Properties of visual pigment analogs.
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1. Introduction.
Retinoids. Historical sketch.

The relationship between "night-blindness", or nyctalopia (severe decline of vision in dim light) and certain component in diets of both humans and animals was known back in ancient Egypt. In 1913 McCollum and Davis reported the discovery of a fat-soluble substance in some foods, which stimulated growth of rats and prevented development of "night-blindness" and xerophtalmia, and have called it "factor A", which was later renamed into "vitamin A". In 1930 Karrer has established its structure. Today three groups of chemical compounds are united under names vitamin A and retinoids: the derivatives of retinol (vitamin A alcohol, **2**), of retinal (vitamin A aldehyde, **3**) and of retinoic acid (RA, **4**) (fig. 1). β-Carotene (provitamin A, **1**) as well as a number of other carotenoids were identified at the same time, however their transformation pathways into retinoids were found much later.

Today vitamin A (*all-E*-retinol, **2**, fig. 1) is considered the most multifunctional fat-soluble vitamin in the human body. It plays key roles in many physiological processes such as vision, reproduction, embryonic growth and development, immune competence, cell differentiation, cell proliferation and apoptosis, maintenance of epithelial tissue, and brain function. Severe vitamin A deficiency can lead to xerophthalmia and "night blindness".

Vitamin A comes into the body exclusively with food in the form of retinol esters or from carotenoids split by a number of enzyme systems located in intestines, and is stored as esters in the liver. The role of vitamin A as dietary component required for normal growth and vision was established, vitamin A deficiency (serum vitamin A levels of <0.7 μmol L^{-1}) is still prevalent in many developing countries, and considered responsible for child and maternal mortality. The administration of vitamin A alone has been shown to decrease preschool mortality in developing countries by 23−34%. Most of the biological processes linked to retinoids are in fact due to the interaction of several metabolites with retinal based proteins or their nuclear biological receptors. These metabolites are generated *in vivo* by redox changes affecting the functional group (retinal, **3**, retinoic acid, **4**), the C4-allylic position oxidation or C5-C6-double bond epoxidation, and the conjugated polyene chain and/or by isomerization of some selected double bonds.

Aside from vision, retinoids perform their function in the form of complexes with protein receptors: covalent complexes (retinal based proteins) and noncovalent complexes (nuclear retinoic acid receptors, RARs and RXRs). Most of the cellular processes influenced by vitamin A and its analogues are mediated by their binding to (and activating) two families of nuclear receptors as well as to the retinoid metabolizing enzymes. The structural and functional studies of nuclear receptors, and the identification of retinoic acid receptor families, RARs [RARα (NR1B1), RARβ (NR1B2), and RARγ (NR1B3)], and retinoid X receptors, RXRs [RXRα (NR2B1), RXRβ (NR2B2), and RXRγ (NR2B3)], that are activated by *all-E*-retinoic acid (**4**) and/or its 9*Z*-isomer have significantly deepened our understanding of the molecular mechanisms by which retinoids as ligands of the nuclear receptor superfamily in general confer the ability onto these inducible transcription factors to regulate target gene transcription.

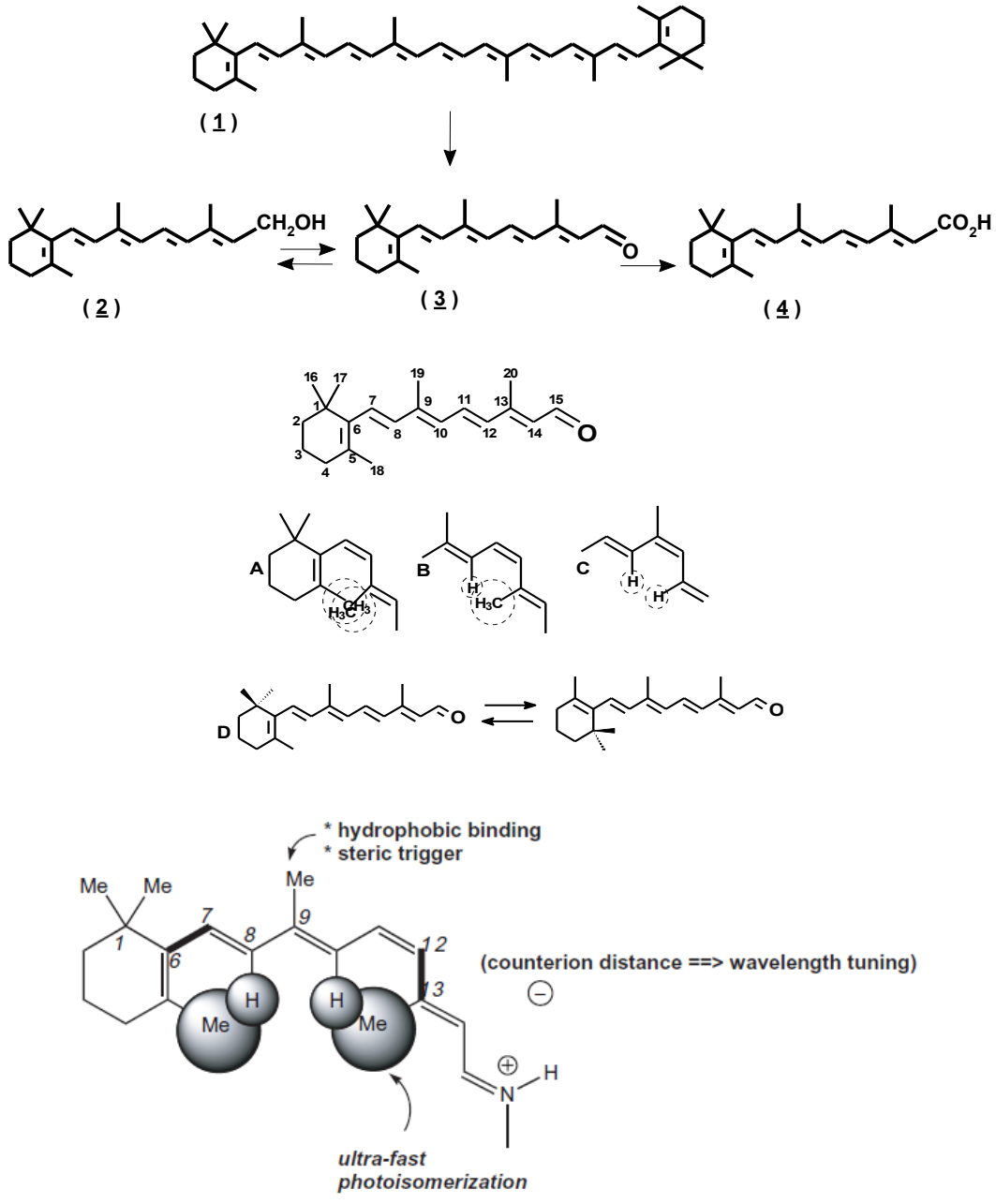
In medicine: *all-E*-retinoic acid/arsenic trioxide combination therapy (together with chemotherapy protocols primarily for post-remission consolidation and maintenance therapy) of acute promyelocytic leukemia (cures more than 90% of patients). As far as RXR ligands (also called rexinoids) are concerned, the U.S. Food and Drug Administration approved bexarotene in 1999 for

the treatment of refractory cutaneous T-cell lymphoma, and efforts are ongoing to dissociate activities that induce hypothyroidism and elevated triglyceride levels, presumably by affecting RXR heterodimer pathways for other nuclear receptors. A limitation of *all-E*-retinoic acid-based therapies is their teratogenicity and hypervitaminosis, the excess intake of vitamin A, may be harmful to the elderly people due to adverse effects of vitamin A toxicity on bone loss [(Álvarez et al., 2014; Domínguez et al., 2003; Khodonov, 1997; Khodonov et al., 2011; Dawson, 2018)].

1.1. Retinoid nomenclature and stereochemistry.

Retinoids are referred to as three groups of fat-soluble vitamin A derivatives that differ in the nature of the terminal group. Their molecules consist of the trimethylcyclohexene ring conjugated via four double bonds with the polar terminal group. The numbering of carbon atoms according to IUPAC-IUB recommendations is presented on fig. 1.

The retinal molecule by its chemical nature contains lipophilic isoprenoid fragment of size C_{20} with a system of five conjugated double bonds, one of which is contained inside the trimethylcyclohexene ring, and the remaining four in the side chain ending with a terminal aldehyde group.



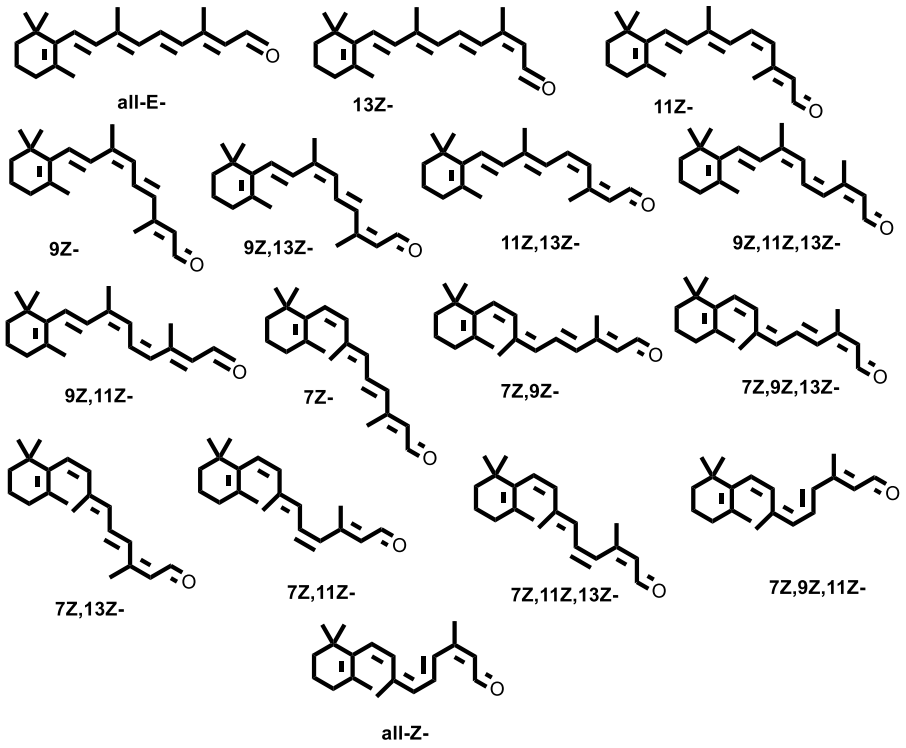


Fig. 1. Retinoid derivatives structures diversity.

Two types of isomery are characteristic for retinoids: *Z*- and *E*-; s-*trans*- and s-*cis*-. Sixteen geometric retinal isomers are possible in total; their structures are presented in fig. 1. All isomers may be subdivided into sterically unhindered - *all-E*-; 9*Z*-; 9*Z*,13*Z*- and 13*Z*-, and sterically hindered – the remaining ones. Isomerization to *E*-series, both spontaneous and induced by various physical factors (irradiation, temperature) is characteristic of the latter ones. This phenomenon is due to presence of steric difficulties of overlapping van der Waals radii of interacting groups (H, CH_3).

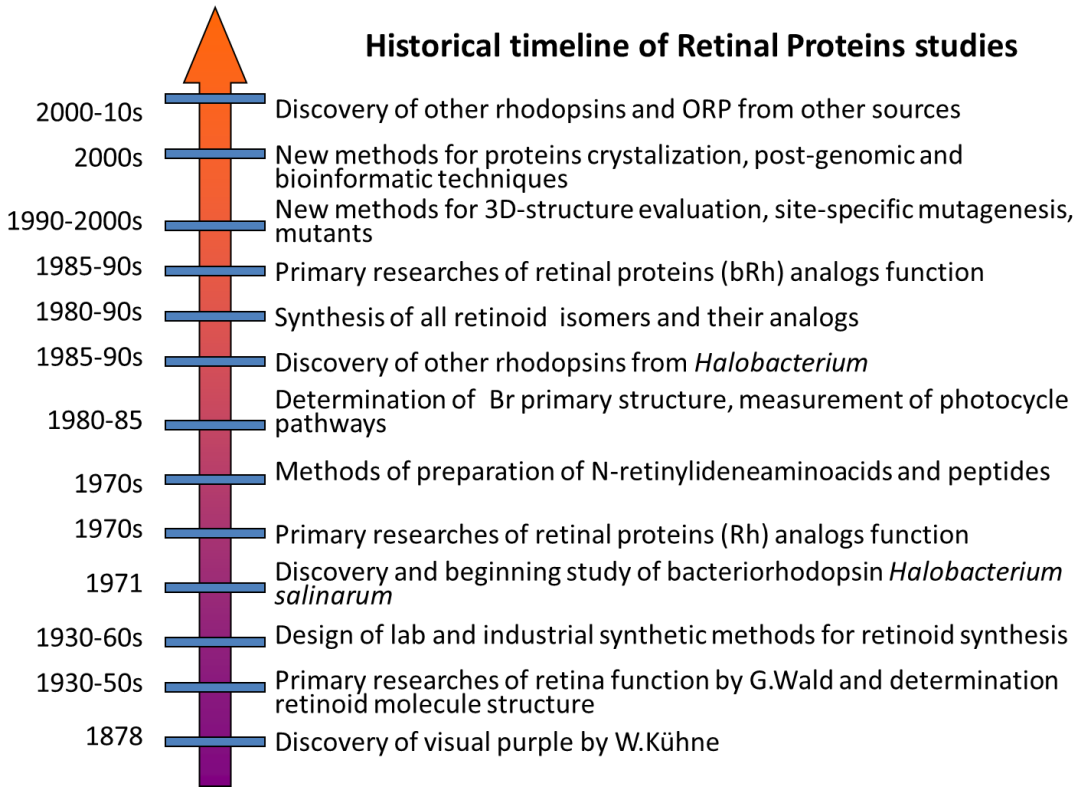


Fig. 2. Historical timeline of Retinal based proteins researches

General features of Retinal based protein structure

Retinal based proteins have the following general features of their structures:

- Their function is closely connected with sun energy conversion into different chemical or physiological responses
- Protein structure — 7 helical *trans*-membrane domain fold - (7TM) helices
- Chromophoric group is definite isomer retinal (*all-E*- for the microbial pigments and *11Z*- for visual pigments) bounded to protein via protonated aldimine bond (Schiff base) with ε-amino group of Lys residue.
- Functional mode: visual pigments (vision), light-driven Cl^- pump, light-driven H^+ pump, light-driven Na^+ pump, inward H^+ pump, light-gated cation channel, light-gated anion channel, light sensor with transmembrane transducer and soluble transducer, and light-activated enzyme.

2. Retinal based proteins (RBP)

The retinoid isomers play the key role in functioning processes in retinal based proteins - visual pigments (rhodopsins and conopsins); ion-pump bacteriorhodopsin (BRh), halorhodopsin (HRh), sensoric rhodopsins (SRhI, SRhII), tundra-rhodopsin (ESRh), and others, as well as in the retinoic acid nuclear receptors.

Upon absorption of light photon, the isomerization of the definite double bond initiates a cascade of events needed for the generation of the physiological or chemical responses. During the evolution process this property of retinoid molecule became the basis for a number of light quantum energy transformation into chemical energy or some physiological response in biological systems, both in higher animals and microorganisms. Retinal based proteins contain a number of defined retinal isomers as part of their chromophoric groups bound via the protonated aldimine bond with the ε-amino group of the Lys residue.

Retinal proteins (Retinal based proteins, RBP) are chromoproteins that function either as sensors or as ion pumps in several species across all domains, Archaea, Eubacteria, and Eukarya. These light-sensitive proteins share a common fold of seven transmembrane (7TM) helices and bind a retinal chromophore through a protonated Schiff base (PSB) with a Lys residue located in helix seven. The absorption maxima of each retinal-based protein are modulated by the ionic environment of the PSB in the binding pocket. Several retinal based proteins with unexpected functions have been discovered and characterized recently.

Retinal based proteins of micrioorganisms are currently considered to be universal and the most abundant biological light energy transducers. Before the 2000s, only microbial rhodopsins from halophilic archaea have been known (bacteriorhodopsin (BRh) and halorhodopsin (HRh)). A 2000 metagenomic study resulted in the discovery of a rhodopsin gene in marine Proteobacteria that was, accordingly, named proteorhodopsin (PRh). Since 2000, thousands of microbial rhodopsins have been identified, in all three domains of life (bacteria, archaea and eukaryota) as well as in large viruses. The renaissance of rhodopsins as a research field has culminated in the development of optogenetics, the revolutionary method for controlling cell behavior in vivo in which microbial rhodopsins play the key role. Several rhodopsins with unexpected functions have been discovered and characterized recently. Among the members of this family are light-driven proton, anion and cation pumps, light-gated anion and cation channels, and photoreceptors. Also, rhodopsins that function as inward proton pumps have been discovered.

The opsin genes are classified into two groups: Type I opsin genes are found in archaea, eubacteria, fungi, and algae, and Type II opsins are found in animals.

Microbial type I opsins, which comprise more than 1000 members, control proton gradients and maintain membrane potential and ionic homeostasis. This group includes the light-driven ion pumps bacteriorhodopsin (BRh), halorhodopsin (HRh) and proteorhodopsin (ESRh) and light-gated ion channels called channel rhodopsins (ChRhs). Other microorganisms use opsin-based photoreceptors, such as sensory rhodopsin (SRh), to modulate flagelar movements in phototaxis. In marine photic ocean zone, the light-activated ion pumps from proteobacteria called proteorhodopsins, PRhs, have been linked to the survival of bacterioplancton. Microbial rhodopsins used by microorganisms to control membrane ion homeostasis and phototaxis are based on light-induced photocycles driven by isomerization of the chromophore *all-E*-retinal (**3**) bound to membrane proteins that are similar to the proteins of the visual cycle [(Belikov et al., 2014, 2024, 2022, 2018;

Dawson, 2018; Ebrey and Koutalos, 2001; Ernst et al., 2014; Khodonov, 1997; Khodonov et al., 2026, 2023, 2020; Kiser et al., 2014; Mitsner and Khodonov, 1985)].

All unicellular organisms use *all-E*-retinal (**3**) (**Ret**) bound to opsin in rhodopsin-like photoreceptors to capture energy and/or information from light sources and transform it into light-activated ion channels and pumps. Light absorption induces isomerization of the chromophore from *all-E*-retinal (**3**) to *13Z*-retinal. In contrast to type II rhodopsin, the activated *13Z*-retinal chromophore in type I (microbial rhodopsins) remains covalently bound to its opsin protein partner and thermally reverts rapidly to the *all-E*-retinal state without detaching from the protein. The efficiency of light absorption depends on the extinction coefficient of the complexes (ε_{max}, typically between 40 000 and 70 000 $M^{-1}cm^{-1}$) and the quantum efficiency (Φ, typically between 0.3 and 0.7). The turnover time of the photocycle for most light-driven pumps (HRh and BRh) is 10−20 ms.

2.1. Photoreceptors.

In the retinas of most vertebrates, there are two types of photoreceptor cells, rods and cones [(De Grip and Ganapathy, 2022; Palczewski, 2012, 2006) and ref. cited there, see figs. 3-6].

A B

Fig. 3. Human (A) and cattle (B) eyes

The oldest representatives from known retinal-based proteins are two visual pigment families – rhodopsins and cone opsins, which responsible for processes dark and color vision.

2.2. Vertebrate retina and rhodopsin.

In the 19th century, groundbreaking research on vision by Müller, Boll and Kühne led to the visual perception, that light capture occurred in the distal part of the human retina (figs. 3-13), in particular the outer segments of the photoreceptor cells.

The reddish-purple coloration of rod cells was noted in 1851 by Heinrich Muller, who attributed it to hemoglobin. In 1876, Franz Boll recognized that frog retina is photosensitive and when exposed to light, the pigment bleached to a yellowish color and then became colorless. Boll demonstrated that frogsxexposed to sunlight and then kept in darkness regenerated the red pigment. After many observations, he concluded, “The basic color of the retina is constantly consumed *in vivo* by the light falling on the eye. In the dark, *in vivo*, the color is regenerated.” Willy Kuhne, pursuing Boll’s findings, determined the pigmented material to be a rod outer segment protein he named “visual purple” (rhodopsin). Kuhne isolated frog retinas and retinal pigment epithelium (RPE) layers in experiments, proving that the RPE is necessary for the regeneration of rhodopsin. He extracted rhodopsin using bile salts, matched its spectral absorption profile to that of dissected retinas, proposed that the yellow and colorless products of bleaching must be chemically distinct substances, and correlated the electrical impulses emitted by isolated retinas to their illumination. Kuhne’s extensive investigation of the visual system began to elucidate the now-familiar story of a photochemical reaction whose products stimulate nerve impulses to the brain [(Palczewski, 2006)].

As of the 1930s it became apparent that a membrane-bound protein in the rod photoreceptor cell was responsible for the red color. This protein was named rhodopsin, after the ancient Greek words *ροδεοσ* (rhodeos, rose-coloured) and *οψισ* (opsis, which appropriately can be translated as sight or eyes). It was found to owe its spectral properties to a covalently bound cofactor, eventually named retinene and then afterward retinal. The typical red color of this tissue disappeared upon illumination, which was termed "bleaching," and could to some extent be regenerated upon subsequent dark adaptation of the isolated eyecup.

George Wald determined in 1935 that *11Z*-retinal (figs. 1, 9) is the chromophore of the visual pigments [(Wald, 1935)]. Thus, Rhodopsin, the founding father of the type-2 family.

Rhodopsin is the first visual pigment identified, namely in the rod photoreceptor cells of the vertebrate retina [(Hofmann and Lamb, 2023; Palczewski, 2006; Wald, 1935) and ref. cited there]. Subsequently, it was discovered that the cone photoreceptors in the vertebrate retina harboured closely related visual pigments. Thereafter, it became known that the invertebrate retina applied structurally very similar, but photochemically slightly differently operating visual pigments [(De Grip and Ganapathy, 2022) and ref. cited there].

2.3. Structure of rod and cone outer segments and ROS internal membranes.

The visual cascade is an archetype of a G-protein-coupled system. In canonical G-protein signalling, an agonist-activated GPCR (R*) binds a heterotrimeric G-protein (Gαβγ), catalysing nucleotide exchange in its α-subunit and dissociation of the GTP-bound α-subunit (Gα-GTP) from the Gβγ heterodimer, and then, depending on cell type, either or both are able to interact with downstream effector proteins. The signal of agonist binding is thus transmitted into the cell and amplified, because a single the G-protein. Receptor signalling is stopped when the active receptor is phosphorylated by a receptor kinase (GRK), and then arrestin binds the active, phosphorylated receptor, thus blocking its further interaction with the G-protein.

Rod photoreceptor pigments had evolved for very-high-sensitivity (single-photon) black-and-white (scotopic) vision. In the vertebrate realm, the absorbance maxima of the rod pigments range from 440 to 520 nm, depending on their habitat. For color discrimination, a closely related set of pigments had evolved that cover the entire UV–deep-red region (350–640 nm), and are confined in the vertebrate cone photoreceptors.

The phylogeny of opsins, including vertebrate 'visual' opsins, has been reviewed in a number of publications, including [(Lamb, 2013) and ref. cited there]. Phylogeny of the gene families of vertebrate visual pigments (i.e. cone opsins and rhodopsins): LWS, SWS1, SWS2, RHB/RH2 and RHA/RH1 was presented on figs. 7, 8 [(Lamb, 2013; Leung and Montell, 2017)]. There are four main groups: c-opsin (*red*), r-opsin (*green*), retinal G protein–coupled receptor (RGR)/Go-opsin (*blue*), and cnidops (*yellow*) (see fig. 8) [(Leung and Montell, 2017)].

The visual transduction cascade on rod disc membranes follows this classical pattern, if one considers the formation of *all-E*-retinal by photoisomerisation of the bound *11Z*-retinal to correspond to the binding of a diffusible agonist molecule. Furthermore, it represents the simplest form, with only one type of G-protein, G_t (transducin), and only one effector, a cyclic GMP phosphodiesterase (PDE6). Activated Gα-GTP dissociates from R* and causes activation of the PDE6. Although activated rhodopsin is capable of interacting with other G-proteins (most notably G_i), it would appear that evolution has tuned rhodopsin and rod transducin (and likewise cone opsins and cone transducin) to interact with each other with high efficiency; a further factor is that no other GPCRs or G-proteins are expressed at high levels in photoreceptor outer segments [(Hofmann and Lamb, 2023)].

Our understanding of the biochemistry and molecular biology of the visual cycle and the retinoid cycle (the conversion of *all-E*-retinal via *11Z*-retinol to *11Z*-retinal) has increased enormously in the last years. A human eye contains roughly 120 million rods and 5 million cones. The visual pigment (rhodopsin or a cone opsin) is incorporated at a very high spatial density (25,000 rhodopsins / μm^{-2}) in the lipid membrane of the "outer segment". Rod cells comprise ~70% of all 6.4 million retinal cells, and cone cells represent <2%. Rods are postmitotic neurons with highly differentiated rod outer segments (ROS) connected to the inner segments (IS), which generate proteins and energy to sustain phototransduction events (see figs. 4-12).

Type II or animal opsins couple to G-protein coupled receptors (GPCR)-dependent signal transduction pathways that affect transmembrane ion currents.

It was shown neuronal organization of a typical mammalian retina (see fig. 6 A). A cross-sectional representation of rod and cone photoreceptors is presented, illustrating their connections to the RPE distally and to relaying cells (bipolar, horizontal, amacrine, and ganglion cells) proximally. The rod structure has a longer outer segment with membrane-enclosed disks tightly packed without connections to the plasma membrane. Cone disks are continuously connected with the plasma membrane. At fig. 6 B depicting the rod cell. The processes in ROS allow rapid transduction of the light signal to graded hyperpolarization of the plasma membrane, ensuing from the decrease of light-sensitive conductance in the ROS cGMP-gated cation channels. In ROS, hundreds of distinct, rhodopsin-loaded disk membranes are enveloped by the plasma membrane.

2.4. Rhodopsin's amino acid sequence, 3D-models and 7-trans-membrane segment (7TM) structure of the disc membrane.

Vertebrate rhodopsin sequences are highly conserved, and across most vertebrate taxa comprise 354 amino acid residues; however, mammalian rhodopsins are slightly shorter, at 348 residues, as a result of minor changes (including the loss of a T(A)SSVS motif) near the C-terminus, in comparison with other vertebrate sequences. The generally-accepted template sequence for comparison with, and numbering of, other visual opsins is bovine rhodopsin, for which the sequence and overall structure are illustrated in figs. 5, 9.

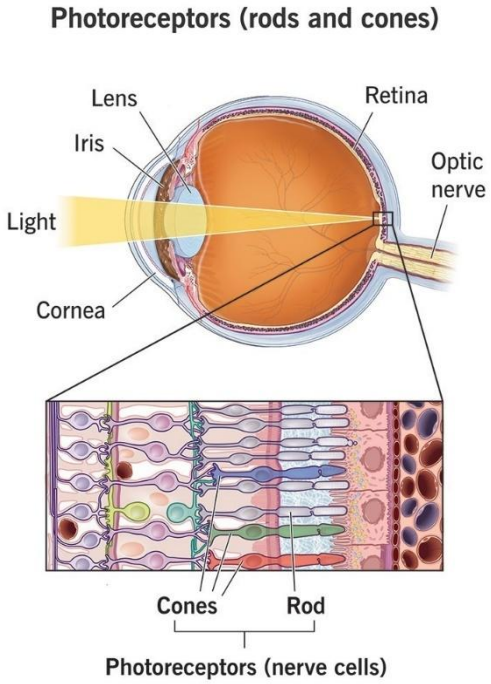


Fig. 4. Photoreceptors.

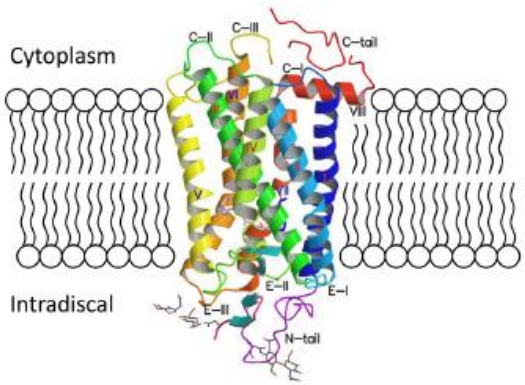


Fig. 5. 3D-rhodopsin model in the membrane of a disc.

Different versions of this figures were published previously, and all of them are refinements of the pioneering work on rhodopsin topology by Paul Hargrave [(De Grip and Ganapathy, 2022; Hofmann and Lamb, 2023)].

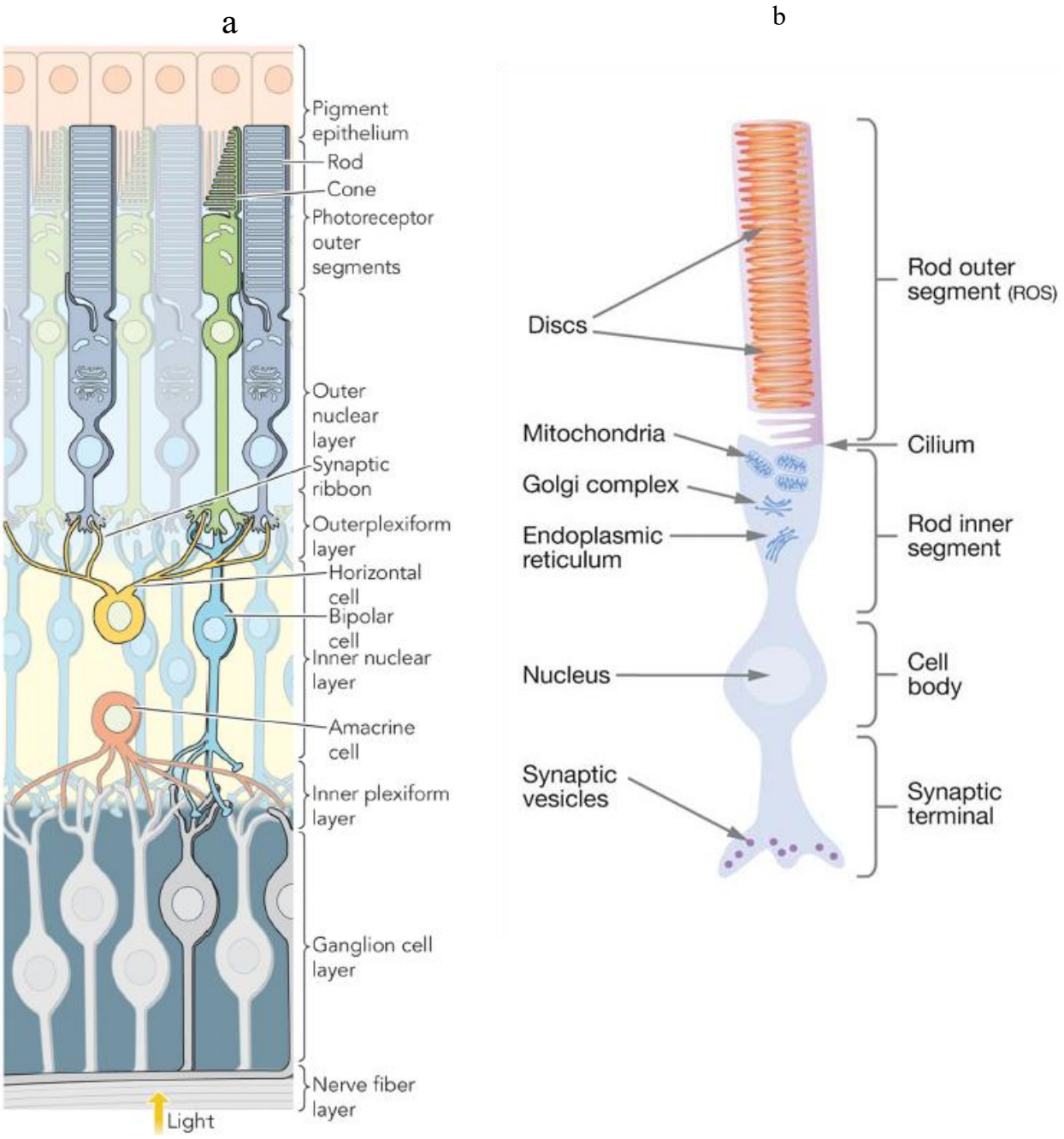


Fig. 6. Structures of rod and cone outer segments and ROS internal membranes. Schematic drawing of vertebrate retina.

Rhodopsin is an integral membrane protein, comprising seven trans-membrane (7TM) helices, here denoted as TM1-TM7 (but sometimes by others as H1–H7 or I-VII), together with an eighth helix, H8 (or VIII), which runs parallel to the membrane surface. The TM helices are interconnected by loops denoted as intracellular or cytoplasmic (CL1- CL3) and extracellular (EL1-EL3), though the latter are in fact intradiscal. These loops, or inter-helical domains, help to constrain the 7TM helix bundle in the compact inactive conformation, and they undergo structural changes upon receptor activation. Fig. 9. Residues are shown using the single-letter amino acid codes. The N-terminus of the polypeptide chain, with two attached carbohydrate chains, is in the intradiscal medium, while the carboxy-terminus (C-term) is in the cytoplasm. The sequence folds into seven trans-membrane helices (TM1-TM7), plus an eighth helix (H8) that runs parallel to the membrane surface. The trans-membrane helices are interconnected by three cytoplasmic loops (CL1-CL3) and by three intradiscal

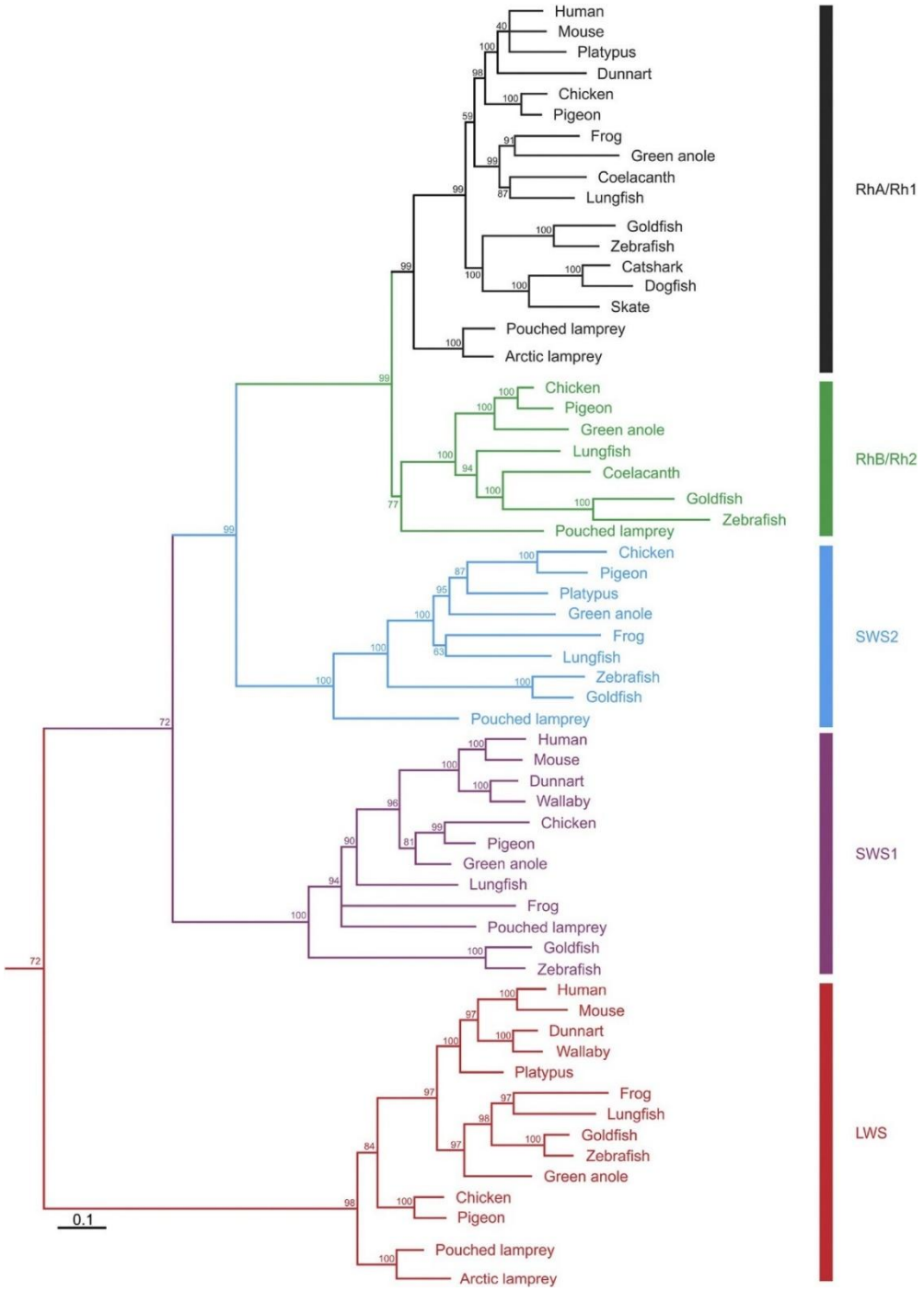


Fig. 7. Phylogeny of vertebrate cone and rod opsins [(Lamb, 2013) **and ref. cited there].**

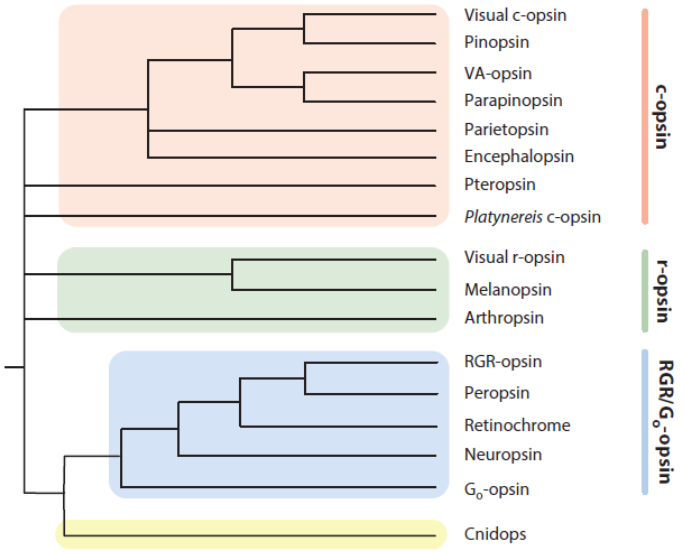


Fig. 8. Phylogenetic tree of selected opsin family members [(Leung and Montell, 2017) **and ref. cited there].**

(so-called extracellular) loops (EL1-EL3). Cys187 forms a disulphide bridge with Cys110. Residues shown in black circles indicate positions associated with retinitis pigmentosa. In the lower part of the figure, *11Z*-retinal *via* protonated Schiff base bond to opsin (K296, black) and *all-E*-retinal are shown; these isomers are involved in the photoactivation of rhodopsin. Rhodopsin, when exposed to light, is phosphorylated by rhodopsin kinase (or G protein–coupled receptor kinase 1). The predominant phosphorylation sites are Ser334, Ser338, and Ser343, and the whole C-terminal region is highly mobile.

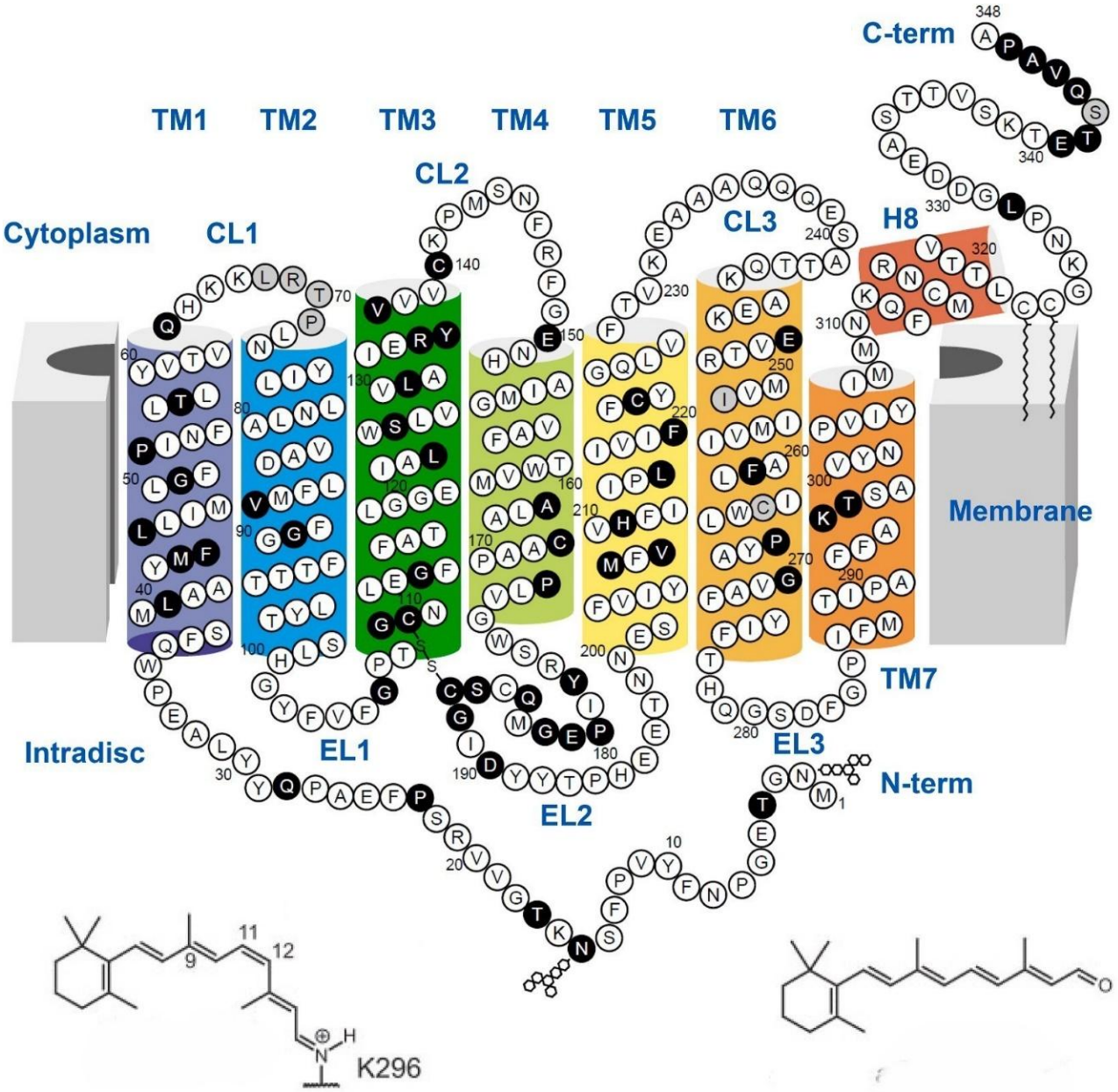


Fig. 9. Amino acid sequence and 2D-model of the bovine rhodopsin molecule [(De Grip and Ganapathy, 2022)].

Rhodopsin's light-sensitive ligand, *11Z*-retinal, is bound via a protonated Schiff base to the ε-amino group of lysine-296 (Lys or K296). When *11Z*-retinal binds to the apoprotein, opsin, it triggers a "mouse trap" conformational change, whereby the Schiff base bond becomes protonated and snaps into a strong salt bridge with its counterion Glu113; this interaction forces the bundle of helices to refold into rhodopsin's dark state, which is exceptionally stable and which exhibits exceedingly low activity. Upon absorption of light, the *11Z*-isomer is photoisomerised to *all-E*-, and rhodopsin undergoes a series of changes that are reflected as photoproducts, each with its own absorption spectrum in the UV/Vis range. When rhodopsin passes from metarhodopsin I to metarhodopsin II, its Schiff base linkage becomes deprotonated and the protein becomes activated. The Schiff base can subsequently be hydrolysed and release *all-E*-retinal isomer. The protein can then rebind *11Z*-retinal and regenerate light-sensitive rhodopsin. Details of the structure of the 3D-model rhodopsin

molecule, its photoproducts and analogs determined from X-ray crystallography and other approaches will be presented in Section 2.4 below.

In the dark, the *11Z*-retinal chromophore is bound to the opsin apoprotein by a protonated Schiff base (figs. 9, 10 A, B, 15, 17), thus forming the rhodopsin dark resting state (top). On absorption of a quantum of light the chromophore isomerises within 200 fs from the *11Z*- to the *all-E*-configuration. The protein then relaxes thermally through a series of intermediates, each characterised by its UV/Vis absorption spectrum, with the indicated wavelength of maximal absorption (λ_{max}), and with approximately the indicated time-course (blue) for mammalian rhodopsin *in vivo*. The active Meta II state, which binds and activates the G-protein transducin, is shown in red. Hydrolysis of the Ret Schiff base linkage generates free opsin and *all-E*-retinal.

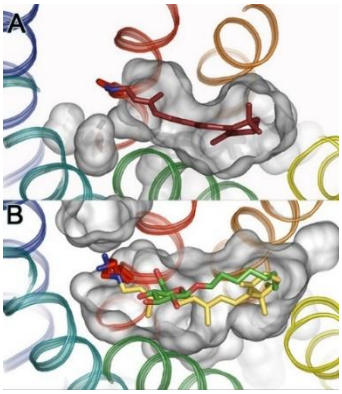


Fig. 10. 3D-model of Retinal binding site of bovine rhodopsin.
(A) Crystal structure of inactive dark state (PDB ID code: 1U19) where *11Z*-retinal is tightly bound deep in the protein with no openings of the retinal binding site toward the lipid environment.
(B) In the active Ops* (or Meta II) conformation the retinal channel allows *all-E*-retinal access and egress, and some detergents like β-D-octylglucoside, mimicking the *all-E*-retinal chromophore, to enter the retinal binding site. Shown is an overlay of the two ligands in the retinal binding pocket as observed in the crystal structures of Meta II (*all-E*-retinal depicted in yellow; PDB ID code: 3PXO) and Ops* in complex with β-D-octylglucoside (depicted in green/red; two rotamers of Lys296 are shown in red; PDB ID code: 4J4Q). Note that the ring moieties of chromophore and detergent are oriented in opposite directions. Whereas *all-E*-retinal is covalently linked by the **PSB** to Lys296, β-D-octylglucoside is fixed in the ligand binding site by hydrogen bonding of its hydroxyl groups to the opsin environment [(Ernst et al., 2014)].

