APPROXIMATION OF VISUAL PIGMENT ABSORPTION SPECTRA

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Single approximational formulas are presented, permitting the calculation from the λ_{max} value of the relative absorption spectra of visual pigments based both on retinal and on 3-dehydroretinal. The principle of the shift in the standard curve in the $\lambda^{1/4}$ scale or in a scale of relative frequencies is used.

The absorption spectra of most visual pigments are similar in shape and differ from one another primarily in the position of the region of absorption on the spectral axis. This makes it possible to characterize them with a single parameter, which is usually provided by the wavelength λ_{max} at which absorption is maximum. It is believed that having determined experimentally the λ_{max} of some visual pigment, its absorption spectrum can then be unambiguously constructed by a standard procedure.

The original hopes [3] of presenting all spectra in the form of a single (nomogram) curve shifted along the frequency axis were not justified. The absorption spectra of long-wavelength pigments were more narrow than the nomogram curves, while those of the short-wavelength were wider [8]. Furthermore, differences were found in the form of the absorption spectra of pigments based on retinal and 3-dehydroretinal. Therefore, to increase the precision of approximation it was proposed that, while retaining Dartnall's principle (shifts in the standard curve along the frequency axis) the entire range of pigments be divided into three ranges according to the λ_{max}, in each of which a special standard curve was used [6]. In addition to its cumbersomeness and the ambiguity of the obtained spectra for pigments with λ_{max} lying at the boundary of the ranges [4], this method suffers from nonuniformity and a varying precision of experimental data on which the standard curves are based. Thus, the absorption spectra of solutions of rhodopsin and porphyropsin, obtained with high precision, are used as standards for the mid-wavelength ranges [2, 3], solutions of iodopsin and cyanopsin are used for long-wavelength ranges, while less reliable data obtained in microspectrophotometric experiments must be used for the short-wavelength ranges [8].

The situation was simplified after Barlow [1], by analyzing all possible scales, found that the width of the major absorption band of light-sensitive pigments with various λ_{max} remains constant if it is measured not in the scale of frequencies but in the scale of $\lambda^{1/4}$. Later, Dartnall et al. [4] showed that the measured microspectrophotometric absorption spectra of various primate rod pigments are described in this scale by a single curve and proposed a tabular specification of this curve.

The use of tables and nomograms to fit standard curves to experimental requires tedious "manual" labor. Approximation formulas permit automation of the procedure. However, the formulas proposed thus far [5, 7, 9] either give an unsatisfactory approximation or are as cumbersome as the nomograms they replace. In particular, the formulas contain many constants specified with an unjustifiably large number of significant digits, which complicates their effective use. Therefore, we attempted to select a single formula (for all ranges) and as simple as possible, approximating the absorption spectra of the visual pigments. The formulas were fitted to the absorption spectra of rhodopsin (tabulated in [3], the course of the curve in the short-wavelength end of the spectrum in the region of the β maximum was taken from [2]) and of porphyropsin (Table 5 in [2]). Although the rhodopsin and porphyropsin absorption spectra were measured quite precisely, we did not attempt a great precision of approximation, since the very principle of the shift in absorption spectra along the $\lambda^{1/4}$ axis is only an empirical approximation and does not provide a good approximation for visual pigments with other λ_{max}.

The relative absorption spectra $a(\lambda, \lambda_{max})$ of light-sensitive pigments, based on retinal (vitamin A_1 system), are described by the equation

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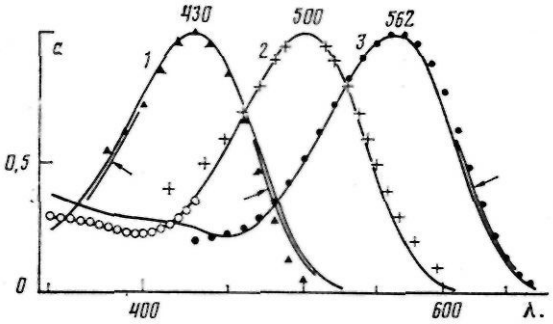

Fig. 1. Relative absorption spectra of visual pigments of the vitamin A_1 system. Solid curves (1-3) show absorption spectra calculated from Eq. (1) for three pigments whose λ_{max} are plotted above the curves; 4 (triangles) - absorption spectrum of green rods of frog [8]; 5 (open circles) — short-wavelength part of rhodopsin absorption spectrum [2]; 6 (crosses) — data from [4] recommended as standard for absorption spectra of primate photoreceptors; 7 (dark circles) — absorption spectrum of iodopsin [12].