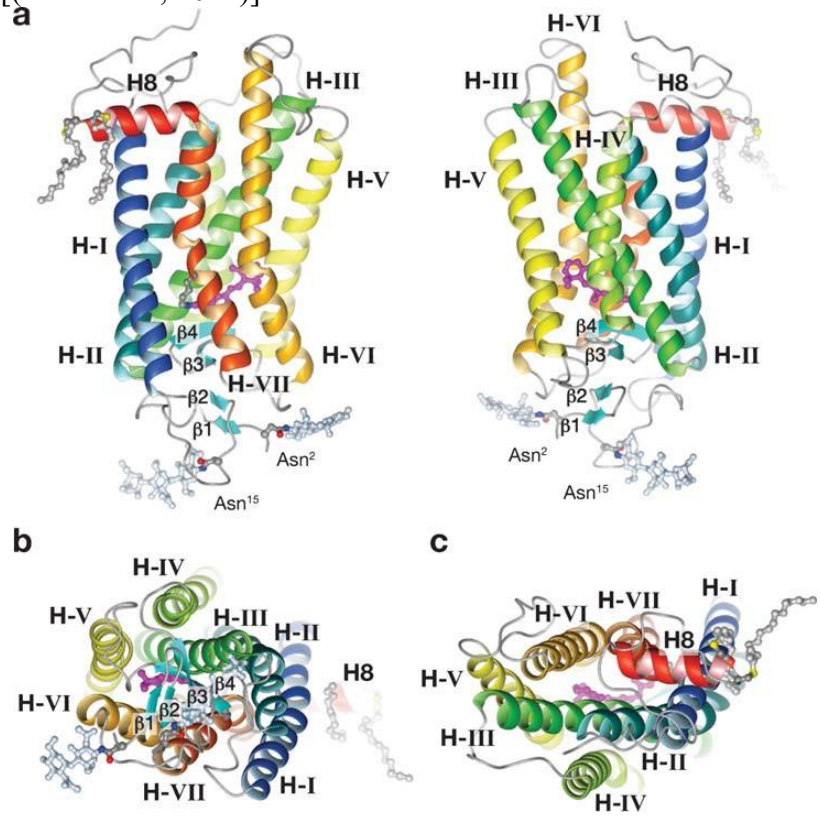


Fig. 11. 3D-model of rhodopsin.

Fig. 11. (*a*) Ribbon drawings of rhodopsin parallel to the plane of the membrane.
(*b*) View into the membrane plane as seen from the intradiscal side of the membrane. The carbohydrate moieties are at Asn2 and Asn15. The pairs of β1-β2 and β3-β4 hairpins, the transmembrane helices (TM) I–VII, and the cytoplasmic helix 8 (TM8) are labeled. A palmitoyl group is attached to each of the two Cys residues at the end of helix 8. The removal of the palmitoyl groups has only a minor effect on phototransduction processes.
(*c*) A view into the membrane plane as seen from the cytoplasmic side. The cytoplasmic side has greater surface area than the intradiscal side [(Palczewski, 2006)].

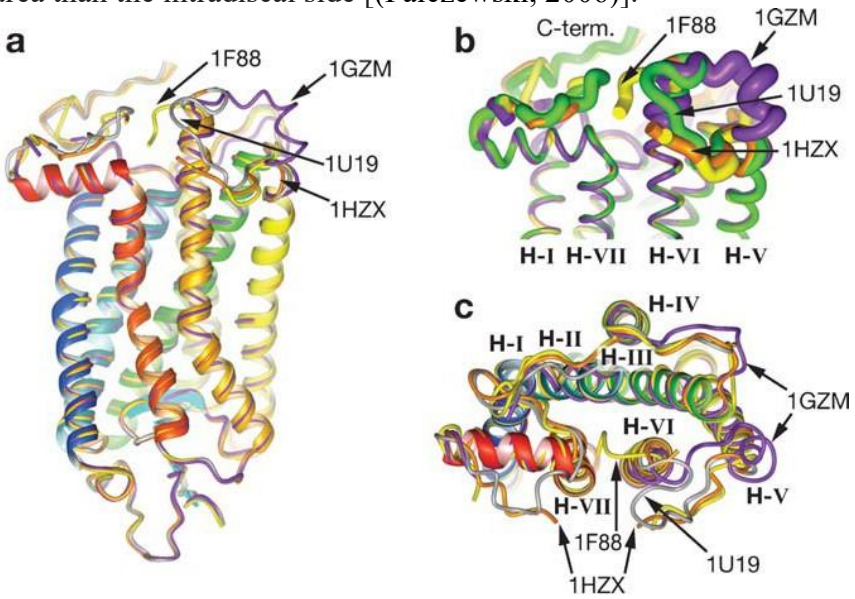


Fig. 12. Comparison of the current 3D-models rhodopsin structure.

(*a*) Side view. (*b*) Side view, with a close-up of the cytoplasmic region. (*c*) View from the cytoplasmic side.

There are currently five crystallographic entries for rhodopsin in the Protein Data Bank (PDB). The structures deposited under the PDB ID codes 1F88, 1HZX, 1GZM, and 1U19 are superimposed. PDB ID codes 1F88 (*yellow thread*), 1HZX (*orange*), 1GZM (*purple*), and 1U19 (*gray*) are represented in the cartoon. Entries with PDB ID code 1F88, 1HZX, 1L9H, and 1U19 are for a tetragonal crystal obtained by very similar methods. Entry PDB ID code 1U19 is at the highest resolution reported, 2.2 Å. Entry PDB ID code 1GZM is for a trigonal crystal form obtained in a different condition than the other listed crystals [(Palczewski, 2006)].

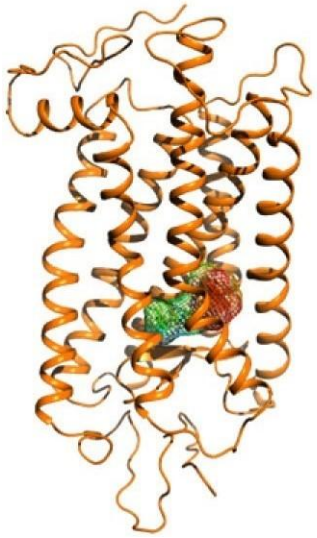


Fig. 13. The structural 3D-model of isoRh analog with *9Z*-retinal (PDB ID: 2PED) with the binding cavity shown in green-orange-red mesh (Pashandi et al., 2025)

Fig. 13 showed the structural model of isoRh analog with *9Z*-retinal (PDB ID code: 2PED) the binding cavity shown in green-orange-red mesh.

2.5. Activation and shut-off of the rhodopsin molecule

In order to activate the transduction cascade and then shut it off, it is necessary (though not sufficient) to activate and then de-activate the rhodopsin molecule. Here we present an overview of the molecular transitions underlying rhodopsin's activation and shut-off. Detailed treatments of the active state, Meta II, and its precursor, Meta I, are provided in Section 2.5 (see figs. 14-18).

2.5.1. An Overview of Opsin Classification

The original classification of opsins is based on the photoreceptor cell type that houses the photopigment: ciliary (c-opsins) or rhabdomeric (r-opsins).

Ciliary photoreceptors, which include human rods and cones, have stacked and flattened membranous discs. Rods are specialized for low-light conditions and express rhodopsin, whereas human cones express three color pigments: OPN1-SW, OPN1-MW, and OPN1-LW.

Rhabdomeric photoreceptors have densely packed membranous microvilli projections, which are present in the compound eyes of flies and in many other invertebrates. These visual photoreceptor cells express r-opsins that are distantly related to c-opsins. The c-opsins and r-opsins couple to distinct signaling cascades that result in hyperpolarization and depolarization of photoreceptor cells, respectively (see figs. 8, 14). Another important difference is that, following light activation of c-opsins in rods and cones, the chromophore dissociates, where upon *all-E*-retinal is regenerated to *11Z*-retinal. However, *all-E*-retinal does not typically dissociate from r-opsins, such as those in the fly eye. Rather, it is converted back to *11Z*-retinal by absorption of a second photon of light.

The early notion was that c-opsins were restricted to vertebrates, whereas r-opsins were exclusive to invertebrates. However, this is an oversimplification. For example, mammalian melanopsin (OPN4) is highly related to r-opsins, such as those in the fly eye, and two opsins in the mosquito, *Anopheles gambiae*, are more similar to c-opsins. The marine ragworm, *Platynereis dumerilii*, expresses an r-opsin in its eyes and a c-opsin in its brain. In addition, other opsins classified as c-opsins on the basis of sequence relationships initiate signaling cascades distinct from the phototransduction cascade observed in rods and cones (green opsin in tilapia, encephalopsin, parapinopsin, VA-opsin, parietopsin, neuropsin, pteropsin) (figs. 8, 14).

A third class of opsins is distinct from c-opsins and r-opsins. This group, comprising retinal GPCR (RGR)/G_o-opsins (also referred to as group 4 opsins), includes RGR, peropsin, and neuropsin (OPN5). These opsins function as photoisomerases or couple to different signaling cascades [(Leung and Montell, 2017)].

2.5.2. Multiple opsin-driven G protein–coupled signaling cascades.

Multiple opsin-driven G protein–coupled signaling cascades are presented on (figs. 14, 16) below.

(*a*) G_t-mediated transduction (e.g., in mammalian rods and cones) couples an activated opsin to a G protein termed transducin (G_t). G_t stimulates a phosphodiesterase (PDE), which causes a decline in cyclic GMP (cGMP) levels and subsequent closure of cyclic nucleotide–gated (CNG) cation channels, resulting in hyperpolarization.

(*b*) G_q-mediated transduction [e.g., in *Drosophila* photoreceptor cells and mammalian intrinsically photosensitive retinal ganglion cells (ipRGCs)] couples an activated opsin to G_q, which stimulates phospholipase C (PLC), resulting in hydrolysis of phosphatidylinositol 4,5-bisphosphate (PIP2). The subsequent openings of Transient Receptor Potential (TRP) channels result in depolarization. Other abbreviations: DAG, diacylglycerol; IP3, inositol triphosphate.

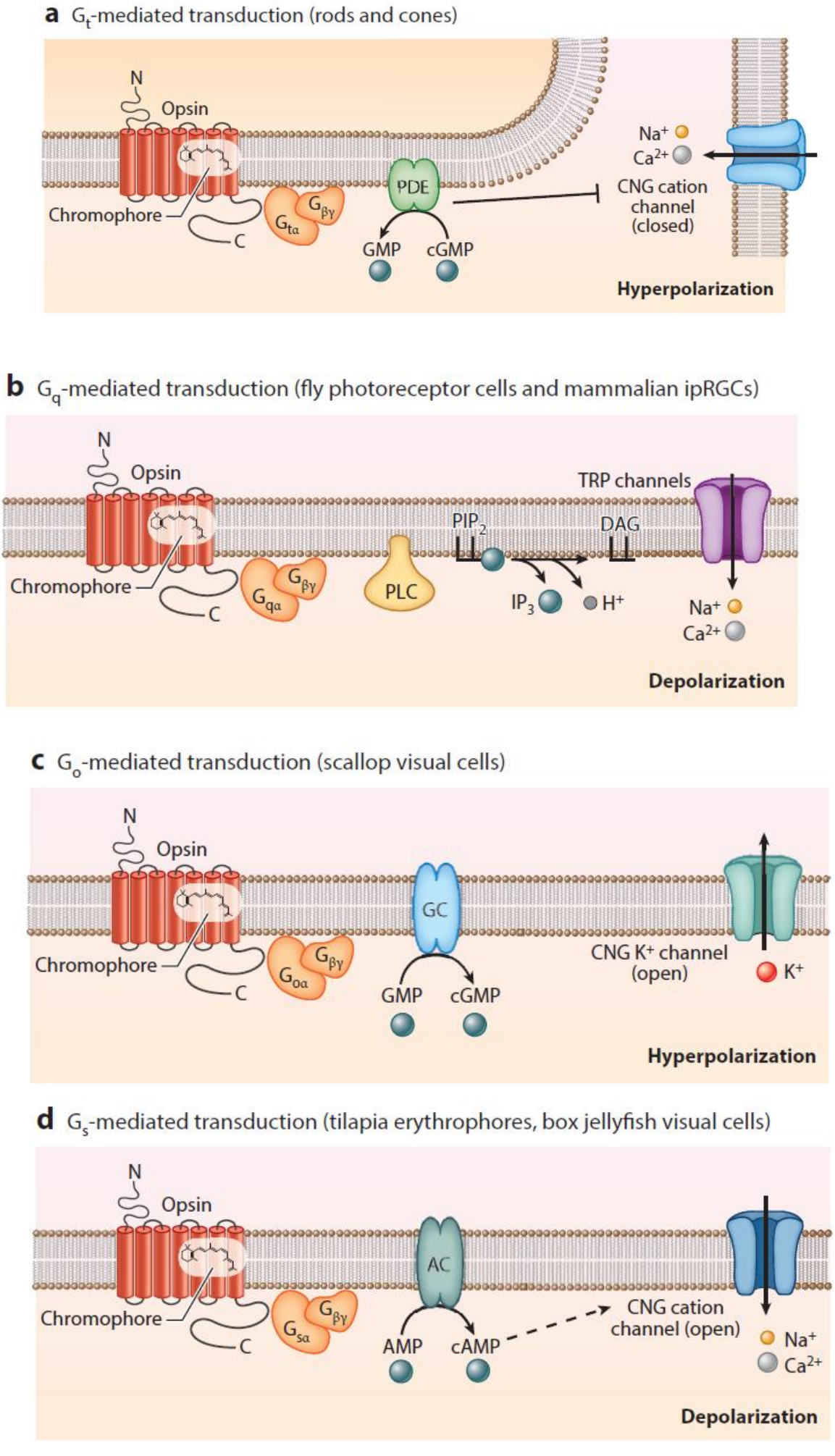


Fig. 14. Multiple opsin-driven G protein–coupled signaling cascades [(Leung and Montell, 2017)].

(*c*) G_o-mediated transduction (e.g., in scallop visual cells) links an activated opsin to G_o, which activates guanylyl cyclase (GC). This leads to opening of CNG K^+ channels and hyperpolarization. G_o-mediated signaling cascades have also been observed in sea slug simple photoreceptors and in the lizard parietal eye. Several encephalopsins (pufferfish TMT and a mosquito homolog (*Anopheles stephensi*, MosOpn3) may couple to G_o and G_i, but the downstream components are less clear. Moreover, vertebrate neuropsins (OPN5) couple to G_i and likely inhibit adenylyl cyclase (AC) activity.
(*d*) G_s-mediated transduction (e.g., in tilapia erythrophores and box jellyfish visual cells) links an activated opsin to G_s, which activates AC. The consequent increase in cAMP opens CNG cation channels, resulting in depolarization. [(Leung and Montell, 2017)].

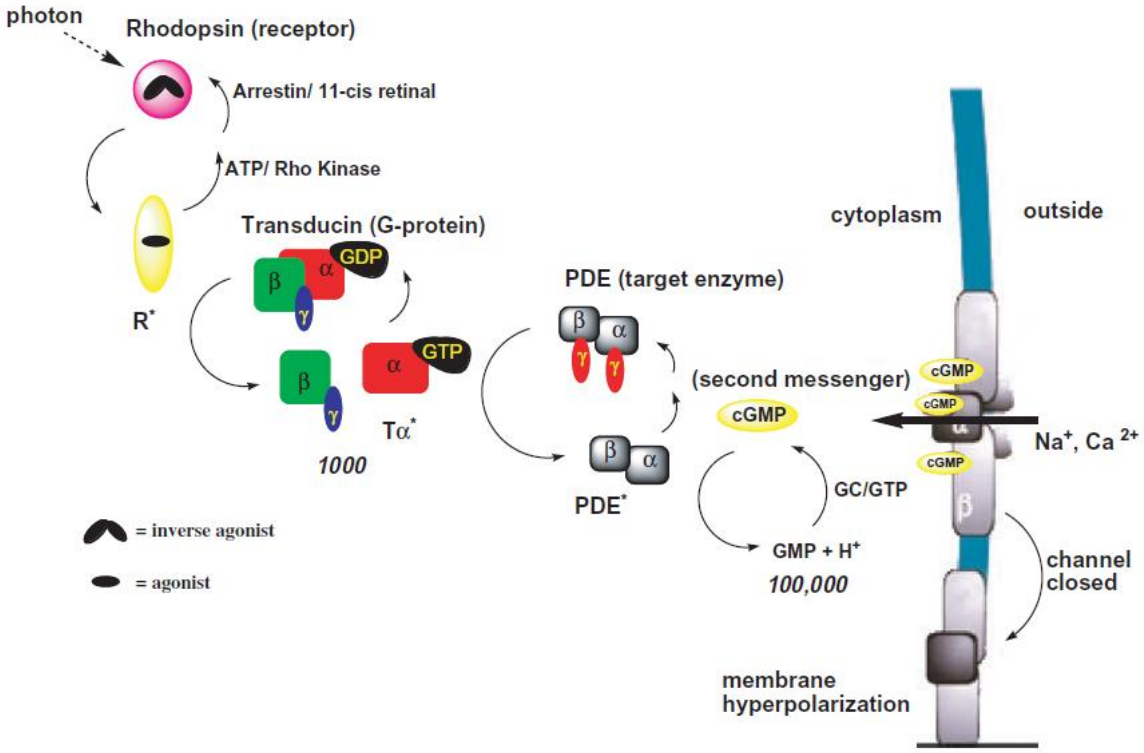


Fig. 15. Schematic overview of the vertebrate visual transduction cascade [(Fishkin et al., 2004)].

2.5.3. Light-cycle of rhodopsin. Photoproducts of rhodopsin photolysis.

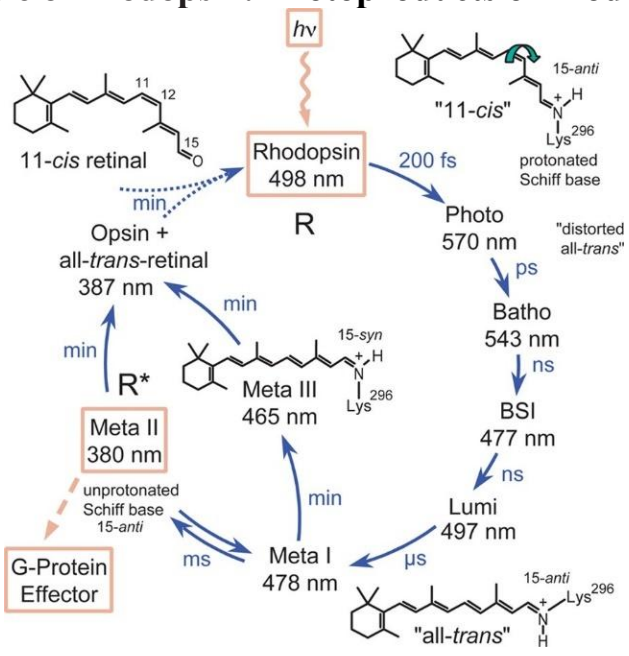


Fig. 16. Spectroscopically detected intermediates of photoactivated bovine rhodopsin [(Ernst et al., 2014; Hofmann and Lamb, 2023; Ostrovsky et al., 2023)**].**

Photoisomerization of the *11Z*-double bond in retinal leads within femtoseconds to photorhodopsin with a highly distorted *11E*-bond. Via thermal relaxation, several intermediates form with distinct λ_{max} values, distinguishable by low-temperature or time-resolved spectroscopy for a review see [(Ostrovsky, 2024; Ostrovsky et al., 2023; Ostrovsky and Nadtochenko, 2021)] (and figs. 15-19). It has long been known that, following a near-instantaneous change upon photoisomerisation, the rhodopsin molecule undergoes a series of transitions through distinct intermediate states and figs. 16, 18 shows a current view of the chromophore of rhodopsin, *11Z*-retinal, is covalently bound via a protonated Schiff base to Lys296 on TM7; the proton at the Schiff base is stabilised by a counterion, at Glu113 on TM3. With extreme rapidity (on a time-scale of fs to ns) the isomerised molecule moves through states named photo-rhodopsin Rh*, bathorhodopsin, and BSI (blue-shifted intermediate), before reaching the state named lumirhodopsin (Lumi), which absorbs maximally at a wavelength of 497 nm, very close to rhodopsin's peak. With the release of strain in the retinoid, energy is transmitted into the protein, but the activation remains near the retinal binding pocket. It is likely that as early as in Lumi, most of the photon energy absorbed by rhodopsin has already been transferred to the apoprotein. In the X-ray structure of Lumi the distortion of the *all-E*-retinal in bathorhodopsin has already relaxed by dislocation of the β-ionone ring, and an outward distortion in the middle of helix TM3 is resolved. Within tens of μs (at body temperature), lumirhodopsin transitions to the first of the so-called metarhodopsin products, metarhodopsin I (Meta I). In the transition from Lumi to Meta I, the *all-E*-retinal and the protein change their relative position, such that the protonated Ret-Schiff base shifts its centre of interaction from Glu113 on TM3 to Glu181 in loop EL2. Up to this point, each of the transitions is essentially irreversible at body temperature, but in contrast the subsequent intermediates exist in equilibria with each other.

Gradual release of the strain in the chromophore leads through Batho and Lumi to Meta I, as seen by the different absorption maxima that arise from changes in chromophore/ protein interaction. A transient blue-shifted intermediate (BSI) cannot be trapped at low temperatures. Time-resolved UV−vis measurements revealed the existence of additional transient forms of Lumi (Lumi II), and Meta I (Meta I380; Meta Ib). The Ret-SBH^+ remains protonated up through Meta I, probably due to the low pK_a of the stabilizing counterion Glu113. Larger protein conformational changes lead to Meta II (comprising substates Meta IIa and Meta IIb) which is in equilibrium with its predecessor Meta I. Meta II is the agonist-bound active receptor state capable of catalyzing GDP/GTP nucleotide exchange in the G protein transducin. Meta II is characterized by a deprotonated Ret-SB resulting in a large blue-shifted value for λ_{max} (380 nm). As a result of Ret-SB hydrolysis Meta II decays to the apoprotein opsin and *all-E*-retinal. Meta I can also form Meta III, involving thermal isomerization of the Ret-SBH^+ (λ_{max} = 465 nm) from *all-E*-15-*anti* to *all-E*-15-*syn*. Meta III decays to opsin and *all-E*-retinal, but can also be photoconverted to Meta I and Meta II.

Unlike in invertebrates, bovine rhodopsin cannot be regenerated *in situ* by reisomerization of retinal with a second photon.

All-E-retinal is reduced to retinol by retinoldehydrogenase and transported out of the photoreceptor cell to adjacent retinal pigment epithelial (RPE) cells, where *11Z*-retinal isomer is regenerated. To regenerate the rhodopsin state, the *all-E*-retinal has to be isomerized into the *11Z*-configuration which, when transported to the opsin site, will spontaneously recombine with opsin, generating rhodopsin, both in vivo and in vitro. In the vertebrate retina, several systems for the production of *11Z*-retinal are operational in the retina pigment epithelium (RPE) and cone photoreceptor cells, employing both enzymatically driven and photoactivated isomerases.

2.5.4. Three-step activation of rhodopsin.

As will be discussed in detail below, these transitions break two of the main constraints that hold the rhodopsin ground state inactive, namely: the retinal Schiff base hydrogen bonding network, which provides a central ionic lock, and the TM3–TM6 ionic lock. In the 3-step transition from Meta I to Meta IIb-H^+, these two main constraints are sequentially broken, and the molecule now has a high probability of being in its active state. Helix motion provides the coupling between the two networks, and it opens the binding crevice for the key binding site on Gαt. The net result of photoisomerisation followed by these transitions is that rhodopsin is converted within ms from being almost totally catalytically inactive to being powerfully catalytically active.

To set a framework for considering rhodopsin's light-induced activation, we now list the main steps that occur, as follows:

- Light-induced *Z*-/*E*- isomerisation (to Batho)
- Counterion shift from E113 to E181 (to Meta I)
- Schiff base deprotonation (to Meta IIa)
- Helix motion and opening of the transducin binding crevice (to Meta IIb)
- Stabilising proton uptake onto E134 (to Meta IIb-H^+).

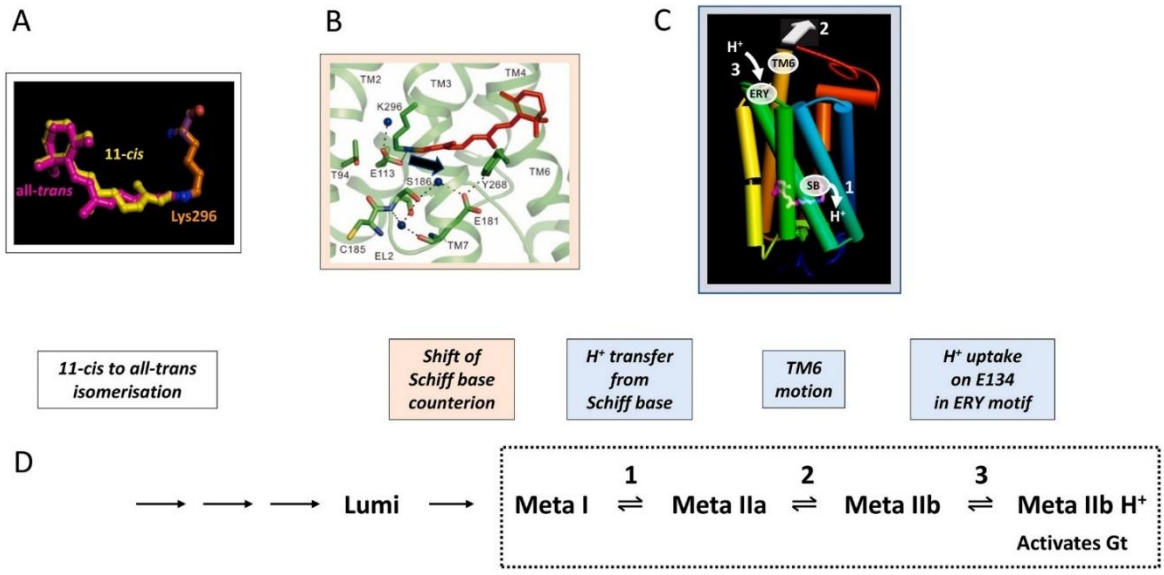


Fig. 17. Three-step activation pathway of rhodopsin.

A number of extremely rapid transitions occur prior to the formation of Meta I, but thereafter three important steps occur on a millisecond time-scale and lead to activation of the protein.

(A) Absorption of a photon induces *11Z*- to *all-E*-isomerisation of the retinal, and energy storage in a twisted *all-E*-Ret-PSB-Lys296 configuration.

(B) In the transition from Lumi to Meta I, changes in the position of *all-E*-retinal and structural changes in the binding pocket cause the protonated retinal Schiff base Ret-PSB to shift its centre of interaction from Glu113 on TM3 towards Glu181 in loop EL2.

(C, D) With the formation of Meta I, the Schiff base is susceptible to deprotonation, and the following reactions steps can proceed: (1) deprotonation of the Ret-Schiff base and protonation of the Glu113 of its complex counterion; (2) motion of TM6; and (3) proton uptake to the ERY domain. Note that the three Meta II sub-states (Meta IIa, Meta IIb and Meta IIb-H^+) are spectrally identical in the UV/Vis range (isochromic). For each step, the protein can either return to the preceding state or progress to the next state, so that after a few milliseconds all states are in equilibrium. In the course of the Meta conversions, two of the main constraints that keep the ground state inactive (the retinal Schiff base hydrogen bonding network and the TM3–TM6 ionic lock) are broken, one after the other, with the result that Meta IIb-H^+ represents an active state, R*, that can bind and activate the G-protein transducin.

In ROS, *11Z*-retinal is bound to opsin, forming rhodopsin. Absorption of a photon of light by rhodopsin causes photoisomerization of *11Z*-retinal to *all-E*-retinal and productive signaling, eventually leading to release of *all-E*-retinal from the chromophore-binding pocket of this opsin. *All-E*-retinal is reduced to *all-E*-retinol in a reaction catalyzed by NADPH-dependent *all-trans*-retinoldehydrogenases. Then, *all-E*-retinol must diffuse into the adjacent RPE cell layer. This process is enabled by esterification of retinol with fatty acids in a reaction catalyzed by lecithin : retinol acyltransferase. In the RPE, these *all-E*-retinyl esters tend to form intracellular structures called retinosomes. These esters serve as substrates for the RPE65 retinoid isomerase, which converts them to *11Z*-retinol, which is further oxidized back to *11Z*-retinal by retinol dehydrogenases. *11Z*-Retinal formed in the RPE diffuses back into the ROS because this reaction is virtually irreversible. This last step also completes the cycle by recombining *11Z*-retinal with opsin to form rhodopsin.

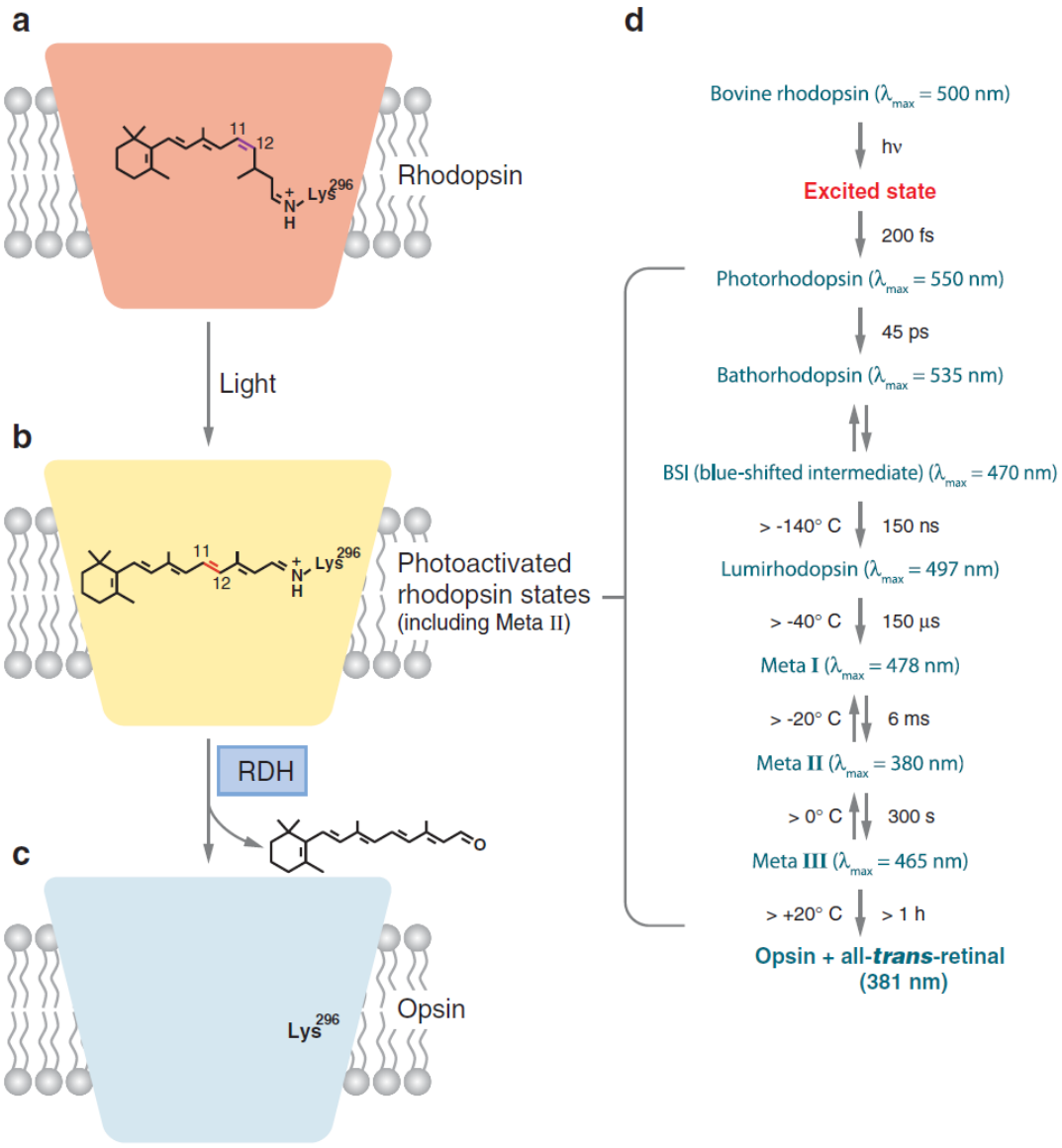


Fig. 18. Light-cycle of rhodopsin. Photoproducts of rhodopsin photolysis.

(*a*) Rhodopsin and *11Z*-retinal. Rhodopsin consists of a colorless protein moiety (the opsin) and the chromophore, *11Z*-Ret-PSB, which imparts a red color to rhodopsin. The chromophore, a geometric isomer of vitamin A in aldehyde form, is coupled to opsin via the protonated Schiff base at Lys296, located in the transmembrane domain of the protein. Bovine rhodopsin absorbs at λ_{max} = 498 nm.
(*b*) Photoactivated rhodopsin. Absorption of light by rhodopsin leads with high probability (~65%) to photoisomerization of the chromophore *11Z*-C11=C12 double bond to *E*-configuration. The probability of isomerization depends only modestly on the wavelength of the light. This reaction, one of the fastest photochemical reactions known in biology, produces multiple intermediates that culminate in the formation of the G protein–activating state, termed meta II, or Meta II.
(*c*) Opsin without chromophore. Ultimately the photoisomerized chromophore, *all-E*-Ret-SB, is released from the opsin as *all-E*-retinal and reduced to alcohol by short-chain alcohol dehydrogenases, such as prRDH, retSDR, and RDH12. The *all-E*-chromophore diffuses to the adjacent retinal pigment epithelium, where it undergoes enzymatic transformation back to *11Z*-retinal in a metabolic pathway known as the retinoid cycle (see fig. 18). Opsin recombines with replenished *11Z*-retinal to form rhodopsin.
(*d*) Reaction scheme of rhodopsin photoactivation. Upon absorption of a photon by rhodopsin and electronic excitation, fast isomerization of *11Z*-Ret-PSB to *all-E*-Ret-SB takes place. At body temperature, the Meta I and Meta II exist in equilibrium shifted toward Meta II. *In vitro*, further decay of rhodopsin to both opsin and free *all-E*-retinal or to Meta III is possible. *In vivo,* Meta III is not formed at significant levels because it decomposes in the presence of G protein transducing. In vitro, prolonged incubation of Meta II involves a thermal isomerization of the chromophore double bond with Lys296 to an *all-E*-15-*syn* configuration. This isomerization step is catalyzed by the opsin itself. On the left are shown maximal temperatures at which indicated intermediates can be trapped, and on

the right is time required for that particular transformation. In the brackets are λ_{max} of absorption for different intermediates [(Hofmann and Lamb, 2023)].

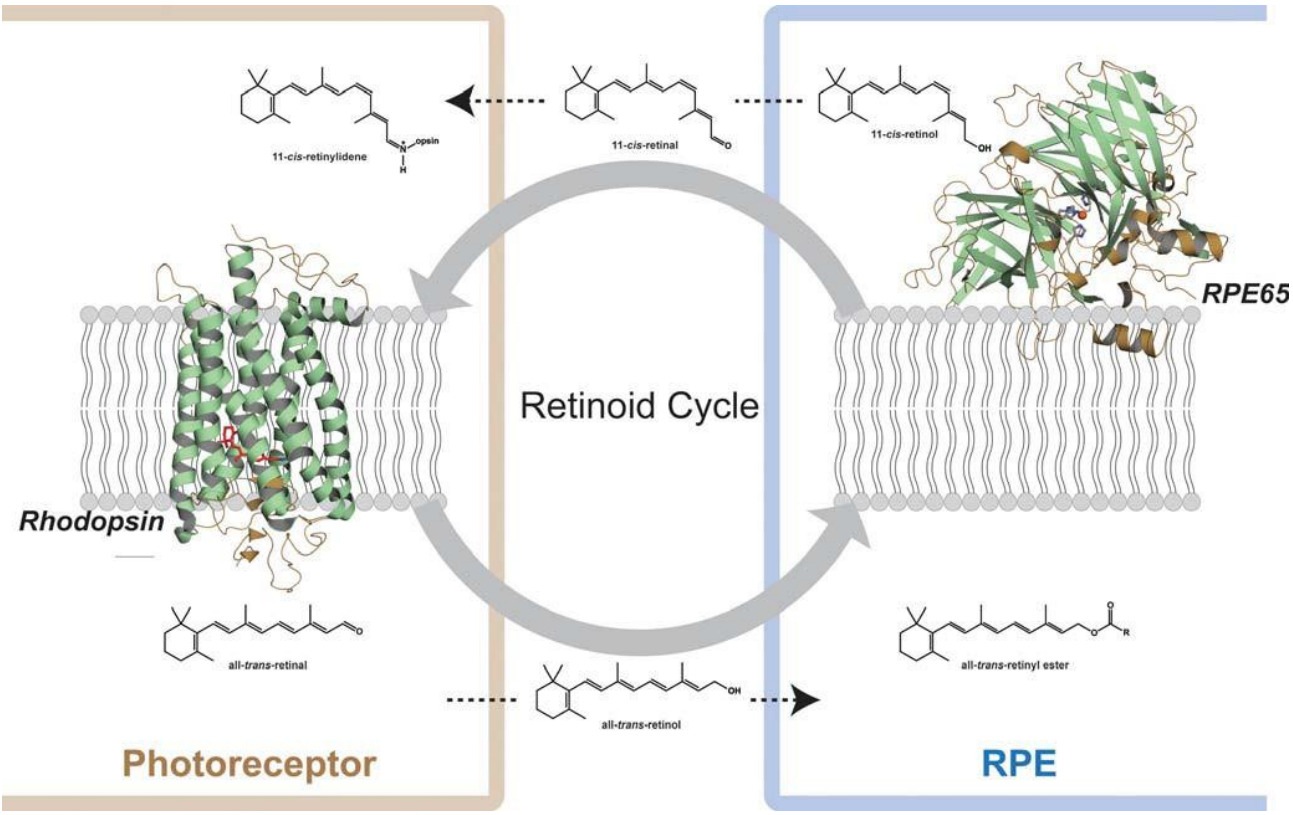


Fig. 19. Retinoid cycle regenerates visual pigment chromophore *11Z*-retinal [(Palczewski, 2012)**].**

2.5.5. Retinoid isomerase (RPE65)

Retinoid-binding protein, (RPE65) has now been recognized as the retinoid isomerase of the canonical retinoid cycle and it was identified in the early 1990s as a conserved, developmentally regulated, RPE-specific, microsomal membrane protein with an apparent molecular mass of 65 kDa. Rpe65−/− mice, exhibited early onset blindness and ocular retinoid abnormalities consisting of a lack of *11Z*-retinoids and overaccumulation of *all-E*-retinyl esters, indicating an important physiological role for RPE65 in the visual cycle. Furthermore, human RPE65 mutations were shown to cause Leber Congenital Amaurosis (LCA), a recessive, severe childhood blinding disease. These two important findings established a key role for RPE65 in retinal physiology (Kiser et al., 2014).

Subsequent treatments of the light-cycle of rhodopsins, their photoproducts, as well as, their function already have been detailed discussed and analyzed in a number of reviews and monographs, its are provided in the refs, cited in [(Hofmann and Lamb, 2023; Ostrovsky et al., 2023; Palczewski, 2012) and others]. They would exclude from present consideration in our database.

3. Spectral Properties of RBPs and its analogs

3.1. Spectral properties of RBPs

Retinal proteins (Retinal based proteins, RBP) - MRs or (Type I) and visual pigments (Type II) are chromoproteins that function either as sensors or as ion pumps in several species across all domains, Archaea, Eubacteria, and Eukarya. These light-sensitive proteins share a common fold of seven transmembrane (7TM) helices and bind a retinal chromophore through a protonated Schiff base (PSB) with a Lys residue located in helix seven. The absorption maxima of each RBP are modulated by the ionic environment of the PSB in the binding pocket.

The absorption of light by the light-adapted BRh form (which contains the *all-E*-15-*anti*-PSB chromophore) induces an ultrafast photocycle (complete in less than 30 ms), which starts with the isomerization of *all-E*-retinal PSB to the *13Z*-isomer (with the 15-*anti*-configuration) on the "vibrationally hot" I state followed by a thermal relaxation process involving conformational changes of the retinal and the protein. Light absorption initiates functions of both microbial and animal rhodopsins, and the wavelength dependence of the absorption efficiency determines the colors of the proteins. The structural features of the protonated Schiff base chromophore and the proton/ion conduction pathway regulate the absorption maxima of the pigments: ChRh, $\lambda_{max} \approx 470$ nm; SRhII, $\lambda_{max} \approx 487$ nm; BRh, $\lambda_{max} \approx 568$ nm; HRhs, $\lambda_{max} \approx 580$ nm; SRhI, $\lambda_{max} \approx 587$ nm; ESRh, $\lambda_{max} \approx 531$ nm.

Rhodopsin was shown to be a photosensitive membrane protein containing a vitamin A aldehyde (retinal) in the *11Z*-configuration, as a chromophore, covalently bound to ε-amino group lysine side chain via a protonated Schiff base (figs. 5, 9). Upon absorption of a visual photon, the chromophore isomerizes in femtoseconds into the *all-E*-configuration, which triggers a sequel of conformational changes in the protein, driving it within milliseconds into the active state, which triggers the photoreceptor cell towards a neural response. This response membrane hyperpolarization is processed by the bipolar and ganglion cells in the retina, and transmitted via the optic nerve towards the visual cortex, where it is translated within several tens of milliseconds into a visual response.

In the early 1980s, evidence was accumulating that rhodopsin was a member of a large family of G-protein coupled receptors (GPCRs). Subsequent studies demonstrated that GPCRs form a family of proteins with a close structural relationship, and the work on rhodopsin gained significance for the function of GPCRs in general. There are remarkable homologies of molecular structure and molecular mechanisms of activation (defined as a stimulus-induced structural change recognised by other proteins) and of inactivation, between vertebrate rhodopsin and other Class A GPCRs.

Animals employ in their eyes and other organs a different type of rhodopsin, which was optimized during evolution to perform a variety of roles pertaining to vision, sensation of light for nonvisual reasons (e.g., circadian rhythms, sensing dawn/dusk, determining the horizon, pupillary constriction, body color change, and seasonal reproduction), and direct utilization for the isomerization of retinal. These animal rhodopsins are GPCRs which are activated by light to catalyze GDP → GTP nucleotide exchange in heterotrimeric G proteins.

Opsins belong to the largest GPCR family (the family of rhodopsin-like GPCRs with ~700 members in humans) and can be roughly subdivided into ciliary and rhabdomeric opsins, which are further diversified by their G protein subtypes, and photoisomerases.

The absorbance band profiles of type-2 rhodopsins are quite similar (figs. 20, 21), but the position of the α-band varies strongly for the visual pigments. The vertebrate rod photoreceptor pigment rhodopsin has quite a broad range in its absorbance maximum (Rh1 subset, 440–520 nm), with fresh-water animals slightly red-shifted and marine animals blue-shifted depending on the depth of their habitat. Vertebrate cone pigments cover the entire visible spectrum, and can be divided into four subsets, the longwavelength (LWS, absorbance maximum range 520–640 nm), green (Rh2, 460–530 nm), blue (SWS2, 400–470 nm), and UV (SWS1, 350–450 nm) sensitive pigments. This classification is not only based upon spectral sensitivity, but also upon sequence similarity. Invertebrate visual pigments are more scattered over the visible region and can range from 340 nm up to 600 nm. Non-visual animal rhodopsins are scattered over the 340–550 nm region [(De Grip and Ganapathy, 2022; Ernst et al., 2014; Hofmann and Lamb, 2023; Leung and Montell, 2017)].

The spectra of cone visual pigments of human (563, 532, and 424 nm), mouse (511 and 358 nm), chicken (571, 508, 455, and 415 nm), salamander (615 (A2), 567 (A1), 444, and 367 nm), and goldfish (566, 516, 447, and 370 nm for retinal A1, and 617, 535, 454, and 382 nm for retinal A2) are shown (see figs. 20, 21). The absorption spectra of the pigments belonging to L, M2, M1, and S group are shown in red, green, blue, and violet, respectively. The spectra of pigments having retinal A2 is shown by broken lines [(Imamoto and Shichida, 2014)].

At the fig. 21 it was shown: **A** - absorbance spectra of the vertebrate cone and rod opsins; (**B**) typical dark state absorbance spectra (red curve) of a purified bovine rhodopsin. Both spectra exhibit a major peak (α-band) and a small satellite (β-band), both originating in the chromophore, and a γ-band near 280 nm, mainly originating in protein (Tyr, Trp) residues. The α-band derives from the whole conjugated polyene system (S0-S1) (see fig. 1), while the β-band derives from a smaller segment, and its intensity also depends on the torsion in the polyene chain. Upon short illumination

of the rhodopsin (**B**) in the presence of hydroxylamine, the liberated retinal is converted into retinaloxime (blue curve).

The length of the π-conjugated polyene chain in the retinal chromophore as well as the protonation of the retinal SB linkage determine the energy gap of the π–π* transition, so that the absorption of most rhodopsins is within the visible region (400−700 nm). While the chromophore molecule is usually the same in all pigments (retinal bound via a (protonated) Schiff base), the absorption maxima differ significantly, implying an active protein control of the energy gap between the ground and excited states of the retinal chromophore.

The mechanism of color tuning has fascinated researchers for a long time, and several factors have been determined to be responsible for it. The protonation state of the chromophore plays a crucial role in color tuning; the unprotonated Ret-SB absorbs in the UV region (λ_{max} ~360−380 nm), and this absorption is quite insensitive to the environment in contrast to the Ret-SBH$^+$ (Ret-PSB), which exhibits a large variation in absorption covering the entire visible light spectrum. Other factors defining the spectral tuning of individual rhodopsins are given by chromophore-protein interactions such as electrostatic interactions with charged and polar amino acids, termed electrostatic tuning and extensively studied, first using retinal analogues, and, later, site-directed mutagenesis.

Interactions of retinal with charged, polar, and aromatic amino acids play a role in changing the electronic energy levels, as do hydrogen-bonding interactions and steric contact effects. Strong hydrogen bonds can lead to charge transfer, and steric contacts can lead to a twist of retinal. All these tuning processes in concert shape the absorbance maxima of retinal in microbial and animal rhodopsins.

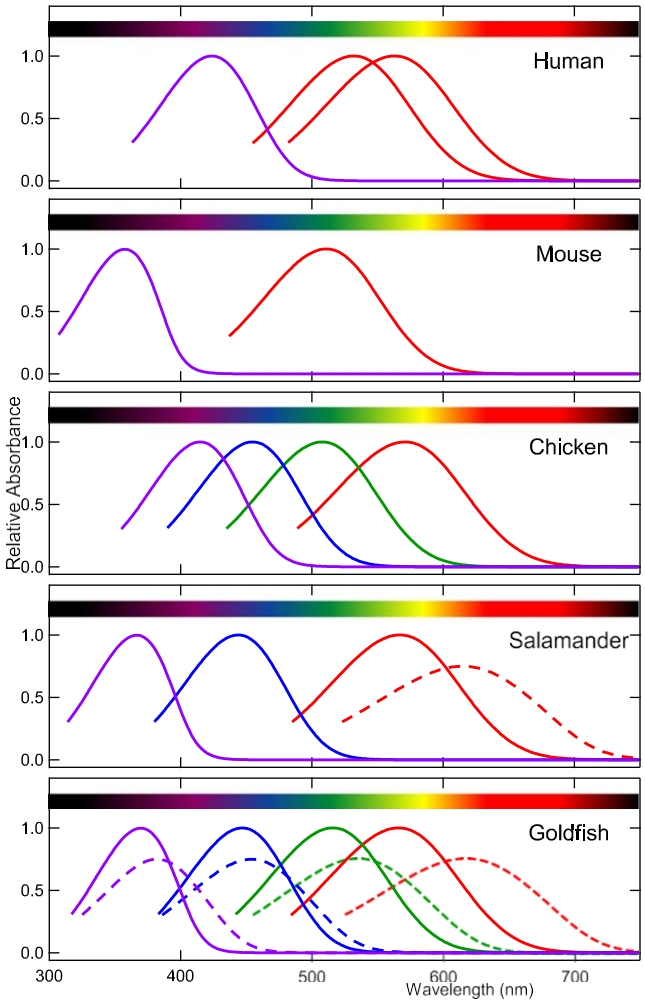


Fig. 20. Absorption spectra of cone visual pigments in representative animals.

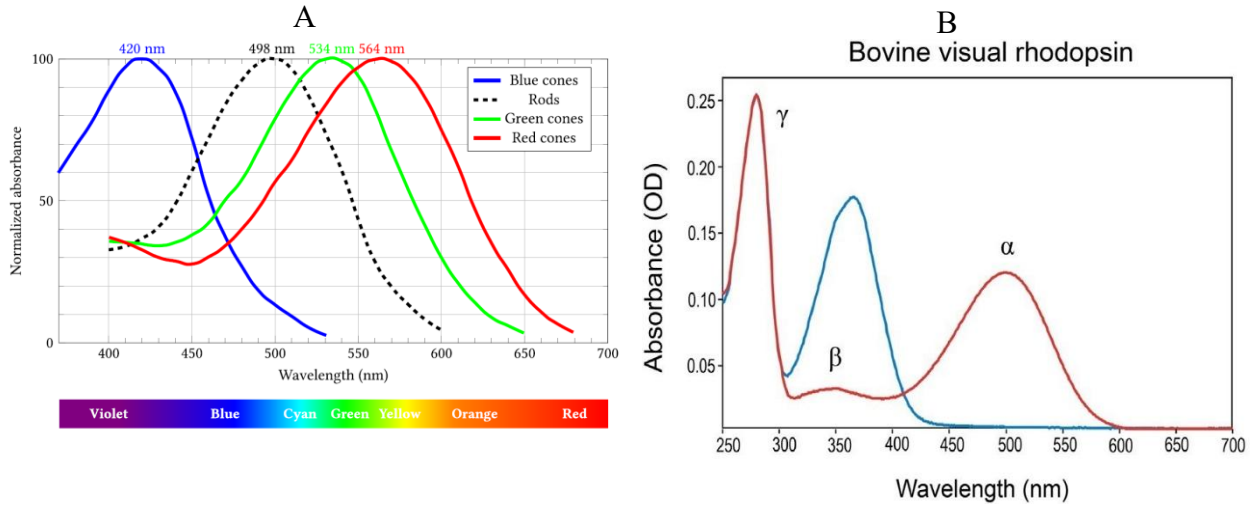


Fig. 21. Spectral characteristics of the vertebrate cone and rod opsins.

One of the most prominent factors in color tuning is the interaction of retinal with the counterion(s). For microbial rhodopsins MRs, however, the C6−C7 bond is 6-s-*trans*, although the C6−C7 6-s-*cis*-conformer is more stable in solution. As a consequence, an extended conjugation of π-electrons becomes possible from the polyene chain to the β-ionone ring, which presumably contributes to the considerable spectral red-shift observed in microbial rhodopsins. In fact, while absorbance spectra of protonated Schiff bases of *all-E*- and *11Z*-retinal in MeOH solution are similar (λ_{max} ~450 nm), most microbial and animal rhodopsins typically possess λ_{max} in 520−580 nm and 480−525 nm ranges, respectively, which can in part be explained by the differences in the C6−C7 bond conformation.

The energy difference between ground (S_0) and excited (S_1) states of the rhodopsin-like proteins was initially considered to depend upon the planarity of the chromophore (a 6-s-*trans*-conformation and an elongated, almost planar polyene chain for BRh), the distance between the Ret-PSB and the counterion, and the interactions of the chromophore with amino acid residues in the binding pocket (the “two-point” charge model, which suggested the presence of a negative charge close to the hydrophobic ring).

The term “opsin shift”, defined as the difference between the protein absorption maximum and that of model retinal N-butylamine-PSB hydrochloride in MeOH, was coined to quantify the effect of the apoprotein on the absorption maximum of the retinal chromophore.

We created and published the data-updated a novel version 3.0. "Properties of artificial bacteriorhodopsin analogs" database, where are presented our own results and data from other laboratories, obtained during a series of structural and functional studies of BRh [Khodonov A.A., Belikov N.E., Demina O.V. Properties of artificial bacteriorhodopsin analogs. From 1975 to 2025, Ed.: Varfolomeev S.D., Version 3, 2026; IBCP, Moscow, Russia 199 pp., access link: BRDT_3.0_final5.pdf].

3.2. Properties of visual pigments and its analogs

Procedures for the regeneration of visual pigment (interaction of opsin with *11Z*-retinal) and formation process of new pigment analogs (opsin with retinal analogs) already have been detailed discussed and analyzed in the literature [(Dawson, 2018)].

There are several ways for visual pigment analogs preparation:

(1) by *in vitro* regeneration of the rhodopsin from a synthetic retinal and opsin, the purified opsin being prepared from the bleached rod outer segment (ROS) membranes,

(2) by *in vitro* displacement of a bound synthetic retinal from the binding site by another retinal to which the opsin has a higher affinity,

(3) by *in vitro* incubation of bleached photoreceptors with a medium containing a synthetic retinal,

(4) by *in vitro* incubation of bleached, perfused retinae with synthetic retinals, and

(5) by *in vivo* delivery (i.p.) of synthetic retinals to animals maintained on a vitamin A-deficient diet.

The majority of pigment analogs discussed below in Table 1 were obtained *in vitro,* by incubation of synthetic retinals with bleached ROS, either in suspension or with ROS solubilized in a suitable detergent. The importance of the solubilizing agent cannot be underestimated. It can affect not only the success of pigment formation and yield of pigment, but can also influence the outcome of the studies carried out with the artificial pigments. Solubilizing in detergents can cause varying degrees of delipidation and ensuing changes in the structure of the apoprotein used for regeneration of the pigments. Further, solubilizing agents can affect the structural features and stability of the reconstituted systems. Digitonin has been the most commonly used detergent to solubilize opsin in early experiments. Recently many new detergents (alkyl glucosides, Triton X-100, CHAPS, and CHAPSO, ALO – Ammonyx LO) have also been employed. ROS (rod outer segment) suspensions have also been used.

Among the methods used to study the rhodopsin analogs, spectroscopic investigations occupy a prominent place. In addition to the classical approaches, such as UV/VIS, CD, resonance Raman, and FTIR spectroscopy, recent advances include the use of difference FTIR, two-photon absorption, and ^{19}F-NMR; ^{13}C-solid state NMR (MASS) spectroscopic techniques as well as innovations in the use of picosecond pulse techniques in monitoring the absorption and fluorescence of the pigments and bleaching intermediates [(Balogh-Nair and Nakanishi, 1990; Liu and Asato, 1990)].

Another important aspect is that the isomeric purity of the synthetic retinals used for the formation of pigment analogs must be checked by high-performance liquid chromatography (HPLC) directly prior to their incubation with opsin, and their stability in the incubation medium must also be ascertained. The bound retinals can be retrieved from the pigment analogs, via denaturation of the protein in such conditions that does not lead to the isomerization of the synthetic retinals, and their integrity can be checked by HPLC. The HPLC technique employing a diode array detector in the UV/VIS region of the spectrum, combined with microprocessor control, allows quick and efficient data comparison especially suitable for this purpose.

Synthetic methods for the retinal isomers and analogs synthesis can be roughly divided into stereoselective and non-stereoselective approaches. The latter include a combination of methods for preparation the most accessible isomer or mixture of them, photoisomerization or interaction with retinal isomerases (e.g., retinochrome), and preparative HPLC [(Borhan et al., 1999, 1997)].

3.2.1. History

Rhodopsin contains *11Z*-retinal as its native chromophore. Visual pigment analog studies began with the classical study of Wald, Hubbard, and co-workers where six geometric isomers of retinal *(all-E-, 13Z-, 11Z-, 9Z-, 9Z,13Z-,* and *11Z,13Z-*) were tested to react with the apoprotein opsin.

In the one of the first publication, where were tested of the binding site shape in visual pigment (cattle Rh) [(Blatz et al., 1968)] by *all-E*-isomer 5,6-dihidroretnal after light illumination of sample (isomers mix), it was shown that it to regenerate cattle opsin in light-sensitive ARh with λ_{max} 463 nm.

Beginning from the mid-1970s - till 2020s, with the involvement of several organic research groups, visual pigment analog studies reached a higher level of activity.

Hubbard and Wald established that the addition of *11Z*-retinal to the pigment that had been exposed to light resulted in regeneration of the rhodopsin pigment. These workers further demonstrated that *9Z*-retinal likewise formed a photosensitive pigment with "bleached" rhodopsin (opsin) and thereby created the first artificial rhodopsin pigment. Then was followed by the use of 3,4-didehydroretinal isomers by the same group and other modified retinals by Blatz and by Kropf see [(Yoshizawa, 1984)]. The observation that in addition to *11Z*-retinal only the structurally similar *9Z*-isomer formed a pigment analog see fig. 22, while the remaining four isomers *(all-E, 13Z-, 9Z,13Z-* and *11Z,13Z-)* either failed to give pigment or did not yield conclusive results led Wald and co-workers to conclude that the binding site of opsin is highly specific.

However, two independent observations in the mid 1970s prompted a reevaluation of this postulate. First, Nakanishi and co-workers showed by extraction of chromophore from the pigment analog derived from *9Z,13Z*-retinal that the pigment analog retained the original geometrical configuration. Second, four new isomers of retinal, all containing the hindered *11Z*-geometry, were shown to form new pigment analogs with absorption properties substantially blue shifted (λ_{max} 440 to 455 nm) from those of other known isomeric rhodopsins (480 to 500 nm).

Subsequently a complete study with all stable isomers of retinals (Table 1) revealed that opsin displayed little selectivity in accepting nearly all singly, doubly, and even triply bent isomers, the only exception being the *all-E-* and the *13Z*-isomers. A similar trend of lack of stereoselectivity extended into other structurally modified retinal analogs (Table 1) although the overall pigment yields were generally lower. Limited data on rates of pigment formation for different isomeric retinals are available in the literature. Therefore, based on the criteria of rates of reaction, the early statement of a highly stereoselective binding site of opsin is still valid. But within each set, the general trend of faster rate of reaction for *11Z-* and the structurally similar *9Z*-isomer is evident. Therefore, the initial structural incompatibility is reflected in reduced rates of reaction but not necessarily in yields of pigments.

In order to determine which structural features of the retinal molecule are essential to fill the binding site of rhodopsin, that we called functionally significant elements of the structure, FSES; thus in turn to use this knowledge in the design of a retinal analog molecule that has the minimum structure required to anchor the retinal into the protein binding site, competition studies were undertaken by following the rate of formation of pigments in the presence of small molecules that mimic portions of the retinal molecule [(Dawson, 2018; De Grip and Ganapathy, 2022; Yoshizawa, 1984)].

Most notable results and achievements were done in the Columbia group under the supervision of the Prof. K. Nakanishi and his collaborators, the pioneer study of examining the effect of methyl substituents at C13 and C14 on conformational properties of the chromophore in RBPs was followed by a steady stream of structurally diversive analogs (more 100 retinoids). They developed a strategy for creating of a chromophore analogs molecule, and studied ARBPs with retinals, modified at the ring-binding site: allenic, acyclic, and aromatic analogs and polyenic chain analogs; a strategy for creating a photoaffinic labeling protocols of a chromophore molecule in RBPs. Using photoaffinity techniques at low temperature and trapping of different intermediates, it was demonstrated that in the dark state as well as in the bathorhodopsin intermediate, the β-ionone ring is located in the vicinity of Trp-265 in the center of helix 6, whereas in the lumirhodopsin, Meta I, and Meta II intermediates, the ring is located in the vicinity of Ala-169 in helix 4.

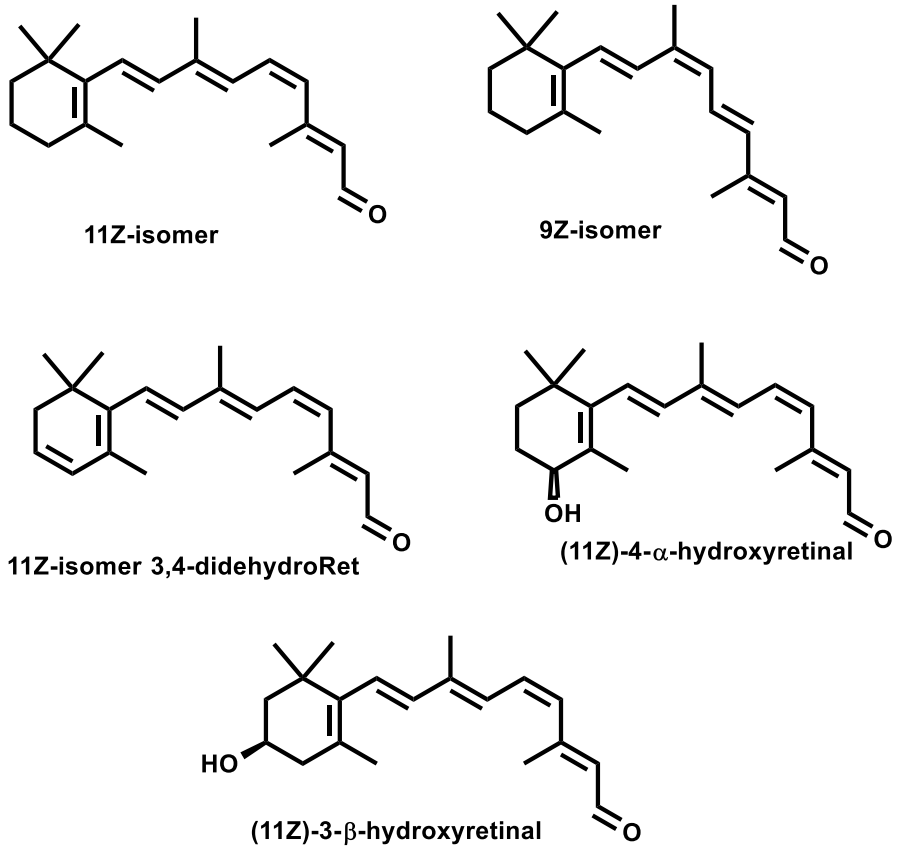


Fig. 22. Structures of the retinal derivatives [(Borhan et al., 1999; Fishkin et al., 2004)**]**

The important role that *11Z*-double bond isomerization plays in initiating the photochemically induced reaction in rhodopsin was demonstrated by studies of a series of *11Z*-locked artificial pigments. These results were interpreted by the gradual increase in the rotational flexibility along the

C11=C12 double bond from a 5- to 8-member ring see [(Balogh-Nair and Nakanishi, 1990; Derguini and Nakanishi, 1986; Lou et al., 2000)].

3.2.2. Opsin Shift (OS) and others parameters

The problem of quantitatively assessing the influence of the retinal molecule's functionally significant elements of the structure on the nature of the chromophore-protein interaction is quite complex. The following parameters were proposed for this purpose: Nakanishi in 1980 proposed the **opsin shift (OS**) and one of the most versatile series of retinal analogs to be made is the dihydro-retinals set in which one double-bond at a time is saturated and bound either *in vitro* or *in vivo* to various opsins. As it was shown, the protonated Schiff base (Ret-PSB), formed from retinal and butylamine absorbs at 440 nm in MeOH. However, bovine rhodopsin absorbs at 500 nm although the chromophore is the same; in other pigments and rhodopsins the maxima vary further, from 440 nm to 640 nm. The difference is attributable to the influence within the protein binding site; it was proposed to call this quantitative parameter, that is calculated as difference between λ_{max} the protonated Schiff bases of retinal analog with *n*-butylamine and the λ_{max} visual pigments.

1) Opsin Shift (OS) which is expressed in cm^{-1} (see fig. 23) [(Balogh-Nair et al., 1981; Crescitelli and Liu, 1988; Khodonov, 1997; Nakanishi et al., 1980)].

Later others ones, a new criterion, also reflecting influence within the protein binding site in RBP, were proposed by Prof. Liu, which allows for a more adequate assessment experimental data:

2) the **total bathochromic shift** (**∑RS) = (OS) + (ΔSB) + (ΔSBH$^+$)**, (**cm^{-1})** which characterizes the overall spectral shift of the analogue relative to the unprotonated aldimine of the *all-E*-isomer of natural retinal;

3) and a new criterion **Percent red shift**; **PRS**, **(%)** [(Liu et al., 1993; López et al., 2005)].

Opsin Shift (OS, cm^{-1}) = 1/ λ_{max} Ret-SBH$^+$ - 1/ λ_{max} (ARh)

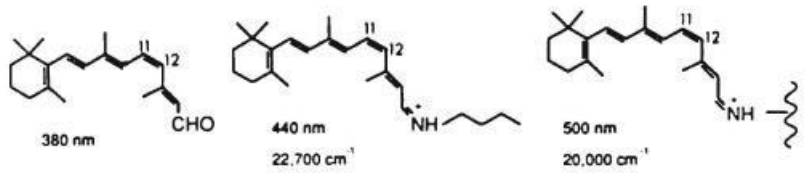


Fig. 23. Rh Opsin Shift (OS, cm^{-1}) = 1/ λ_{max} Ret-SBH$^+$ (AR) - 1/ λ_{max} (ARh) = 2700 cm^{-1}

Total red shift, (∑RS) = (OS) + (ΔSB) + (ΔSBH$^+$), (cm^{-1})

Certain components reflect the contributions of:

- **(OS): (OS) = 1/ λ_{max} SBH$^+$ (AR) - 1/ λ_{max} (ARh)** - interactions with the microenvironment of the RPB chromophore center;

- **(ΔSB): (ΔSB) = 1/ λ_{max} SB (AR) - 1/ λ_{max} SB (RetCHO) -** shifts in the position of λ_{max} upon replacement of natural retinal in unprotonated aldimine by its analogue;

- **(ΔSBH$^+$): (ΔSBH$^+$) = 1/λ_{max} SB (AR) - 1/λ_{max} SBH$^+$ (AR)** - shifts in λ_{max} accompanying protonation of the aldimine analogue of retinal.

Nakanishi in the dihydroretinal series (see fig. 24), it is seen that the **OS** has the largest value of 5300 cm^{-1} for 11,12-dihydroretinal, this analog with the shortest chromophore. These data strongly suggest the presence of significant electrostatic interactions in the vicinity of the chromophore, from C-11 to the nitrogen atom. Semi-empirical calculations on this trend indicated that the absorption maxima of rhodopsin and analogs could be accounted for by placing, in addition to the counter-anion of the protonated Schiff base, another negative charge near C-12 and C-14 of the polienic chain; these experimental and theoretical results led to the external point charge model (fig. 25) [(Nakanishi, 1991; Nakanishi et al., 1980, 1979)].

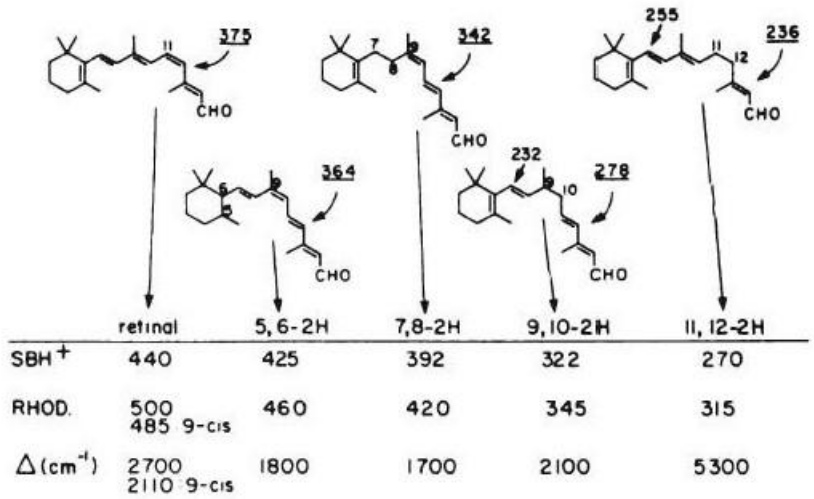


Fig. 24. Opsin shift (OS, cm^{-1}) in Rhodopsins and Dihydrorhodopsins series

With the exception of the substituent steric effects, all other factors (functionally significant elements of the structure, **FSES**) affecting spectral shifts are associated with changes in the intrinsic properties of the chromophore in going from a neutral retinal to its **SB** and to its charged **PSB** form in the protein. An additional factor contributing to the red-shift is the protein perturbation on different retinal analogs. The relative magnitude of protein perturbations had previously been compared under the concept **OS**. For the purpose of comparing effectiveness inducing red-shift for various chromophore derivatives, prof. R.S.H. Liu and colleagues demonstrated and pointed out earlier the inadequacy of the **OS** concept and introduced the new concept of **percent red shift (PRS)** a slightly modified form is expressed as:

Percent red shift, **PRS: PRS = [1/ λ_{max} (AR) - 1/λ_{max} (ARh)] / [1/λ_{max} (AR)] x 100 (%).**

External point charge model for bovine rhodopsin

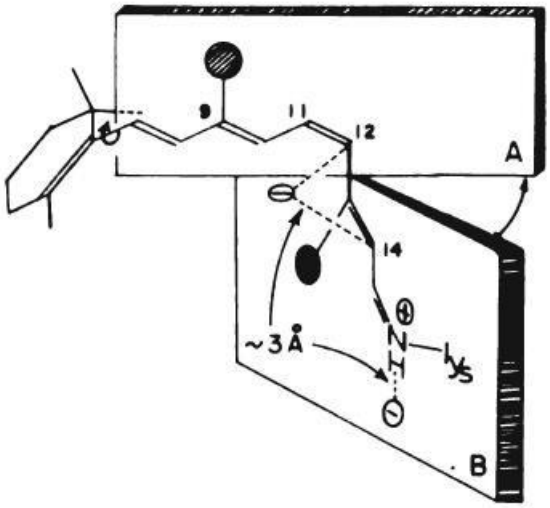


Fig. 25. External point-charge model for bovine rhodopsin molecule.

From the early 1970s - till 2010s the research group of Prof. R.S.H. Liu and co-workers at Hawaii established a photochemical entry to the previously unknown sterically crowded. This finding paved the way for the synthesis of other missing retinal geometric isomers. The unexpected finding of stable pigment formation of *11Z*-isomers of retinal not only revived the interest in reexamining the stereospecificity of the binding site of opsin, but also launched an independent program of visual pigment analog studies at Hawaii.

Prof. Liu and his colleagues demonstrated with success two variants stategy of creation of *Z*-geometry in compounds in the vitamin A series: stereoselective and combination non-stereoselictive

variants with preparative HPLC. This effort culminated in the successful synthesis of the last two hindered isomers (*all-Z-;* and *7Z,9Z,11Z-)* of vitamin A in 1983. Since that time, have shown that all the *Z*-isomers of retinal, with the exception of *13Z-,* will form pigments of varying stability.

R.S.H. Liu's researches on retinal analogs have been pioneering in understanding the **(OS)** (bathochromic shift) of visual pigments, where the absorption maximum moves to longer wavelengths to enhance sensitivity: series of the alkyl-, fluoro- and other halogeno-substituted, aromatic and azulenic analogs. It is necessary to separately note the development of the method ^{19}F-NMR for fluorolabelled RBPs study. The cyclohexyl ring could also be replaced with aromatic and heteroaromatic rings or removed in several modified retinals without affecting the regeneration yield of rhodopsin analogs, provided that the aromatic ring had substituents in positions *ortho* to the polyene side chain.

In Leiden group of Prof. J. Lugtenburg and Prof. W.J. de Grip with collaborators have obtained the following outstanding results:

1) a strategy for creating a polyene chain of a chromophore molecule was developed, including a two-fold repetition of a combination of the Horner-Emmons olefination procedure of suitable carbonyl precursors using C5-phosphonate anions with a terminal nitrile function, followed by reduction of the nitrile function using DIBAL;

2) the synthesis of a numerous sets of diverse retinal analogs was conducted;

3) a strategy for introducing stable isotopes (^{2}H, ^{13}C and ^{15}N) into virtually any given site of the retinoid molecule and in the protein parts and the preparation RBP analogs based on them was developed;

4) their investigation of RBP analogs was carried out by NMR or FTIR spectroscopy and other technics;

5) for the first time, the configuration of the ring - polyenic chain in chromophore group was established and proven in MRs [(De Grip and Ganapathy, 2022; De Grip and Lugtenburg, 2022)].

Prof. Crouch R.K. and her co-workers (Medical University of South Carolina) studied stereo and chiroptical requirements of the binding site RBPs (see fig. 26) with retinal analogs and showed that rhodopsin regeneration is inhibited best by compounds which mimic the structure of *9Z*- and *11Z*-retinal up to C-11, thus suggesting the presence of two binding sites within the receptor - one for the β-ionone ring and another for the protonated Schiff base.

Comparison of Binding Restraints of Rhodopsin and Bacteriorhodopsin

	Rhodopsin	**Bacteriorhodopsin**
Isomeric specifications	All-*cis* isomers except 13-*cis*	13-*cis*, all-*trans* only
Ring portion: methyl groups	At least *one* required	None required
Cyclic ring	Not required	Not required
Bulky substituents	Limits binding	No limitations
Side chain: length	Length between aldehyde and ring methyl groups critical to pigment formation	Side chain lengths of eight to eleven carbons adequate
C_9 and C_{13} methyl group	Not required; absorption sensitive to C_9 substitution	Not required; C_{13} methyl may effect proton pumping
Bulky substituents	Moderate tolerance	Low tolerance

Fig. 26. Comparison of binding restraints of Rhodopsin and Bacteriorhodopsin [(Crouch, 1990)**]**

However, incubation with acyclic analogs showed that the cyclohexyl ring is not essential for pigment formation; rather a methyl group corresponding to the C-1 or C-5 methyl groups in retinal ring is required. In the addition they to develop methods for spin labelled retinoids and RBPs preparation and study a serie of RBPs with modified trimethylcyclohexenic ring in the chromophore.

In addition to the above-mentioned groups and laboratories, it is necessary to note the great contribution of individual researchers mentioned below at certain stages of this field of photobiology and bioorganic chemistry of the retinoid and RBPs: Prof. A de Lera with co-workers (Spain); Japanese researches (Prof. M. Ito, Prof. H. Kandori, Prof. T. Yoshizawa, Dr. K. Yoshihara and others); Prof. Spudich J. L. group (Dr. Sineshchekov, Dr. O. A., Govorunova E. G.); (Dr. Gushchin I., Dr. Gordeliy V.) and many other persons.

3.3. Summary results

[(Fishkin et al., 2004) **and others refs]**

Properties of visual pigments and its analogs (ARhs) already have been discussed in detail and analyzed in a multiple number of reviews and monographs, here we presented them in [see refs and remarks in the Table 1].

The *11Z*-geometry of the retinylidene chromophore keeps the partially active opsin protein locked in its inactive state (inverse agonist). Several ARs with defined configurations and stereochemistry, and containing various reporter groups, have been incorporated into the apoprotein (opsin) to give ARhs. These incorporation results along with the spectroscopic properties of the ARhs clarify the mode of entry of the chromophore into the apoprotein and the biologically relevant conformation of the chromophore in the rhodopsin binding site.

In addition, difference UV, CD, and photoaffinity labeling studies with a 3-diazo-4-oxo analog of *11Z*-retinal have been used to chart the movement of the retinylidene chromophore through the various intermediate stages of visual transduction. This is the first of such studies performed on a GPCR.

The following mechanism of this dark activity was proposed based on resuls with 13-desmethyl-**Ret**, 11,12-dihydro-13-desmethyl-**Ret**, and a further analog, locked *11Z*-6-membered ring-retinal. The opsin cavity is divided into three domains, site I for the ring moiety (A), site II for the polyene chain (B), and site III for the protonated Schiff base (**PSB**) (C) [(Fishkin et al., 2004)].

Enantioselective binding studies with 6-*s*-α-(16,7)-locked retinal and *11Z*-locked analog β-cyclopropyl-cycloheptatrienylidene retinal defined the twist sense of the retinylidene chromophore in dark adapted rhodopsin (see fig. 27), and these results generally are in agreement with those found from the crystal structure of rhodopsin. Incorporation of a cyclopropyl ring at the C11/C12 bond yields a retinal analogue with a rigid structure where the twist around the 12-*s* bond is predetermined by the absolute configuration of the analogue. Namely, α- and β-enantiomers adopt opposite twists around the C12/C13 bond; it was therefore expected that binding of the certain enantiomer to bovine opsin with the right absolute geometry would occur preferentially over the other enantiomer.

Analysis of transient dark activity in pigments containing 13-desmethyl-**Ret**; 11,12-dihydro-13-desmethyl-**Ret**; and locked *11Z*-6-membered ring-retinal chromophore analogs reveal a potential mechanism for entry of retinoids into opsin which involves three discrete binding sites (see fig. 28). Moreover, data obtained with *11Z*-7-membered ring- and *11Z*-8-membered ring - retinals seems to suggest the existence of a potential binding cleft on opsin which can detect slight changes in the bottom portion of the *11Z*-retinal chromophore.

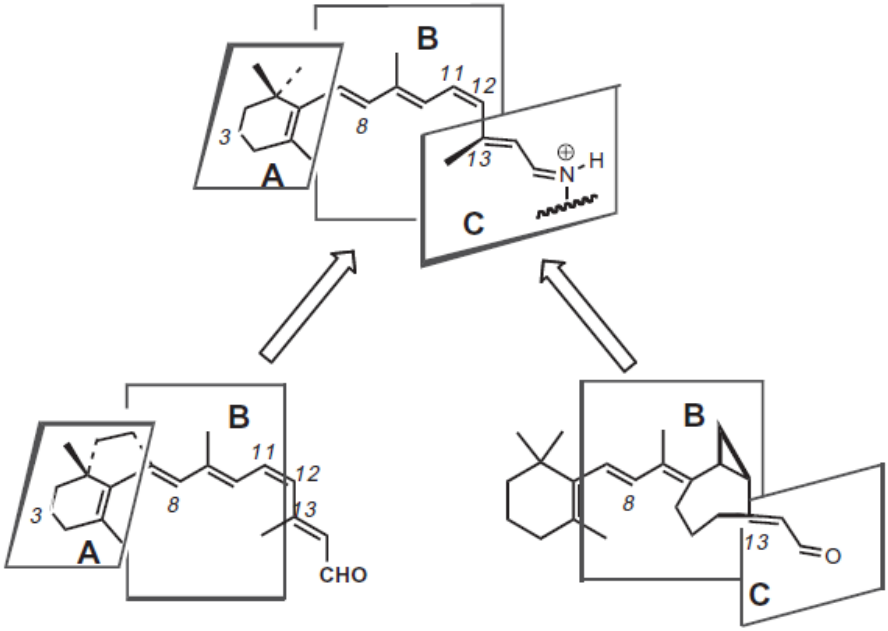


Fig. 27. Chromophore conformation in dark Rh based on combined data from binding studies opsin with 6-*s*-α-(16,7)-locked retinal and *11Z*-locked analog β-cyclopropyl-cycloheptatrienylidene retinal [(Fishkin et al., 2004)].

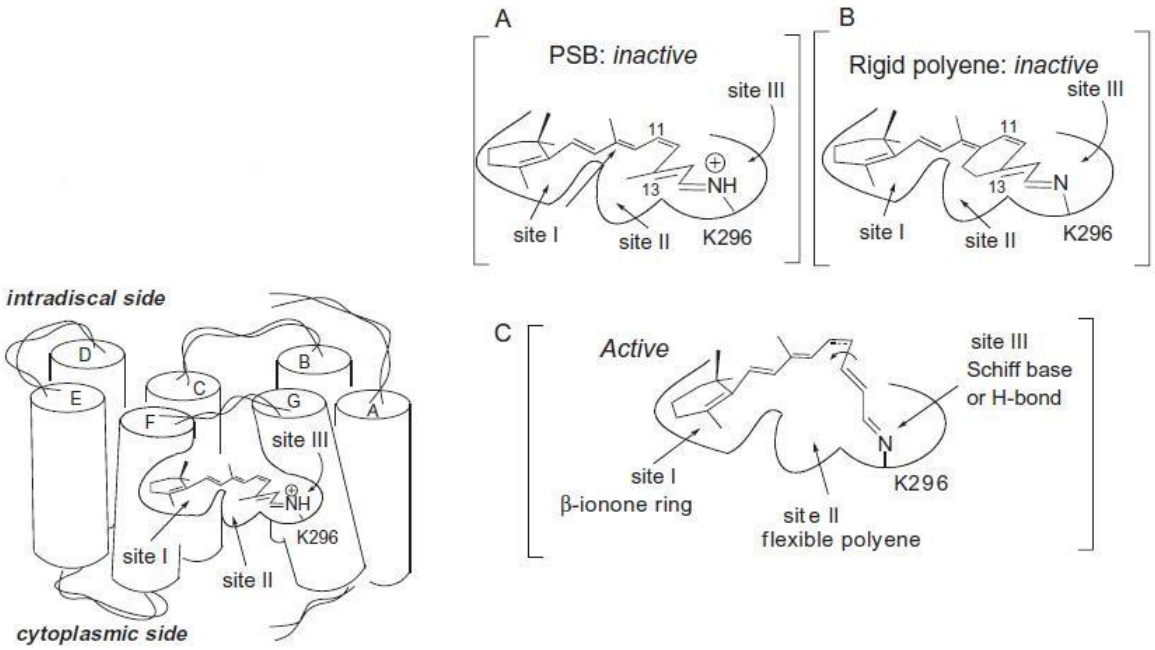


Fig. 28. Transient dark activity in opsin studied with **Ret**, 11,12-dihydro-13-desmethyl-Ret, and locked *11Z*-6-membered ring-retinal chromophore analogs [(Fishkin et al., 2004)]

Sites I, II, and III shown bound to A) native chromophore (inactive); B) locked *11Z*-6-membered ring-retinal (inactive); C) 13-desmethyl-**Ret**, / 11,12-dihydro-13-desmethyl-**Ret**.
Step I: The β-ionone ring of *11Z*-retinal settles into opsin site I first. This is based on the observation that pretreatment of opsin with β-ionone completely blocks any formation of a **PSB** when *11Z*-retinal is applied.
Step II: Transient dark activity requires Schiff base formation, but protonation of the imine nitrogen immediately destroys the transient activity. When **SB** formation is blocked by dimethylation of Lys296 there is no transient activity. Moreover, it was found that as **PSB** formation in the 13-desmethyl-**Ret** pigment increases, there is a corresponding decrease in transient transducin activation.
Step III: As the chromophore enters the binding site with its cyclohexene ring in site I and the unprotonated Schiff base in site III, the polyene enters site II and adjusts its torsional angles. It is at this intermediate stage when the flexible polyene chain is about to settle into site II that transient activity is detected. Interesting, the 13-desmethyl-**Ret** pigment shows a characteristic Meta-II-like CD (negative band around 280 nm during the dark activity period).

The ring-locked and rigid locked *11Z*-6-membered ring-retinal chromophore analogs cannot achieve this and hence induces no dark activity. In addition, no dark activity has been reported for *11Z*-retinal; an explanation for this is that since the binding of *11Z*-retinal is 10-fold faster than 13-desmethyl-**Ret**, the retinal and opsin rapidly attain the inactive state.

The results of these research groups work's have been summarized in number reviews, books and monographies [(Dawson, 2018; Derguini and Nakanishi, 1986; Liu and Asato, 1990; Yoshizawa, 1984)].

4. Basic directions in the retinal molecule modification strategy

In 1972, the "Rhodopsin program" was created in the USSR under the leadership of Academician Yu.A. Ovchinnikov. Its main goals were to develop methods for determining the structure of light-sensitive RBPs: bacteriorhodopsin (BRh) and the visual pigment rhodopsin (Rh), and to comprehensively study their functions. The first participants in the program were teams from four laboratories: the laboratory of Academician Yu.A. Ovchinnikov himself at the Institute of Bioorganic Chemistry of the USSR Academy of Sciences, Academician V.P. Skulachev at the A.N. Belozersky Institute of Physicochemical Biology of the M.V. Lomonosov Moscow State University,

L.P. Kayushin at the Institute of Biophysics of the USSR Academy of Sciences in Pushchino, and Academician M.A. Ostrovsky at the Institute of Chemical Physics of the USSR Academy of Sciences.

The main goals and objectives of the “Rhodopsin project”

1. Selection of target proteins from available RBPs: MRhs or Rh visual pigments;

2. Development and research of methods for culturing/isolating RBPs from producer biomass or from animal models; obtaining mutants and developing methods for creating recombinant RBP producers;

3. Determination of RBP structural parameters: amino acid composition, primary and tertiary polypeptide sequences, the binding site of the retinal molecule to the polypeptide chain, the isomeric composition of the chromophore group, production of 3D crystal preparations suitable for X-ray diffraction analysis, and obtaining and decoding high-resolution 3D structures of RBPs using X-ray diffraction and other methods;

4. Determination of the functional properties and characteristics of target proteins: study of the photochemistry and electrogenesis of MRhs and their analogs; study of the biophysical and physiological aspects of visual pigment function; signal transduction pathways from visual rhodopsin to the brain, etc;

5. Development of methods for obtaining RBP models: a) mutants with single- and multi-point amino acid substitutions along the MRhs polypeptide chain; b) MRhs derivatives modified along the polypeptide chain with various types of reporter groups; c) model MRhs analogs with a modified chromophore group; d) aldimines of retinal analogs with various amino components: amino acids and/or polypeptides;

6. Search for practical applications of MRhs in various fields.

An excellent reviews of the “Rhodopsin project” was recently published for its 50th anniversary [(Ostrovsky, 2024; Ostrovsky et al., 2023)].

Our research team participated in the implementation of the “Rhodopsin project” in close collaboration with a number of other scientific organizations and universities (M.M. Shemyakin and Yu.A. Ovchinnikov Institute of Bioorganic Chemistry of the RAS; A.N. Belozersky Institute of Physicochemical Biology of the M.V. Lomonosov Moscow State University; Photochemistry Center of the RAS; M.V. Lomonosov Moscow Institute of Fine Chemical Technologies (MITKHT); Institute of Biophysics of the RAS; etc.).

The main areas of our group's research included: 1) the development and practical implementation of an integrated approach to the study of structure-function relationships in RBP through chemical modification of functionally significant elements of the retinoid molecule structure.

The overall objective was to provide other groups participating in the project with sets of reference compounds - individual retinoid isomers, their derivatives and analogs, as well as ARs - necessary for structural studies of RBPs.

1. Developing synthetic routes for retinal isomers and analogs and methods for their isolation, producing sample compounds;

2. Studying the interaction of MRh family apoproteins with the obtained retinal analogs;

3. Synthesizing model compounds - aldimines of retinal analogs.

To implement this, it was necessary to solve the following set of problems:

1. Searching for and creating new synthetic approaches to various modifications of the retinoid molecule and methods for their separation, producing samples in quantities sufficient to support the entire cycle of subsequent experiments;

2. Studying the physicochemical properties and spectral characteristics of the synthesized compounds;

3. Studying the interaction of MR family apoproteins with the obtained retinal analogs;

4. Synthesis of model compounds – aldimines of retinal analogs;

5. Studying the effects of various modifications of the chromophore groups of bcteriorhodopsin (BRh) from the purple membranes of *H. salinarum* and proteorhodopsin (ESRh) from *Exiguobacterium sibiricum* on their photochemical properties and proton transport, and modeling the spatial constraints of the chromophore binding site in these proteins;

6. Creation of the "Properties of artificial bacteriorhodopsin analogs" database, version 3.0.

In the USSR and later in Russia, the chemistry and biochemistry of retinoids were limited to a few scientific schools and laboratories at several research institutes and universities. The foundation for this research area was laid by Professor N.A. Preobrazhensky's work in the 1950s and 1960s at the M.V. Lomonosov Moscow Institute of Fine Chemical Technologies (MITKHT). This work was closely linked to the vitamin industry, implemented at the Belgorod Vitamin Plant, and aimed at developing and improving the domestic vitamin industry.

The development of Professor N.A. Preobrazhensky's scientific legacy in the synthesis of vitamin A and its derivatives led to the formation of two scientific schools: 1) at the Department of Biotechnology at the MITKHT and 2) at the Laboratory of Polyene Compounds at the Scientific Production Association "Vitamins" (Professor G.I. Samokhvalov). After 1965, this topic was further developed at the Department of Biotechnology of the MITKHT in the works of the co-workers of prof. N.A. Preobrazhensky: Academician of the RAS V.I. Shvets, professors E.N. Zvonkova, A.A. Khodonov, associated professors B.I. Mitsner, E.N. Karnaukhova and others (now from the Department of Biotechnology and Industrial Pharmacy of the Russian Technical University - MIREA). Among other achievements in this area, it is necessary to note a series of works devoted to the synthesis of retinoids and their analogues, carried out under the supervision of prof. S.M. Makin at the Department of Organic Chemistry of the MITKHT in the 1970s - 1996s.

After the mid-1990s, it was successfully continued at Lab. 0501 of the N.M. Emanuel Institute of Biochemical Physics of the RAS (under the direction of Corresponding Member of the RAS, Professor S.D. Varfolomeev and Professor A.A. Khodonov). This laboratory conducted comprehensive, systematic research aimed at developing a synthetic methodology for the preparation retinoids of various structures, as well as analyzing the effects of modifications of individual structural elements of the retinoid molecule on the functioning of various retinoid-protein complexes.

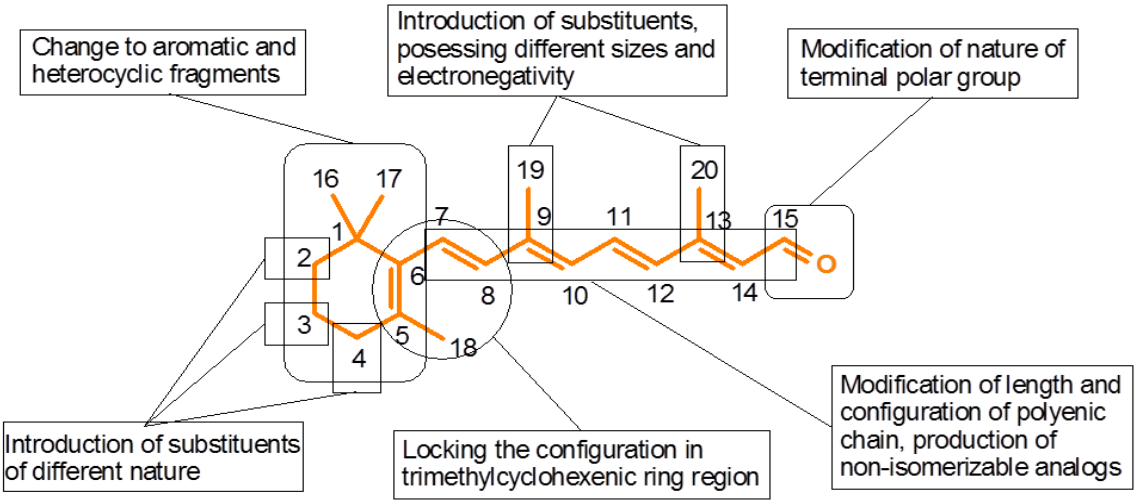


Fig. 29. Basic directions in the retinal molecule modification strategy

All retinal molecule modification variants were divided in next charts:

A. Natural chromophore - retinal and its isomers
B. Terminal polar group modification
C. Polyenic chain modification
D. Alteration of the bond types and its disposition in the chromophore polyenic chain
E. Alteration of the polyenic chain length and bond disposition and terminal group types
F. Alteration or locking of the bond configuration. Non-isomerizable analogs
G. Alteration of the trimethylcyclohexenic ring. Ring modification
H. Alteration of the trimethylcyclohexenic ring. Replacement ring to aromatic or heterocyclic fragments
I. Alteration of the trimethylcyclohexenic ring. Acyclic analogs
J. Miscellaneous modifications
K. Labelled Rh derivatives (radioactive, photo-affinic, fluorophoric, heavy-atom, paramagnetic (SL), ionophoric and photochromic probes)

During the course of the research cycle implemented within the framework of the “Rhodopsin program”, it was developed novel methods for synthesizing retinoids with virtually any given

structure, including those containing various types of reporter groups isotopic, fluorescent, spin, affinity, photoaffinity and electron-dense labels, as well as fluorine atoms.

Below, we present results obtained by the various authors during a series of structural and functional studies of ARh. In this database, a summary of these results are presented [(Liu and Asato, 2003, 1990; Liu and Liu, 2011) and others] and see Table 1.