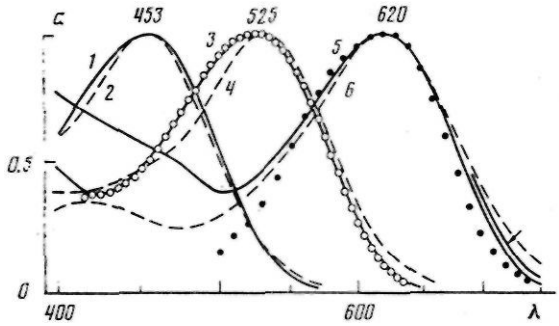

Fig. 2. Relative absorption spectra of visual pigments of vitamin A_2 system. Solid curves (1, 3, 5) show absorption spectra calculated from Eq. (2) for three pigments whose λ_{max} are plotted above the curves; dashed curves (2, 4, 6) — Harosi's approximations for absorption spectra of goldfish cones [7]; 7 (open circles) — absorption spectrum of porphyropsin [2]; 8 (solid circles) — absorption spectrum of cyanopsin [11].

$$a = \exp(-\psi^2 \xi^2).$$

where $\psi = \lambda^{1/4} - \lambda_{max}^{1/4}$,

$$\xi = 6 + 6\psi + \frac{2}{3}\arctan(21\psi + 6). \qquad (1)$$

The wavelengths λ and λ_{max} in this equation are specified in nanometers, and the argument of the arctan function in radians. The first term of the sum (1) determines the bell-shaped form of the curve; the second makes it asymmetric: Its short-wavelength arm is more open than the long-wavelength; the third term is introduced to obtain a rise in the curve in the region of the β maximum of visual pigment absorption.

Assigning λ_{max} = 500 nm, from this equation we obtain a spectrum (Fig. 1, curve 2) visually coinciding with the absorption spectrum of frog rhodopsin. In the scale of Fig. 1 the initial points from [3] in the range from 400 to 620 nm lie directly on the approximation curve. Therefore, they were not plotted on the graph. The greatest deviations were obtained in the region of 530 nm, where the proposed equation gives absorption values 2.5% too low. In this region crosses indicate the standard curve from [4]. In contrast to the earlier-proposed nomogram [3, 4, 6] and the approximation equations [5, 9], our formulas expand the range of approximation into the short-wavelength region. When λ_{max} = 500 nm, it is applicable

up to 350 nm, where a second rhodopsin absorption maximum is located (further toward shorter wavelengths the curve has a rise, which differs appreciably from the rhodopsin absorption spectrum).

The wavelengths along the abscissa in Fig. 1 are plotted in $\lambda^{1/4}$ scale, which makes it possible to obtain absorption spectra of light-sensitive pigments with other λ_{max} by a simple shift in the initial 2 along the abscissa. Figure 1 presents such spectra for λ_{max} equal to 430 (curve 1) and 562 nm (curve 3). Shown for comparison is the absorption spectrum of green rods of the frog retina — points 4 — obtained microspectrophotometrically [8], as well as the iodopsin absorption spectrum — points 7 [12]. The latter two curves were made the basis of nomograms [6] and polynomial approximations [5] as standard curves for the absorption spectra of short-wavelength and long-wavelength visual pigments.

Visual pigments based on 3-dehydroretinal (vitamin A_2 system) have a wider band of primary absorption. Their spectra are well described by an analogous equation. The necessary expansion of the absorption band is achieved simply by an increase in the first term of the function $\xi(\psi)$ by 1, i.e., to approximate the absorption spectra of light-sensitive pigments based on vitamin A_2 one must assume:

$$\xi = 5 + 6\psi + \frac{2}{3}\arctan(21\psi + 6). \qquad (2)$$

Thus, assuming λ_{max} = 525 nm, by this equation we obtain curve 3 (Fig. 2), virtually indistinguishable from the porphyropsin absorption spectrum (plotted with the circles in Fig. 2), tabulated by Bridges [2], which is usually the basis of nomograms for pigments of the vitamin A_2 system [6].