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Table 1. Properties of visual pigment analogs

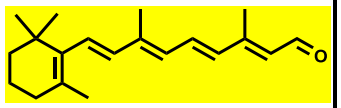
No	Structure	Isomer	Target	λ_{max} (nm); ε 10^{-4} (M^{-1} cm^{-1})				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
A. Natural chromophore — retinal and its isomers														
1.		all-E-	Cattle Rh	380 381 (4.86) 383[a] (4.29) 368[c]			NO							(Yoshizawa, 1984)
		all-E-	Octopus Rh			445	510			2864			stable photoproduct of rhodopsin, acid metarhodopsin λ = 510 nm; since the pH is 7.0 and the pK of the acid-alkaline transition is about 9.5.	(Koutalos et al., 1989)
		all-E-	Human red cone opsin in COS-1 cells										Human red cone opsin was transiently expressed in COS-1 cells. AR tested on the human red cone opsin's ability to activate transducin. Ability of opsins to activate transducin was measured using a radioactive filter-binding assay as described previously. All-E-retinal is agonist.	(Kono and Crouch, 2011)

Table 1. Properties of visual pigment analogs

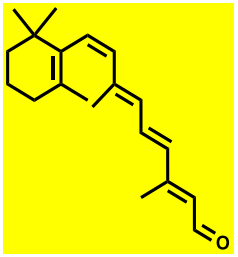
No	Structure	Isomer	Target	λ_{max} (nm); ε 10^{-4} (M^{-1} cm^{-1})				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		all-E-	Cattle Rh	380			NO						in ROS suspension or D.	(Liu and Asato, 1990) (Liu and Asato, 1984) (Matsumoto et al., 1980b)
		all-E-	ApoRetinochrome	381		444	496			2400			CD ARh 330 (-) / 495 (+).	(Kinumi et al., 1993)
		all-E-	ApoRetinochrome				495						Aporetinochrome in 0.67% digitonin at pH 6.8.	(Seki et al., 1985)
2.		7Z-	Cattle Rh	359[c] 377[a] (3.8)			450						Yield 40% in D.	(Yoshizawa, 1984)
		7Z-	R-photopsin from chicken red-sensitive cone visual pigment (iodopsin)			432	463 CHAPS-PC			1550			$t_{1/2}$ half-life of pigment formation < 0.4 min. Like scotopsin, R-photopsin failed to form a pigment with 13Z- or all-E-retinal.	(Fukada et al., 1990)
		7Z-	scotopsin from bovine rod pigment - rhodopsin			432	451 CHAPS-PC 450 D			975 926			$t_{1/2}$ half-life of pigment formation 204 min. Like scotopsin, R-photopsin failed to form a pigment with 13Z- or all-E-retinal	(Fukada et al., 1990)

Table 1. Properties of visual pigment analogs

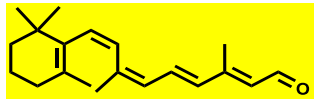
No	Structure	Isomer	Target	λ_{max} (nm); ε 10^{-4} (M^{-1} cm^{-1})				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		7Z-	Cattle Rh				+						The photochemical and subsequent thermal reactions of 7Z-rhodopsin prepared from cattle opsin and 7Z-retinal were investigated by low-temperature spectrophotometry and laser photolysis, and compared with those of 11Z-rhodopsin prepared from cattle opsin and 11Z-retinal.	(Shichida et al., 1991)
		7Z-	Cattle Rh	359[c] (4.41) 377[a] (3.8)			450				unstable		Yield 30-70% in ROS suspension. In 1% digitonin solution. Yield 51% in ROS suspension. K_2 1 (M^{-1} s^{-1}) in ROS. CD ARh 330 (+) / 450 (+).	(Liu and Asato, 1990) (Liu and Asato, 1984) (Matsumoto et al., 1980b)
3.		7Z,9Z-	Cattle Rh	351[c]			460							(Yoshizawa, 1984)
		7Z,9Z-	Cattle Rh	351[c] (4.25)			460				unstable		Yield 30-70% in ROS suspension. Yield 41% in ROS suspension. K_2 1.3 (M^{-1} s^{-1}) in ROS.	(Liu and Asato, 1990) (Liu and Asato, 1984)
4.		7Z,9Z, 11Z-	Cattle Rh				NO							(Yoshizawa, 1984)

Table 1. Properties of visual pigment analogs

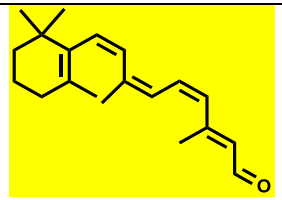
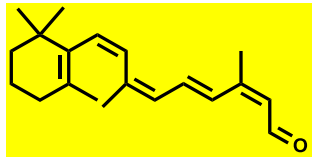
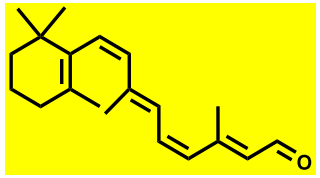
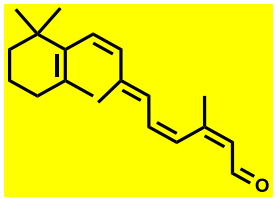
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		7Z,9Z, 11Z-	Cattle Rh	346[c] (2.2)			462						Yield 30-70% in D. Yield 35% in ROS suspension. K_2 0.02 ($M^{-1}\,s^{-1}$) in D. CD ARh 458 (+).	(Liu and Asato, 1990) (Liu and Asato, 1984)
5.		7Z,9Z, 13Z-	Cattle Rh	346[c]			455							(Yoshizawa, 1984)
		7Z,9Z, 13Z-	Cattle Rh	346[c] (3.66)			455				unstable		Yield 30-70% in D. Yield 40% in ROS suspension. K_2 0.3 ($M^{-1}\,s^{-1}$) in ROS. CD ARh 450 (+).	(Liu and Asato, 1990) (Liu and Asato, 1984)
6.		7Z,11Z-	Cattle Rh	355[c]			465							(Yoshizawa, 1984)
		7Z,11Z-	Cattle Rh	355[c] (1.88) 374[a] (1.6)			455				unstable		Yield 30-70% in D. Yield 45% in ROS suspension. K_2 0.04 ($M^{-1}\,s^{-1}$) in D. CD ARh 455 (+).	(Liu and Asato, 1990) (Liu and Asato, 1984)
7.		7Z,11Z, 13Z-	Cattle Rh	302[c]										(Yoshizawa, 1984)
		7Z,11Z, 13Z-	Cattle Rh				?							(Liu and Asato, 1990) (Liu and Asato, 1984)

Table 1. Properties of visual pigment analogs

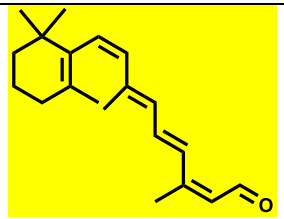
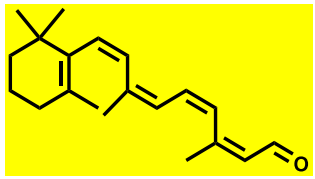
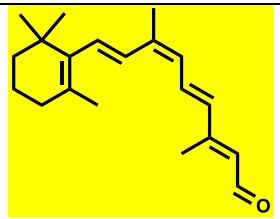
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
8.		7Z,13Z-	Cattle Rh	357[c]			460							(Yoshizawa, 1984)
		7Z,13Z-	Cattle Rh				455						Yield 3-30% in D Yield >5% in D K_2 0.007 ($M^{-1}\,s^{-1}$) in D.	(Liu and Asato, 1990) (Liu and Asato, 1984)
9.		7Z,9Z, 11Z,13 Z-	Cattle Rh											(Yoshizawa, 1984)
		7Z,9Z, 11Z,13 Z-	Cattle Rh				?							(Liu and Asato, 1990) (Liu and Asato, 1984)
10.		9Z-	bovine Rh (IRh)				485	kinetics of pigment photobleaching. The half-life ($t_{1/2}$) of pigment Meta-II state formation 0.6 min			Stable 2 h, in the dark in the presence of 40 mM hydroxyl amine		(ROS 20 mM BTP at pH 7.5 and 120 mM NaCl were incubated with 10 mM DDM). (*K*d) binding affinity 57.6 nM. $t_{1/2}$ of pigment regeneration 2.0 min. Kinetics of pigment stability to HCl $t_{1/2}$ 13 min.	(Pashandi et al., 2025)
		9Z-	Cattle IRh	363[c] (3.7) 372 (3.58) 373[a] (3.6)			485						Yield > 90% in D.	(Yoshizawa, 1984)

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		9Z-	bovine Rh (IRh) ROS from bovine eyes				486						FTIR spectra Binding level >90% Φ 0.26	(Bovee-Geurts et al., 2017)
		9Z-	bovine Rh (IRh) ROS from bovine eyes					Batho 525 nm BSI 483 nm Lumi 487 nm						(Szundi et al., 2002)
		9Z-	bovine Rh (IRh) ROS from bovine eyes				485						9Z-Retinylidene Chromophore of Isorhodopsin. Uniformly ^{13}C-labeled chromophore ^{13}C-labeled 9Z-retinal and Isorhodopsin is shown above the 2D homonuclear (^{13}C-^{13}C) and heteronuclear (^{1}H-^{13}C) correlation spectra.	(Creemers et al., 2004)
		9Z-	Cattle IRh					Meta I 480 nm Meta II 380 nm					FTIR spectroscopy to examine the pH dependence of the Meta I / Meta II conformational equilibrium. pK_A values were determined from pH series of FTIR spectra.	(Vogel et al., 2005)
		9Z-	bovine Rh (IRh)				483						Rh in **2%** Ammonyx LO. CD ARh 432 (+)? / 480 (+).	(Ebrey et al., 1975)
		9Z-	bovine Rh (IRh)										Activation of bovine rod phosphodiesterase (PDE) by 9Z-RetCHO Dark PDE activity (nmol/min) 18; Light PDE activity (nmol/min) 118.	(Ebrey et al., 1980)

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); ε 10^{-4} (M^{-1} cm^{-1})				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		9Z-	bovine Rh (IRh)	363[c] (3.7)				9Z-Rh 486 nm Batho 543 nm Lumi 497 nm Meta I 478 nm					The photobleaching processes of 9Z-Rh at at liquid nitrogen temperatures.	(Shichida et al., 1981)
		9Z-	Octopus Rh				460							(Koutalos et al., 1989)
		9Z-	R-photopsin from chicken red-sensitive cone visual pigment (iodopsin)			433	534 CHAPS-PC			4368			$t_{1/2}$ half-life of pigment formation < 0.25 min. Like scotopsin, R-photopsin failed to form a pigment with 13Z- or all-E-retinal.	(Fukada et al., 1990)
		9Z-	scotopsin from bovine rod pigment - rhodopsin			433 433	484 CHAPS-PC 483 D			2434 2391			$t_{1/2}$ half-life of pigment formation < 0.85 min. Like scotopsin, R-photopsin failed to form a pigment with 13Z- or all-E-retinal.	(Fukada et al., 1990)
		9Z-	bovine Rh (IRh)				483						ARh in a 2% digitonin solution. ARh were investigated by low-temperature spectrophotometry and nanosecond laser photolysis. Irradiation of each pigment at -180^0 **C** produced a photosteady-state mixture containing the original 9Z-pigment, its 11Z-pigment, and a photoproduct, indicating that the primary process of each pigment is a photoisomerization of its	(Okada et al., 1991)

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
													chromophore. It should be noted that each pigment was stable in the presence of 100 mM NH_2OH at 4^0C.	
		9Z-	bovine Rh (IRh)				485	9Z-Rh 485 nm Batho 525 nm BSI 483nm Lumi 487 nm					Nanosecond laser photolysis measurements	(Lewis et al., 1997) (Lewis et al., 1995)
		9Z-	cone visual pigment, P521, of the Tokay gecko *Gekko gekko*) retina				488 2% D pH 7.0	9Z- P521 488 nm Batho 560 nm BSI 508 nm Lumi 508 nm Meta I 503 nm					Nanosecond laser photolysis measurements	(Lewis et al., 1997)
		9Z-	bovine Rh (IRh)			433[a]	483			2391	stable		Yield >70% in ROS suspension or in D. Yield > 90% in ROS suspension. K_2 80 ($M^{-1}\,s^{-1}$) in ROS. CD ARh 330 (+) / 484 (+).	(Liu and Asato, 1990) (Liu and Asato, 1984)
		9Z-	bovine Rh (IRh)			433[a]	484			2434				(Iwasa et al., 1998)
		9Z-	Octopus Rh			433[a]	463			1496				(Iwasa et al., 1998)
		9Z-	bovine Rh (IRh)	373[c]		433[a]	484			2400			Yield >70% in 2% CHAPS.	(Colmenares et al., 1996)

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		9Z-	Red cone Rod Blue cone				542 489 418			4400 2400 -1000			Salamander visual pigments. AR were used to determine how saturating particular double bonds in the chromophore affected the spectrum and opsin shift (OS) of salamander red rod and red and blue cone visual pigments.	(Makino et al., 1999)
		9Z-	goldfish visual pigments cone pigments and the rod pigment				Cone pigments longwave-sensitive (LWS) 526 nm middle-wave-sensitive (MWS) 493 nm short-wave-sensitive (SWS) 427 nm ultraviolet-sensitive (UVS) cone pigments 370 nm rod pigment 490 nm						λ_{max} of the native porphyropsins (visual pigments based on 11Z-3-dehydroretinal and its analogs) of the rods and four spectral classes of cone in the goldfish. Cone pigments and the rod pigment were measured with each chromophore, demonstrating that all the goldfish visual pigments were reconstituted by the above protocol.	(Parry and Bowmaker, 2000)

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		9Z-	bovine Rh (IRh)			440	483	9Z-Rh 483 nm Batho 530 nm BSI 475nm Lumi 488 nm		2000			Nanosecond time-resolved and continuous illumination, low-temperature, spectroscopic studies reveal a new photolysis intermediate in a wide variety of ARhs.	(Randall et al., 1991)
		9Z-	bovine Rh (IRh)				483						In 2 % Ammonyx LO / phosphate buffer (67 mM, pH 7.4) at 23°C. Photosensitivity 0.45.	(Crouch, 1976)
		9Z-	Rat Rh (IRh)				485						In 2 % Ammonyx LO / phosphate buffer (67 mM, pH 7.4) at 23°C. Photosensitivity 0.4.	(Crouch, 1976)
		9Z-	Iodopsin				534 (Cl^-) 493 (NO_3^-)						Iodopsin analog in buffer A (0.6% CHAPS, 0.8 mg/mL egg phosphatidylcholine, 50 mM HEPES, 140 mM NaCl, 1 mM dithiothreitol, 200 mM methyl-α-D-mannopyranoside (MMP), pH 6.5 at 4°C). Chloride replacement with nitrate in the analogs was accompanied with a blue shift.	(Imai et al., 1999)
		9Z-	Iodopsin			440	500			2750				(Chen et al., 1989)

Table 1. Properties of visual pigment analogs

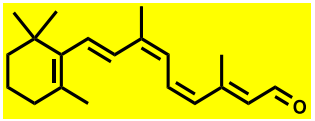
No	Structure	Isomer	Target	λ_{max} (nm); ε 10^{-4} (M^{-1} cm^{-1})				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		9Z-	bovine Rh (IRh)				486						AR and ROS in buffer A: 20mM (PIPES), 130 mM NaCl, 5 mM KCl, 2 mM $CaCl_2$, 0.1 mM EDTA, 1 mM dithioerythritol, pH 6.5) with a 5-10-fold molar excess of the retinal derivative at room temperature. Yield 100%. Quantum yield Φ 0.26. Transducin activation 104%.	(De Grip et al., 2011)
		9Z-	cone visual pigment, P521, of the Tokay gecko *Gekko gekko*) retina				488						Extract with NaCl, Yield 81%.	(Crescitelli and Liu, 1988)
		9Z-	Midship man fish *Porichthys notatus* (IRh)				487						Yield 37%.	(Crescitelli and Liu, 1988)
11.		9Z,11Z-	Cattle Rh	352[c]			480							(Yoshizawa, 1984)

Table 1. Properties of visual pigment analogs

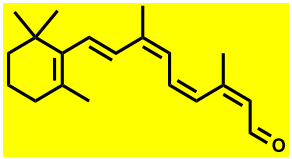
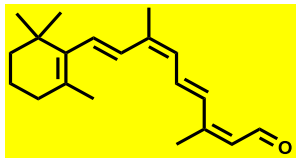
No	Structure	Isomer	Target	λ_{max} (nm); ε 10^{-4} (M^{-1} cm^{-1})				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		9Z,11Z-	Cattle Rh				444						Low-temperature photochemistry, UV/vis spectroscopy, and chromophore extraction experiments that 7Z,9Z-rhodopsin undergoes one-photon-two-bond photoisomerization to a batho intermediate containing the all-E-geometry.	(Zhu and Liu, 1993)
		9Z,11Z-	Cattle Rh	352[c] (3.06) 358[a] (2.7)			480				unstable		Yield 3-30% in D Yield 21% in ROS suspension. K_2 0.34 (M^{-1} s^{-1}) in D. CD ARh 338 (+) / 475 (+).	(Liu and Asato, 1990) (Liu and Asato, 1984)
12.		9Z,11Z, 13Z-	Cattle Rh	302[c]			NO							(Yoshizawa, 1984)
		9Z,11Z, 13Z-	Cattle Rh				?							(Liu and Asato, 1990) (Liu and Asato, 1984)
13.		9Z,13Z-	Cattle Rh	359[c]			481							(Yoshizawa, 1984)
		9Z,13Z-	Cattle Rh				481						Rh in **2%** Ammonyx LO. CD ARh 431 (+)/ 477 (+).	(Ebrey et al., 1975)
		9Z,13Z-											Activation of bovine rod phosphodiesterase (PDE) by 9Z,13Z-RetCHO	(Ebrey et al., 1980)

Table 1. Properties of visual pigment analogs

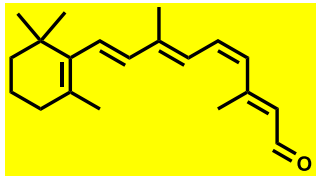
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
													Dark PDE activity (nmol/min) 14; Light PDE activity (nmol/min) 102.	
		9Z,13Z-	Cattle Rh				485						Yield 90% in D.	(Asato et al., 1986)
		9Z,13Z-	Cattle Rh				481						In 2 % Ammonyx LO / phosphate buffer (67 mM, pH 7.4) at 23°C. Photosensitivity 0.45.	(Crouch, 1976)
		9Z,13Z-	Rat Rh				483						In 2 % Ammonyx LO / phosphate buffer (67 mM, pH 7.4) at 23°C. Photosensitivity 0.4.	(Crouch, 1976)
		9Z,13Z-	Cattle Rh				478 485				unstable Stable		9Z,13Z-retinal with cattle opsin in 2% digitonin at 20 ^{O}C produced two pigments, one unstable (λ 478 nm) and the other stable (λ 485 nm) in hydroxylamine. Yield < 30% in D. CD ARh / 465 (+).	(Shichida et al., 1988)
		9Z,13Z-	Cattle Rh				481						Yield >70% in D.	(Liu and Asato, 1990) (Liu and Asato, 1984)
14.		11Z-	Cattle Rh	254, 290sh, 377 (2.5) 365[c] (2.6)			498	Hypso 430 nm Batho 543 nm Lumi 497 nm Meta I 478 nm					Rod opsin. Yield 100% in D.	(Yoshizawa, 1984)

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		11Z-	Iodopsin	380[a] (2.5)			562						Iodopsin Cone opsin	(Yoshizawa, 1984)
		11Z-	Rh Squid				480	Hypso 446 nm Batho 534 nm Lumi 515 nm Meta I 482 nm					squid Rh	(Yoshizawa, 1984)
		11Z-	Chikken Rh				508	Hypso 430 nm Batho 550 nm					Chikken Rh	(Yoshizawa, 1984)
		11Z-	Frog Rh				502	Hypso 430 nm Batho 555 nm Lumi 516 nm Meta I 461 nm					Frog Rh	(Yoshizawa, 1984)
		11Z-	Cattle Rh				279 (10.58) 340 (2.03) 500 (4.2)						67 mM phosphate buffer (pH 7.0) at 25°C for *5* h / 23 mM octyl glucoside solution at pH **7.0**. CD ARh 337 (+)/ 480 (+)	(Tan et al., 1997)
		11Z-	ROS from bovine eyes				498							(Kropf et al., 1973)
		11Z-	ROS from bovine eyes				498	Batho 531 nm BSI 473 nm Lumi 493 nm Meta II 377 nm					FTIR spectra Binding level >90% Φ 0.66	(Szundi et al., 2002)

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); ε 10^{-4} (M^{-1} cm^{-1})				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		11Z-	salamander rod pigment	376[a] (2.6)			499				stable		Salamander rod and cone pigments. Pigments were generated by combining proteins expressed in COS-1 cells. All spectra were recorded with the pigments in 0.1% dodecyl maltoside and 10 mM MES buffer with 150 mM NaCl at pH 6.0. 9-methyl group of retinal is not important in the activation pathway of the red cone and blue cone/green rod pigments.	(Das et al., 2004) (Ma et al., 2001)
		11Z-	salamander red cone pigment				558				unstable			
		11Z-	salamander blue cone/green rod pigment				432				unstable			
		11Z-	salamander UV cone pigment				356				stable			
		11Z-	ROS from bovine eyes	379[a]			498 (4.2)						Rh in **2%** Ammonyx LO. CD ARh 335 (+)/ 486 (+).	(Ebrey et al., 1975)
		11Z-	Cattle Rh										Activation of bovine rod phosphodiesterase (PDE) by 11Z-RetCHO Dark PDE activity (nmol/min) 23; Light PDE activity (nmol/min) 121.	(Ebrey et al., 1980)
		11Z-	Cattle Rh	379[a]		440	498 (4.0)			2700				(Koutalos et al., 1989)
		11Z-	Octopus Rh			440	475 (2.7)			1700				(Koutalos et al., 1989)

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		11Z-	R-photopsin from chicken red-sensitive cone visual pigment (iodopsin)			442	571 CHAPS-PC			5111			$t_{1/2}$ half-life of pigment formation < 0.25 min. Like scotopsin, R-photopsin failed to form a pigment with 13Z- or all-E-retinal.	(Fukada et al., 1990)
		11Z-	scotopsin from bovine rod pigment - rhodopsin			442	500 CHAPS-PC 498 D			2624 2544			$t_{1/2}$ half-life of pigment formation < 0.85 min. Like scotopsin, R-photopsin failed to form a pigment with 13Z- or all-E-retinal.	(Fukada et al., 1990)
		11Z-	Cattle Rh										The photochemical and subsequent thermal reactions of 11Z-rhodopsin prepared from cattle opsin and 11Z-retinal were investigated by low-temperature spectrophotometry and laser photolysis.	(Shichida et al., 1991)
		11Z-	chicken green cone visual pigment				508 at 0^0C 514 at -185^0C	Chicken Green 508 nm Batho 549 nm Lumi 511 nm Meta I 460 nm Meta II 360 nm Meta III 460 nm					The photochemical and subsequent thermal reactions of chicken green cone visual pigment were investigated by low-temperature spectrophotometry and laser photolysis, and compared with those of 11Z-rhodopsin prepared from cattle opsin and 11Z-retinal.	(Imai et al., 1995)

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		11Z-	Cattle Rh				498 (4.06)						in 10 mM Hepes CD ARh 340 (+)/ 498 (+) Relative PDE Activity 100%. Φ 0.67	(Karnaukhova et al., 1999)
		11Z-	Cattle Rh	380[c]	350[a]	442	498				stable		Yield >70% in D% in ROS suspension or in D. Yield 100% in ROS suspension. K_2 5600 ($M^{-1}\,s^{-1}$) in ROS. K_2 50 ($M^{-1}\,s^{-1}$) in D.	(Liu and Asato, 1990) (Liu and Asato, 1984)
		11Z- 11Z-	Cattle Rh Octopus Rh			442 442	500 476			2624 1616				(Iwasa et al., 1998) (Iwasa et al., 1998)
		11Z-	Cattle Rh					498 nm Batho 529 nm BSI 475 nm Lumi 492 nm						(Lewis et al., 1995) (Lewis et al., 1997)
		11Z-	Cattle Rh	380[c]	350[a]	442	500			2600			Yield >70% in 2% CHAPS. CD Rh 335 (+)/ 485 (+)	(Colmenares et al., 1996)
		11Z-	human blue cone opsin, green cone opsin, red cone opsin bovine Rh				415 530 560 497						Specific chromophore–protein interactions that govern spectral tuning in human visual pigments, here was presented unique compared binding properties of 11Z-ReCHO and 11Z-6-membered-ring-retinal (11Z-6mr-retinal) with human blue, green, and red cone opsins. To unravel the	(Katayama et al., 2019)

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
													specificity of the chromophore-binding pocket of cone opsins, we applied 11Z-6mr-retinal analog-binding analyses to human blue, green, and red cone opsins. These results revealed that among the three cone opsins, only blue cone opsin can accommodate the 11Z-6mr-retinal in its chromophore binding pocket, resulting in the formation of a synthetic blue pigment (B6mr) that absorbs visible light.	
		11Z-	Red cone Rod Blue cone				562 502 462			4800 2700 -500			Salamander visual pigments. AR were used to determine how saturating particular double bonds in the chromophore affected the spectrum and opsin shift (OS) of salamander red rod and red and blue cone visual pigments.	(Makino et al., 1999)
		11Z-	Human red cone opsin in COS-1 cells.										Human red cone opsin was transiently expressed in COS-1 cells. 11Z-RetCHO tested on the human red cone opsin's ability to activate transducin. Ability of opsins to activate transducin was measured using a radioactive filter-binding assay as described previously.	(Kono and Crouch, 2011)

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
													11Z-retinal is an inverse agonist.	
		11Z-	goldfish visual pigments cone pigments and the rod pigment				Cone pigments longwave-sensitive (LWS) 566 nm middle-wave-sensitive (MWS) 516 nm short-wave-sensitive (SWS) 446 nm ultraviolet-sensitive (UVS) cone pigments 370 nm rod pigment 503 nm						λ_{max} of the native porphyropsins (visual pigments based on 11Z-3-dehydroretinal and its analogs) of the rods and four spectral classes of cone in the goldfish. Cone pigments and the rod pigment were measured with each chromophore, demonstrating that all the goldfish visual pigments were reconstituted by the above protocol.	(Parry and Bowmaker, 2000)
		11Z-	isolated rods from the tiger salamander				502						11Z-Retinal, when delivered to isolated rods from liposomes, combines with free opsin to form a bleachable photopigment that fully restores sensitivity.	(Corson et al., 1990)
		11Z-	in frog ROS membrane	376[a]			502						Activation of GTPase 60% at illumination.	(Fukada et al., 1982)

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		11Z-	Cattle Rh				498	Rh 498 nm Batho 529 nm BSI 477 nm Lumi 490 nm		2650			Nanosecond time-resolved and continuous illumination, low-temperature, spectroscopic studies reveal a new photolysis intermediate in a wide variety of ARhs.	(Randall et al., 1991)
		11Z-	Iodopsin				571 (Cl^-) 538 (NO_3^-)						Iodopsin analog in buffer A (0.6% CHAPS, 0.8 mg/mL egg phosphatidylcholine, 50 mM HEPES, 140 mM NaCl, 1 mM dithiothreitol, 200 mM methyl-α-D-mannopyranoside (MMP), pH 6.5 at 4°C). Chloride replacement with nitrate in the analogs was accompanied with a blue shift.	(Imai et al., 1999)
		11Z-	Iodopsin			440	562			4950				(Chen et al., 1989)
		11Z-	Cattle Rh	380	360	440	500						SBH^+ pK_a 7.4	(Steinberg et al., 1993)
		11Z-	Cattle Rh				498						AR and ROS in buffer A: 20mM (PIPES), 130 mM NaCl, 5 mM KCl, 2 mM $CaCl_2$, 0.1 mM EDTA, 1 mM dithioerythritol, pH 6.5) with a 5-10-fold molar excess of the retinal derivative at room temperature. Yield 100%. Quantum yield Φ 0.65. Transducin activation 100%.	(De Grip et al., 2011)

Table 1. Properties of visual pigment analogs

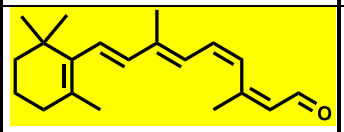
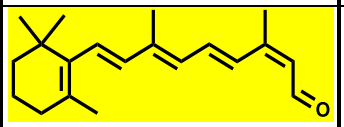
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		11Z-	cone visual pigment, P521, of the Tokay gecko *Gekko gekko*) retina				521						Extract with NaCl, Yield 80%.	(Crescitelli and Liu, 1988)
		11Z-	Midship man fish *Porichthys notatus* (Rh)				496						Yield 36%.	(Crescitelli and Liu, 1988)
		11Z-	opossum shrimps *Mysis relicta* Rh				529 nm Sea form 554 nm Lake form						both forms *Mysis relicta* visual pigment has contained only the same chromophore *11Z*-retinal and not *11Z*-3,4-didehydroretinal	(Belikov et al., 2014)
15.		11Z,13Z-	Cattle Rh	356[c] 303 (1.82)			?							(Yoshizawa, 1984)
		11Z,13Z-	Cattle Rh				?						in D%	(Liu and Asato, 1990) (Liu and Asato, 1984)
16.		13Z-	Cattle Rh	363[c] (3.88) 375 (3.57)			NO							(Yoshizawa, 1984)

Table 1. Properties of visual pigment analogs

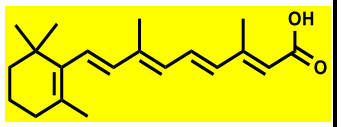
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		13Z-	Octopus Rh				502						13Z-pigment (λ = 502 nm) is actually acid metarhodopsin or not?	(Koutalos et al., 1989)
		13Z-	Cattle Rh				465? NO						in D%	(Liu and Asato, 1990) (Liu and Asato, 1984) (Matsumoto et al., 1980b)
		13Z-	Human red cone opsin in COS-1 cells.										Human red cone opsin was transiently expressed in COS-1 cells. 13Z-RetCHO tested on the human red cone opsin's ability to activate transducin. Ability of opsins to activate transducin was measured using a radioactive filter-binding assay as described previously. 13Z-retinal is agonist.	(Kono and Crouch, 2011)
		13Z-	ROS				467 ???? 425 after light						ARh in Tris-HCl (pH 7.4), 100 mmol/L NaCl, 1 mmol/L magnesium acetate, 0.1 mmol/L PMSF, 5 mmol/L β-mercaptoethanol. Yield 24% ???.	(Araujo, 2014)
B. Terminal polar group modification														
17.		all-E-					NO						Retinoic acid (all-E) has no effect on the activity of the opsin	(Wong and Rando, 1984) (Wong and Rando, 1982)

Table 1. Properties of visual pigment analogs

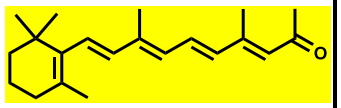
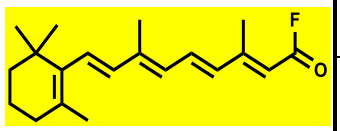
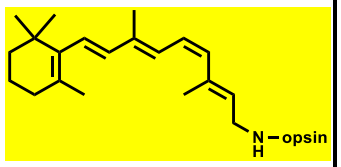
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
18.		mix	Cattle Rh	367[c]			NO NO							(Yoshizawa, 1984) (Ebrey et al., 1975)
19.		all-E-												
		9Z-	Cattle Rh				365						It is shown here that 9Z-retinoyl fluoride reacts with opsin in a time dependent fashion t = 9 min at 25 μM to form a new, nonbleachable pigment with a λ 365 nm. 9Z-Retinoyl fluoride is approximately 4-fold more potent than all-E-retinoyl fluoride as an inactivator of bovine opsin.	(Wong and Rando, 1984) (Wong and Rando, 1982)
		13Z-	Cattle Rh										13Z-retinoyl fluoride is inactive.	(Wong and Rando, 1984) (Wong and Rando, 1982)
20.		all-E- 11Z-	Cattle Rh										all-E-retinylopsin was prepared by irradiation of rhodopsin in the presence of 100 mM $NaBH_4$.11Z-retinylopsin was prepared by reaction with $NaCNBH_3$, in the dark. Rhodopsin-mediated activation of GTPase data.	(Calhoon and Rando, 1985)

Table 1. Properties of visual pigment analogs

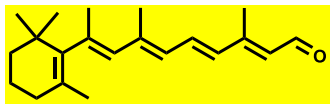
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
			in frog ROS membrane				330						Activation of GTPase 20%. It was shown that Schiff-base linkage between opsin and retinal is not always necessary for this enzyme activation.	(Fukada et al., 1982)
C. Polyenic chain modification														
21.		11Z-	Cattle Rh	368			500 490	After illumination 373 / 467 nm					The 11Z-AR 1) was added to the purifed rhodopsin in dodecyl maltoside (DM) detergent solution. 2) to WT protein expressed in transiently transfected COS-1 cells. After 2 h initial spectrum in the dark shows the typical absorbance bands at 280 and 500 nm and a band at 376 nm corresponding to the free 11Z-7-methyl AR. After 10 s illumination with light of >495 nm, ARh was bleached and the chromophore band at 500 nm was converted to a specie 380 nm. After 2h regeneration in the dark blue-shift of the visible band to 490 nm can be detected. ARh at 490 nm was not fully converted to Meta II species with maximum at 380 nm, but rather two bands of similar intensity are detected at 373 and 467 nm, respectively, indicating that the methyl group introduced at C7 in	(Bosch et al., 2006) (Aguilà et al., 2009)

Table 1. Properties of visual pigment analogs

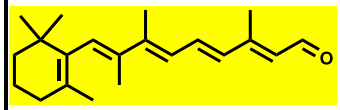
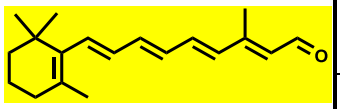
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
													retinal causes a stability change in photointermediates. ARh stability at 55°C in the dark was reduced ($t_{1/2}$ 4.6 min, Rh $t_{1/2}$ 13.1 min). Relative total Gt activation 0.55.	
22.		9Z-	Cattle IRh	342 344[a]			NO							(Alvarez et al., 2003)
		11Z-	Cattle Rh	368			NO							(Alvarez et al., 2003)
23.		all-E-		360[c] 373[a]		430								(Blatz et al., 1969)
		9Z-	bovine Rh (IRh)				464	kinetics of pigment photobleaching. The half-life ($t_{1/2}$) of pigment Meta-II state formation 10.8 min			Stable 2 h, in the dark in the presence of 40 mM hydroxyl amine		ROS 20 mM BTP at pH 7.5 and 120 mM NaCl were incubated with 10 mM DDM). (*Kd*) binding affinity 9.1 nM. $t_{1/2}$ of pigment regeneration 0.6 min. Kinetics of pigment stability to HCl $t_{1/2}$ 3.2 min.	(Pashandi et al., 2025)
		9Z-	Clattle IRh				453						CD ARh 335 (+)/ 459 (+)	(Yoshizawa, 1984) (Kropf et al., 1973)
		9Z-	Clattle IRh	361[c]		431	465			1700			ARh in 1% DDM solution (pH 6.5). Yield >80%.	(Wang et al., 2004a) (Wang et al., 2004b)

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		9Z-	Cattle IRh	367[a]			462 D						ARh in 2 % aqueous digitonin 23^{0}C, pH 6.8.	(Blatz et al., 1969)
		9Z-	Cattle IRh	366[a]			457	9-Desmethyl IRh forms a Meta II photoproduct only at very acidic pH					FTIR spectroscopy to examine the pH dependence of the Meta I / Meta II conformational equilibrium. pK_A values were determined from pH series of FTIR spectra. *t* pigment regeneration 4 h, yield < 90%. pK_A of the Meta I / Meta II equilibrium was found to be 4.5.	(Vogel et al., 2006a)
		9Z-	Cattle IRh			422	461			2000			Nanosecond time-resolved and continuous illumination, low-temperature, spectroscopic studies reveal a new photolysis intermediate in a wide variety of ARhs.	(Randall et al., 1991)
		11Z-	Cattle Rh				465							(Balogh-Nair and Nakanishi, 1990)
		11Z-	Cattle Rh				461							(Derguini and Nakanishi, 1986)
		11Z-	Cattle Rh				459						CD ARh 330 (+)/ 478 (+)	(Yoshizawa, 1984) (Kropf et al., 1973)
		11Z-	Cattle Rh	359[c]		454	466			1580			ARh in 1% DDM solution (pH 6.5). Yield >80%.	(Wang et al., 2004a)

Table 1. Properties of visual pigment analogs

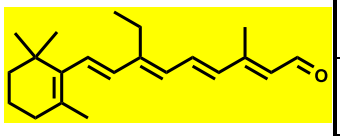
No	Structure	Isomer	Target	λ_{max} (nm); ε 10^{-4} (M^{-1} cm^{-1})				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
														(Wang et al., 2004b)
		11Z-	Cattle Rh				464 (3.8)				Stable 1 h, in the dark in DM		ROS in dodecylmaltoside (DM). Schiff base hydrolysis rates. FTIR spectroscopy. Inhibition of transducin activation in rhodopsin.	(Vogel et al., 2000)
		11Z-	Cattle Rh	370[a]			465 D						ARh in 2 % aqueous digitonin 23^{0}C, pH 6.8.	(Blatz et al., 1969)
		11Z- 11Z- 11Z- 11Z-	salamander rod pigment salamander red cone pigment salamander blue cone/green rod pigment salamander UV cone pigment	357[c]			468 509 412 347				stable unstable unstable stable		Salamander rod and cone pigments. Pigments were generated by combining proteins expressed in COS-1 cells. All spectra were recorded with the pigments in 0.1% dodecylmaltoside and 10 mM MES buffer with 150 mM NaCl at pH 6.0. 9-methyl group of retinal is not important in the activation pathway of the red cone and blue cone/green rod pigments. Initial Transducin activation and Meta II decay rates data.	(Das et al., 2004) (Ma et al., 2001)
24.		all-E-												
		9Z-	Cattle IRh				493							(Yoshizawa, 1984)

Table 1. Properties of visual pigment analogs

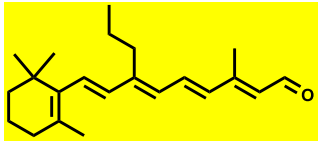
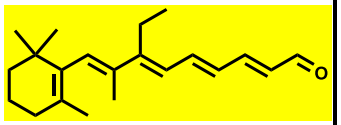
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		9Z-	Cattle IRh				500	ARh 500 nm Batho 540 nm BSI 483 nm Lumi 485 nm						(Lewis et al., 1995)
		11Z-	Cattle Rh				497							(Yoshizawa, 1984)
		11Z-	Cattle Rh				497							(Balogh-Nair and Nakanishi, 1990)
		11Z-	COS cell membranes containing wild-type opsins										Transducin activation by mutant opsins in the presence of C9-retinal analogues measured in COS.	(Han et al., 1997)
25.		11Z-	COS cell membranes containing wild-type opsins										Transducin activation by mutant opsins in the presence of C9-retinal analogues measured in COS.	(Han et al., 1997)
26.		all-E- 9Z- 11Z-	 Cattle Rh Cattle Rh				 NO NO							(Liu and Asato, 1990)
27.		all-E-												

Table 1. Properties of visual pigment analogs

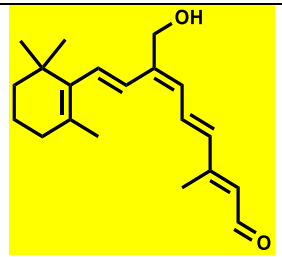
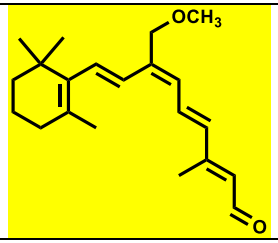
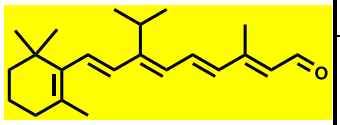
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		9Z-	Cattle IRh				473						Formed a pigment with absorption maximum at 473 nm within 10 min.	(Sen et al., 1984)
28.		9Z-	Cattle IRh	366[a]			473						in 2% digitonin buffered with HEPES (pH 7.0)	(Ito et al., 1984)
29.		all-E-												
		9Z-	Cattle IRh				490 D						Yield 3-30% in D	(Liu and Asato, 1990)
		9Z-	Cattle IRh				485						AR and ROS in buffer A: 20mM (PIPES), 130 mM NaCl, 5 mM KCl, 2 mM $CaCl_2$, 0.1 mM EDTA, 1 mM dithioerythritol, pH 6.5) with a 5-10-fold molar excess of the retinal derivative at room temperature. Yield 5%.	(De Grip et al., 2011)

Table 1. Properties of visual pigment analogs

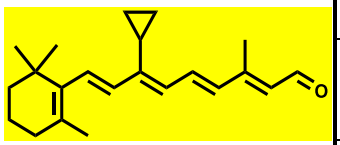
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		11Z-	Cattle Rh				504						AR and ROS in buffer A: 20mM (PIPES), 130 mM NaCl, 5 mM KCl, 2 mM $CaCl_2$, 0.1 mM EDTA, 1 mM dithioerythritol, pH 6.5) with a 5-10-fold molar excess of the retinal derivative at room temperature. Yield 2%.	(De Grip et al., 2011)
		11Z-	Cattle Rh				494 D						Yield 3-30% in D	(Liu and Asato, 1990)
		13Z-	Cattle Rh				NO							(Liu and Asato, 1990)
30.		all-E-												
		9Z-	ROS from bovine eyes				504						FTIR spectra Binding level 30-40% Φ 0.39	(Bovee-Geurts et al., 2017)
		9Z-	Cattle IRh				504						Φ 0.39	(De Grip and Lugtenburg, 2022)
		9Z-	Cattle IRh				504						AR and ROS in buffer A: 20mM (PIPES), 130 mM NaCl, 5 mM KCl, 2 mM $CaCl_2$, 0.1 mM EDTA, 1 mM dithioerythritol, pH 6.5) with a 5-10-fold molar excess of the retinal derivative at room temperature. Yield 36%. Quantum yield Φ 0.39. Transducin activation 60%.	(De Grip et al., 2011)
		11Z-	Cattle Rh				492						AR and ROS in buffer A: 20mM (PIPES), 130 mM NaCl, 5 mM KCl, 2 mM $CaCl_2$, 0.1 mM EDTA, 1	(De Grip et al., 2011)

Table 1. Properties of visual pigment analogs

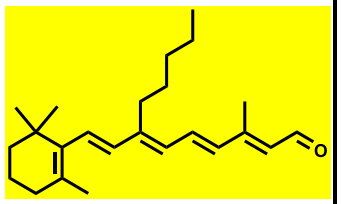
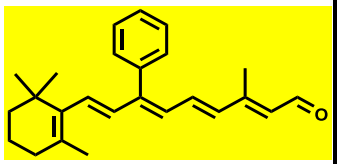
No	Structure	Isomer	Target	λ_{max} (nm); ε 10^{-4} (M^{-1} cm^{-1})				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
													mM dithioerythritol, pH 6.5) with a 5-10-fold molar excess of the retinal derivative at room temperature. Yield 30%. Quantum yield Φ 0.08. Transducin activation 83%.	
		11Z-	Cattle Rh				492						Φ 0.08	(De Grip and Lugtenburg, 2022)
		11Z-	ROS from bovine eyes				492						FTIR spectra Binding level 20-30% Φ 0.08	(Bovee-Geurts et al., 2017)
31.		all-E- 7Z- 9Z- 11Z-	 Cattle Rh Cattle Rh Cattle Rh				 462 D NO 480 D						 Yield 3-30% in D Yield 3-30% in D	(Liu and Asato, 1990)
32.		all-E- 9Z- 11Z-	 Cattle Rh Cattle Rh				 NO NO							(Liu and Asato, 1990)
33.		all-E-												

Table 1. Properties of visual pigment analogs

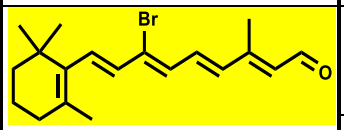
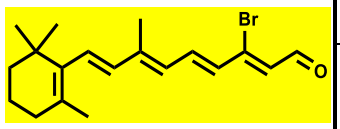
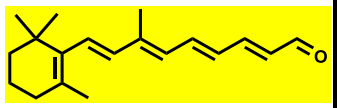
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		9Z-	Cattle IRh	365		462	465 D			140			in 2% digitonin, pH 7.0, phosphate buffer for 23 h. CD ARh 322 (+)/ 452 (+)	(Motto et al., 1980)
		9Z-	Cattle IRh	352[c]		422	474			2770			ARh in 1% DDM solution (pH 6.5). Yield 50-70%.	(Wang et al., 2004a) (Wang et al., 2004b)
		11Z-	Cattle Rh	363[c]		425	485			2910			ARh in 1% DDM solution (pH 6.5). Yield 50-70%.	(Wang et al., 2004a) (Wang et al., 2004b)
34.		all-E-												
		11Z-	Cattle Rh	383		467	520 D			2182			in 2% digitonin, pH 7.0, phosphate buffer for 23 h. CD ARh 355 (+)/ 520 (+)	(Motto et al., 1980)
35.		all-E-	Cattle Rh	377 379[a]	362	439	NO							(Liu and Asato, 1990) (Blatz et al., 1969)
		9Z-	Cattle IRh				483 D						Yield >70% in D	(Liu and Asato, 1990) (Liu and Mirzadegan, 1988)
		9Z-	Cattle IRh	369[a]			488 D						ARh in 2 % aqueous digitonin 23^{0}C, pH 6.8.	(Blatz et al., 1969)
		9Z-	Cattle IRh	370[a]			485	Batho 532 nm Lumi 497 nm Meta I 512 nm						(Yoshizawa, 1984)

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		9Z-	Cattle IRh				488	13-demethyl Iso in PC membranes formed Meta II only at pH 5.1, while the photoproduct at pH 8.6 was pure Meta I.					FTIR spectroscopy to examine the pH dependence of the Meta I / Meta II conformational equilibrium. pK_A values were determined from pH series of FTIR spectra. *t* pigment regeneration 4 h, yield < 90%. pK_A of the Meta I / Meta II equilibrium was found to be 5.9.	(Vogel et al., 2006a)
		9Z-	Cattle IRh				+						ARh in **2%** digitonin solution pH 6.5. CD ARh 330 (+)/ 478 (+).	(Kropf et al., 1973)
		9Z-	Cattle IRh				490	13-dm-rhodopsin 488 nm Batho 532 nm BL 475 nm Lumi 517 nm Meta I 512 nm					The photobleaching processes of 9Z-13-dm-rhodopsin at liquid nitrogen temperatures	(Shichida et al., 1981)
		9Z-	Cattle IRh				477 D	Meta I 485 nm Meta II 380 nm					Deletion of the13-methyl group on the isoprenoid chain did not affect metarhodopsin formation	(Renk and Crouch, 1989)
		9Z-	Cattle IRh				486							(De Grip and Lugtenburg, 2022)
		9Z-	Cattle IRh										Activation of bovine rod phosphodiesterase (PDE) by 9Z-13desmethyl-RetCHO Dark PDE activity (nmol/min) 27; Light PDE activity (nmol/min) 104.	(Ebrey et al., 1980)

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); ε 10^{-4} (M^{-1} cm^{-1})				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		9Z,11Z-	Cattle Rh				484 D 477 D						Yield 30-70% in D Yield 3-30% in D	(Liu and Asato, 1990) (Liu and Mirzadegan, 1988)
		9Z,13Z-	Cattle Rh				485 CHAPS						Yield 30-70% in D	(Liu and Asato, 1990)
		9Z,11Z, 13Z-	Cattle Rh				495						Yield 30-70% in CHAPS	(Liu and Asato, 1990)
		11Z-	Cattle Rh	377[a]			500							(Yoshizawa, 1984)
		11Z-	Cattle Rh				497						11Z-13dm **AR** and opsin induced dark activation of phosphodiesterase, a subsequent assay for rhodopsin kinase activity showed that the dark activity decayed with time, i.e., it is transient.	(Tan et al., 1998) (Fishkin et al., 2004)
		11Z-	Cattle Rh				496						Φ 0.46	(De Grip and Lugtenburg, 2022)
		11Z-	Cattle Rh										Activation of bovine rod phosphodiesterase (PDE) by 11Z-13desmethyl-RetCHO Dark PDE activity (nmol/min) 56; Light PDE activity (nmol/min) 108.	(Ebrey et al., 1980)

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		11Z-	Cattle Rh				495							(Balogh-Nair and Nakanishi, 1990)
		11Z-	Cattle Rh	377[a]			500 D						ARh in 2 % aqueous digitonin 23^{0}C, pH 6.8.	(Blatz et al., 1969)
		11Z-	Cattle Rh					In the pH range from 5.0 to 9.0, 13-demethyl Iso formed exclusively a 380 nm photoproduct state indicative of Meta II.					FTIR spectroscopy to examine the pH dependence of the Meta I / Meta II conformational equilibrium. pK_A values were determined from pH series of FTIR spectra. *t* pigment regeneration 4 h, yield < 50%. pK_A of the Meta I / Meta II equilibrium was found to be 6.0.	(Vogel et al., 2006a)
		11Z-	Cattle Rh										ARh in **2%** digitonin solution pH 6.5. CD ARh 325 (+)/ 485 (+).	(Kropf et al., 1973)
		11Z-	Cattle Rh				497	Meta I 485 nm Meta II 380 nm					Deletion of the13-methyl group on the isoprenoid chain did not affect metarhodopsin formation	(Renk and Crouch, 1989)
		11Z-	Cattle Rh				498 (4.4) CHAPSO						ARh resonance Raman spectra and CD spectra. ARh photoproduct formation times and quantum yield 0.35.	(Kochendoerfer et al., 1996)
		11Z-	Cattle Rh				498 CHAPS 498 D						Yield 30-70% in CHAPS. Yield 30-70% in D	(Liu and Asato, 1990) (Liu and Mirzadegan, 1988)

Table 1. Properties of visual pigment analogs

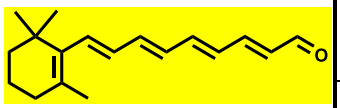
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		11Z-	Cattle Rh				495	13-dm-ARh 495 nm Batho 530 nm BIS 470 nm Lumi 480 nm					Nanosecond time-resolved and continuous illumination, low-temperature, spectroscopic studies reveal a new photolysis intermediate in a wide variety of ARhs.	(Randall et al., 1991)
		11Z-	Cattle Rh										Quantum yield Φ 0.44. Transducin activation rate 53%. Opsin membranes were suspended in buffer A (20 mM Pipes (pH 6.5), 130 mM NaCl, 4 mM KCl, 2 mM $CaCl_2$, 0.1 mM EDTA, 1 mM dithioerythritol), to a final concentration of opsin of about 50 μM.	(Verhoeven et al., 2006)
		11Z,13Z-	Cattle Rh				500 D						Yield 30-70% in D	(Liu and Mirzadegan, 1988)
36.		all-E-		370[a]										(Blatz et al., 1969)
		9Z-	Cattle IRh	363[a]			481 D						ARh in 2 % aqueous digitonin 23°C, pH 6.8.	(Blatz et al., 1969)
		9Z-	Cattle IRh				458 (4.2)						CD ARh 330 (+)/ 446 (+)	(Yoshizawa, 1984) (Kropf et al., 1973)

Table 1. Properties of visual pigment analogs

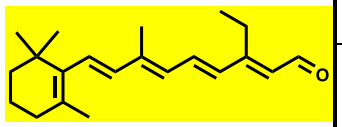
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		11Z-	Cattle Rh				483							(Yoshizawa, 1984)
		11Z-	Cattle Rh				483							(Balogh-Nair and Nakanishi, 1990)
		11Z-	Cattle Rh	368[a]			483 D						ARh in 2 % aqueous digitonin 23^{0}C, pH 6.8.	(Blatz et al., 1969)
37.		all-E-												
		9Z-	Cattle IRh				488	ARh 488 nm Batho 539 nm BIS 498 nm Lumi 489 nm					Nanosecond laser photolysis measurements	(Lewis et al., 1997) (Lewis et al., 1995)
		9Z-	Cattle Rh				495							(Balogh-Nair and Nakanishi, 1990)
		11Z-	Cattle Rh				495 (3.6)				stable		ARh in 10 mM Hepes, the regeneration was complete in 1 h. CD ARh 334 (+)/ 480 (+) Relative PDE Activity 100%. Φ 0.52	(Karnaukhova et al., 1999)
		11Z-	Cattle Rh	250 277 360[c]			495	485 after illumination 1 min and store in the dark 48 h			stable		ARh in CHAPSO, pH 7.0. CD ARh 335 (+)/ 495 (+)	(Nakanishi, 1985)
38.		9Z-	Cattle IRh				490							(Balogh-Nair and Nakanishi, 1990)

Table 1. Properties of visual pigment analogs

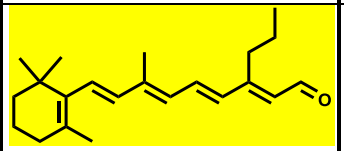
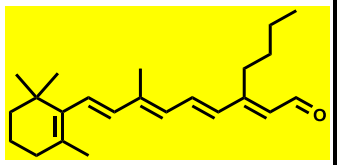
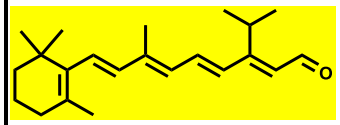
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		11Z-					+	after illumination 1 min and store in the dark 48 h ARh regenerated					ARh in CHAPSO, pH 7.0.	(Nakanishi, 1985)
39.		all-E- 9Z- 11Z-	Cattle IRh Cattle Rh				NO NO							(Liu and Asato, 1990)
40.		9Z-	Cattle IRh				490						AR and ROS in buffer A: 20mM (PIPES), 130 mM NaCl, 5 mM KCl, 2 mM $CaCl_2$, 0.1 mM EDTA, 1 mM dithioerythritol, pH 6.5) with a 5-10-fold molar excess of the retinal derivative at room temperature. Yield 31%. Quantum yield Φ 0.23. Transducin activation 139%.	(De Grip et al., 2011)
		11Z-	Cattle Rh				500						AR and ROS in buffer A: 20mM (PIPES), 130 mM NaCl, 5 mM KCl, 2 mM $CaCl_2$, 0.1 mM EDTA, 1 mM dithioerythritol, pH 6.5) with a 5-10-fold molar excess of the retinal derivative at room temperature. Yield 6%.	(De Grip et al., 2011)

Table 1. Properties of visual pigment analogs

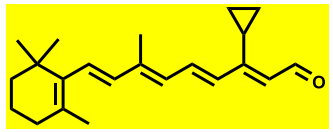
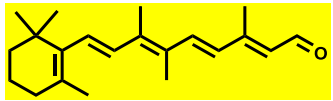
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
41.		9Z-	Cattle IRh				488						AR and ROS in buffer A: 20mM (PIPES), 130 mM NaCl, 5 mM KCl, 2 mM $CaCl_2$, 0.1 mM EDTA, 1 mM dithioerythritol, pH 6.5) with a 5-10-fold molar excess of the retinal derivative at room temperature. Yield 81%. Quantum yield Φ 0.1. Transducin activation 53%.	(De Grip et al., 2011)
		11Z-	Cattle Rh				506						AR and ROS in buffer A: 20mM (PIPES), 130 mM NaCl, 5 mM KCl, 2 mM $CaCl_2$, 0.1 mM EDTA, 1 mM dithioerythritol, pH 6.5) with a 5-10-fold molar excess of the retinal derivative at room temperature. Yield 28%. Quantum yield Φ 0.18.	(De Grip et al., 2011)
42.		all-E-		374[c]										
		7Z-	Cattle Rh	356[c]			506 D						Yield 3-30% in D	(Liu and Asato, 1990) (Liu and Mirzadegan, 1988)
		7Z-	Cattle Rh	356[c]			505 D						Yield 12% in D.	(Asato et al., 1986)

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		9Z-	Cattle IRh	376[a]			500	10-Methyl ARh forms Meta II photoproduct only at very acidic pH. Meta I 490 nm Meta II 380 nm					FTIR spectroscopy to examine the pH dependence of the Meta I / Meta II conformational equilibrium. pK_A values were determined from pH series of FTIR spectra. *t* pigment regeneration 4 h, yield < 90%. pK_A of the Meta I / Meta II equilibrium was found to be 5.0.	(Vogel et al., 2006a)
		9Z-	Cattle IRh	362[c] 280			498						Yield 94% in D. Φ 0.08% Yield >70% in D	(Asato et al., 1986) (Liu and Asato, 1990) (Liu and Mirzadegan, 1988)
		9Z-	Cattle IRh				485							(Balogh-Nair and Nakanishi, 1990)
		9Z-	Gecko pigment 521				497 D						Yield 70% in D.	(Liu et al., 1986)
		9Z-	cone visual pigment, P521, of the Tokay gecko *Gekko gekko*) retina				499						Extract with NaCl, Yield 43%.	(Crescitelli and Liu, 1988)
		9Z-	Midship-man fish *Porichthys notatus* (IRh)				495						Yield 41%	(Crescitelli and Liu, 1988)

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); ε 10^{-4} (M^{-1} cm^{-1})				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		9Z-	Cattle IRh				498						Φ 0.55%	(De Grip and Lugtenburg, 2022)
		11Z-	Cattle Rh				506						Φ <0.2%	(De Grip and Lugtenburg, 2022)
		11Z-	Cattle Rh	375[a]			497						Yield 100% in D for 4 h. The pK_A of the transition to Meta I is 5.1.	(Vogel et al., 2006a)
		11Z-	Cattle Rh	340[c] 270			508						Yield 83% in D. Φ 0.32%	(Asato et al., 1986)
		11Z-	Cattle Rh				506 (2.4)						Conformational changes in the photointermediates of the 10-methyl pigment are basically identical with those observed in the native pigment. CD ARh 330 (+)/ 500 (+)	(DeLange et al., 1998)
		11Z-	Gecko pigment 521				NO							(Liu et al., 1986)
		11Z-	cone visual pigment, P521, of the Tokay gecko *Gekko gekko*) retina				NO						Extract with NaCl, Yield 0%.	(Crescitelli and Liu, 1988)
		11Z-	Midship-man fish *Porichthys notatus* (Rh)				495						Yield 18%.	(Crescitelli and Liu, 1988)

Table 1. Properties of visual pigment analogs

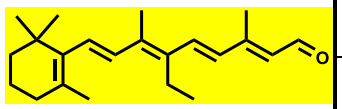
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		11Z-	Cattle Rh				508 D 498 D						Yield 3-30% in D	(Liu and Asato, 1990) (Liu and Mirzadegan, 1988)
		11Z-	Cattle Rh										Quantum yield Φ 0.55. Transducin activation rate 35%. Opsin membranes were suspended in buffer A (20 mM Pipes (pH 6.5), 130 mM NaCl, 4 mM KCl, 2 mM $CaCl_2$, 0.1 mM EDTA, 1 mM dithioerythritol), to a final concentration of opsin of about 50 μM.	(Verhoeven et al., 2006)
43.		all-E-		376[c]										
		7Z-	Cattle Rh	280[c] 259			480-490 D						Yield 1% in D	(Asato et al., 1986)
		9Z-	Cattle IRh	365[c] 280			494 D						Yield 8% in D. Yield 3-30% in D	(Asato et al., 1986) (Liu and Asato, 1990) (Liu and Mirzadegan, 1988)
		9Z-	Gecko pigment 521				NO NO							(Liu et al., 1986) (Crescitelli and Liu, 1988)

Table 1. Properties of visual pigment analogs

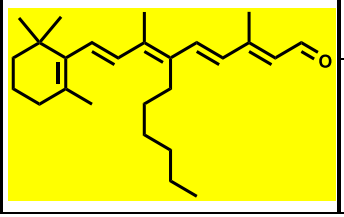
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		9Z-	Midship-man fish *Porichthys notatus* (IRh)				NO							(Crescitelli and Liu, 1988)
		9Z,13Z-	Cattle Rh	359[c] 288			493 D						Yield 6% in D.	(Asato et al., 1986) (Liu and Asato, 1990)
		11Z-	Gecko pigment 521				NO NO							(Liu et al., 1986) (Crescitelli and Liu, 1988)
		11Z-	Midship-man fish *Porichthys notatus* (Rh)				NO							(Crescitelli and Liu, 1988)
		11Z-	Cattle Rh	335[c] 250			480 D						Yield 2-3% in D.	(Asato et al., 1986) (Liu and Asato, 1990) (Liu and Mirzadegan, 1988)
44.		all-E-												
		9Z- 11Z-	Cattle Rh Cattle Rh				NO NO							(Liu and Asato, 1990)

Table 1. Properties of visual pigment analogs

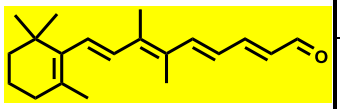
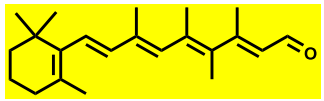
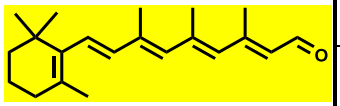
No	Structure	Isomer	Target	λ_{max} (nm); ε 10^{-4} (M^{-1} cm^{-1})				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
45.		all-E-												
		9Z-	Cattle IRh				NO						Interaction of 9Z-AR with opsin were nearly unsuccessful and led to only a minimal absorbance increase around 505 nm.	(Koch and Gärtner, 1997)
		11Z-	Cattle Rh				500 (4.4) in CHAPSO						ARh resonance Raman spectra and CD spectra. ARh photoproduct formation time 400 fs and quantum yield 0.47.	(Kochendoerfer et al., 1996)
		11Z-	Cattle Rh				505				unstable		The **11Z-**isomer of 10-methyl-13-dm-retinal formed ARh (λ_{max} 505 nm) with remarkably slow regeneration kinetics. Complete ARh formation required several hours. Φ 0.59.	(Koch and Gärtner, 1997)
46.		11Z-	Cattle Rh				480							(Balogh-Nair and Nakanishi, 1990)
47.		all-E-												
		9Z-	Cattle IRh				479 D						Yield 3-30% in D Yield 9%	(Liu and Asato, 1990) (Dawadi et al., 2011)

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		11Z-	Cattle Rh				490							(Balogh-Nair and Nakanishi, 1990)
		11Z-	Cattle Rh				498 D						Yield 3-30% in D Yield 12%	(Liu and Asato, 1990) (Dawadi et al., 2011)
		11Z-	Cattle Rh	250 280 353[c]			496				stable		ARh form with much slower kinetics and lower efficiency than the native pigment. The initial photochemistry and the signaling activity of the analog pigments were investigated by UV-vis and FTIR spectroscopy, and by a G protein activation assay. Data indicate that the ultrafast formation of the first photointermediate is strongly perturbed by the presence of 11-methyl substituent, but much less by a 12-methyl substituent. These results support the current concept of the mechanism of the primary photoisomerization event in rhodopsin. It is concluded that the 11-methyl analog of 11Z-retinal does not optimally fit into the binding site. Regeneration rate relative to rhodopsin <0.01.	(Verhoeven et al., 2006)

Table 1. Properties of visual pigment analogs

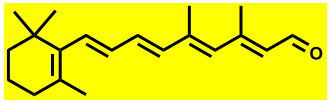
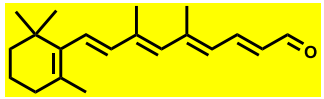
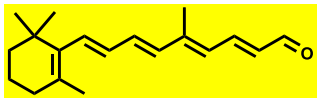
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
													Regeneration efficiency 54%. Quantum yield Φ 0.28. Transducin activation rate 29%. Opsin membranes were suspended in buffer A (20 mM Pipes (pH 6.5), 130 mM NaCl, 4 mM KCl, 2 mM $CaCl_2$, 0.1 mM EDTA, 1 mM dithioerythritol), to a final concentration of opsin of about 50 μM.	
48.		11Z-	Cattle Rh			433	475			2040			Yield 26%. CD ARh 338 (+)/ 478 (+)	(Colmenares and Liu, 1991)
49.		11Z-	Cattle Rh										Quantum yield Φ 0.18. Transducin activation rate 70%. Opsin membranes were suspended in buffer A (20 mM Pipes (pH 6.5), 130 mM NaCl, 4 mM KCl, 2 mM $CaCl_2$, 0.1 mM EDTA, 1 mM dithioerythritol), to a final concentration of opsin of about 50 μM.	(Verhoeven et al., 2006)
50.		9Z-	Cattle lRh			438	459			1050			Yield 13%. CD ARh 320 (+)/ 461 (+)	(Colmenares and Liu, 1991)
		9Z,13Z-	Cattle Rh				459						Yield 7%.	(Colmenares and Liu, 1991)
		11Z-	Cattle Rh				NO							(Colmenares and Liu, 1991)
51.		all-E-												

Table 1. Properties of visual pigment analogs

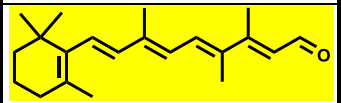
No	Structure	Isomer	Target	λ_{max} (nm); ε 10^{-4} (M^{-1} cm^{-1})				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		9Z-	cone-type visual pigment, P521				490 2% D pH 7.0						Nanosecond laser photolysis measurements were conducted on digitonin extracts of ARh prepared from the cone-type visual pigment, P521, of the Tokay gecko (*Gekko gekko*) retina.	(Lewis et al., 1997)
		9Z-	Cattle Rh				487 CHAPS-PC						Yield >70% in CHAPS-PC	(Liu and Asato, 1990) (Liu and Mirzadegan, 1988)
		11Z-	Cattle Rh	375[a]			487	12-Methyl rhodopsin formed a Meta II photoproduct only at very acidic pH.					FTIR spectroscopy to examine the pH dependence of the Meta I / Meta II conformational equilibrium. pK_A values were determined from pH series of FTIR spectra. *t* pigment regeneration 4 h, yield < 90%. pK_A of the Meta I / Meta II equilibrium was found to be 5.1.	(Vogel et al., 2006a)

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		11Z-	R-photopsin from chicken red-sensitive cone visual pigment (iodopsin)			440	534 CHAPS-PC			4001			$t_{1/2}$ half-life of pigment formation 3.0 min. Like scotopsin, R-photopsin failed to form a pigment with 13Z- or all-E-retinal.	(Fukada et al., 1990)
		11Z-	scotopsin from bovine rod pigment - rhodopsin			440	507 CHAPS-PC 489 D			3003 2277	unstable		$t_{1/2}$ half-life of pigment formation 166 min. Like scotopsin, R-photopsin failed to form a pigment with 13Z- or all-E-retinal.	(Fukada et al., 1990)
		11Z-	Cattle Rh				500							(Balogh-Nair and Nakanishi, 1990)
		11Z-	Cattle Rh				489 CHAPS-PC						Yield 3-30% in CHAPS-PC	(Liu and Asato, 1990) (Liu and Mirzadegan, 1988)
		11Z-	Cattle Rh	285 350[c]			500	Since with 500 nm light it was found the efficiency of the primary step in the photoreaction of 12-methylRh (Φ=0.54) not much reduced compared to that of native rhodopsin (Φ=0.65), this would imply that the 12-methyl group in 12-methylRh performs an out-of-					ARh form with much slower kinetics and lower efficiency than the native pigment. The initial photochemistry and the signaling activity of the analog pigments were investigated by UV-vis and FTIR spectroscopy, and by a G protein activation assay. Data indicate that the ultrafast formation of the first photointermediate is strongly perturbed by the	(Verhoeven et al., 2006)

Table 1. Properties of visual pigment analogs

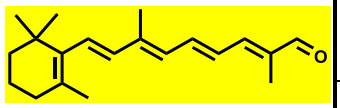
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
								plane movement comparable to the trajectory of the C-12 hydrogen in rhodopsin. These results support the current concept of the mechanism of the primary photoisomerization event in rhodopsin.					presence of 11-methyl substituent, but much less by a 12-methyl substituent. Regeneration rate relative to rhodopsin <0.004. Regeneration efficiency 37%. Quantum yield Φ 0.54. Transducin activation rate 6%. Opsin membranes were suspended in buffer A (20 mM Pipes (pH 6.5), 130 mM NaCl, 4 mM KCl, 2 mM $CaCl_2$, 0.1 mM EDTA, 1 mM dithioerythritol), to a final concentration of opsin of about 50 μM.	
		11Z,13Z-	Cattle Rh				486 CHAPS-PC						Yield 3-30% in CHAPS-PC	(Liu and Asato, 1990) (Liu and Mirzadegan, 1988)
52.		all-E-		377[a] (5.0)										(Ebrey et al., 1975)
		9Z-	Cattle IRh	372[a] (3.6)			492						In 2% Triton X-100 CD ARh 330 (+)/ 487 (+)	(Ebrey et al., 1975)
		9Z-	Cattle IRh				492						In 2 % Ammonyx LO / phosphate buffer (67 mM, pH 7.4) at 23°C. Photosensitivity 0.33.	(Crouch, 1976)
		9Z-	Rat IRh				490						In 2 % Ammonyx LO / phosphate buffer (67 mM, pH 7.4) at 23°C. Photosensitivity 0.28.	(Crouch, 1976)

Table 1. Properties of visual pigment analogs

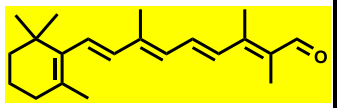
No	Structure	Isomer	Target	λ_{max} (nm); ε 10^{-4} (M^{-1} cm^{-1})				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		9Z-	Cattle IRh				492							(Balogh-Nair and Nakanishi, 1990)
		11Z-	Cattle Rh	378[a] (3.38)			NT							(Ebrey et al., 1975)
		13Z-	Cattle Rh											(Ebrey et al., 1975)
53.		all-E-		382[a] (4.2) 373[c] (4.6)			NO							(Ebrey et al., 1975) (Liu and Asato, 1990)
		9Z-	Cattle IRh				493							(Yoshizawa, 1984)
		9Z-	Cattle IRh	374[a] 378[a] (3.1)			492	14-Methyl IRh forms a regular Meta II state with deprotonated Schiff base					FTIR spectroscopy to examine the pH dependence of the Meta I / Meta II conformational equilibrium. pK_A values were determined from pH series of FTIR spectra. *t* pigment regeneration 20 h, yield < 70%. pK_A of the Meta I / Meta II equilibrium was found to be 7.4.	(Vogel et al., 2006a)
		9Z-	Cattle IRh				492 In 2% OG	ARh 492 nm Batho 592 nm BSI 453 nm Lumi 480 nm					Nanosecond laser photolysis measurements. The regeneration gave a pigment absorbing at 492 nm with a yield of 86%	(Lewis et al., 1997)

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		9Z-	cone visual pigment, P521, of the Tokay gecko (*Gekko gekko*) retina				490 D	P521 490 nm Batho 560 nm BSI 475 nm Lumi 500 nm Meta I 502 nm					Nanosecond laser photolysis measurements.	(Lewis et al., 1997)
		9Z-	Cattle IRh	365[c]			493 Triton X-100							(Liu and Asato, 1990)
		9Z-	Cattle IRh				502							(Balogh-Nair and Nakanishi, 1990)
		9Z,13Z-	Cattle Rh	353[c]			494 Triton X-100							(Liu and Asato, 1990)
		11Z-	Cattle Rh	350[a] (1.67)			502 (4.0)						ARh in **2%** Ammonyx LO. CD ARh 338 (+)/ 497 (+).	(Yoshizawa, 1984) (Ebrey et al., 1975)
		11Z-	Cattle Rh				505 (3.8)				unstable		ARh in 10 mM Hepes, the regeneration was complete in 3 h. CD ARh 334 (+)/ 480 (+) Relative PDE Activity 80%. Φ 0.55	(Karnaukhova et al., 1999)
		11Z-	Cattle Rh	338[c]			508 Triton X-100							(Liu and Asato, 1990)

Table 1. Properties of visual pigment analogs

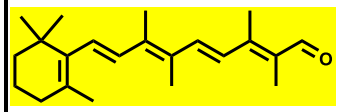
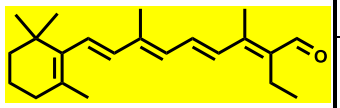
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		11Z-	cone visual pigment, P521, of the Tokay gecko (*Gekko gekko*) retina				NO							(Crescitelli and Liu, 1988)
		11Z-	Midship-man fish *Porichthys notatus* (Rh)				NO							(Crescitelli and Liu, 1988)
		13Z-	Cattle Rh	372[a] (3.0) 358[c] (3.5)			NO							(Ebrey et al., 1975)
54.		9Z-	Cattle IRh				500							(Balogh-Nair and Nakanishi, 1990)
55.		all-E-												
		9Z-	Cattle IRh				NO							(Liu and Asato, 1990)
		11Z-	Cattle Rh				NO							(Liu and Asato, 1990)

Table 1. Properties of visual pigment analogs

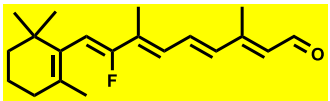
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		11Z-	cone visual pigment, P521, of the Tokay gecko (*Gekko gekko*) retina				NO							(Crescitelli and Liu, 1988)
		11Z-	Midship-man fish *Porichthys notatus* (Rh)				NO							(Crescitelli and Liu, 1988)
56.		all-E-	Cattle Rh				NO						Yield 0% in CHAPS	(Liu and Asato, 1990)
		7Z-	Cattle Rh				453						Yield 3-30% in CHAPS	(Liu and Asato, 1990)
		7Z,13Z-	Cattle Rh				440						Yield 3-30% in CHAPS	(Liu and Asato, 1990)
		9Z-	Cattle IRh				460						Yield >70% in CHAPS Φ 0.22	(Liu and Asato, 1990)
		9Z-	Cattle IRh	354[c]	341[a]	410[a]	459			2600			Yield >70% in 2% CHAPS. CD Rh 324 (+)/ 450 (+) ^{19}F NMR spectra of 11Z and 9Z- isomers of fluorinated ARh	(Colmenares et al., 1996)

Table 1. Properties of visual pigment analogs

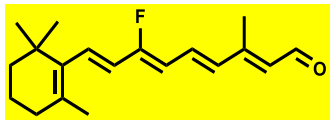
No	Structure	Isomer	Target	λ_{max} (nm); ε 10^{-4} (M^{-1} cm^{-1})				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		11Z-	Cattle Rh				463						Yield >70% in CHAPS Φ 0.60	(Liu and Asato, 1990)
		11Z-	R-photopsin from chicken red-sensitive cone visual pigment (iodopsin)			410[a]	514 CHAPS-PC			4935			$t_{1/2}$ half-life of pigment formation < 0.6 min. Like scotopsin, R-photopsin failed to form a pigment with 13Z- or all-E-retinal.	(Fukada et al., 1990)
		11Z-	scotopsin from bovine rod pigment - rhodopsin			410[a] 410[a]	463 CHAPS-PC 463 D			2792 2792			$t_{1/2}$ half-life of pigment formation 12.5 min. Like scotopsin, R-photopsin failed to form a pigment with 13Z- or all-E-retinal.	(Fukada et al., 1990)
		11Z-	Cattle Rh	354[c]	340[a]	413[a]	463			2615			Yield >70% in 2% CHAPS. CD Rh 335 (+)/ 485 (+) ^{19}F NMR spectra of 11Z and 9Z- isomers of fluorinated ARh	(Colmenares et al., 1996)
57.		all-E-												
		9Z-	Cattle IRh				463							(Colmenares et al., 1999)
		9Z-	Cattle IRh	354[c]		410	465			2880			ARh in 1% DDM solution (pH 6.5). Yield 50-70%.	(Wang et al., 2004a) (Wang et al., 2004b)

Table 1. Properties of visual pigment analogs

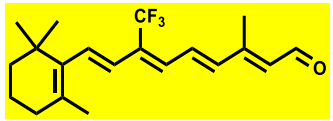
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		11Z-	Cattle Rh	348[c]		420	466			2350			ARh in 1% DDM solution (pH 6.5). Yield 50-70%.	(Wang et al., 2004a) (Wang et al., 2004b)
58.		all-E-					NO							
		9Z-	Cattle IRh	336[c]	334[a]	386[a]	454			3900			Yield 30-70% in CHAPS CD Rh 335 (+)/ 448 (+) ^{19}F NMR spectra of 11Z and 9Z- isomers of fluorinated ARh.	(Colmenares et al., 1996)
		9Z-	Cattle IRh				447 D							(Liu and Liu, 2011) (Liu and Asato, 1990)
		9Z,13Z-	Cattle Rh				453 CHAPS							(Liu and Asato, 1990) (Liu and Liu, 2011)
		11Z-	Cattle Rh			391[a]	456 D			3600				(Liu and Asato, 1990)
		13Z-	Cattle Rh				NO							(Liu and Asato, 1990)

Table 1. Properties of visual pigment analogs

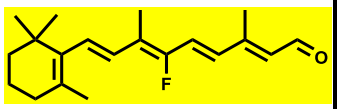
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
59.		all-E-	Cattle Rh	373[c]			NO						Yield 0% in CHAPS	(Liu and Asato, 1990)
		7Z-	Cattle Rh	360[c] 284 347[c]			484 C						Yield 3-30% in CHAPS Yield 22% in D.	(Liu and Asato, 1990) (Asato et al., 1986) (Liu and Mirzadegan, 1988)
		7Z-	Gecko pigment 521	347[c]			NO						Yield 0%	(Liu et al., 1986)
		7Z,9Z-	Cattle Rh				464						In D. Yield 31% In D.	(Asato et al., 1986) (Liu and Asato, 1990)
		7Z,9Z, 13Z-	Cattle Rh				460						In D.	(Liu and Asato, 1990)
		9Z-	Cattle IRh	358[c]			486 486 486 C						Yield >70% in CHAPS Yield 100% in D. Yield 68% in CHAPS. Φ 0.09	(Liu and Asato, 1990) (Asato et al., 1986) (Liu and Mirzadegan, 1988)

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		9Z-	Gecko pigment 521				487						Yield 52% in D.	(Liu et al., 1986)
		9Z-	cone visual pigment, P521, of the Tokay gecko (*Gekko gekko*) retina				490						Extract with NaCl, Yield 45%.	(Crescitelli and Liu, 1988)
		9Z-	cone visual pigment, P521, of the Tokay gecko (*Gekko gekko*) retina				492						Extract with NaCl, At 15^0C the 9Z-10-F AR replaces the 11Z--chromophore by at least 30% in about 15 hr.	(Crescitelli, 1988)
		9Z-	Midship-man fish *Porichthys notatus* (Rh)				487						Yield 34%.	(Crescitelli and Liu, 1988)
		9Z-	Cattle IRh				486							(Yoshizawa, 1984)

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		9Z-	Cattle Rh										The ARh was extracted from the ROS with 2% digitonin or 2% Ammonyx-LO. Photochemical reactions of fluorinated rhodopsin analogues were investigated by means of low-temperature spectrophotometry. Irradiation of 9Z-10-F-rhodopsin with 440-nm light at -191°C showed only a slight bathochromic shift.	(Shichida et al., 1987)
		9Z- 9Z-	Cattle Rh Octopus Rh	359[c] 359[c]		420[a] 420[a]	486 465			3233 2304			.^{19}F NMR spectra of 10-F ARh and their photoproducts. ^{19}F NMR spectra of 10-F ARh and their photoproducts.	(Iwasa et al., 1998) (Iwasa et al., 1998)
		9Z-	Cattle Rh	370[c]		420[a]	486			3233			Yield >70% in 2% CHAPS. CD Rh 332 (+)/ 478 (+) ^{19}F NMR spectra of 11Z and 9Z- isomers of fluorinated ARh	(Colmenares et al., 1996)
		9Z,13Z-	Cattle Rh				484						Yield 3-30% in 2% CHAPS. Yield 50% in D.	(Liu and Asato, 1990) (Asato et al., 1986)
		11Z-	Gecko pigment 521	356[c] 283			523						Yield 38% in D.	(Liu et al., 1986)

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		11Z-	cone visual pigment, P521, of the Tokay gecko (*Gekko gekko*) retina				523						Extract with NaCl, Yield 27%.	(Crescitelli and Liu, 1988)
		11Z-	Midship-man fish *Porichthys notatus* (Rh)				492						Yield 13%.	(Crescitelli and Liu, 1988)
		11Z-	Cattle Rh				502							(Yoshizawa, 1984)
		11Z-	Cattle Rh	356[c] 283			502 500 489 C						Yield 100% in D. Yield 90% in CHAPS. Φ 0.65	(Asato et al., 1986) (Liu and Asato, 1990) (Liu and Mirzadegan, 1988)

Table 1. Properties of visual pigment analogs

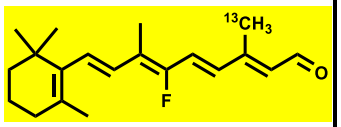
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		11Z-	Cattle Rh				498 495 at -191 ^{0}C	10-F-ARh at -191^o**C** had two peaks at 495 and 530 nm Batho 562 nm at -191 ^{0}C		2286			The rhodopsin analogue was extracted from the ROS with 2% digitonin or 2% Ammonyx-LO. Photochemical reactions of fluorinated rhodopsin analogues were investigated by means of low-temperature spectrophotometry. Batho-10-F-rhodopsin had absorption maximum at 562 nm. Absorption spectrum of 10-F-rhodopsin at -191^o**C** had two peaks at 495 and 530 nm.	(Shichida et al., 1987)
		11Z-	R-photopsin from chicken red-sensitive cone visual pigment (iodopsin)			428	574 CHAPS-PC			5943			$t_{1/2}$ half-life of pigment formation < 0.25 min. Like scotopsin, R-photopsin failed to form a pigment with 13Z- or all-E-retinal	(Fukada et al., 1990)
		11Z	scotopsin from bovine rod pigment - rhodopsin			428	499 CHAPS-PC			3324			$t_{1/2}$ half-life of pigment formation < 0.6 min. Like scotopsin, R-photopsin failed to form a pigment with 13Z- or all-E-retinal	(Fukada et al., 1990)
						428	498 D			3284				

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); ε 10^{-4} (M^{-1} cm^{-1})				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		11Z	Cattle Rh				502 (4.0)						The 10-F ARh exhibits a quantum yield similar to that of rhodopsin (0.65) but strongly perturbed thermodynamics of the structural transitions following photoactivation and only 20% of the native signaling activity.	(Bovee-Geurts et al., 2009)
		11Z 11Z	Cattle Rh Octopus Rh			428[a] 428[a]	499 466			3324 1905			^{19}F NMR Spectra of 10-F ARh and Their Photoproducts ^{19}F NMR Spectra of 10-F ARh and Their Photoproducts	(Iwasa et al., 1998) (Iwasa et al., 1998)
		11Z	Cattle Rh										^{19}F,^{13}C doubly-labeled retinal, i.e. the title compound, 10-fluoro-20-^{13}C-retinal. ARh prepared in good yields (>50%).	(Ni et al., 2001)
		11Z	Cattle Rh	350[c]	346[a]	428[a]	499			3324			Yield >70% in 2% CHAPS. CD Rh 337 (+)/ 495 (+) ^{19}F NMR spectra of 11Z and 9Z- isomers of fluorinated ARh	(Colmenares et al., 1996)
		11Z,13Z-	Cattle Rh				461 461						Yield 30-70% in CHAPS. Yield 61% in CHAPS.	H., Asato Alfred E., 1990) (Asato et al., 1986) (Liu and Mirzadegan, 1988)

Table 1. Properties of visual pigment analogs

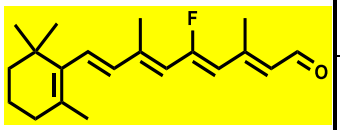
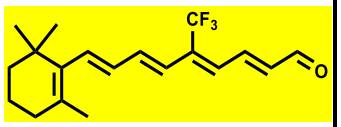
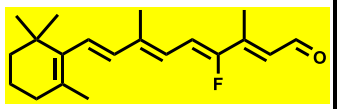
No	Structure	Isomer	Target	λ_{max} (nm); ε 10^{-4} (M^{-1} cm^{-1})				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		13Z-	Gecko pigment 521	355[c] 284			NO						Yield 0%	(Liu et al., 1986)
		13Z-	Cattle Rh	355[c] 284			NO						Yield 0% in CHAPS.	(Liu and Asato, 1990)
60.		all-E-					NO							(Colmenares et al., 1999)
		9Z-	Cattle Rh				474							(Colmenares et al., 1999)
		11Z-	Cattle Rh				488							(Colmenares et al., 1999)
61.		all-E- 9Z- 11Z-	Cattle Rh Cattle Rh				NO NO							(Liu and Asato, 1990)
62.		all-E-	Cattle Rh				NO							(Liu and Asato, 1990) (Liu and Mirzadegan, 1988)
		7Z-	Cattle Rh				NO							(Liu and Asato, 1990) (Liu and Mirzadegan, 1988)

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		7Z,11Z-	Cattle Rh				500							(Liu and Asato, 1990)
		9Z-	Cattle IRh				485							(Yoshizawa, 1984)
		9Z-	Cattle IRh				493						Yield >70% in D.	(Liu and Asato, 1990) (Liu and Mirzadegan, 1988)
		9Z-	Cattle IRh	375[c]	357[a]	436[a]	493			2650			Yield >70% in 2% CHAPS. CD Rh 334 (+)/ 484 (+) ^{19}F NMR spectra of 11Z and 9Z- isomers of fluorinated ARh	(Colmenares et al., 1996)
		9Z,11Z-	Cattle Rh				484						ARh was found to be stable in NH_2OH, although prolonged standing at room temperature is known to result in isomerization to the 9Z-isomer. By low-temperature photochemistry, UV/vis spectroscopy, and chromophore extraction experiments. 9Z,11Z-12-fluoroARh undergoes one-photon one-bond isomerization to the corresponding 9Z-isomer and then the all-E batho intermediate.	(Zhu and Liu, 1993)

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		9Z,11Z-	Cattle Rh	367[c]			484						^{19}F-NMR study of 9Z,11Z-12-fluororhodopsin and its photobleached product. ARh in 2% CHAPS.	(Colmenares and Liu, 1992)
		9Z,11Z-	Cattle Rh	374	350	443	484			1900			Yield 30-70% in 2% CHAPS.	(Colmenares et al., 1996)
		11Z-	Cattle Rh				506 514 at -191^{0}C	Batho 572 nm at -191^{0}C					The ARh was extracted from the ROS with 2% digitonin or 2% Ammonyx-LO. Photochemical reactions of fluorinated rhodopsin analogues were investigated by means of low-temperature spectrophotometry. On irradiation of 12-F-rhodopsin with 437-nm light at -191^{0}C, the spectrum shifted to longer wavelengths with an isosbestic point at 532 nm during the early stage of the irradiation, owing to the formation of a bathoproduct (batho-12-F-rhodopsin). Prolonged irradiation yielded a photosteady- state mixture composed of 12-F-rhodopsin, 9Z-12-F-rhodopsin, and batho-12-F-rhodopsin.	(Shichida et al., 1987)
		11Z-	Cattle Rh				505							(Yoshizawa, 1984)

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		11Z	R-photopsin from chicken red-sensitive cone visual pigment (iodopsin)	362[a]		446	586 CHAPS-PC			5357			$t_{1/2}$ half-life of pigment formation < 0.25 min. Like scotopsin, R-photopsin failed to form a pigment with 13Z- or all-E-retinal.	(Fukada et al., 1990)
		11Z	scotopsin from bovine rod pigment - rhodopsin			446	507 CHAPS-PC 506 D			2698 2658			$t_{1/2}$ half-life of pPigment formation < 0.4 min. Like scotopsin, R-photopsin failed to form a pigment with 13Z- or all-E-retinal.	(Fukada et al., 1990)ukada et al., 1990)
		11Z	Cattle Rh				507						Yield >70% in D	(Liu and Asato, 1990) (Liu and Mirzadegan, 1988)
		11Z	Cattle Rh				510 (3.4)	ARh 507 nm Batho 572 nm Lumi 514 nm Meta I 495 nm					The 12-F ARht exhibits a significantly decreased quantum yield (0.47) and signaling activity (30%).	(Bovee-Geurts et al., 2009)
		11Z	Cattle Rh			446[a]	510 (3.5)						ARh in 1% digitonin, pH 7.0 at 25**°C**, in Ammonyx LO stable <O^0C. ^{19}F NMR spectrum of the ARh is reported.	(Liu et al., 1981)
		11Z	Cattle Rh	382[c]		446[a]	507		2700				Yield >70% in 2% CHAPS. CD Rh 346 (+)/ 508 (+) ^{19}F NMR spectra of 11Z and 9Z- isomers of fluorinated ARh.	(Colmenares et al., 1996)

Table 1. Properties of visual pigment analogs

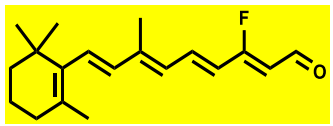
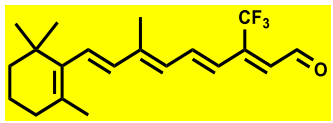
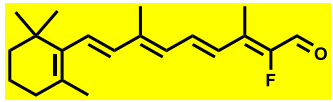
No	Structure	Isomer	Target	λ_{max} (nm); ε 10^{-4} (M^{-1} cm^{-1})				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		13Z-	Cattle Rh				NO							(Liu and Mirzadegan, 1988)
63.		all-E- 11Z-	Cattle Rh				502							(Colmenares et al., 1999)
64.		all-E-					NO							(Liu and Liu, 2011)
		9Z-	Cattle IRh			390	516 CHAPS 520			1200				(Liu and Asato, 1990)
		9Z-	Cattle IRh	400	367	467	512			1882			SBH^+ pK_a 1.8	(Steinberg et al., 1993)
		11Z-	Cattle Rh				542 D							(Liu and Liu, 2011) (Liu and Asato, 1990)
65.		all-E-	Cattle Rh				NO							(Liu and Asato, 1990)
		7Z-	Cattle Rh				NO							(Liu and Asato, 1990)
		9Z-	Cattle IRh				511 D						Φ 0.40	(Yoshizawa, 1984)

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
														(Liu and Asato, 1990)
		9Z-	Cattle IRh	377[c]	360[a]	451[a]	510			2600			Yield >70% in 2% CHAPS. CD Rh 343 (+)/ 508 (+) ^{19}F NMR spectra of 11Z and 9Z- isomers of fluorinated ARh.	(Colmenares et al., 1996)
		9Z-	Cattle IRh				510						Φ 0.40	(De Grip and Lugtenburg, 2022)
		9Z-	Cattle IRh	378[a]			511	ARh formed, at acidic pH, a Meta II photoproduct absorbing at 392 nm.					AR reacted readily with opsin, regenerating within 2 h at room temperature. pK_a ARh 8.2. FTIR data	(Vogel et al., 2006b)
		9Z-	Cattle IRh	388	372	460	510			2131			SBH^+ pK_a 5.0	(Steinberg et al., 1993)
		9Z-	cone visual pigment, P521, of the Tokay gecko (*Gekko gekko*) retina				518						Extract with NaCl, Yield 87%.	(Crescitelli and Liu, 1988)
		9Z-	Midship-man fish *Porichthys notatus* (Rh)				507						Yield 17%.	(Crescitelli and Liu, 1988)
		11Z-	cone visual pigment, P521, of the Tokay gecko (*Gekko gekko*) retina				548						Extract with NaCl, Yield 69%.	(Crescitelli and Liu, 1988)

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); ε 10^{-4} (M^{-1} cm^{-1})				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		11Z-	Midship-man fish *Porichthys notatus* (Rh)				522						Yield 25%.	(Crescitelli and Liu, 1988)
		11Z-	Cattle Rh	384	370	460	522			2582			SBH^+ pK_a 5.0	(Steinberg et al., 1993)
		11Z-	Cattle Rh				528						Φ 0.55	(De Grip and Lugtenburg, 2022)
		11Z-	Cattle Rh				527 D						Φ 0.51	(Yoshizawa, 1984) (Liu and Asato, 1990)
		11Z-	Cattle Rh				529 (4.0)						14-F ARh did not significantly impair rhodopsin properties, quantum yield (0.55) and signaling activity (80%).	(Bovee-Geurts et al., 2009)

Table 1. Properties of visual pigment analogs

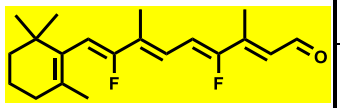
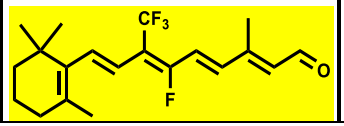
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		11Z	R-photopsin from chicken red-sensitive cone visual pigment (iodopsin)			455	607 CHAPS-PC			5504			$t_{1/2}$ half-life of pigment formation < 0.25 min.	(Fukada et al., 1990)
		11Z	scotopsin from bovine rod pigment - rhodopsin			455 455	527 CHAPS-PC 527 D			3003 3003			$t_{1/2}$ half-life of pigment formation 1 min.	(Fukada et al., 1990)
		11Z	Cattle Rh	378[c]	357[a]	459[a]	527			2800			Yield >70% in 2% CHAPS. CD Rh 351 (+)/ 529 (+) ^{19}F NMR spectra of 11Z- and 9Z- isomers of fluorinated ARh.	(Colmenares et al., 1996)
66.		all-E-												
		9Z-	Cattle Rh											
		11Z-	Cattle Rh	356[c]	341[a]	423[a]	476			2600			Yield 30-70% in 2% CHAPS. CD Rh 346 (+)/ 480 (-) ^{19}F NMR spectra of 11Z- and 9Z- isomers of fluorinated ARh.	(Colmenares et al., 1996)
67.		all-E- 9Z-	Cattle Rh				NO							(Liu and Asato, 1990)

Table 1. Properties of visual pigment analogs

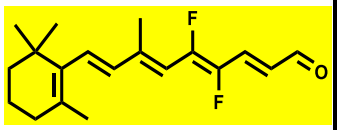
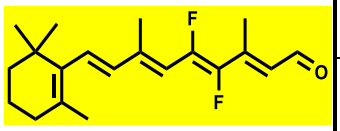
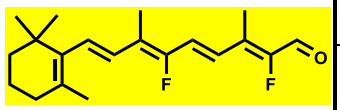
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		11Z-	Cattle Rh				NO							
68.		all-E- 9Z- 11Z-	Cattle Rh Cattle Rh				NO							(Colmenares et al., 1999)
69.		all-E-					NO							(Colmenares et al., 1999)
		11Z-	Cattle Rh				504 D						11,12-Difluoro ARh, solubilized in 2% CHAPS, were prepared in good yield (80%).	(Colmenares et al., 1999)
70.		all-E-												
		9Z-	Cattle Rh	373[c]	361[a]	446[a]	512			2900			Yield 30-70% in 2% CHAPS. ^{19}F NMR spectra of 11Z and 9Z- isomers of fluorinated ARh.	(Colmenares et al., 1996)
		9Z,13Z-	Cattle Rh				510							(Yoshizawa, 1984) (Liu and Asato, 1990)
		11Z-	Cattle Rh	348[c]	341[a]	432[a]	526			4100			Yield >70% in 2% CHAPS. ^{19}F NMR spectra of 11Z and 9Z- isomers of fluorinated ARh.	(Colmenares et al., 1996)