Figure 2 also presents approximations for two other fish visual pigments (based on 3-dehydroretinal). Also plotted there for comparison are the dashed curves constructed from Harosi's approximation equations [7] for the pigments of goldfish cones with λ_{max} equal to 453, 533, and 620 nm, as well as the absorption spectrum of cyanopsin — points 8 [11]. It should be noted that Harosi's equations, first, were based on unreliable microspectrophotometric changes; second, as the author himself notes, a not-entirely-successful family of approximation function was used (sum of three Gaussians in frequency scale). Therefore, the corresponding curves apparently correctly reflect the position and general form of the visual-pigment absorption bands but do not provide a detailed description of their spectra. In particular, Harosi considered as completely satisfactory the agreement of its approximation for pigments of green-sensitive cones (curve 4) with the porphyropsin absorption spectrum (curve 7) and that of the approximation for the pigment of red-sensitive cones (curve 6) with the cyanopsin absorption spectrum (curve 8).

Equation (2), proposed by us, satisfactorily describes the spectra only in the principle absorption band. The course of the porphyropsin absorption spectrum in the region of the β maximum is not known with the necessary precision. Furthermore, as can be seen from a comparison of the curves in Fig. 2, the very principle of a shift in the standard curve in $\lambda^{1/4}$ scale is inapplicable for the short-wavelength part of the spectrum: It does not give the correct position on the spectral axis of the second absorption maximum and the magnitude of absorption in this region.

As MacNichol notes [10], for pigments based both on retinal and on 3-dehydroretinal, differing strongly in their λ_{max} from rhodopsin and porphyropsin, respectively, a shift in $\lambda^{1/4}$ scale does not absolutely precisely reproduce the spectra even in the region of principal absorption. Instead of this, MacNichol proposes the use of a scale of relative frequencies. An appropriate modification can easily be introduced into Eqs. (1) and (2). It is necessary only to alter the scale of the argument of the function $a(\psi)$: ψ should be increased by $(500/\lambda_{max})^{1/4}$ for pigments of the vitamin A_1 system and by $(525/\lambda_{max})^{1/4}$ for pigments of the vitamin A_2 system. Such a correction slightly expands the absorption band in long-wavelength pigments and narrows it in short-wavelength pigments. However, this is manifested only at extreme λ_{max} values. For the pigments whose spectra are depicted in Figs. 1 and 2, the differences in the curves using the principle of a shift in the scale of relative frequencies and in the $\lambda^{1/4}$ scale are negligible. At those sites where they are marked, the corresponding portions of the curves constructed in the scale of relative frequencies are plotted in Figs. 1 and 2 and indicated by arrows.

It has become the practice to characterize visual pigments by their λ_{max} value of the wavelength at which absorption is maximum. Insofar as there is no direct method for measur-

ing λ_{max}, it is found by fitting a standard curve to the absorption curve obtained experimentally. This is usually done from the long-wavelength branch of the curve, where the experimental data are most reliable [4, 10]. When Dartnall's nomogram [3] was still used for this certain λ_{max} values were obtained for visual pigments that do not serve as names for the corresponding pigments. However, the transition to other more suitable nomograms may either yield other λ_{max} values, which would be extremely inconvenient, requiring a reexamination of the nomenclature of all visual pigments thus far investigated, or the λ_{max} parameter will lose its original meaning. Thus, as apparent from an analysis of polynomial approximations [5] for nomograms [6], the maxima of all six standard curves in general do not lie on the λ_{max} adopted for the corresponding pigments. This is indicated by the nonzero values of the first term of the corresponding approximation. For example, the standard curve for porphyropsin $P523_2$ has a maximum at 525 nm, while that for the $P432_1$ pigment of the green rods of the frog has a maximum at 430 nm. The greatest contrast is for the absorption curve of the $P438_2$ pigment of green rods of the tadpole, which had a maximum at 444 nm. In the equations we proposed the λ_{max} parameter does in fact correspond to the maximum of the curve. However, when our equations are used the obtained λ_{max} may differ from their values obtained earlier, including those for the pigments providing the basis of approximation: As already mentioned, according to our equations the absorption spectrum of $P502_1$ frog rhodopsin was obtained for λ_{max} = 500 nm, and the absorption spectrum of $P523_2$ porphyropsin, for λ_{max} = 525 nm. Unfortunately, no systematic "corrections" to the equations (making it possible to obtain acceptable λ_{max} values for previously investigated pigments) exist, since these acceptable values were obtained at a different time by fitting various nomogramic curves by various methods.

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