Table 1. Properties of visual pigment analogs

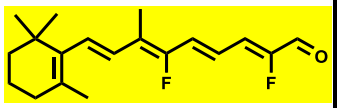
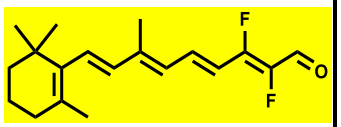
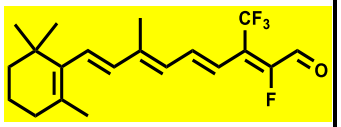
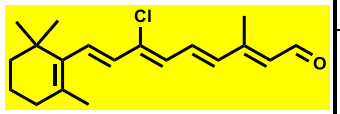
No	Structure	Isomer	Target	λ_{max} (nm); ε 10^{-4} (M^{-1} cm^{-1})				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
71.		all-E-	Cattle Rh				NO						Yield 3-30% in 2% D.	(Liu and Asato, 1990)
		9Z,11Z-	Cattle Rh				492 D							
		13Z-	Cattle Rh				NO							
72.		all-E-	Cattle Rh				NO						Yield 3-30% in 2% D.	(Liu and Asato, 1990)
		9Z-	Cattle Rh				520 D							
		13Z-	Cattle Rh				NO							
73.		all-E-												
		9Z-	Cattle IRh				NO							(Liu and Asato, 1990)
		11Z-	Cattle Rh				NO							
74.		all-E-												
		9Z-	Cattle IRh	363[c]		419	474			2770			ARh in 1% DDM solution (pH 6.5). Yield 50-70%.	(Wang et al., 2004a) (Wang et al., 2004b)
		11Z-	Cattle Rh	345[c]		415	485			3480			ARh in 1% DDM solution (pH 6.5). Yield 50-70%.	(Wang et al., 2004a) (Wang et al., 2004b)

Table 1. Properties of visual pigment analogs

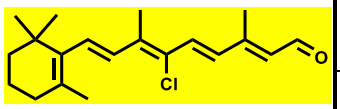
No	Structure	Isomer	Target	λ_{max} (nm); ε 10^{-4} (M^{-1} cm^{-1})				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
75.		all-E-		366[c] 280										
		9Z-	Cattle IRh	360[c] 281			474 D 488						Yield 30% in D. Φ 0.07 Yield 30-70% in D	(Asato et al., 1986) (Liu and Asato, 1990) (Liu and Mirzadegan, 1988)
		9Z-	Gecko pigment 521				487 D						Yield 30% in D.	(Liu et al., 1986)
		9Z-	cone visual pigment, P521, of the Tokay gecko (*Gekko gekko*) retina				482						Extract with NaCl, Yield 38%.	(Crescitelli and Liu, 1988)
		9Z-	Midship-man fish *Porichthys notatus* (Rh)				477						Yield 21%.	(Crescitelli and Liu, 1988)
		11Z-	Cattle Rh	335[c] 269			480 D						Yield 79% in D. Φ 0.33	(Asato et al., 1986) (Liu and Asato, 1990) (Liu and Mirzadegan, 1988)

Table 1. Properties of visual pigment analogs

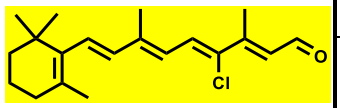
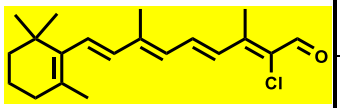
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
							NO D							
		11Z-	cone visual pigment, P521, of the Tokay gecko (*Gekko gekko*) retina				NO						Extract with NaCl, Yield 0%.	(Crescitelli and Liu, 1988)
		11Z-	Midship-man fish *Porichthys notatus* (Rh)				476						Yield 11%.	(Crescitelli and Liu, 1988)
76.		all-E-												
		9Z-	Cattle Rh				488 D						Yield 30-70% in D.	(Liu and Asato, 1990) (Liu and Mirzadegan, 1988)
		11Z-	Cattle Rh				? NO							(Liu and Asato, 1990) (Liu and Mirzadegan, 1988)
77.		all-E-												
		9Z-	Cattle Rh				524 D						Yield 30-70% in D.	(Liu and Asato, 1990)

Table 1. Properties of visual pigment analogs

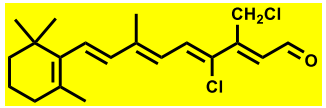
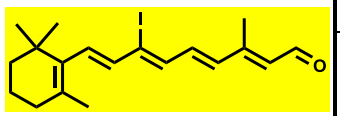
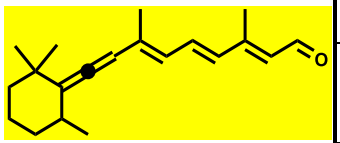
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		11Z-	Cattle Rh				544 D						Yield 3-30% in D.	(Liu and Asato, 1990)
78.		9Z-	Cattle IRh	402	370	454	520			2795			SBH^+ pK_a 3.8	(Steinberg et al., 1993)
79.		all-E-												
		9Z-	Cattle IRh	368[c]		425	482			2780			ARh in 1% DDM solution (pH 6.5). Yield < 20%.	(Wang et al., 2004a) (Wang et al., 2004b)
		11Z-	Cattle Rh	353[c]		414	484			3490			ARh in 1% DDM solution (pH 6.5). Yield 20-40%.	(Wang et al., 2004a) (Wang et al., 2004b)
D. Alteration of the bond types and its disposition in the chromophore polyenic chain														
80.		all-E-		353[c]										
		9Z-	Cattle IRh				456							(Yoshizawa, 1984)
		9Z- 5S,6R-/5S,6S-Mix	Cattle IRh	351[c]		430	456 462			1517			ARh in 1.5% Triton X-100. CD ARh 320 (+)/ 455 (+)	(Blatchly et al., 1980) (Nakanishi et al., 1976)
		9Z,13Z- 5S,6R-/5S,6S-mix	Cattle Rh				455						ARh in 1.5% Triton X-100. CD ARh 325 (+)/ 455 (+)	(Nakanishi et al., 1976) (Blatchly et al., 1980)

Table 1. Properties of visual pigment analogs

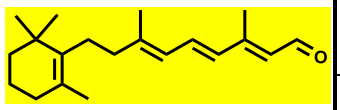
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		11Z-	Cattle Rh				462							(Yoshizawa, 1984)
81.		all-E-		342 320[c]		392								
		9Z-	Cattle IRh	321[c]		392	425			4532			ARh in 1.5% Triton X-100	(Yoshizawa, 1984) (Blatchly et al., 1980)
		9Z-	Cattle IRh				428 (5.1)						*p*Ka Meta I / Meta II < 6.5. G-protein activation 70%. Φ 0.39	(DeGrip et al., 2007)
		9Z-	Cattle IRh	342		392	420			1700			The opsin shifts of bovine rhodopsins formed from hydroretinals constituted the experimental basis for the external-point charge model. This model was proposed to explain the color of bovine rhodopsin as well as to account for a general mechanism by which opsins regulate the absorption maxima of visual pigments in nature.	(Nakanishi, 1985) (Nakanishi et al., 1980)
		9Z-	Cattle IRh							1700			The opsin shifts of bovine rhodopsins formed from hydroretinals constituted the experimental basis for the external-point charge model. This model was proposed to explain the color of bovine rhodopsin as well as to account for a	(Balogh-Nair and Nakanishi, 1990)

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); ε 10^{-4} (M^{-1} cm^{-1})				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
													general mechanism by which opsins regulate the absorption maxima of visual pigments in nature.	
		9Z-	Cattle IRh			392	420			1700			In 0.5% digitonin, 67 mM phosphate buffer, pH 7.0. Spectroscopic data of the dihydrorhodopsins now make it possible for the first time to locate a group on the opsin which plays a major role in determining the absorption maximum of bovine rhodopsin.	(Honig et al., 1979)
		9Z-	Cattle IRh	342		392	420			1700			In 0.5% digitonin, 67 mM phosphate buffer, pH 7.0.	(Arnaboldi et al., 1979)
		9Z-	ROS from bovine eyes				428						FTIR spectra Binding level >90% Φ 0.39	(Bovee-Geurts et al., 2017)
		9Z-	Cattle IRh	342		392	420			1700			The opsin shifts of bovine rhodopsins formed from hydroretinals constituted the experimental basis for the external-point charge model. This model was proposed to explain the color of bovine rhodopsin as well as to account for a general mechanism by which opsins regulate the absorption maxima of visual pigments in nature. In 0.5% digitonin, 67 mM phosphate buffer, pH 7.0.	(Derguini and Nakanishi, 1986)
		9Z-	Cattle IRh				428						Φ 0.39	(De Grip and Lugtenburg, 2022)

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		9Z-	Cattle IRh				427						photoreaction of 9Z-7,8-dihydroRh was examined at liquid nitrogen temperatures (- 180^0C) bathochromic product (λ_{max} roughly 465 nm).	(Muto et al., 1984)
		9Z-	Iodopsin			392	423			1850				(Chen et al., 1989)
		11Z-	Iodopsin			392	440			2800				(Chen et al., 1989)
		11Z-	Cattle Rh				426						Φ 0.68	(De Grip and Lugtenburg, 2022)
		9Z- 11Z-	Cattle IRh Cattle Rh				420 in 0.5% digitonin 427 in dodecyl maltoside 425 in dodecyl maltoside						Both 11Z-7,8-dihydroretinal and 9Z-7,8-dihydroretinal form bleachable pigments when combined with opsin. Photolysis of these pigments in the presence of G-protein results in the activation of the latter as revealed by its GTPase activity.	(Calhoon and Rando, 1985)
		11Z-	ROS from bovine eyes				426						FTIR spectra Binding level >90% Φ 0.68	(Bovee-Geurts et al., 2017)
		11Z-	Cattle Rh	323[c]			426 (3.7)						p*Ka* Meta I / Meta II < 6.5. G-protein activation 75%. Φ 0.68	(DeGrip et al., 2007)

Table 1. Properties of visual pigment analogs

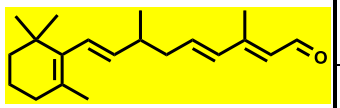
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		11Z-	Cattle Rh			392	428			2200			Both 11Z-7,8-dihydroretinal and 9Z-7,8-dihydroretinal form bleachable pigments when combined with opsin. Photolysis of these pigments in the presence of G-protein results in the activation of the latter as revealed by its GTPase activity.	(Koutalos et al., 1989)
		11Z-	Octopus Rh			392	417			1500				(Koutalos et al., 1989)
		all-E-	Octopus Rh			392	433			2400				(Koutalos et al., 1989)
82.		all-E-	Cattle Rh				345							(Yoshizawa, 1984)
		9Z-	Cattle Rh	232 278		322	345			2100			The opsin shifts of bovine rhodopsins formed from hydroretinals constituted the experimental basis for the external-point charge model. This model was proposed to explain the color of bovine rhodopsin as well as to account for a general mechanism by which opsins regulate the absorption maxima of visual pigments in nature.	(Nakanishi, 1985) (Nakanishi et al., 1980)
		9Z-	Cattle Rh			322	345		2100				In 0.5% digitonin, 67 mM phosphate buffer, pH 7.0. Spectroscopic data of the dihydrorhodopsins now make it possible for the first time to locate a group major role in determining the absorption maximum of bovine rhodopsin.	(Honig et al., 1979)

Table 1. Properties of visual pigment analogs

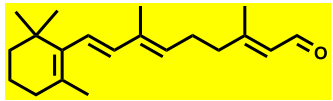
No	Structure	Isomer	Target	λ_{max} (nm); ε 10^{-4} (M^{-1} cm^{-1})				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		9Z-	Cattle Rh	232 278		322	345			2100			The opsin shifts of bovine rhodopsins formed from hydroretinals constituted the experimental basis for the external-point charge model. This model was proposed to explain the color of bovine rhodopsin as well as to account for a general mechanism by which opsins regulate the absorption maxima of visual pigments in nature	(Derguini and Nakanishi, 1986)
		9Z-	Cattle Rh	232 278		322	345			2100			In 0.5% digitonin, 67 mM phosphate buffer, pH 7.0. Bleachable and nonbleachable pigments, respectively, upon exposure room light.	(Arnaboldi et al., 1979)
		11Z-	Cattle Rh			320	336			1600				(Koutalos et al., 1989)
		11Z-	Octopus Rh			320	332			900				(Koutalos et al., 1989)
83.		all-E-	Cattle Rh				315							(Yoshizawa, 1984)
		all-E-	bovine opsin	236 255^{sh}		255^{sh} 270	279 (2.68)						67 mM phosphate buffer (pH 7.0) at 25°C for *5* h / 23 mM octyl glucoside solution at pH **7.0**. CD ARh 275 (+)/ 295 (-)	(Tan et al., 1997)
		all-E-	Cattle Rh	236 255		255 270	275 295						Dihydroretinal in which the saturation of the 11,12-double bond eliminates the possibility of 11Z- to all-E-	(Lou et al., 2000) (Nakanishi, 1985)

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
						270	315 OG			5300			isomerization formed the first known nonbleachable rhodopsin analog, thus supporting the important role attributed to the isomerization of this bond in the bleaching of rhodopsin. The opsin shifts of bovine rhodopsins formed from hydroretinals constituted the experimental basis for the external-point charge model. This model was proposed to explain the color of bovine rhodopsin as well as to account for a general mechanism by which opsins regulate the absorption maxima of visual pigments in nature. in octylglucoside solution.	(Nakanishi et al., 1980)
		all-E-	Cattle Rh						5300				Dihydroretinal in which the saturation of the 11,12-double bond eliminates the possibility of 11Z- to all-E- isomerization formed the first known nonbleachable rhodopsin analog, thus supporting the important role attributed to the isomerization of this bond in the bleaching of rhodopsin. The opsin shifts of bovine rhodopsins formed from hydroretinals constituted	(Balogh-Nair and Nakanishi, 1990)

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
													the experimental basis for the external-point charge model. This model was proposed to explain the color of bovine rhodopsin as well as to account for a general mechanism by which opsins regulate the absorption maxima of visual pigments in nature.	
		all-E-	Cattle Rh	236 255		270	315		5300				Bleachable and nonbleachable pigments, respectively, upon exposure room light. Although the "NB" pigments derived from 11,12-dihydro- and 9,10, 11,12-tetrahydroretinals are stable to room light, they undergo photolysis when exposed to UV light nonbleachable pigment.	(Arnaboldi et al., 1979)
		all-E-	Cattle Rh	236 255		270	315			5300				(Derguini and Nakanishi, 1986)
		all-E-	Cattle Rh	236		270	345						2% ALO, P-Buffer pH 7.0 nonbleachable pigment, upon exposure room light	(Nakanishi et al., 1979)
		all-E-	Cattle Rh	236 255		270	315			5300				(Honig et al., 1979)
		all-E-	Cattle Rh										Incorporation of 11,12-dihydroretinal into the retinae of vitamin A deprived rats. [15-^{3}H]11,12-dihydroretinal	(Crouch et al., 1981)

Table 1. Properties of visual pigment analogs

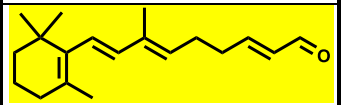
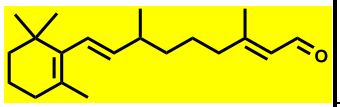
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		all-E-	Cattle Rh			270	294			3023				(Koutalos et al., 1989)
		all-E-	Octopus Rh			270	286			2072				(Koutalos et al., 1989)
84.		all-E-	Cattle Rh				270						11Z-11,12-didihydro13dm **AR** and opsin induced dark activation of phosphodiesterase, a subsequent assay for rhodopsin kinase activity showed that the dark activity decayed with time, As was shown 11Z-11,12-didihydro13dm **AR** exhibited transient activity on PDE similar to 13dmAR.	(Tan et al., 1998) (Fishkin et al., 2004)
85.		all-E-	Cattle Rh				310							(Yoshizawa, 1984)
		all-E-	Cattle Rh										Bleachable and nonbleachable pigments, respectively, upon exposure room light. Although the "NB" pigments derived from 11,12-dihydro- and 9,10, 11,12-tetrahydroretinals are stable to room light, they undergo photolysis when exposed to UV light nonbleachable pigment, upon exposure room light. In 0.5% digitonin, 67 mM phosphate buffer, pH 7.0.	(Nakanishi et al., 1979)

Table 1. Properties of visual pigment analogs

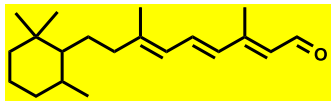
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		all-E-	Cattle Rh			275	310			4100			In 0.5% digitonin, 67 mM phosphate buffer, pH 7.0. Spectroscopic data of the dihydrorhodopsins now make it possible for the first me to locate a group major role in determining the absorption maximum of bovine rhodopsin.	(Honig et al., 1979)
		all-E-	Cattle Rh	234		275	310			4100			Bleachable and nonbleachable pigments, respectively, upon exposure room light. Although the "NB" pigments derived from 11,12-dihydro- and 9,10, 11,12-tetrahydroretinals are stable to room light, they undergo photolysis when exposed to UV light nonbleachable pigment, upon exposure room light. In 0.5% digitonin, 67 mM phosphate buffer, pH 7.0.	(Arnaboldi et al., 1979)
86.		all-E-	Cattle Rh											
		9Z-	Cattle Rh				426 D						Yield 30-70% in D.	(Liu and Asato, 1990)
		9Z,13Z-	Cattle Rh				426 D						Yield 3-30% in D.	(Liu and Asato, 1990)
		11Z-	Cattle Rh				424 D						Yield 30-70% in D.	(Liu and Asato, 1990)

Table 1. Properties of visual pigment analogs

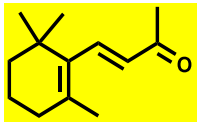
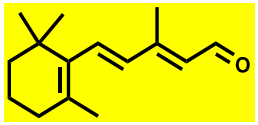
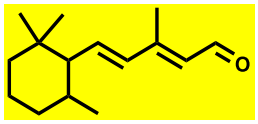
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
E. Alteration of the polyenic chain length and bond disposition and terminal group types														
87.			Cattle Rh	222, 292[b]			NO							(Yoshizawa, 1984)
			Cattle Rh				NO						Inhibitor of ARh formation.	(Crouch, 1990)
			Cattle Rh				302 ?						Inhibitor of ARh formation. ARh in Tween-80/buffer solution.	(Towner et al., 1981)
88.		all-E-	Cattle Rh	264, 330[b]			NO NO						ARh in **2%** digitonin solution pH 6.5.	(Yoshizawa, 1984) (Kropf et al., 1973)
		all-E-	Cattle Rh	280, 328[b]			330						Inhibitor of ARh formation. ARh in Tween-80/buffer solution.	(Towner et al., 1981) (Crouch, 1990)
		9Z-	Cattle IRh	266, 326[b]			322						Inhibitor of ARh formation. ARh in Tween-80/buffer solution.	(Towner et al., 1981) (Crouch, 1990)
89.		all-E- 9Z-	Cattle Rh	264, 330[b]			NO NO						ARh in **2%** digitonin solution pH 6.5.	(Yoshizawa, 1984) (Kropf et al., 1973)

Table 1. Properties of visual pigment analogs

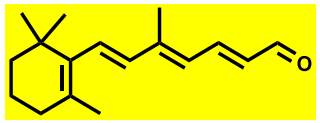
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
90.		all-E-	Cattle Rh	340[a] (3.3)			NO							(Liu and Asato, 1990)
		all-E-	Cattle Rh	350[b]			360						Inhibitor of ARh formation. ARh in Tween-80/buffer solution.	(Towner et al., 1981)
		9Z- 11Z-	Cattle IRh Cattle Rh	323[a] 336[a] (2.9)			NO NO							
		9Z-	Cattle IRh	322[b]			345						Inhibitor of ARh formation. ARh in Tween-80/buffer solution.	(Towner et al., 1981) (Crouch, 1990)
		9Z-	Human red cone opsin in COS-1 cells										Human red cone opsin was transiently expressed in COS-1 cells. AR tested on the human red cone opsin's ability to activate transducin. Ability of opsins to activate transducin was measured using a radioactive filter-binding assay as described previously. Lowered activity in the presence of the 9Z- AR indicates that it is an inverse agonist and contrasts the findings of the same compound on the rod opsin.	(Kono and Crouch, 2011)

Table 1. Properties of visual pigment analogs

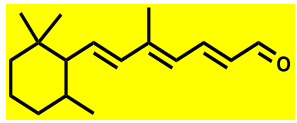
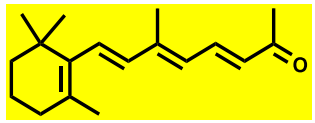
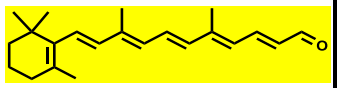
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
91.		all-E-	Cattle Rh				NO NO						ARh in **2%** digitonin solution pH 6.5.	(Yoshizawa, 1984) (Kropf et al., 1973)
92.		9Z-	Cattle IRh	302, 344[b]			342						Inhibitor of ARh formation. ARh in Tween-80/buffer solution.	(Towner et al., 1981)
93.		all-E-	Cattle Rh	398 (4.5) 392[a]			NO NO						ARh in **2%** digitonin solution pH 6.5.	(Yoshizawa, 1984) (Kropf et al., 1973)
		all-E-	Human red cone opsin in COS-1 cells										Human red cone opsin was transiently expressed in COS-1 cells. AR tested on the human red cone opsin's ability to activate transducin. Ability of opsins to activate transducin was measured using a radioactive filter-binding assay as described previously. AR appeared to be neither an agonist nor an inverse agonist.	(Kono and Crouch, 2011)
		all-E-	in frog ROS membrane	393[a]			?						No activation of phosphodiesterase in the membrane was observed. Activation of GTPase <2%. It was shown that Schiff-base linkage between opsin and retinal	(Fukada et al., 1982)

Table 1. Properties of visual pigment analogs

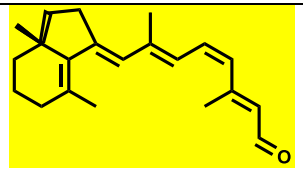
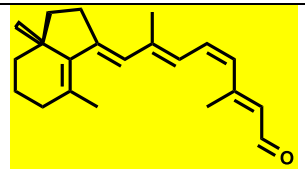
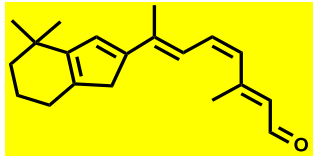
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
													is not always necessary for this enzyme activation.	
F. Alteration or locking of the bond configuration. Non-isomerizable analogs														
94.		11Z- 1R-	Cattle Rh				539						6α-Locked (11Z)-Retinal CD AR 226 (-) / 280 (+)/ 390 (+) t of pigment formation 1.5 h. ARh was measured in 10 mM CHAPSO / HEPES buffer (pH 6.6). CD ARh 329 (+) / 536 (+) CD ARh closely resembles that of native Rh.	(Fujimoto et al., 2001) (Fishkin et al., 2004)
95.		11Z- 1S-	Cattle Rh				NO						6β-Locked (11Z)-Retinal does'n t formed ARh. CD AR 227 (+) / 280 (-)/ 389 (-)	(Fujimoto et al., 2001) (Fishkin et al., 2004)
96.		all-E-	Aporetino chrome	425		505	537			1200			CD ARh 530 (+)/ 324 (-)	(Kinumi et al., 1993)
		9Z-	Cattle Rh				NO							
		11Z-	Cattle Rh	425[a] 295 (2.9)		502	535						ARh were fixed in a 6-s-cis form with a five-embered ring. Low-temperature spectrophotometry of ARh.	(Imamoto et al., 1996)

Table 1. Properties of visual pigment analogs

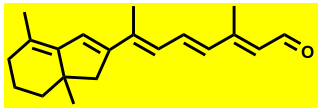
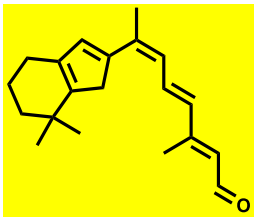
No	Structure	Isomer	Target	λ_{max} (nm); ε 10^{-4} (M^{-1} cm^{-1})				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		11Z-	Cattle Rh	422[a] 229 299 422[a]		506 506	539 In CHAPS–PC mixture. 539			1200 1200			In CHAPS–PC mixture. CD ARh 526 (+)/ 332 (+)	(Ito et al., 1992) (Wada et al., 2001)
97.		all-E-	Aporetino chrome	410 411[a]		495	NO							(Kinumi et al., 1993)
		11Z-	Cattle Rh	227sh 258 310 405[a]		495	545			1853			CD ARh 537 (+)/ 348 (+)	(Ito et al., 1992)
98.		9Z-	Cattle Rh	417[a] 295 (2.5)		503	519			613			CD ARh 512 (+)/ 326 (-)	(Ito, 1990)
99.		9Z-	Cattle IRh	370[a] 335			539						CD ARh 527 (+)/ 328 (-)	(Ito, 1990)

Table 1. Properties of visual pigment analogs

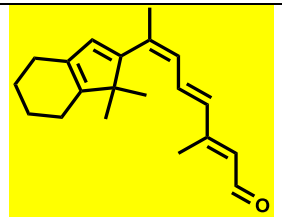
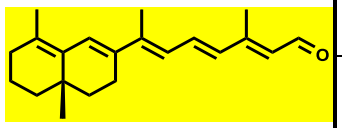
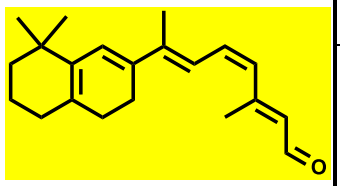
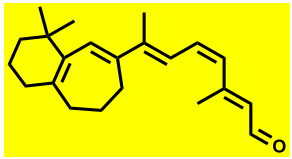
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		9Z-	Cattle IRh	370[a] (1.3) 335[a] (1.5)		473	539			2110			AR with cattle opsin in 2% digitonin, 10 mmol HEPES buffer (pH 6.86) to give the novel 9Z-ARh CD ARh 527 (+)/ 328 (-)	(Ito et al., 1985)
100.		all-E-		400	376	465								(Yoshizawa, 1984)
		9Z-	Cattle IRh				475	Batho 532 nm BSI 474 nm Lumi 518 nm Meta II 406 nm					Yield of pigment 50%. ROS in LM detergent	(Szundi et al., 2002)
101.		all-E-												
		11Z-	Cattle Rh	416[a]		496	546 In CHAPS–PC mixture			1846			In CHAPS–PC mixture. CD ARh 545 (+)/ 340 (+)	(Wada et al., 2001)
102.		all-E-	ApoRetino chrome	382		449	498			2200			In 2% digitonin solution / 67 mM phosphate buffer (pH *6.5)*. CD ARh 488 (+)/ 308 (-)	(Wada et al., 1994) (Wada et al., 1993)
		all-E-	ApoRetino chrome	382		449	498			2200			In 2% digitonin solution / 67 mM phosphate buffer (pH *6.5)*. CD ARh 488 (+)/ 308 (-)	(Kinumi et al., 1993)

Table 1. Properties of visual pigment analogs

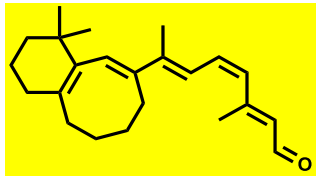
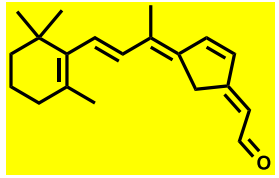
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		11Z-	Cattle Rh				503						ARh were fixed in a 6-s-cis form with and a seven-membered ring. Low-temperature spectrophotometry of ARh data.	(Imamoto et al., 1996)
		11Z-	Cattle Rh	386[a]		457	503 In CHAPS–PC mixture			2000			In CHAPS–PC mixture. CD ARh 491 (+)/ 335(+)	(Wada et al., 1997) (Wada et al., 2001)
103.		all-E-												
		11Z-	Cattle Rh	374[a]		440	483 In CHAPS–PC mixture			2000			In CHAPS–PC mixture. CD ARh 475 (+)/ 340 (+)	(Wada et al., 2001)
104.		11Z-	Cattle Rh	405[a] 263 (1.85)	353	464	495	P495 P466	HPLC analysis of the chromophore extracted from this new pigment P466 shows that it is still 11Z-ret5				ARh5 in 2% digitonin buffered with 10 mM HEPES (pH 7.0). Irradiation of P-495 at -196**^{0}C** with either blue light or orange light caused no spectral change, supporting the cis-trans isomerization hypothesis for formation of bathorhodopsin. Upon irradiation of P-495 at 0^{O}C with orange light, however, its absorption spectrum shifted to a shorter wavelength owing to formation of a hypsochromic product P466. This result	(Fukada et al., 1984)

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
													suggests that the isomerization of the retinylidene chromophore of rhodopsin is indispensable in the phototransduction process. P495 pigment only displays CD ARh 336 nm (+). P466 shows that CD ARh 466 nm (+) nm.	
		11Z-	Cattle Rh		353	464							Primary photochemical behaviors of cattle rhodopsin analogue Rh5 having cyclopenta-11Z-locked retinals Ret5 were studied by excitation with a picosecond laser pulse. Fluorescence maximum was located at about 620 nm.	(Kandori et al., 1989)
		11Z-	Cattle Rh				495						Picosecond spectroscopy of ARh5, only a long-lived excited state (*t* 85 ps) and no product formation were observed.	(Kandori et al., 1996)

Table 1. Properties of visual pigment analogs

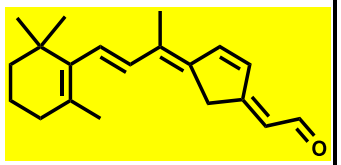
No	Structure	Isomer	Target	λ_{max} (nm); ε 10^{-4} (M^{-1} cm^{-1})				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		11Z-	Cattle Rh	405[a] 263 (1.85)	353	464	495 D			1350			11Z-ret5 forms a ARh (Rh5, 495 nm) only in digitonin solution at a very slow rate; Rh5 is nonfunctional. Rh5, with the most rigid chromophore, does not form any photointermediate under laser flash photolysis due to the complete inhibition of rotation around 11-12 double bond. Only emits strong fluorescence. ^{1}H NMR spectral data confirm that the 11Z-locked-retinal has a high degree of coplanarity, particularly in the C9-C14 triene region.	(Hu et al., 1994) (Ito, 1990)
		11Z,13Z-	Cattle Rh	392[a] (1.0)			NO?							
		11Z-	Cattle Rh	405[a] (1.85)			498 D 503						ARh in 2% digitonin solution. ARh in ROS. ARh prepared from retinal AR5 which has a 11Z-locked and fixed 12-*s*-*trans* geometry, and hence a completely planar configuration of the C9-C12 side-chain moiety, showed a CD spectrum with rhodopsin-like β-band at 336 nm. However, no α-band was observed corresponding to the pigment's absorption maximum at 498 nm.	(Ito et al., 1982) (Balogh-Nair and Nakanishi, 1990)
105.		9Z,11Z-	Cattle Rh	402[a]			NO?							(Hu et al., 1994)

Table 1. Properties of visual pigment analogs

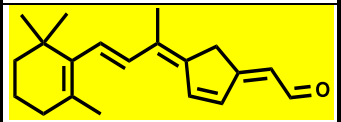
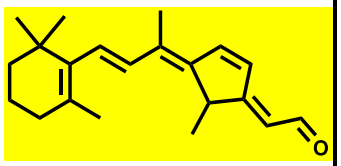
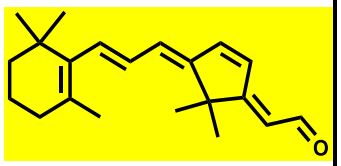
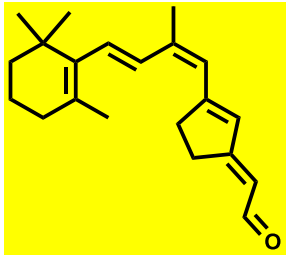
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		9Z,11Z-	Cattle Rh	402[a] (1.15)										(Ito et al., 1982)
106.		11Z-	Cattle Rh	400 260			NO							(Ito, 1990)
107.		11Z-					NO							(Ito, 1990)
108.		11,13 Ring-fused 9Z-retinal 11,13 Ring-fused 9Z,13Z-retinal	Cattle Rh Cattle Rh	366[c] 360[c]			480 (482)						results of the photoconversion of the analogs and the photochemical process elucidated with the computational methods.	(Hirano et al., 2002)

Table 1. Properties of visual pigment analogs

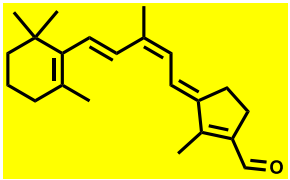
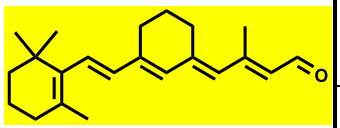
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
109.		all-E-12,14 Ring-fused retinal 9Z-12,14 Ring-fused retinal	Cattle Rh Cattle Rh				509 (510)						results of the photoconversion of the ARh and the photochemical process elucidated with the computational methods.	(Hirano et al., 2002)
110.		all-E-	Cattle Rh				NO							(Liu and Asato, 1990)
		11Z-	Cattle Rh				483 D						Yield 3-30% in D.	(Liu and Asato, 1990) (Liu and Mirzadegan, 1988)
		11Z-	Cattle Rh				488 485							(Balogh-Nair and Nakanishi, 1990)
		11Z-	Cattle Rh				482	ARh 482 nm Batho 535 nm BSI 475 nm Lumi 499 nm						(Lewis et al., 1995)
		11Z,13Z	Cattle Rh				471 D						Yield 3-30% in D.	(Liu and Asato, 1990) (Liu and Mirzadegan, 1988)
		13Z-	Cattle Rh				NO							(Liu and Asato, 1990)

Table 1. Properties of visual pigment analogs

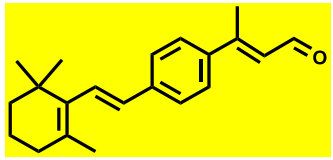
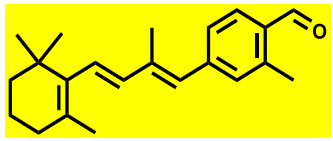
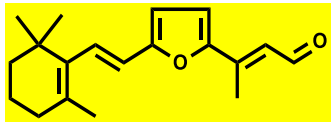
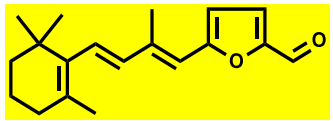
No	Structure	Isomer	Target	λ_{max} (nm); ε 10^{-4} (M^{-1} cm^{-1})				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
111.		all-E- 9Z- 11Z-	Cattle IRh Cattle Rh				NO NO							(Liu and Asato, 1990) (Balogh-Nair and Nakanishi, 1990)
112.		all-E- 9Z- 11Z-	Cattle IRh Cattle Rh				NO NO							(Liu and Asato, 1990)
113.		all-E- 9Z- 11Z-	Cattle IRh Cattle Rh				NO NO							(Liu and Asato, 1990)
114.		all-E- 9Z- 11Z-	Cattle IRh Cattle Rh				NO NO							(Liu and Asato, 1990)
115.		all-E- 9Z-	Cattle Rh Cattle IRh				NO 489 D						Yield 3-30% in D.	(Liu and Asato, 1990)

Table 1. Properties of visual pigment analogs

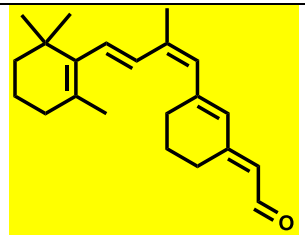
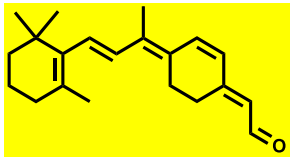
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		13Z-	Cattle Rh				NO							
116.		11Z-	Cattle Rh	374[c]	368	449	510 NG			2660			Similar to native Rh, it exhibited two maxima at 340 and **5**13 nm; however, unlike native Rh, **5**13-nm maximum is not bleached upon irradiation but instead undergoes a blue-shift to 494 nm upon prolonged illumination. CD ARh 293 (+)/ 340 (+) nm, this latter shifts to 493 nm after irradiation. These data suggest that the chromophoric environment of Rh6 is quite different from that of natural Rh.	(Hu et al., 1994)
		11Z,13Z-	Cattle Rh	369[c]	362		NO?							

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		11Z-	Cattle Rh				+						Mechanism of Rhodopsin activation process in ARh6 has been investigated by biochemical methods. The activity of transducin was determined by following the light-dependent binding of [^{35}S] GTPγS. Activities of 11Z-retinol dehydrogenase (11Z-RDH) in retinal pigment (prRDH) epithelium microsomes or all-*E*-retinol dehydrogenase (all-*E*-RDH) in rod outer segments were assayed.	(Jang et al., 2001)
		11Z,13Z-	Cattle Rh											
		11Z-	Cattle Rh				508						Relative activities of incubation mixture measured by transducin assay. Inactive.	(Tan et al., 1998) (Fishkin et al., 2004)
		11Z-	human blue cone opsin, green cone opsin, red cone opsin bovine Rh				440 NO NO 505						Specific chromophore–protein interactions that govern spectral tuning in human visual pigments, here was presented unique compared binding properties of 11Z-ReCHO and 11Z-6-membered-ring-retinal (11Z-6mr-retinal) with human blue, green, and red cone opsins. To unravel the specificity of the chromophore-binding pocket of cone opsins, we applied 11Z-6mr-retinal analog-binding analyses	(Katayama et al., 2019)

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
													to human blue, green, and red cone opsins. These results revealed that among the three cone opsins, only blue cone opsin can accommodate the 11Z-6mr-retinal in its chromophore binding pocket, resulting in the formation of a synthetic blue pigment (B6mr) that absorbs visible light.	
		11Z-	Cattle Rh				512 DM	Illumination of ARh6 for 10 s caused **3** nm blue-shift and **3%** loss of visible absorbance. Prolonged illumination caused a maximal blueshift up to 20 nm and -40% loss of visible absorbance.		2600			ARh6 λ_{max} 512 nm formed from opsin and AR6 in dodecyl maltoside (DM) showed ground state properties very similar to those of rhodopsin, but was not entirely stable to light. The rate of formation of ARh6 from AR6 wasin 10 times slower. Complete bleaching of ARh6 by hydroxylamine required >12.5 min and illumination. ARh6 activates Transducin and undergoes phosphorylation.	(Bhattacharya et al., 1992) (Ridge et al., 1992)
		11Z-	Abca4-/-Rdh8-/- mice eye										It was evaluated the effect of a locked chromophore analog, 11Z-6-membered ring-AR against bright light–induced retinal degeneration in Abca4-/-Rdh8-/- mice.	(Gao et al., 2018)

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		11Z-											Rh regenerated with retinal analogs with different ring sizes, which prevent isomerization around the C11=C12 double bond, the activation mechanism of this G-protein-coupled receptor was investigated. In bleaching 11Z-ARh6-ring-Rho modestly activates phototransduction *in vivo* and at low pH *in vitro*. These results reveal that partial activation is caused by isomerization along other double bonds in more rigid 6-locked retinal isomers and protonation of key residues by lowering pH in 11Z-ARh6. Full activation is not achieved, because isomerization does not induce a complete set of conformational rearrangements of Rh.	(Kuksa et al., 2002)

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		11Z-											It was investigated whether the 6-member ring locked ARh6 is capable of producing an active conformation following light absorption, we have studied the photochemistry of ARh6 by UV-visible spectroscopy at different pH levels. Furthermore, FTIR spectroscopy was employed to monitor protein conformational changes following light absorption. It was revealed that the photochemistry of ARh6 is pH dependent. An active Meta II-like intermediate with a protonated Schiff base is produced, particularly at low pH, while at high pH, presumably photoequilibration processes between the11Z-like inactive isomers dominate the photochemistry.	(Fan et al., 2002)
		11Z-											ARh6, in which the retinal chromophore is locked in an 11Z-geometry by the introduction of a six-member ring structure, an activated receptor may be formed by light-induced isomerization around other double bonds. It was have examined this activation of ARh6 by UV-visible and FTIR	(Vogel et al., 2002)

Table 1. Properties of visual pigment analogs

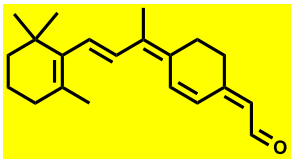
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
													spectroscopy and have revealed that ARh6 is a nonbleachable pigment. It was showed that the activated receptor consists of two different subspecies corresponding to 9E- and 9Z- isomers of the chromophore. Both subspecies relax in the dark via separate pathways back to their respective inactive states by thermal isomerization presumably around the C13=C14 double bond. ARh6 can be repeatedly photolyzed to undergo identical activation-relaxation cycles.	
117.		9Z,11Z-	Cattle Rh	366[c]	350		NO?						Similar to native Rh, it exhibited two maxima at 340 and **5**13 nm; however, unlike native Rh, **5**13-nm maximum is not bleached upon irradiation but instead undergoes a blue-shift to 494 nm upon prolonged illumination.	(Hu et al., 1994)
		9Z,11Z,13Z-	Cattle Rh	360[c]	354	451	494 NG		1930					
		9Z,11Z-	Cattle Rh				+						Mechanism of Rhodopsin activation process in ARh6 has been investigated by biochemical methods. The activity of transducin was determined by following the light-dependent binding of [^{35}S] GTPγS. Activities of 11Z-retinol dehydrogenase	(Jang et al., 2001)
		9Z,11Z,13Z-	Cattle Rh											

Table 1. Properties of visual pigment analogs

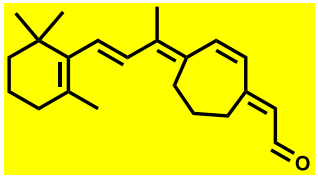
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
													(11Z-RDH) in retinal pigment (prRDH) epithelium microsomes or all-*E*-retinol dehydrogenase (all-*E*-RDH) in rod outer segments were assayed.	
118.		11Z-	Cattle Rh				490							(Yoshizawa, 1984)
		11Z-	Cattle Rh		355	437	490	Rh7(580) Rh7(630)		2475			Primary photochemical behaviors of cattle rhodopsin ARh7 having cycloheptatrienylidene-11Z-locked retinals Ret7 were studied by excitation with a picosecond laser pulse.	(Kandori et al., 1989)
		11Z-	Cattle Rh				490						Excitation of ARh7, yielded an appearance of the ground-state photoproduct that had a spectrum similar to that of photorhodopsin, the primary intermediate of rhodopsin. ARh7→P580 nm, t < 44 ps. In the case of ARh7, whose quantum yield is 5 times less than that of rhodopsin.	(Kandori et al., 1996)
		11Z-	Cattle Rh	376[c]	355	447	496 NG			2210			The seven-membered ring retinal AR7 has been shown by ultraviolet / visible absorption and circular dichroism spectra to occupy the same binding site in ARh7 as 11Z-retinal does in native Rh.	(Hu et al., 1994)

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
													11Z-Ret7, readily forms ARh (Rh7, 496 nm, which was totally stable to light and did not lead to visual transduction, neither in vitro nor in vivo. CD ARh 333 (+)/ 491 (+) nm.	
		11Z,13Z-	Cattle Rh	371[c]	351	436	488 NG			2444			CD ARh 330 (+)/ 490 (+) nm. In ARh7 isomerization around C11=C12 is blocked and no enzymatic activity is reported.	(Hu et al., 1994)
		11Z-	bullfrog retina				497						By comparison with rhodopsin, ARh formed in the bullfrog retina, that is degraded slowly by hydroxylamine and relatively resistant to photolysis.	(Crouch, 1990) (Crouch et al., 1984)
		11Z-	Cattle Rh	230 265 295 376 (2.5)	355	447	490			1963			Data for 2% digitonin, 67 mM phosphate buffer, pH 7.0 CD ARh 330 (+)/ 488 (+) nm.	(Akita et al., 1980)
		11Z,13Z-	Cattle Rh	225 295 371 (2.2)	351	436	488 D			2444			Data for 2% digitonin, 67 mM phosphate buffer, pH 7.0 CD ARh 330 (+)/ 484 (+) nm.	(Akita et al., 1980)

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		11Z-	Cattle Rh				490 D	(P580)					Key question that remains to be solved is the mechanistic aspects leading to visual transduction. There is no doubt that an 11Z- to all-E-isomerization has to occur. Thus, ARh7 was readily formed from the AR7 in which the 11Z--ene is locked into the *Z*-geometry via a side-chain 7-membered ring. As was expected nonplanar conformation of the 7-membered ring simulates that of the native chromophore in the binding site as judged from the UV/vis and CD spectra which were similar to those of native Rh. ARh7 was totally stable to light, and was enzymatically inactive, both *in vivo* and *in vitro,* thus showing that 11Z-isomerization is a prerequisite for visual transduction. The UV/vis and CD spectra of ARh7 are similar to those of native Rh; thus, the chromophoric binding site in ARh7 closely resembles that of native Rh, i.e., both ends of the chromophore are fixed in the binding site. Picosecond flash photolysis showed that	(Nakanishi et al., 1994)

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
													the nonbleachable ARh7 absorbing at 490 nm yielded in 7 ps a pigment with a maximum at 580 nm (P580) corresponding to photo-R; this decayed to the original ARh7 in 44 ps. Quantum yields of ca. 13 %	
		11Z-	Cattle Rh				490 D						Data for 2% digitonin, 67 mM phosphate buffer, pH 7.0. CD ARh 330 (+)/ 488 (+) nm. Flash photolysis ARh7 experiments showed that ARh7 cannot form a Meta I intermediate and also that at 77 K, where the batho product of natural rhodopsin can be observed, irradiation of ARh7 led to no changes in its absorption spectrum. This confirmed the original premise that 11Z- to *E*- isomerization is a prerequisite to rhodopsin activation in the primary event of vision. Picosecond kinetic absorption and fluorescence measurements further demonstrated that although ARh7 can undergo photochemical changes at the picosecond timescale, none of the species formed from ARh7 was the equivalent of the	(Balogh-Nair and Nakanishi, 1990)

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
													batho intermediate found in the bleaching sequence of natural rhodopsin but was instead a species which could have been obtained also from natural rhodopsin if the primary event in vision did not involve the crucial 11,12-double bond isomerization. The fluorescence characteristics of ARh7 differed considerably from those of rhodopsin. These include the slower rise time (25 ps) and decay time (55 ps) of its emission (< 12 ps for both, in Rh), as well as its much larger fluorescence quantum yield.	
		11Z-	rods from the tiger salaman der				+						11Z-Retinal, when delivered to isolated rods from liposomes, combines with free opsin to form a bleachable photopigment that fully restores sensitivity. 11Z-Locked AR combine with opsin to form unbleachable ARh in isolated bleached rods from the tiger salamander.	(Corson et al., 1990)
		11Z,13Z-	rods from the tiger salaman der				+						11Z-Retinal, when delivered to isolated rods from liposomes, combines with free opsin to form a bleachable photopigment that fully restores sensitivity. 11Z-Locked	(Corson et al., 1990)

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
													AR combine with opsin to form unbleachable ARh in isolated bleached rods from the tiger salamander.	
		11Z- 11Z,13Z-	Cattle Rh				+ +						11Z-locked AR7 forms nonbleachable pigments with opsins from various sources, however, 11Z-locked AR7, upon addition to bleached salamander rod outer segments, restores some light sensitivity through a mechanism apparently unrelated to the photoexcitation of the pigment. Properties of AR7 and ARh7 which are necessary and sufficient for transduction, were tested by phosphorylation of rhodopsin kinase and by difference FTIR spectroscopy.	(Zankel et al., 1990)

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		11Z-	Cattle Rh				+	P580 nm					The vibrational degrees of freedom of the only photophysical intermediate formed during the photoreaction of ARh7 containing AR with 7-membered ring blocking 11Z-isomerization in ARh7 is measured via picosecond time-resolved coherent anti-Stokes Raman spectroscopy (PTR/CARS). The structural changes occurring as ARh7 is formed can be derived from vibrational mode assignments in the PTR/CARS spectra such as the 955-cm^{-1} band assigned as the HC11=C12H hydrogen-out-of-plane (HOOP) mode (shifts to 946 cm^{-1}), increases intensity, and broadens its width in ARh7 and the 1551-cm^{-1} band assigned as the C=C stretching mode (shifts to 1546 cm^{-1} in ARh7). These PTR/CARS data show that incorporation of an 11-ene, AR7 permits some flexibility for torsional motion around the C11=C12 bond and within the seven-membered ring.	(Jäger et al., 1998)

Table 1. Properties of visual pigment analogs

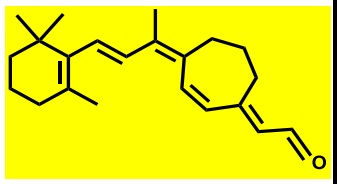
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		11Z-	Cattle Rh				+						AR7 11Z-locked analog, gave the pigment ARh7, which was nonbleachable and nonfunctional flash photolysis detected a transient primary photoproduct (but in only 25% quantum yield of native rhodopsin), which reverted to starting ARh7.	(Caldwell et al., 1993)
		11Z-											Rh regenerated with retinal analogs with different ring sizes, which prevent isomerization around the C11=C12 double bond, the activation mechanism of this G-protein-coupled receptor was investigated. It was demonstrated that 11Z-ARh7 does not activate G-protein *in vivo* and *in vitro*, and that it does not isomerize along other double bonds, suggesting that it fits tightly into the binding site of opsin.	(Kuksa et al., 2002)
119.		9Z,11Z-	Cattle Rh	371[c]	351	441	489 NG			2230			11Z-Ret7, readily forms ARh (Rh7, 496 nm, which was totally stable to light and did not lead to visual transduction, neither in vitro nor in vivo. CD ARh 333 (+)/ 491 (+) nm.	(Hu et al., 1994)
		9Z,11Z, 13Z-	Cattle Rh	366[c]	346	430	483 NG			2550			11Z-Ret7, readily forms ARh (Rh7, 496 nm, which was totally stable to light and did not lead to visual transduction, neither in vitro nor in vivo.	(Hu et al., 1994)

Table 1. Properties of visual pigment analogs

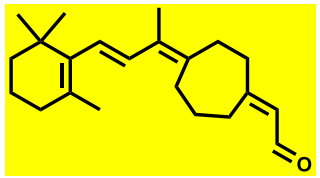
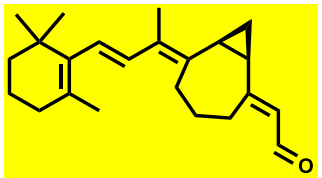
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
													CD ARh 333 (+)/ 491 (+) nm.	
		9Z,11Z-	Cattle Rh	230 295 371 (2.0)	351	441	489			2226			Data for 2% digitonin, 67 mM phosphate buffer, pH 7.0 CD ARh 330 (+)/ 485 (+) nm.	(Akita et al., 1980)
		9Z,11Z, 13Z-	Cattle Rh	225 285 366 (1.6)	346	430	483			2552			Data for 2% digitonin, 67 mM phosphate buffer, pH 7.0 CD ARh 330 (+)/ 481 (+) nm.	(Akita et al., 1980)
120.		11Z, 13E-	Cattle Rh	244		272	283 (2.8)			1429		Don't replaced by 11Z-RetCHO	CD ARh 273 (+)/ 297 (-) nm. 67 mM phosphate buffer (pH 7.0) at 25°C for 5 h / 23 mM octyl glucoside solution at pH 7.0.	(Tan et al., 1997) (Lou et al., 2000)
		11Z, 13Z-	Cattle Rh	244		272	284 (2.9)			1554		Don't replaced by 11Z-RetCHO	CD ARh 272 (+)/ 298 (-) nm	(Tan et al., 1997) (Lou et al., 2000)
121.		11Z-	Cattle Rh	266	260	284	312 270 316						11Z-Seven-membered ring-locked ARs with a cyclopropyl ring incorporated to the C-11 / C-12 bond have been designed for opsin binding studies. It was observed in the binding of AR to opsin. A new band absorbing at 312 rim was formed during a 1 h incubation at room temperature, with bovine opsin solubilized in CHAPSO/HEPES buffer.	(Lou et al., 2000, 1999) (Fishkin et al., 2004)

Table 1. Properties of visual pigment analogs

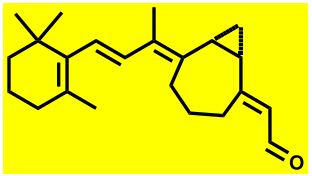
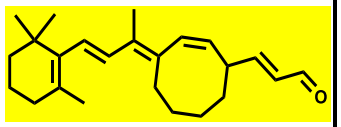
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
													CD AR 245 (-)/ 281 (+) / 343 (-) nm.	
122.		11Z-	Cattle Rh	266	260	284	NO						AR does not bind to opsin CD AR 244 (+)/ 281 (-) / 342(+) nm.	(Lou et al., 2000, 1999)
123.		11Z-	Cattle Rh	346[c] 276[c]	285 335	315 435	425 OG 425 502 CHAPSO/ HEPES			3070	unstable		Incubation of 11Z-ret8 with bovine opsin, either suspended in buffer or solubilized in octyl glucoside, yielded only a single pigment absorbing at 425 nm (P425) under various conditions; no pigment with higher λ was observed. However, an additional pigment absorbing at 502 nm (P502) was formed when fresh opsin in 10 mM CHAPSO/10 mM HEPES (pH 7.0) was used. At 37°C, P502 reached its maximum in 30 min and then decreased gradually with time. After 14 h, P502 disappeared, while P425 remained. In contrast, the three other 11Z-ret8 isomers formed only a single pigment, each between 410 and 430 nm, throughout the incubation. Unlike ARh5 and ARh6,	(Hu et al., 1994)

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
													ARh8 (P502) was completely stable to light. ARh8 was stable under prolonged illumination; however, flash photolysis experiments revealed that a primary product absorbing at 585 nm in 15 ps. This photoproduct corresponds to photo-ARh8, which then thermally decays in 1 ns to batho-ARh8 (577 nm). The latter, however, reverts to the starting ARh8 (502 nm) in 50 ns. ARh8 is a much less stable pigment. It decomposed gradually in 20 mM nonylglucose at 22^{O}C. P425 did not show any CD band.	
		11Z,13Z-	Cattle Rh	337[c] 286[c]	318		NO 425						In contrast, the three other ret8 isomers formed only a single pigment, each between 410 and 430 nm, throughout the incubation.	(Hu et al., 1994)
		11Z-	methylated ROS				502 CHAPSO/ HEPES							(Hu et al., 1994)
		11Z,13Z -	methylated ROS				NO CHAPSO/ HEPES							(Hu et al., 1994)

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		11Z-	Cattle Rh				500						Incubation of bovine opsin with 11Z-locked Ret8 formed two pigments absorbing at 425 nm (P425) and 500 nm (P500). P425, however, is an artificial pigment because it formed from thermally denatured opsin or other proteins and Ret8. Results on ARh8, which possesses a more flexible ring, upon excitation of ARh8 with a 21-ps pulse, two photoproducts were observed, not only photorhodopsin-like, but also bathorhodopsin-like products. ARh8→P585→P577→ ARh8 nm, t_1 = 780 ps. t_2 <10 ns. These facts indicate that the primary photochemical nature of ARh8 is close to that of the native rhodopsin.	(Kandori et al., 1996)
		11Z-	Cattle Rh	346[c] 276[c]	285 335	315 435								(Caldwell et al., 1993)

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		11Z-	Cattle Rh	346[c] 276[c]			430? 515 CHAPSO	P585					ARh8 in bovine ROS in CHAPSO, 28^0C. Only the 11Z-isomer AR8 yields a pigment. In the case of ARh8 with increased flexibility in the chromophore, the highly distorted photo-Rh-like intermediate P585 can relax one step further to a batho-like intermediate P577 in 1 ns before returning to the original ground state. Importantly, the quantum yield of P585 formation is high and similar to that of native Rh (100%).	(Nakanishi et al., 1994)
		11Z-	Cattle Rh				430? 515 CHAPSO						ARh8 in bovine ROS in CHAPSO, 28^0C. Incubation of AR8 at room temperature yielded a photolabile species with a broad absorption and a maximum at 430 nm as determined from its second derivative spectrum. At 37°C, however, a ARh8, absorbing at 515 nm, was also obtained together with the 430-nm species. Irradiation at wavelengths longer than 410 nm "bleached" the 430-nm species but the absorption of ARh8 at 515 nm remained unchanged. ARh8 is a nonbleachable rhodopsin.	(Balogh-Nair and Nakanishi, 1990)

Table 1. Properties of visual pigment analogs

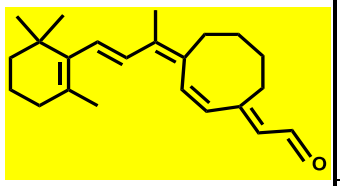
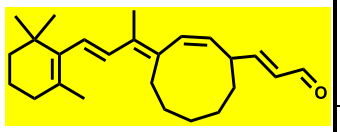
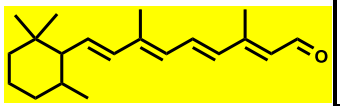
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
124.		9Z,11Z-	Cattle Rh	350[c] 275[c]			NO 415						In contrast, the three other ret8 isomers formed only a single pigment, each between 410 and 430 nm, throughout the incubation. Interaction of AR8 with opsin in CHAPSO at 37°C.	(Hu et al., 1994)
		9Z,11Z, 13Z-	Cattle Rh	335[c] 278[c]			NO 410						In contrast, the three other ret8 isomers formed only a single pigment, each between 410 and 430 nm, throughout the incubation. Interaction of AR8 with opsin in CHAPSO at 37°C.	(Hu et al., 1994)
125.		11Z-	Cattle Rh	245[c] 281[c] 330[c]	286	324	NO							(Hu et al., 1994)
		11Z-	Cattle Rh	245[c] 281[c] 330[c]	285	324								(Caldwell et al., 1993)
		11Z-	Cattle Rh				?							(Nakanishi et al., 1994)
		11Z-	Cattle Rh	280			407?						AR9 with the 9-membered ring produced a 407-nm absorbing and light-sensitive species when incubated with bovine ROS solublized in CHAPSO.	(Balogh-Nair and Nakanishi, 1990)
G. Alteration of the trimethylcyclohexenic ring. Ring modification														
126.		all-E-		370 363[a]		430								(Yoshizawa, 1984)

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
				356[c]										
		9Z-	Cattle IRh				465							(Yoshizawa, 1984); (Kropf et al., 1973)
		9Z-	Cattle Rh	364		425	460			1800				(Nakanishi, 1985); (Honig et al., 1979); (Nakanishi et al., 1980)
		9Z-	Cattle Rh	347[c]		425	460			1800			Dihydroretinal in which the saturation of the 11,12-double bond eliminates the possibility of *11Z-* to *all-E-* isomerization formed the first known nonbleachable ARh, thus supporting the important role attributed to the isomerization of this bond in the bleaching of rhodopsin. The opsin shifts of bovine rhodopsins formed from hydroretinals constituted the experimental basis for the external-point charge model. This model was proposed to explain the color of bovine rhodopsin as well as to account for a general mechanism by which opsins regulate the absorption maxima of visual pigments in nature.	(Balogh-Nair and Nakanishi, 1990)

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		9Z-	Cattle IRh	356[a]			465 D						ARh in 2 % aqueous digitonin 23^{0}C, pH 6.8.	(Blatz et al., 1969)
		9Z-	Red cone Rod Blue cone				492 467 415			3200 2100 -600			Salamander Visual Pigments. AR were used to determine how saturating particular double bonds in the chromophore affected the spectrum and opsin shift (OS) of salamander red rod and red and blue cone visual pigments.	(Makino et al., 1999)
		9Z-	Cattle IRh				465						ARh in 2 % digitonin solution.	(Blatz et al., 1970)
		9Z- cis-5,6-dihydro-	Cattle IRh				461	ARh 461 nm Batho 508 nm BSI 430 nm Lumi 480 nm Meta I 473 nm Meta II 370 nm					ARh in 2% octyl-fl-D-glucopyranoside (octyl-glucoside), in pH 7.0 Tris buffer. Low-temperature nanosecond photolysis.	(Albeck et al., 1989)
		9Z-	Cattle IRh			422	461	461 nm Batho 510 nm BSI 430 nm Lumi 470 nm		2000			Nanosecond time-resolved and continuous illumination, low-temperature, spectroscopic studies reveal a new photolysis intermediate in a wide variety of ARhs.	(Randall et al., 1991)
		9Z-	Iodopsin			425	475			2500				(Chen et al., 1989)
		11Z-	Iodopsin			433	505			3300				(Chen et al., 1989)

Table 1. Properties of visual pigment analogs

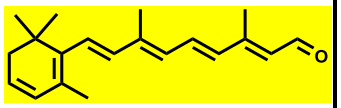
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		11Z-	Cattle Rh				465							(Yoshizawa, 1984) (Kropf et al., 1973)
		11Z-	Cattle Rh	360[a]			465 D						ARh in 2 % aqueous digitonin 23^{0}C, pH 6.8. $NaBH_4$ on ARh in the dark caused very little change. but under illumination caused progressive disappearance of ARh.	(Blatz et al., 1969)
		11Z-	Cattle Rh	356[a]	338[a]	415[a]	465						ARh in 2 % digitonin solution.	(Blatz et al., 1970)
		11Z-	Cattle Rh			433	473			1950				(Koutalos et al., 1989)
		11Z-	Octopus Rh			433	464			1500				(Koutalos et al., 1989)
		all-E-	Octopus Rh			430	471			2100				(Koutalos et al., 1989)
127.		all-E-	Cattle Rh	396 401 387[c] 401[a] 400	381	471 463	NO							(Liu and Asato, 1990) (Azuma et al., 1973)
		all-E-	Octopus Rh			471	520			2000				(Koutalos et al., 1989)
		all-E-	Aporetinichrome				515						Aporetinochrome in 0.67% digitonin at pH 6.8.	(Seki et al., 1985)

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		7Z-	Cattle Rh				464 D						In D.	(Liu and Asato, 1990) (Matsumoto et al., 1979)
		9Z-	Cattle IRh				498 D						In D.	(Liu and Asato, 1990)
		9Z-	Cattle IRh				500						CD ARh 500 (+)	(Yoshizawa, 1984)
		9Z-	Cattle IRh	390			500				stable		ARh in 2 % aqueous digitonin CD data	(Azuma et al., 1973)
		9Z-	Cattle IRh	391[a]			501 D						ARh in 2 % aqueous digitonin 23^{0}C, pH 6.8.	(Blatz et al., 1969)
		9Z-	Red cone Rod Blue cone				582 503 422			4700 2000 -1900			Salamander visual pigments. AR were used to determine how saturating particular double bonds in the chromophore affected the spectrum and opsin shift (OS) of salamander red rod and red and blue cone visual pigments.	(Makino et al., 1999)
		9Z-	in frog ROS membrane	393[a]			522						Activation of GTPase 38% under illumination. It was shown that Schiff-base linkage between opsin and retinal is not always necessary for this enzyme activation.	(Fukada et al., 1982)

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		9Z-	Cattle IRh			450	500	ARh 500 nm Batho 560 nm BSI 500 nm Lumi 505 nm		2200			Nanosecond time-resolved and continuous illumination, low-temperature, spectroscopic studies reveal a new photolysis intermediate in a wide variety of ARhs.	(Randall et al., 1991)
		9Z-	Cattle IRh				500						Φ 0.1	(De Grip and Lugtenburg, 2022)
		9Z-	Iodopsin			471	575			3750				(Chen et al., 1989)
		9Z-	Iodopsin				585 (Cl^-) 533 (NO_3^-)						Iodopsin analog in buffer A (0.6% CHAPS, 0.8 mg/mL egg phosphatidylcholine, 50 mM HEPES, 140 mM NaCl, 1 mM dithiothreitol, 200 mM methyl-α-D-mannopyranoside (MMP), pH 6.5 at 4°C). Chloride replacement with nitrate in the analogs was accompanied with a blue shift.	(Imai et al., 1999)
		11Z-	Iodopsin				624 (Cl^-) 588 (NO_3^-)						Iodopsin analog in buffer A (0.6% CHAPS, 0.8 mg/mL egg phosphatidylcholine, 50 mM HEPES, 140 mM NaCl, 1 mM dithiothreitol, 200 mM methyl-α-D-mannopyranoside (MMP), pH 6.5 at 4°C). Chloride replacement with nitrate in the analogs was accompanied with a blue shift.	(Imai et al., 1999)

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		11Z-	Iodopsin			471	613			4900				(Chen et al., 1989)
		11Z-	Cattle Rh				518						Φ 0.63	(De Grip and Lugtenburg, 2022)
		11Z-	Cattle Rh	392			517				stable		ARh in 2 % aqueous digitonin CD data	(Azuma et al., 1973)
		11Z-	in frog ROS membrane	391[a]			504						Activation of GTPase 42% under illumination. It was shown that Schiff-base linkage between opsin and retinal is not always necessary for this enzyme activation.	(Fukada et al., 1982)
		11Z-	Goldfih Cyanopsin				625							(Yoshizawa, 1984)
		11Z-	Rod opsin Carp Porphyro Opsin				522	Batho 592 nm Lumi 542 nm Meta I 509 nm						(Yoshizawa, 1984)
		11Z-	Red cone Rod Blue cone				620 521 440			5300 2300 -1300			Salamander visual pigments. AR were used to determine how saturating particular double bonds in the chromophore affected the spectrum and opsin shift (OS) of salamander red rod and red and blue cone visual pigments.	(Makino et al., 1999)

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		11Z-	salamander rod pigment				520						Salamander rod and cone pigments. Pigments were generated by combining proteins expressed in COS-1 cells. All spectra were recorded with the pigments in 0.1% dodecyl maltoside and 10 mM MES buffer with 150 mM NaCl at pH 6.0. 9-methyl group of retinal is not important in the activation pathway of the red cone and blue cone/green rod pigments	(Ma et al., 2001) (Das et al., 2004)
		11Z-	salamander red cone pigment											
		11Z-	salamander blue cone/green rod pigment				440							
		11Z-	salamander UV cone pigment				360							
		11Z-	Cattle Rh				517						CD ARh 350 (+)/ 510 (+)	(Kropf et al., 1973)
		11Z-	Cattle Rh	400[a]	380[a]	460[a]	517						ARh in 2 % digitonin solution.	(Blatz et al., 1970)
		11Z-	goldfish visual pigments cone pigments and the rod pigment				Cone pigments longwave-sensitive (LWS) 618 nm middle-wave-sensitive (MWS) 535 nm short-wave-sensitive (SWS) 454 nm						λ_{max} of the native porphyropsins (visual pigments based on 11Z-3-dehydroretinal and its analogs) of the rods and four spectral classes of cone in the goldfish. Cone pigments and the rod pigment were measured with each chromophore, demonstrating that all the goldfish visual pigments were reconstituted by the above protocol.	(Parry and Bowmaker, 2000)

Table 1. Properties of visual pigment analogs

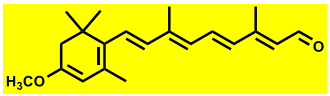
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
							ultraviolet-sensitive (UVS) cone pigments 380 nm rod pigment 522 nm							
		11Z-	Cattle Rh	396[a]			517 D						ARh in 2 % aqueous digitonin 23^{0}C, pH 6.8.	(Blatz et al., 1969)
		11Z- 11Z-	Cattle Rh Octopus Rh			471 471	520 486			2000 700				(Koutalos et al., 1989) (Koutalos et al., 1989)
		11Z-	Cattle Rh				505 D						In D.	(Liu and Asato, 1990)
		11Z-	rods from the tiger salamander				519							(Corson et al., 1990)
		13Z-	Cattle Rh				NO							(Liu and Asato, 1990)
128.		9Z-	Iodopsin				663 (Cl^-) 578 (NO_3^-)						Iodopsin analog in buffer A (0.6% CHAPS, 0.8 mg/mL egg phosphatidylcholine, 50 mM HEPES, 140 mM NaCl, 1 mM dithiothreitol, 200 mM methyl-α-D-mannopyranoside (MMP), pH 6.5 at 4°C). Chloride	(Imai et al., 1999) (Liu and Asato, 2003)

Table 1. Properties of visual pigment analogs

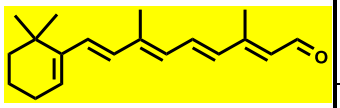
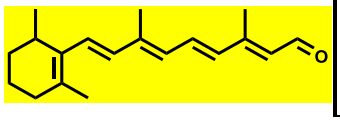
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
													replacement with nitrate in the analogs was accompanied with a blue shift.	
129.		all-E-		388 362[a]		453								
		9Z-	Cattle IRh				480							(Yoshizawa, 1984)
		9Z-	Cattle IRh					pigment 474 nm Batho 530 nm BSI 466 nm Lumi 482 nm					ARh was solubilized in sufficient 2% octylglucoside detergent in buffer (pH 7.0, 10 mM TRIS, 60 mM KCl, 30 mM NaCl, 2 mM $MgCl_2$, 0.1 mM EDTA). ARh formed much more slowly, and after the first 2 h, incubation was continued at room temperature for 4 days.	(Lewis et al., 2001)
		11Z-	Cattle Rh				480							(Yoshizawa, 1984)
		11Z-	Cattle Rh				485							(Derguini and Nakanishi, 1986)
		11Z-	Cattle Rh	385 (2.0)			492						Yield of pigment formation 70%.	(Domínguez et al., 2006)
		?	Cattle Rh				NO							(Kropf et al., 1973)
130.		all-E-	Cattle Rh	364[a]			NO NO							(Yoshizawa, 1984) (Kropf et al., 1973)

Table 1. Properties of visual pigment analogs

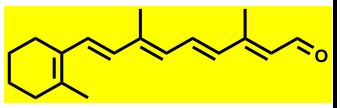
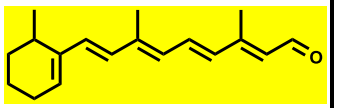
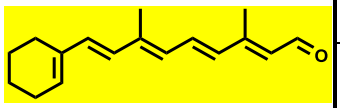
No	Structure	Isomer	Target	λ_{max} (nm); ε 10^{-4} (M^{-1} cm^{-1})				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		11Z-	Cattle Rh	394 (1.9)			522						Yield of pigment formation 33%.	(Domínguez et al., 2006)
131.		all-E-	Cattle Rh	401		474	NO							(Domínguez et al., 2006)
		9Z-	Cattle IRh	388[a]			505						FTIR spectroscopy to examine the pH dependence of the Meta I / Meta II conformational equilibrium. pK_A values were determined from pH series of FTIR spectra. *t* pigment regeneration 6 h, yield < 10%. pK_A of the Meta I / Meta II equilibrium was found to be 5.8.	(Vogel et al., 2005)
132.		11Z-	Cattle Rh	389 (2.2)			516						Yield of pigment formation 24%.	(Domínguez et al., 2006)
133.		all-E-		387		458								
		9Z-	Cattle IRh	381[a]			500						FTIR spectroscopy to examine the pH dependence of the Meta I / Meta II conformational equilibrium. pK_A values were determined from pH series of FTIR spectra. *t* pigment regeneration 20 h, yield < 5%. pK_A of the Meta I /Meta II equilibrium was found to be 5.2.	(Vogel et al., 2005)

Table 1. Properties of visual pigment analogs

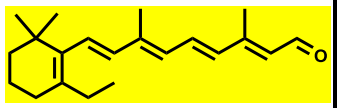
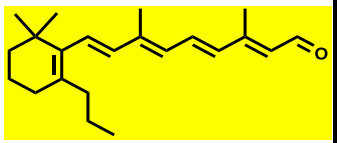
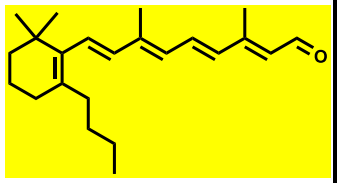
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		11Z-	Cattle Rh	387 (2.2)			NO							(Domínguez et al., 2006)
134.		9Z-	Cattle IRh				484	Batho 532 nm BSI 435 nm Lumi 500 nm Meta I 473 nm Meta II 380 nm					ROS in 1% Ammonyx LO detergent. Yield of pigment 20%.	(Szundi et al., 2002)
		11Z-	Cattle Rh	377 (1.6)			500						Yield of pigment 105%.	(Domínguez et al., 2006)
135.		all-E-	Cattle Rh				NO							(Liu and Asato, 1990)
		7Z-	Cattle Rh				470 D						Yield of pigment 3-30% in D.	(Liu and Mirzadegan, 1988)
		9Z-	Cattle IRh				482 D						Yield of pigment 3-30% in D.	
		11Z-	Cattle Rh				475 D						Yield of pigment 30-70% in D.	
		11Z,13Z-	Cattle Rh				480 D						Yield of pigment 3-30% in D.	
		13Z-	Cattle Rh				NO							
136.		all-E-	Cattle Rh											(Liu and Asato, 1990)
		9Z-	Cattle IRh				458 D						Yield of pigment 3-30% in D.	
		11Z-	Cattle Rh				NO							

Table 1. Properties of visual pigment analogs

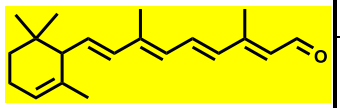
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
137.		all-E-		368										
		9Z-	ROS from bovine eyes				461						FTIR spectra Binding level >90% Φ 0.28	(Bovee-Geurts et al., 2017)
		9Z-	ROS from bovine eyes				459						ARh in a 2% digitonin solution. ARh were investigated by low-temperature spectrophotometry and nanosecond laser photolysis. Irradiation of each pigment at -180^0 **C** produced a photosteady-state mixture containing the original 9Z-pigment, its 11Z-pigment, and a photoproduct, indicating that the primary process of each pigment is a photoisomerization of its chromophore. It should be noted that each pigment was stable in the presence of 100 mM NH_2OH at 4^{0}C	(Okada et al., 1991)
		9Z-	cone visual pigment, P521, of the Tokay gecko (*Gekko gekko*) retina				455 D	P521 455 nm BSI 430 nm Lumi 463 nm Meta I 455 nm					Nanosecond laser photolysis measurements	(Lewis et al., 1997)

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		9Z-	Cattle IRh	348[c]		417	461 (4.0) 461			2290			G protein activation. Φ 0.28. ARh in 1% DDM solution (pH 6.5). Yield >70%.	(Wang et al., 2008) (Wang et al., 2004a)
		9Z-	Cattle IRh			422	461	ARh 461 nm Batho 515 nm BSI 428 nm Lumi 470 nm		2000			Nanosecond time-resolved and continuous illumination, low-temperature, spectroscopic studies reveal a new photolysis intermediate in a wide variety of ARhs.	(Randall et al., 1991)
		9Z-	Cattle IRh				461						AR and ROS in buffer A: 20mM (PIPES), 130 mM NaCl, 5 mM KCl, 2 mM $CaCl_2$, 0.1 mM EDTA, 1 mM dithioerythritol, pH 6.5) with a 5-10-fold molar excess of the retinal derivative at room temperature. Yield 90%. Quantum yield Φ 0.28.	(De Grip et al., 2011)
		11Z-	Cattle Rh				469						AR and ROS in buffer A: 20mM (PIPES), 130 mM NaCl, 5 mM KCl, 2 mM $CaCl_2$, 0.1 mM EDTA, 1 mM dithioerythritol, pH 6.5) with a 5-10-fold molar excess of the retinal derivative at room temperature. Yield 50%.	(De Grip et al., 2011)
		11Z-	Cattle Rh	352[c]		424	469 (3.7) 469			2260			ARh in 1% DDM solution (pH 6.5). Yield 50-70%.	(Wang et al., 2008) (Wang et al., 2004a)

Table 1. Properties of visual pigment analogs

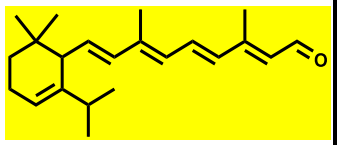
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		11Z-	ROS from bovine eyes				469						FTIR spectra Binding level >50%	(Bovee-Geurts et al., 2017)
		mix	Cattle Rh				467							(Yoshizawa, 1984)
138.		9Z-	Cattle IRh				462						ARh in a 2% digitonin solution. ARh were investigated by low-temperature spectrophotometry and nanosecond laser photolysis. Irradiation of each pigment at -180^0 **C** produced a photosteady-state mixture containing the original 9Z-pigment, its 11Z-pigment, and a photoproduct, indicating that the primary process of each pigment is a photoisomerization of its chromophore. It should be noted that each pigment was stable in the presence of 100 mM NH_2OH at 4^{0}C	(Okada et al., 1991)
		9Z-	Cattle IRh				462 D						Yield of pigment 30-70% in D.	(Liu and Asato, 1990)
		13Z-	Cattle Rh				NO							(Liu and Asato, 1990)

Table 1. Properties of visual pigment analogs

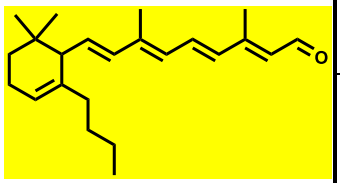
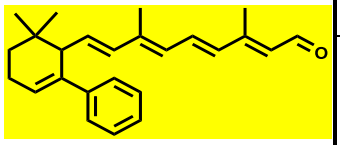
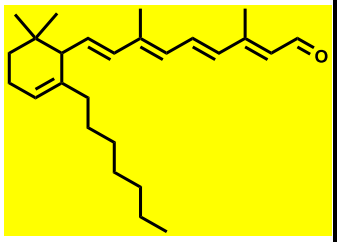
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
139.		all-E-	Cattle Rh				NO							
		9Z-	Cattle Rh				NO						Yield of pigment 3-30% in D.	(Liu and Asato, 1990)
		11Z-	Cattle Rh				462 D							
140.		all-E-												
		9Z-	Cattle Rh				NO							(Liu and Asato, 1990)
		11Z-	Cattle Rh				NO							
141.		9Z-	Cattle Rh				460 D						Yield of pigment >70% in D.	(Liu and Asato, 1990)
142.		all-E-												

Table 1. Properties of visual pigment analogs

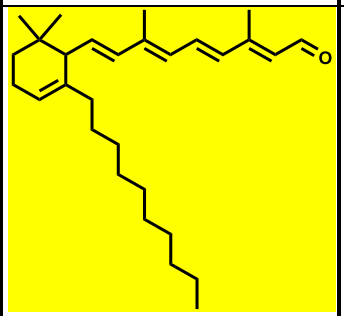
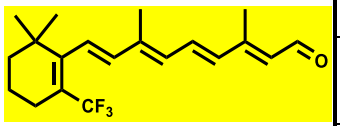
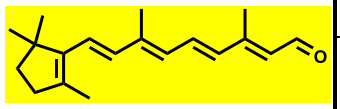
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		9Z-	Cattle Rh				NO							
		11Z-	Cattle Rh				NO							
143.		all-E-												
		9Z-	Cattle IRh				454 D							(Liu and Liu, 2011)
		11Z-	Cattle Rh				457 D							(Liu and Asato, 1990); (Liu and Liu, 2011)
144.		all-E-												
		9Z-	Cattle IRh				485 (4.3)						CD ARh 330 (+)/ 464 (+)	(Yoshizawa, 1984)
		11Z-	Cattle Rh											(Kropf et al., 1973)
145.		all-E-		362; 365[a]		420								(Ito et al., 1983)

Table 1. Properties of visual pigment analogs

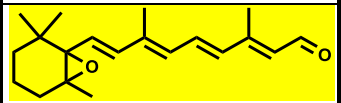
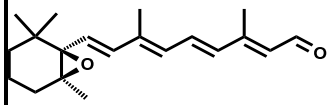
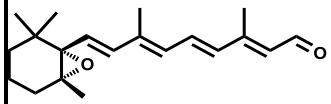
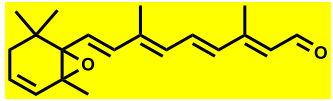
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
	 rac-	9Z-	Cattle IRh	358[a]			458 457 (3.4)						CD ARh 450 (+)	(Yoshizawa, 1984) (Kropf et al., 1973) (Ito et al., 1983) (Ito et al., 1979)
	 (5S,6R)	9Z-	Cattle IRh			416	459	ARh 459 nm Batho 490 nm BSI 440 nm Lumi 460 nm		2250			Nanosecond time-resolved and continuous illumination, low-temperature, spectroscopic studies reveal a new photolysis intermediate in a wide variety of ARhs.	(Randall et al., 1991)
	 (5R,6S)	11Z-	Cattle Rh	252 362[a]			468							(Yoshizawa, 1984) (Kropf et al., 1973) (Ito et al., 1983) (Ito et al., 1979)
146.		all-E- (5S,6R) (5R,6S)	Aporetinochrome Aporetinochrome	388		453	464 458						Aporetinochrome in 0.67% digitonin at pH 6.8. addition of all-E-*rac*-AR to aporetinochrome, an absorption maximum around 464 nm appeared, but during incubation the λ_{max} shifted to about 458 nm.	(Seki et al., 1985) (Seki et al., 1985)

Table 1. Properties of visual pigment analogs

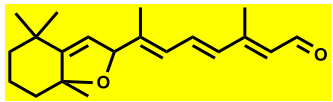
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		all-E-	Cattle Rh	367										(Azuma et al., 1973)
		9Z-	Cattle IRh				465 (2.4)						CD ARh 455 (+)	(Yoshizawa, 1984) (Kropf et al., 1973)
		9Z-	Cattle IRh	361			465				stable		ARh in a 2% digitonin solution CD ARh	(Azuma et al., 1973)
		11Z-	Cattle Rh				465 (3.0)						CD ARh 460 (+)	(Yoshizawa, 1984) (Kropf et al., 1973)
		11Z-	Cattle Rh	361			465				stable		ARh in a 2% digitonin solution CD ARh	(Azuma et al., 1973)
		11Z-	Cattle Rh				460 (474)						These results suggest strongly that the combination of chiral 11Z-AR with cattle opsin formed a mixture of two diastereomeric pigments.	(Seki et al., 1985)
147.		all-E-		331		380								
		9Z-	Cattle IRh											(Yoshizawa, 1984) (Kropf et al., 1973)
		11Z-	in frog ROS membrane	329[a]			407						Activation of GTPase 25% under illumination and 6% in the dark.	(Fukada et al., 1982)

Table 1. Properties of visual pigment analogs

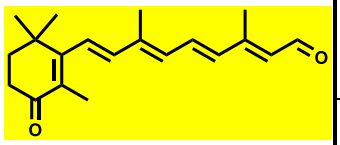
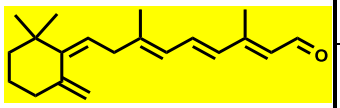
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		mix	Cattle Rh				411							(Yoshizawa, 1984) (Kropf et al., 1973)
148.		all-E-		294, 380 (4.4)		445								
		9Z-	Cattle IRh				470							(Yoshizawa, 1984)
		11Z-	Cattle Rh				464							(Yoshizawa, 1984)
149.		all-E-		340[a] (2.4)										
		9Z-	Cattle IRh	339[a] (2.34) 343[a]	323[a]	390[a]	420 D 425 (-185°C)	Batho 465 nm					In D.	(Ito, 1990) (Yoshizawa, 1984) (Kawamura et al., 1979) (Ito et al., 1978)
		9Z-	in frog ROS membrane	338[a]			420						Opsin membrane and 9Z- equal molar ratio were incubated at 20°C for 6 h, (80-90% yield). Activation of GTPase 20% under illumination and 15% in the dark. 9Z-Retro-ARh gradually decomposed in the presence of 25 mM NH_2OH with a half-time of about 2 h at 20°C, but at	(Fukada et al., 1982)

Table 1. Properties of visual pigment analogs

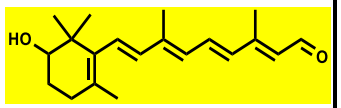
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
													0°C this decay was very slow. It was shown that Schiff-base linkage between opsin and retinal is not always necessary for this enzyme activation.	
		11Z-	Cattle Rh	228, 339[a] (1.39)			415							(Ito, 1990) (Yoshizawa, 1984) (Kawamura et al., 1979) (Ito et al., 1978)
150.		all-E- 9Z- 11Z- mix	fly visual pigment	381[a] (4.2) 372[a] (3.2) 376[a] 285sh 254 (2.3)			NO Not found							(Ito, 1990)

Table 1. Properties of visual pigment analogs

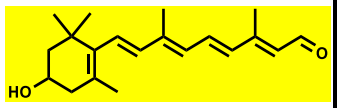
No	Structure	Isomer	Target	λ_{max} (nm); ε 10^{-4} (M^{-1} cm^{-1})				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
151.		all-E- 9Z- 11Z-	fly visual pigment	379[a] (4.4) 372[a] (3.2) 375[a] 282sh 254 (2.1)										(Ito, 1990)
		11Z-	fly visual pigment										In the class Insecta, retinal and 3-hydroxyretinal are used as chromophores of visual pigments, but the absolute configuration of the 3-hydroxyretinal chromophore has yet to be clarified. It was investigated the chirality of 3-hydroxyretinal in the compound eyes of five representative orders of insects. In the orders Odonata, Hemiptera, Neuroptera and Lepidoptera, and suborders Nematocera and Brachycera of the Diptera, only (3R)-3-hydroxyretinal isomers were detected, but dipterans of the suborder Cyclorrhapha (higher flies) had the (3S)-11Z-enantiomer and a mixture of (3R)-all-E and (3S)-all-E 3-hydroxyretinal enantiomers.	(Seki et al., 1994)

Table 1. Properties of visual pigment analogs

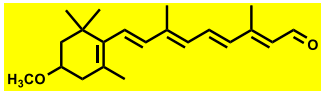
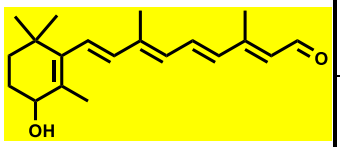
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		mix	fly visual pigment				+							
152.		9Z-	Iodopsin				529 (Cl^-)						Iodopsin analog in buffer A (0.6% CHAPS, 0.8 mg/mL egg phosphatidylcholine, 50 mM HEPES, 140 mM NaCl, 1 mM dithiothreitol, 200 mM methyl-α-D-mannopyranoside (MMP), pH 6.5 at 4°C). AR give pigments at low yields ((10%).	(Imai et al., 1999)
		11Z-	Iodopsin				536 (Cl^-)						Iodopsin analog in buffer A (0.6% CHAPS, 0.8 mg/mL egg phosphatidylcholine, 50 mM HEPES, 140 mM NaCl, 1 mM dithiothreitol, 200 mM methyl-α-D-mannopyranoside (MMP), pH 6.5 at 4°C). AR give pigments at low yields ((10%).	(Imai et al., 1999)
153.		all-E-		254, 375 (4.01										
		9Z-	Cattle IRh			426	471	ARh 471 nm Batho 506 nm BSI 477 nm Lumi 479 nm		2300			Nanosecond time-resolved and continuous illumination, low-temperature, spectroscopic studies reveal a new photolysis intermediate in a wide variety of ARhs.	(Randall et al., 1991)
		9Z-	Cattle IRh				460	Meta I 450 nm Meta II 390 nm						(Renk and Crouch, 1989)

Table 1. Properties of visual pigment analogs

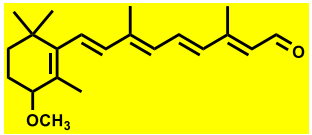
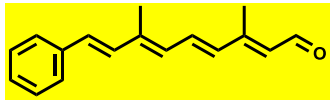
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		11Z-	Cattle Rh				470	Meta I 450 nm Meta II 390 nm						(Renk and Crouch, 1989)
		11Z-	firefly squid, *Watasenia scintillans*				470						third pigment from eye (λ_{max} 470 nm). Spectral and HPLC data.	(Matsui et al., 1988)
		11Z-	firefly squid, *Watasenia scintillans*	254 373[a]			470						(-)-R-isomer (11Z)-4-hydroxyretinal. It was to determine the absolute configuration of a visual pigment chromophore in *Watasenia scintillans*. CD spectra of the native chromophore and its anti-oxime agreed with those of synthetic (4R)-compounds. (4R)- CD ARh 254 (-)/ 375 (-). (4S)- CD ARh 253 (+)/ 375 (+).	(Katsuta et al., 1994)
154.		9Z-	Cattle IRh			426	472	ARh 472 nm Batho 490 nm BSI 465 nm Lumi 475 nm		2300			Nanosecond time-resolved and continuous illumination, low-temperature, spectroscopic studies reveal a new photolysis intermediate in a wide variety of ARhs.	(Randall et al., 1991)
H. Alteration of the trimethylcyclohexenic ring. Replacement ring to aromatic or heterocyclic fragments														
155.		all-E-		391[a] (5.7) 388 375[c] 390[a]	371 357 372 387	452 453	NO							(Derguini et al., 1984) (Matsumoto et al., 1980a)

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		9Z-	Cattle IRh	383[a] 370[c]			NO? D						Yield of pigment <2% in D. in **0.5%** digitonin **(10** mM Hepes buffer, pH 7.0).	(Matsumoto et al., 1980a)
		9Z-	Cattle IRh			443	485			1960			in 2% digitonin, pH 7.0, phosphate buffer. ARh, even in the absence of NH_20H, is bleached in 40 s on illumination.	(Motto et al., 1980)
		9Z-	Cattle IRh				480						Yield of pigment <2% in D. in **0.5%** digitonin (10 mM Hepes buffer, pH 7.0).	(Liu and Asato, 1990)
		9Z-	Cattle IRh				?							(Yoshizawa, 1984)
		9Z-	Cattle IRh			445	485			1850			Retinal analogs with aromatic rings have been bound to bovine opsin. The aromatic retinal pigments obtained from the 9Z-and 11Z-AR have much slower rates of formation than the natural rhodopsin but exhibit similar absorption properties. Methyl-substituted chromophores gave higher regeneration yields (ca. 80%) and stabler pigments compared to the non-methylated counterparts. The SBs of unsubstituted chromophores display fine structure, thus implying that the ring and side-chain are close to planarity. The maxima of unsubstituted retinals and	(Balogh-Nair and Nakanishi, 1990)

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
													their derivatives are red-shifted in comparison to substituted aromatic retinals and derivatives. This is due to the planar structures of the former group. An interesting observation with this aromatic series was that the unmethylated analogs had absorption maxima red shifted from those seen for the methylated ones. This was interpreted as a result of ring-side chain planarization, possible only in the unmethylated analogs. This suggests that the methyl groups of the aromatic ring and presumably of the β-ionine ring, are involved in an anchoring hydrophobic interaction with the binding site.	
		9Z-	Cattle IRh	382	351 367 385	445	485			1850			Retinal analogs with aromatic rings have been bound to bovine opsin. The aromatic retinal pigments obtained from the 9Z-and 11Z-AR have much slower rates of formation than the natural rhodopsin but exhibit similar absorption properties. Methyl-substituted chromophores gave higher regeneration yields	(Derguini et al., 1984) (Derguini and Nakanishi, 1986)

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
													(ca. 80%) and stabler pigments compared to the non-methylated counterparts. The SBs of unsubstituted chromophores display fine structure, thus implying that the ring and side-chain are close to planarity. The maxima of unsubstituted retinals and their derivatives are red-shifted in comparison to substituted aromatic retinals and derivatives. This is due to the planar structures of the former group. An interesting observation with this aromatic series was that the unmethylated analogs had absorption maxima red shifted from those seen for the methylated ones. This was interpreted as a result of ring-side chain planarization, possible only in the unmethylated analogs.	
		11Z-	Cattle Rh	384[a]			494							(Yoshizawa, 1984)
		11Z-	Cattle Rh	384[a] 374[c]			494 D				unstable		reduced rate of pigment formation. Yield of pigment <7% in D.	(Matsumoto et al., 1980a)

Table 1. Properties of visual pigment analogs

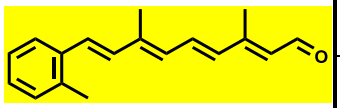
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		11Z-	Cattle Rh				494						reduced rate of pigment formation. Yield of pigment 3-30% in D.	(Liu and Asato, 1990)
		13Z-	Cattle Rh	388[a] 370[c]			NO							(Matsumoto et al., 1980a)
156.		all-E-		387[a] 375[c]		453	NO							(Matsumoto et al., 1980a)
		9Z-	Cattle IRh				482							(Yoshizawa, 1984)
		9Z-	Cattle IRh	380[a] 372[c]			482 D						Yield of pigment <10% in D. reduced rate of pigment formation. Methyl substitution of the aromatic rings assured good regeneration yields of ARh and also contributed to the stability of the latter.	(Matsumoto et al., 1980a) (Liu and Asato, 1990)
		11Z-	Cattle Rh				496							(Yoshizawa, 1984)
		11Z-	Cattle Rh	379[a] 368[c]			496 D						Yield of pigment <10% in D. reduced rate of pigment formation.	(Matsumoto et al., 1980a) (Liu and Asato, 1990)
		13Z-	Cattle Rh	381[a] 373[c]			NO							(Matsumoto et al., 1980a) (Liu and Asato, 1990)

Table 1. Properties of visual pigment analogs

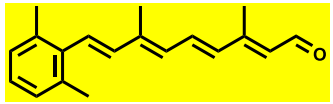
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
157.		all-E-					NO							(Derguini et al., 1984) (Balogh-Nair and Nakanishi, 1990)
		9Z-	Cattle IRh	365 355[c]	353	425	457			1650			The aromatic retinal pigments obtained from the 9Z-and 11Z-chromophores have much slower rates of formation than the natural rhodopsin but exhibit similar absorption properties. Methyl substitution of the aromatic rings assured good regeneration yields of ARh and also contributed to the stability of the latter. An interesting observation with this aromatic series was that the unmethylated analogs had absorption maxima red shifted from those seen for the methylated ones. This was interpreted as a result of ring-side chain planarization, possible only in the unmethylated analogs. Methyl-substituted chromophores gave higher regeneration yields (ca. 80%) and stabler pigments compared to the non-methylated counterparts. The Schiff bases of unsubstituted	(Balogh-Nair and Nakanishi, 1990) (Derguini et al., 1984) (Derguini and Nakanishi, 1986)

Table 1. Properties of visual pigment analogs

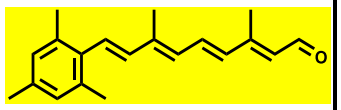
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
													chromophores display finestructure, thus implying that the ring and side-chain are close to planarity. The maxima of unsubstituted retinals and their derivatives are red-shifted in comparison to substituted aromatic retinals and derivatives. This is due to the planar structures of the former group. CD ARh 320 (+)/ 460 (+)	
158.		all-E-	Cattle Rh	359 380 (5.1) 368[c] 380[a]		439	NO							(Matsumoto et al., 1980a)
		9Z-	Cattle IRh				470						Yield of pigment 3-30% in D. reduced rate of pigment formation. An interesting observation with this aromatic series was that the unmethylated analogs had absorption maxima red shifted from those seen for the methylated ones. This was interpreted as a result of ring-side chain planarization, possible only in the unmethylated analogs.	(Liu and Asato, 1990)

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		9Z-	Cattle IRh				470							(Yoshizawa, 1984)
		9Z-	Cattle IRh	368[a] 355[c]			465 (470) D						Yield of pigment <15%. reduced rate of pigment formation. An interesting observation with this aromatic series was that the unmethylated analogs had absorption maxima red shifted from those seen for the methylated ones. This was interpreted as a result of ring-side chain planarization, possible only in the unmethylated analogs. Methyl substitution of the aromatic rings assured good regeneration yields of ARh and also contributed to the stability of the latter.	(Matsumoto et al., 1980a)
		11Z-	Cattle Rh				480							(Yoshizawa, 1984)
		11Z-	Cattle Rh				480	pigment 480 nm Batho 506 nm BSI 464 nm Lumi 458 nm					ARh was solubilized in sufficient 2% octylglucoside detergent in buffer (pH 7.0, 10 mM TRIS, 60 mM KCl, 30 mM NaCl, 2 mM MgC_{l2}, 0.1 mM EDTA).	(Lewis et al., 2001)

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
													ARh forms within the first hour of incubation	
		11Z-	Cattle Rh	376[a]			478						The aromatic ring analogue does not regenerate well, indicating possibly mild steric incompatibility with the binding pocket. In this analogue, the ring and its connection to the polyene is planar, in contrast to the cyclohexenyl ring of retinal. This changes the positioning of the ring in the binding pocket and induces distortions of the protein backbone. FTIR spectroscopy to examine the pH dependence of the Meta I / Meta II conformational equilibrium. pK_A values were determined from pH series of FTIR spectra. *t* pigment regeneration 20 h, yield < 20%.	(Vogel et al., 2005)
		11Z-	Cattle Rh	364[c] 375[a]			475 (480) D						Yield of pigment <40%. reduced rate of pigment formation. Methyl substitution of the aromatic rings assured good regeneration yields of ARh and also contributed to the stability of the latter. An interesting observation with this aromatic series was that the unmethylated analogs had absorption maxima	(Matsumoto et al., 1980a) (Liu and Asato, 1990)

Table 1. Properties of visual pigment analogs

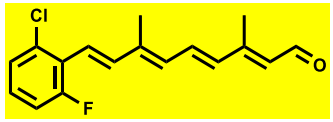
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
													red shifted from those seen for the methylated ones. This was interpreted as a result of ring-side chain planarization, possible only in the unmethylated analogs.	
		13Z-	Cattle Rh	363[c] 374[a]			NO							(Liu and Asato, 1990) (Matsumoto et al., 1980a)
159.		all-E-		378[a] 380[a] 371[c]		434	NO							(Matsumoto et al., 1980a)
		9Z-	Cattle IRh	370[a] 366[c]			470 D						Yield of pigment <6% in D. reduced rate of pigment formation.	(Liu and Asato, 1990) (Yoshizawa, 1984) (Matsumoto et al., 1980a)
		11Z-	Cattle Rh	373[a] 368[c]			460 D						Yield of pigment <8% in D. reduced rate of pigment formation.	(Liu and Asato, 1990) (Yoshizawa, 1984) (Matsumoto et al., 1980a)

Table 1. Properties of visual pigment analogs

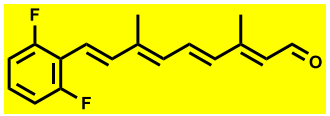
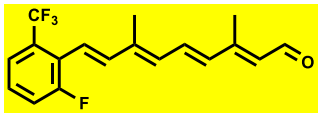
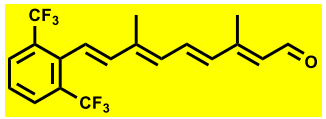
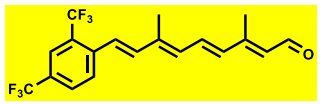
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
160.		9Z-	Cattle IRh	369[a]		425[a]	435 CHAPS			540			Pigment yield in CHAPS 6%. ^{19}F NMR spectra of 11Z- and 9Z- isomers of fluorinated ARh.	(Colmenares and Liu, 1996)
		11Z-	Cattle Rh	368[a]		430[a]	454 CHAPS			1230			Pigment yield in CHAPS 3%. ^{19}F NMR spectra of 11Z- and 9Z- isomers of fluorinated ARh.	(Colmenares and Liu, 1996)
161.		9Z-	Cattle IRh	369[a]		416[a]	451 CHAPS			1870			Pigment yield in CHAPS 32%. ^{19}F NMR spectra of 11Z- and 9Z- isomers of fluorinated ARh.	(Colmenares and Liu, 1996)
		11Z-	Cattle Rh	367[a]		421[a]	454 CHAPS			2060			Pigment yield in CHAPS 51%. ^{19}F NMR spectra of 11Z- and 9Z- isomers of fluorinated ARh.	(Colmenares and Liu, 1996)
162.		9Z-	Cattle IRh	352[a]		404[a]	442 CHAPS			2130			Pigment yield in CHAPS 53%. ^{19}F NMR spectra of 11Z- and 9Z- isomers of fluorinated ARh.	(Colmenares and Liu, 1996)
		9Z,11Z-	Cattle Rh	345[a]		401[a]	442 CHAPS			2310			Pigment yield in CHAPS 9%. ^{19}F NMR spectra of 11Z- and 9Z- isomers of fluorinated ARh.	(Colmenares and Liu, 1996)
		11Z-	Cattle Rh	350[a]		403[a]	456 CHAPS			2880			Pigment yield in CHAPS 58%. ^{19}F NMR spectra of 11Z- and 9Z- isomers of fluorinated ARh.	(Colmenares and Liu, 1996)
163.		9Z-	Cattle IRh	376[a]		421[a]	NO							(Colmenares and Liu, 1996)

Table 1. Properties of visual pigment analogs

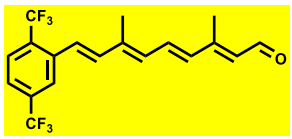
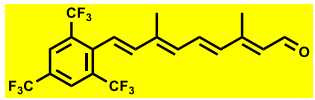
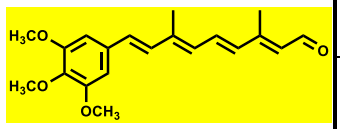
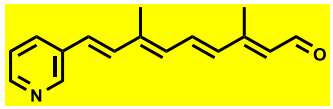
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		11Z-	Cattle Rh	376[a]		420[a]	NO							(Colmenares and Liu, 1996)
164.		9Z-	Cattle IRh	370[a]		419[a]	450 CHAPS			1640			Pigment yield in CHAPS 3%. ^{19}F NMR spectra of 11Z- and 9Z- isomers of fluorinated ARh.	(Colmenares and Liu, 1996)
165.		all-E-	Cattle Rh	351[a]		398[a]	443 CHAPS			2550			Pigment yield in CHAPS 63%. ^{19}F NMR spectra of 11Z- and 9Z- isomers of fluorinated ARh	(Colmenares and Liu, 1996)
166.		all-E-		393[c]			NO							(Matsumoto et al., 1980a)
		9Z-	Cattle Rh	383[c]			NO							(Liu and Asato, 1990) (Yoshizawa, 1984) (Matsumoto et al., 1980a)
167.		all-E-		378[a] 380[a]	350 367 375	419	NO							(Derguini et al., 1984) (Balogh-Nair and Nakanishi, 1990)
		9Z-	Cattle IRh	374	352 365 381	416	465 D			2530			Yield of pigment <6% in D. reduced rate of pigment formation. Retinal analogs with aromatic rings have been bound to bovine opsin.	(Derguini et al., 1984) (Balogh-Nair and Nakanishi, 1990)

Table 1. Properties of visual pigment analogs

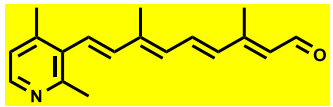
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
													An interesting observation with this aromatic series was that the unmethylated analogs had absorption maxima red shifted from those seen for the methylated ones. This was interpreted as a result of ring-side chain planarization, possible only in the unmethylated analogs. This suggests that the methyl groups of the aromatic ring and presumably of the β-ionine ring, are involved in an anchoring hydrophobic interaction with the binding site.	(Derguini and Nakanishi, 1986)
168.		all-E-		368	351	410	NO							(Derguini et al., 1984) (Balogh-Nair and Nakanishi, 1990)
		9Z-	Cattle IRh	350[c] 358	348	403	447			2380			Yield of pigment <6% in D. reduced rate of pigment formation (1 h). ROS in CHAPS. CD ARh 455 (+). An interesting observation with this aromatic series was that the unmethylated analogs had absorption maxima red shifted from those seen for the methylated ones. This was interpreted as a result of	(Derguini et al., 1984) (Balogh-Nair and Nakanishi, 1990) (Derguini and Nakanishi, 1986)

Table 1. Properties of visual pigment analogs

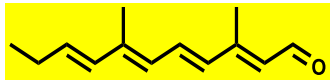
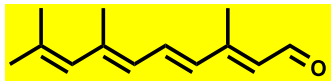
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
													ring-side chain planarization, possible only in the unmethylated analogs. Methyl substitution of the aromatic rings assured good regeneration yields of ARh and also contributed to the stability of the latter.	
I. Alteration of the trimethylcyclohexenic ring. Acyclic analogs														
169.		mix	Cattle Rh				NO							(Kropf et al., 1973)
170.		mix	Cattle Rh				NO							(Kropf et al., 1973)
171.		mix	Cattle Rh				NO							(Kropf et al., 1973)
172.		all-E-	Cattle Rh				NO							(Yoshizawa, 1984)
		all-E-	aporetino chrome	364		422	456			1800			AReT from aporetinochrome in 2% digitonin in phosphate buffer. CD ARh 455 (+)	(Kinumi et al., 1993)
173.		mix	Cattle Rh				NO						Isomers of the AR found inactive when incubated with bovine opsin.	(Liu and Asato, 1990) (Rao et al., 1985)

Table 1. Properties of visual pigment analogs

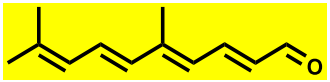
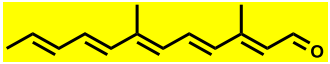
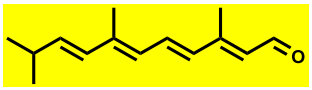
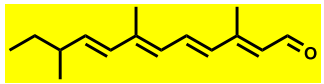
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
174.		mix	Cattle Rh				NO						Isomers of the AR found inactive when incubated with bovine opsin.	(Liu and Asato, 1990) (Rao et al., 1985)
175.		all-E-	aporetino chrome	388		458	490			1400			ARet from aporetinochrome in 2% digitonin in phosphate buffer. CD ARh 484 (+)	(Kinumi et al., 1993)
		10Z-	Cattle Rh				NO							(Yoshizawa, 1984)
176.		all-E-	Cattle Rh	364[a] 346[c]			NO						Pigment is not obtained with any isomer of AR even on prolonged incubation with bovine opsin. AR containing no ring "methyl groups" did not form pigment, supporting the hypothesis that ring methyls are essential to pigment formation.	(Crouch, 1990) (Crouch and Or, 1983)
		9Z-		358[a] 341[c]			NO							
		9Z,13Z-		356[a] 339[c]			NO							
		13Z-		358[a] 343[c]			NO							
177.		all-E-	Cattle Rh	364[a] 347[c]			NO							(Crouch and Or, 1983)

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); ε 10^{-4} (M^{-1} cm^{-1})				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		9Z-	Cattle IRh	361[a]			456	Meta I / Meta II					FTIR spectroscopy to examine the pH dependence of the Meta I / Meta II conformational equilibrium. pK_A values were determined from pH series of FTIR spectra. *t* pigment regeneration 2 h. pK_A of the Meta I/Meta II equilibrium was found to be 4.8.	(Vogel et al., 2005)
		9Z-	Cattle IRh			420	460			2100			Nanosecond time-resolved and continuous illumination, low-temperature, spectroscopic studies reveal a new photolysis intermediate in a wide variety of ARhs.	(Randall et al., 1991)
		9Z-	bovine Rh (IRh)				460	kinetics of pigment photobleaching. The half-life ($t_{1/2}$) of pigment Meta-II state formation 1.3 min.			Stable 2 h, in the dark in the presence of 40 mM hydroxyl amine		(ROS 20 mM BTP at pH 7.5 and 120 mM NaCl were incubated with 10 mM DDM). (*K*d) binding affinity 100 nM. $t_{1/2}$ pigment regeneration 5.1 min. Kinetics of pigment stability to HCl $t_{1/2}$ 0.2 min.	(Pashandi et al., 2025)
		9Z-	Cattle IRh	350[a] 344[c]			455						ARh is stable to the addition of hydroxylamine and 11Z-retinal over several hours, which demonstrates that the analogs are in the binding site.	(Crouch, 1990) (Crouch and Or, 1983)
		9Z,13Z-	Cattle Rh	358[a] 345[c]			453							(Crouch and Or, 1983)

Table 1. Properties of visual pigment analogs

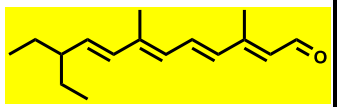
No	Structure	Isomer	Target	λ_{max} (nm); ε 10^{-4} (M^{-1} cm^{-1})				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		13Z-	Cattle Rh	361[a] 344[c]			NO							(Crouch and Or, 1983)
178.		all-E-	Cattle Rh	373[a] 366[a] 347[c]			NO							(Crouch and Or, 1983)
		9Z-	Cattle IRh	360[a]			461	Meta I / Meta II					FTIR spectroscopy to examine the pH dependence of the Meta I / Meta II conformational equilibrium. pK_A values were determined from pH series of FTIR spectra. *t* pigment regeneration 2 h. pK_A of the Meta I / Meta II equilibrium was found to be 5.0.	(Vogel et al., 2005)
		9Z-	Cattle IRh	360[c] 343[c]			454 460						ARh was obtained in 92% yield. ARh formation was complete in 15 min. ARh is stable to the addition of hydroxylamine and 11Z-retinal over several hours, which demonstrates that the analogs are in the binding site.	(Renk and Crouch, 1989) (Crouch, 1990) (Crouch, 1982) (Crouch and Or, 1983)
		9Z-	Cattle IRh			420	460			2100			Nanosecond time-resolved and continuous illumination, low-temperature, spectroscopic studies reveal a new photolysis intermediate in a wide variety of ARhs.	(Randall et al., 1991)

Table 1. Properties of visual pigment analogs

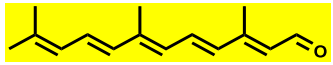
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		9Z,13Z-	Cattle Rh	358[a] 340[c]			460							(Crouch and Or, 1983)
		13Z-	Cattle Rh	359[a] 344[c]			NO							(Crouch and Or, 1983)
179.		all-E-	Cattle Rh	400	373	468 pK_a 7.4	NO							(Liu and Asato, 1990)
		9Z-	Cattle IRh	380[a]			510						FTIR spectroscopy to examine the pH dependence of the Meta I / Meta II conformational equilibrium. pK_A values were determined from pH series of FTIR spectra. *t* pigment regeneration 20 h. Slow and incomplete regeneration	(Vogel et al., 2005)
		9Z-	Cattle IRh				508 CHAPS						Yield of pigment 30-70%.	(Liu and Asato, 1990)
		9Z-	Cattle IRh				508 CHAPS 513 D				stable		Yield of ARh in 2% digitonin 10%. Yield of ARh in CHAPS 52%.	(Rao et al., 1985)
		9Z-	Cattle IRh			462	505			1850			Nanosecond time-resolved and continuous illumination, low-temperature, spectroscopic studies reveal a new photolysis intermediate in a wide variety of ARhs.	(Randall et al., 1991)

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		9Z-	Cattle IRh				513							(Derguini and Nakanishi, 1986)
		11Z-	Cattle Rh				506							(Derguini and Nakanishi, 1986)
		11Z-	Cattle Rh				507 CHAPS 507 D				stable		Yield of ARh in 2% digitonin 6%. Yield of ARh in CHAPS 12%.	(Rao et al., 1985)
		11Z-	Cattle Rh				507 CHAPS						Yield of pigment 3-30%.	(Liu and Asato, 1990)
		13Z-	Cattle Rh				NO							(Liu and Asato, 1990)
180.		all-E-												

Table 1. Properties of visual pigment analogs

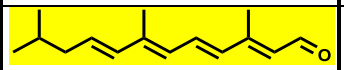
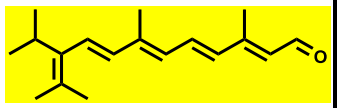
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		9Z-	Cattle IRh				457						ARh in a 2% digitonin solution. ARh were investigated by low-temperature spectrophotometry and nanosecond laser photolysis. Irradiation of each pigment at -180^0**C** produced a photosteady-state mixture containing the original 9Z-pigment, its 11Z-pigment, and a photoproduct, indicating that the primary process of each pigment is a photoisomerization of its chromophore. It should be noted that each pigment was stable in the presence of 100 mM NH_2OH at 4^{0}C.	(Okada et al., 1991)
181.		all-E-	Cattle Rh				NO							(Liu and Asato, 1990)
		7Z-	Cattle Rh				473 D						In 2% digitonin. Yield of pigment 3-30%.	(Liu and Asato, 1990)
		9Z-	Cattle IRh				481 D						In 2% digitonin. Yield of pigment >70%.	(Liu and Asato, 1990)

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		9Z-	Cattle IRh				481						ARh in a 2% digitonin solution. ARh were investigated by low-temperature spectrophotometry and nanosecond laser photolysis. Irradiation of each pigment at -180^0 **C** produced a photosteady-state mixture containing the original 9Z-pigment, its 11Z-pigment, and a photoproduct, indicating that the primary process of each pigment is a photoisomerization of its chromophore. It should be noted that each pigment was stable in the presence of 100 mM NH_2OH at 4^{0}C.	(Okada et al., 1991)
		9Z-	Cattle IRh	362[c]			481						In 2% digitonin. Yield of pigment 30-70%.	(Zhang et al., 1989)
		9Z,13Z-	Cattle Rh	364[c]			473						In 2% digitonin. Yield of pigment >70%.	(Zhang et al., 1989)
		11Z-	Cattle Rh	369[c]			496						In 2% digitonin. Yield of pigment >70%.	(Zhang et al., 1989)
		11Z-	Cattle Rh				490							(Yoshizawa, 1984)
		11Z-	Cattle Rh				496 (4.52)				stable hore then Rh		Binding of ARh is much faster in 10 mM Hepes (10 min). CD ARh 334 (+)/ 480 (+) Relative PDE Activity 80%.	(Karnaukhova et al., 1999)

Table 1. Properties of visual pigment analogs

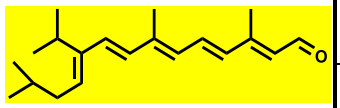
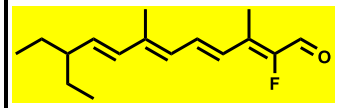
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
													Φ 0.48	
		11Z-	Cattle Rh				496 D						In 2% digitonin. Yield of pigment >70%.	(Liu and Asato, 1990)
182.		all-E-												
		9Z-	Cattle IRh	366[c]			485						In 2% digitonin. Yield of pigment >70%.	(Zhang et al., 1989)
		5Z,9Z-	Cattle Rh	370[c]			493						In 2% digitonin. Yield of pigment 30-70%	(Zhang et al., 1989)
		5Z,11Z-	Cattle Rh	375[c]			505						In 2% digitonin. Yield of pigment >70%.	(Zhang et al., 1989)
		11Z-	Cattle Rh	371[c]			495						In 2% digitonin. Yield of pigment >70%.	(Zhang et al., 1989)
J. Miscellaneous modifications														
183.		9Z-	Cattle IRh	362[a]			481						pK_a ARh 5.0. Removal of the β-ionone ring in acyclic ARh had been shown recently to shift considerably the Meta I / Meta II equilibrium toward inactive Meta I. Likewise, in the 14-F acyclicARh, the apparent pK_a of the equilibrium is shifted by roughly 3 units compared with that of the 14-F ARh. FTIR data.	(Vogel et al., 2006b)

Table 1. Properties of visual pigment analogs

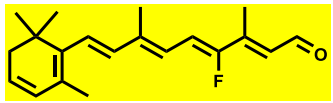
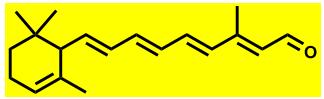
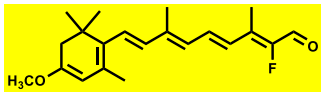
No	Structure	Isomer	Target	λ_{max} (nm); ε 10^{-4} (M^{-1} cm^{-1})				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
184.		all-E-	Cattle Rh				NO							(Liu and Asato, 1990)
		11Z-	Cattle Rh				520 D						In D.	(Liu and Asato, 1990)
185.		9Z-	Cattle IRh	342[c]		411	444			1810			ARh in 1% DDM solution (pH 6.5). Yield >70%.	(Wang et al., 2004a)
		11Z-	Cattle Rh	344[c]		413	446			1790			ARh in 1% DDM solution (pH 6.5). Yield >70%.	(Wang et al., 2004a)
186.		9Z-	Iodopsin Cattle Rh				720 nm (Cl^-) 611 nm (NO_3^-)						Iodopsin analog in buffer A (0.6% CHAPS, 0.8 mg/mL egg phosphatidylcholine, 50 mM HEPES, 140 mM NaCl, 1 mM dithiothreitol, 200 mM methyl-a-D-mannopyranoside (MMP), pH 6.5 at 4°C). AR was found to react with opsin at too slow a rate, while with iodopsin at a detectable rate giving a 720 nm pigment at low yield (-10%). Chloride replacement with nitrate in the analogs was accompanied with a blue shift.	(Imai et al., 1999) (Liu and Asato, 2003)

Table 1. Properties of visual pigment analogs

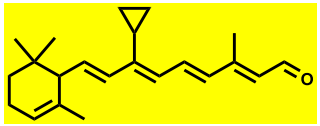
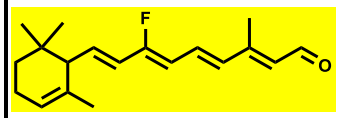
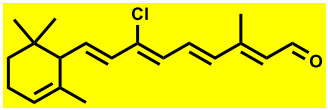
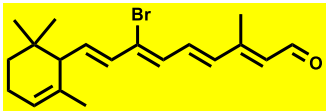
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
187.		9Z-	Cattle Rh				485						AR and ROS in buffer A: 20mM (PIPES), 130 mM NaCl, 5 mM KCl, 2 mM $CaCl_2$, 0.1 mM EDTA, 1 mM dithioerythritol, pH 6.5) with a 5-10-fold molar excess of the retinal derivative at room temperature. Yield 10%.	(De Grip et al., 2011)
		11Z-	Cattle Rh				476						AR and ROS in buffer A: 20mM (PIPES), 130 mM NaCl, 5 mM KCl, 2 mM $CaCl_2$, 0.1 mM EDTA, 1 mM dithioerythritol, pH 6.5) with a 5-10-fold molar excess of the retinal derivative at room temperature. Yield 5%.	(De Grip et al., 2011)
188.		9Z-	Cattle IRh	337[c]		399	437			2180			ARh in 1% DDM solution (pH 6.5). Yield >70%.	(Wang et al., 2004a)
		11Z-	Cattle Rh	340[c]		406	448			1790			ARh in 1% DDM solution (pH 6.5). Yield >70%.	(Wang et al., 2004a)
189.		9Z-	Cattle IRh	343[c]		405	443			2120			ARh in 1% DDM solution (pH 6.5). Yield 20-40%.	(Wang et al., 2004a)
		11Z-	Cattle Rh	346c		408	454			2480			ARh in 1% DDM solution (pH 6.5). Yield 20-40%.	(Wang et al., 2004a)
190.		9Z-	Cattle IRh	341[c]		397	448			2870			ARh in 1% DDM solution (pH 6.5). Yield 20-40%.	(Wang et al., 2004a)
		11Z-	Cattle Rh				NO						ARh in 1% DDM solution (pH 6.5).	(Wang et al., 2004a)

Table 1. Properties of visual pigment analogs

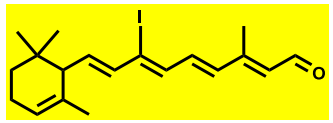
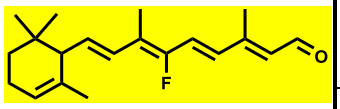
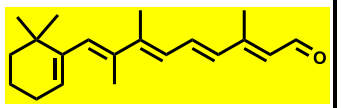
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
191.		9Z-	Cattle IRh				NO						ARh in 1% DDM solution (pH 6.5).	(Wang et al., 2004a)
		11Z-	Cattle Rh				NO						ARh in 1% DDM solution (pH 6.5).	(Wang et al., 2004a)
192.		all-E-	Cattle Rh				NO							(Liu and Asato, 1990)
		9Z-	Cattle Rh				460 D						In 2% digitonin. Yield of pigment 30-70%.	(Liu and Asato, 1990)
		9Z,13Z-	Cattle Rh				458 D						In 2% digitonin. Yield of pigment >70%.	(Liu and Asato, 1990)
		11Z-	Cattle Rh				463 D						In 2% digitonin. Yield of pigment 30-70%.	(Liu and Asato, 1990)
		13Z-	Cattle Rh				NO							(Liu and Asato, 1990)
193.		9Z-	Cattle IRh	345 343[a]			450 525?	Batho 523 nm BSI 438 nm Lumi 469 nm Meta II 370 nm					Yield of pigment 20%. ROS in LM detergent	(Szundi et al., 2002) (Alvarez et al., 2003)
		11Z-	Cattle Rh	371			NO						Yield of pigment <5%.	(Alvarez et al., 2003)

Table 1. Properties of visual pigment analogs

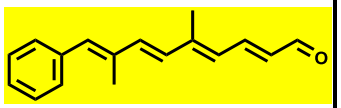
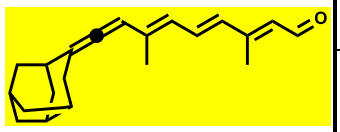
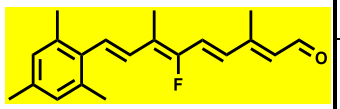
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
194.			Cattle Rh				NO NO						ARh in **2%** digitonin solution pH 6.5.	(Yoshizawa, 1984) (Kropf et al., 1973)
195.		all-E-		365[c]			NO							(Yoshizawa, 1984) (Matsumoto et al., 1980a)
		11Z-	Cattle Rh	357[c]			NO							(Yoshizawa, 1984) (Matsumoto et al., 1980a)
		11Z,13Z-	Cattle Rh	357[c]			NO							(Yoshizawa, 1984) (Matsumoto et al., 1980a)
196.		all-E-		355[c]										
		9Z-	Cattle IRh	335[c]		398	410			736	unstable		ARh in 1.5% Triton X-100. Formation yield of 9Z-ARh was - 3%. ARh was completely destroyed after 2 h in digitonin, after 35 min in Triton, and immediately in A-LO. It is also not stable in 0.1 M hydroxylamine (Triton, pH 7.0).	(Yoshizawa, 1984) (Blatchly et al., 1980)
197.		all-E-												
		9Z-	Cattle IRh				462 D						In 2% digitonin. Yield of pigment >70%.	(Liu and Asato, 1990)

Table 1. Properties of visual pigment analogs

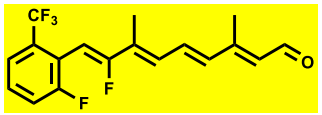
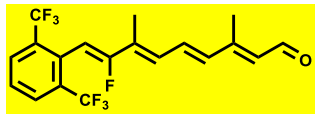
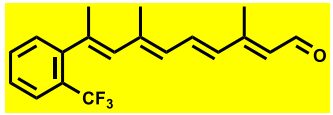
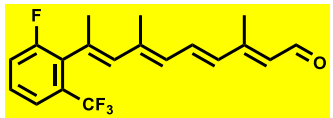
No	Structure	Isomer	Target	λ_{max} (nm); ε 10^{-4} (M^{-1} cm^{-1})				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		9Z,13Z-	Cattle Rh				468 D						In 2% digitonin. Yield of pigment 30-70%.	(Liu and Asato, 1990)
		11Z-	Cattle Rh				472 D						In 2% digitonin. Yield of pigment 30-70%.	(Liu and Asato, 1990)
198.		11Z-	Cattle Rh	346[a]		394[a]	437 CHAPS			2650			Pigment yield in CHAPS 44%. ^{19}F NMR spectra of 11Z- and 9Z- isomers of fluorinated ARh.	(Colmenares and Liu, 1996)
199.		11Z-	Cattle Rh	344[a]			NO							(Colmenares and Liu, 1996)
200.		9Z-	Cattle IRh	362[a]		414[a]	452 CHAPS			2030			Pigment yield in CHAPS 60%. ^{19}F NMR spectra of 11Z- and 9Z- isomers of fluorinated ARh.	(Colmenares and Liu, 1996)
		11Z-	Cattle Rh	362[a]		426[a]	454 CHAPS			1450			Pigment yield in CHAPS 45%. ^{19}F NMR spectra of 11Z- and 9Z- isomers of fluorinated ARh.	(Colmenares and Liu, 1996)
201.		9Z-	Cattle IRh	362[a]		406[a]	453 CHAPS			2800			Pigment yield in CHAPS 63%. ^{19}F NMR spectra of 11Z- and 9Z- isomers of fluorinated ARh.	(Colmenares and Liu, 1996)
202.		9Z-	Cattle IRh	343[a]			445						Pigment yield in CHAPS 21%. ^{19}F NMR spectra of	(Colmenares and Liu, 1996)

Table 1. Properties of visual pigment analogs

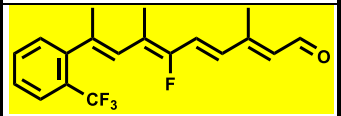
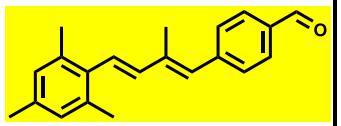
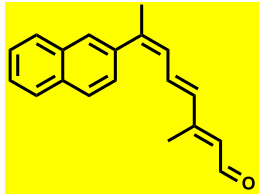
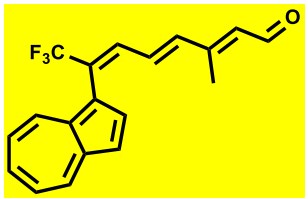
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments							
							ARh				NH_2OH	RETCHO		
							CHAPS						11Z- and 9Z- isomers of fluorinated ARh.	
203.		all-E- 9Z-	Cattle Rh Cattle Rh	350[c] 340[c]			NO NO							(Yoshizawa, 1984) (Matsumoto et al., 1980a)
204.		9Z-	Cattle IRh iodopsin				NO NO						AR was found not to yield ARh upon incubation with bovine opsin or the more reactive chicken red opsin.	(Imai et al., 1999) (Liu and Asato, 2003)
205.		9Z-	Cattle IRh iodopsin				NO NO						AR was found not to yield ARh upon incubation with bovine opsin or the more reactive chicken red opsin.	(Imai et al., 1999) (Liu and Asato, 2003)
K. Labelled BR derivatives (radioactive, photo-affinic, fluorophoric, heavy-atom, paramagnetic (SL), ionophoric and photochromic probes														
206.		all-E-	380[a]				NO						Easy hydrolyzed in 4-hydroxy-ARh after 0.5 h. ESR spectrum.	(Renk et al., 1981) (Crouch, 1990)
		9Z-	Cattle IRh				NO						SLB AR contained the spin label connected to the retinal molecule by an ester linkage. This	(Crouch, 1990)

Table 1. Properties of visual pigment analogs

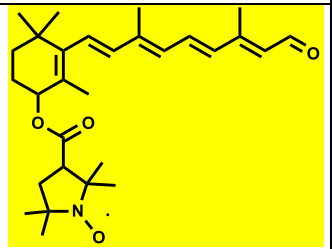
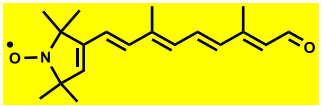
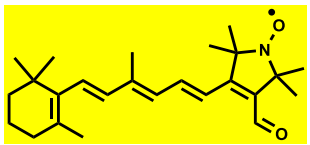
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
													derivative proved to be unsuitable in these studies due to the labile allylic ester linkage at C4 and the large steric bulk in the ring portion which prevents binding.	
		11Z-	Cattle Rh				NO						SLB AR contained the spin label connected to the retinal molecule by an ester linkage. This derivative proved to be unsuitable in these studies due to the labile allylic ester linkage at C4 and the large steric bulk in the ring portion which prevents binding.	(Crouch, 1990)
207.		all-E-												
		9Z-	Cattle IRh				NO						The pyrrolinyl derivative SLB AR eliminated the problems with steric bulk and the labile ester linkage. However, pigment was not formed between the *9Z*- or *11Z*-isomer and bovine opsin, possibly due to the lack of ring mobility which should allow it to twist into the native binding site.	(Renk et al., 1987) (Crouch, 1990)
208.		all-E-		258 384[a]		440	NO							(Kálai et al., 2014)

Table 1. Properties of visual pigment analogs

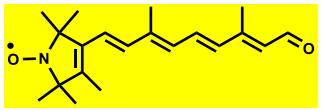
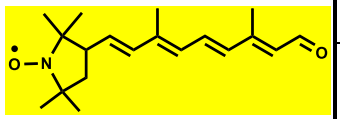
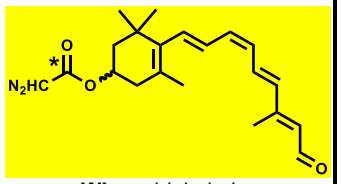
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
209.		all-E-		270 377[a]										(Kálai et al., 2014)
210.		all-E-		360[a]		440								
		9Z-	Cattle IRh				448	Meta I 440 nm Meta II 380 nm			stable	stable	meta II state pigment forms only if the pH is lowered to 4.5. ARh is stable to hydroxylamine and 11Z-retinal.	(Renk and Crouch, 1989) (Renk et al., 1987) (Crouch, 1990)
211.	 **Where** * labeled **3-(O-^{14}COCHN$_2$)-** 3S-enantiomer	all-E-		360[c] 245										(Sen et al., 1983) (Ok et al., 1988) (Nakanishi, 2000)

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
	3R-enantiomer	9Z-	Cattle IRh	356[c]	327	427	365 465 D 465 465			2020			Retinal analogs designed to photoaffinity label rhodopsin should satisfy the following requirements: (1) the labeled retinal should be able to bind readily, i.e. should not cause conformational distortions of the opsin; (2) the photolabel bearing retinal should be reasonably stable in aqueous buffers and detergents, and to the conditions employed in binding studies; (3) the photolabile group should undergo facile photolysis at a wavelength where irradiation would result in the least protein damage; (4) the intermediate, generated by light should undergo little or no rearrangement, but should react rapidly and indiscriminately with its immediate environment; (5) a reasonably simple route should be available not only for the synthesis of the photoaffinity-label-bearing retinal but also for its ^3H- or ^{14}C-labeled analog at high levels of radioactivity. in 2% digitonin / 67mM phosphate buffer, pH 7.0. Diazoacetoxy group could be activated by irradiation at 4^0C with a low-pressure Hg lamp (90% emission	(Sen et al., 1982) (Sen et al., 1984) (Derguini and Nakanishi, 1986) (Balogh-Nair and Nakanishi, 1990) (Souto et al., 2000)

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
													at 254 nm) of low intensity (4W). CD ARh 325 (+)/ 473 (+). Racemic ^{14}C-labeled 9Z- -3-diazoacetate and subsequently the 3*R* and 3*S* enantiomers were incorporated into Rh and photo-crosslinked, the results were not published because too many amino acids were affinity labeled. 3-Diazoacetoxy-9Z-ARh was formed from retinal in bleached ROS suspension and absorbs at 465 nm in 2% (w/v) digitonin solution. It was demonstrated that the chromophore of this pigment analog occupies the natural binding site and that the opsin binds only the 3S-enantiomer. Attemps to sequence the cross-linked amino acids using 3(S)-([^{14}C]-diazoacetoxy)-9Z-retinal**.** However, multiple cross-linking and difficulty in separating the sticky peptide fragments prevented **us** from deducing any clear-cut results.	
212.		all-E-												

Table 1. Properties of visual pigment analogs

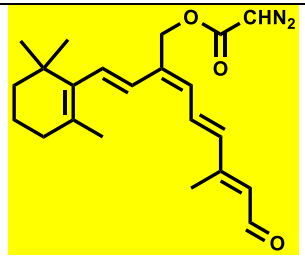
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
		9Z-	Cattle IRh	356 275^{sh} 245			340 460				unstable		Retinal analogs designed to photoaffinity label rhodopsin should satisfy the following requirements: (1) the labeled retinal should be able to bind readily, i.e. should not cause conformational distortions of the opsin; (2) the photolabel bearing retinal should be reasonably stable in aqueous buffers and detergents, and to the conditions employed in binding studies; (3) the photolabile group should undergo facile photolysis at a wavelength where irradiation would result in the least protein damage; (4) the intermediate, generated by light should undergo little or no rearrangement, but should react rapidly and indiscriminately with its immediate environment; (5) a reasonably simple route should be available not only for the synthesis of the photoaffinity-label-bearing retinal but also for its ^3H- or ^{14}C-labeled analog at high levels of radioactivity. In 10 mM CHAPS in 10 mM HEPES buffer pH 7.0. Due to its lability even under argon at – 70^0C only minute amounts of	(Sen et al., 1984) (Balogh-Nair and Nakanishi, 1990)

Table 1. Properties of visual pigment analogs

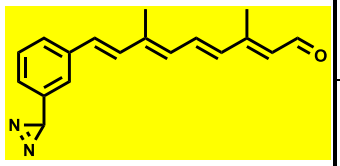
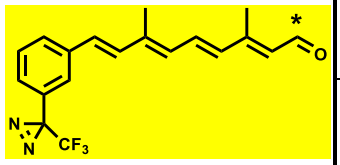
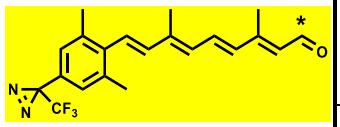
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
													compound could be isolated. ARh was obtained in 90% in CHAPS solution of bleached ROS for 22 hr. CD ARh 360 (+)/ 467 (+).	
213.		all-E-		390[a] (4.9)										(Nakayama and Khorana, 1990a)
		11Z-	Cattle Rh	385[a]			NO							(Nakayama and Khorana, 1990a) (Nakayama and Khorana, 1990a)
214.	 **Where** * labeled by ^3H-isotope	all-E-		393 (3.2)										(Nakayama and Khorana, 1990a)
		11Z-	Cattle Rh	385 (2.0)			NO							(Nakayama and Khorana, 1990b) (Nakayama and Khorana, 1990a)
215.	 **Where** * labeled by ^3H-isotope	all-E-		370 (4.6)										(Nakayama and Khorana, 1990a)
		11Z- -	Cattle Rh	365 (2.2)		424	460 (4.6) 458 (4.6)			1800			ARh in 10 mM Tris.HCl buffer, pH **6.8,** containing 1% lauryl maltoside. ARh in ROS regenerated about 80% ARh with λ 460 nm. ARh was stable for several weeks at -20^{0}C in 40% glycerol.	(Nakayama and Khorana, 1990a) (Nakayama and Khorana, 1990a)

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
													To regenerate of bleached opsin in ROS by AR. It gave ARh with λ at 458 nm. The linkage site of the analog to the opsin was confirmed to be Lys-296 as in 11Z-retinal rhodopsin. The reconstituted ARh-activated transducin and was phosphorylated by rhodopsin kinase on illumination. On photolysis of ARh containing the radioactively labeled at 365 nm at -15^{0}C, 20-25% of the analog was covalently linked to the protein. In contrast, photoaffinity labeling of rhodopsin by using a photoisomerizable trifluoromethyldiazirene analog led to two and six crosslinking sites on helices F and C, respectively. In this study, photolyzed a functional ARh containing o-dimethyl p-(trifluoromethy)diazirine phenyl AR as its chromophore, to cross-link to six aminoacids located in helices C and F; this indicated that the β-ionone ring was in close proximity to these two helices, perhaps residing between them.	

Table 1. Properties of visual pigment analogs

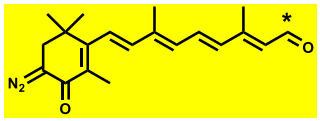
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
216.	 **Where** * labeled by ^3H-isotope	all-E-	apo-retinochrome				458						All-E-3-diazo-4-oxo-retinal was added to a suspension of apo-retinochrome at pH 6.5 to yield a stable pigment with λ at 458 nm. HPLC separation of this mixture afforded pure 11Z-AR in 45% yield.	(Borhan et al., 1997)
		11Z-	Cattle Rh				467 rod outer segment (ROS)	Batho 543 nm (-140°C) Lumi 438 nm (-40°C) Meta I 480 nm (-15°C) Meta II 380 nm (0°C)					The changes in chromophore and opsin interactions were then tracked by: (i) performing photoaffinity labeling at the respective optimal temperatures, (ii) pyridiethylate the crosslinked protein prior to separation of the protein from the membrane, (iii) BrCN cleavage, (iv) separate peptidic fragments by HPLC, (v) collect the tritiated HPLC peak and sequence by Edman degradation. Photoreactive 11Z-retinal analog in which the 11-ene is not locked showed that the C-3 region cross-linked to both helices C and F; recent studies with spin labels also showed that movements of these two helices were involved in the light activation process. It is thus possible that the Z → E-isomerization results in a "flip-over motion of the ring" from the proximity of	(Borhan et al., 1997) (Nakanishi, 2000) (Borhan et al., 2000) (Souto et al., 2000) (Fishkin et al., 2004)

Table 1. Properties of visual pigment analogs

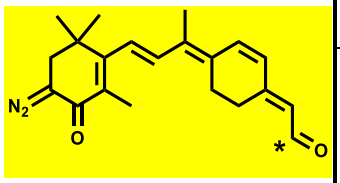
No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
													helix F to helix C as well as movements of helices F and C and that this induces the conformational changes responsible for the enzymatic cascade. In ARh and Batho the β-ionone ring is close to Trp265 in helix F. In Lumi the ring flips over with concomitant changes in helical structure and resides close to Ala169 in helix D. The conformation of the extra membrane loops connecting helices C/D and E/F activates the G protein. CD ARh 306 (+)/ 462 (+).	
217.	 **Where** * labeled by ^{3}H-isotope	all-E-												
		11Z-	Cattle Rh			435	483			2300			Photoreactive AR was synthesized and used in photo-cross-linking studies to determine the orientation of the chromophore in bovine rhodopsin. Incubation of AR with bovine opsin for 1 day gave a pigment, λmax 483 nm, reconstitution yield ca. 50%. Photolysis of a pigment incorporating the nonisomerizable 11Z-locked retinal analog) resulted in clear-cut cross-linking to Leu-266, thus revealing that the	(Zhang et al., 1994) (Nakanishi et al., 1995) (Borhan et al., 2000) (Fishkin et al., 2004)

Table 1. Properties of visual pigment analogs

No	Structure	Isomer	Target	λ_{max} (nm); $\varepsilon\ 10^{-4}$ ($M^{-1}\,cm^{-1}$)				Photochemistry	Isomer ratio	OS cm^{-1}	Reactions with		Remarks	Ref.
				"CHO"	SB	SBH^+	Visual Pigments ARh				NH_2OH	RETCHO		
													ionone C-3 is in close contact with helix F of rhodopsin in the dark. Present exclusive labeling of helix F with the nonisomerizable AR indicates that C-3 of the β-ionone ring is in contact with helix F in rhodopsin, and that light-induced isomerization moves the C-3 region to come in contact with helix C. This AR almost exclusively cross-linked to Trp-265 and Leu-266 located around the middle of helix F, thus yielding one of the most clear-cut results in retinal protein photoaffinity labeling. CD ARh 308 (+) in 67 mM phosphate buffer solution of ARh containing 2% digitonin.	

Notes:

[1]* Abbreviations:

ABRh - Bacteriorhodopsin analog; AC - adenylate cyclase; ALO – Ammonyx LO; AM –apomembranes; ARh – Rhodopsin analog; AR – retinal analog; BO - Bacterioopsin; BRh - Bacteriorhodopsin; CD – circular dichroism; CHAPS (CHAPSO) - 3-((3-cholamidopropyl)dimethylammonio)-1-propanesulfonate; DDM - dodecylmaltoside; D – digitonin; ESRh - tundra-rhodopsin; FSES - functionally significant elements of the structure; HPLC – high-performance liquid chromatography; HRh - halorhodopsin; GPCR - G-protein coupled receptors; IS -inner segments; MES - 2-(N-morpholino)ethanesulfonic acid; NC - noncovalent complex; OG - octyl glucoside; OS - opsin shift; P - pigment (covalent complex, containing protonated aldimine bond); PC – phosphatidylcholine; PDB - Protein Data Bank; PDE Activity – Phosphodiesterase activity; pK_a - pK of aldimine group of retinal or its analog in SBH^+ and in ARh; PM – purple membranes; PRh – proteorhodopsin; (RARs and RXRs - nuclear retinoic acid receptors; RBP - Retinal based proteins; (**Ret**) - *all-E*-retinal (**3**); Rh – Rhodopsin; ROS – rod outer

segments; RPE – retinal pigment epitelium; SRhI, SRhII - sensoric rhodopsins; sh – shoulder; SB - the Schiff base; SBH^+ or PSB - protonated form of the Schiff base; T – Triton X-100; 7TM - seven trans-membrane helices domen; TRP - Transient Receptor Potential channel;

Usually, synthesis of RBP and study of their properties are carried out at pH close to neutral (pH 6-7); if pH and temperature at which the reaction of opsin with polyenal and other measurements were performed are given in the publication, these values are presented in "Remarks" column.
In the same column, data on transitional spectral forms from their photocycles and their transitions in alkaline medium as well as some other non-standart properties of pigments (times of pigments formation, if ones differ substantially from natural Rh parametres, CD-; X-rays or ESR-data, etc.) are presented.
(+) - quality without quantitative assesment; (-) or (NO) - lack of quality; (blank) - no data.
[2]* Polyenals' structures are only given for *all-E*-isomers as their 6-*s*-*cis*-forms.
[3]* λ_{max} values for compounds (CHO, SB, SBH^+) are given for solutions in methanol (no index), ethanol (a), isopropanol (b), hexane (c),
[4]* (OS) = $1/\lambda(SBH^+)$ - $1/\lambda$(pigment)

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