and the ε-amino group of lysine has been demonstrated by Dupuis, Mitchell & Towers (1974). Dupuis, Benezra, Schlewer & Stampf (1980) successfully reacted alantolactone with model proteins and with guinea pig skin protein extract.

Intermolecular distances were calculated up to 3·6 Å with ORFFE (Busing et al., 1971). There are no C—H···O interactions between neighbouring molecules; the structure consists of discrete molecules.

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References

BLEUMINK, E., MITCHELL, J. C., GEISSMAN, T. A. & TOWERS, G. H. N. (1976). Contact Dermatitis, 2, 81–88.

BUSING, W. R., MARTIN, K. O., LEVY, H. A., BROWN, G. M., JOHNSON, C. K. & THIESSEN, W. E. (1971). ORFFE. Oak Ridge National Laboratory, Tennessee.

COCKER, W. & McMURRY, T. B. H. (1960). Tetrahedron, 8, 181–204.

DUAX, W. L. & NORTON, D. A. (1975). In Atlas of Steroid Structure. New York, Washington, London: Plenum.

DUPUIS, G., BENEZRA, C., SCHLEWER, G. & STAMPF, J.-L. (1980). Mol. Immunol. 17, 1045–1051.

DUPUIS, G., MITCHELL, J. C. & TOWERS, G. H. N. (1974). Can. J. Biochem. 52, 575–581.

HJORTH, N. (1970). Contact Dermatitis Newslett. 8, 180.

JOHNSON, C. K. (1971). ORTEP. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee.

KARLE, I. L. (1972). Acta Cryst. B28, 2000–2007.

MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data. Univs. of York, England, and Louvain, Belgium.

MARSHALL, J. A. & COHEN, N. (1964). J. Org. Chem. 29, 3727–3729.

MARSHALL, J. A., COHEN, N. & HOCHSTETLER, A. R. (1966). J. Am. Chem. Soc. 88, 3408–3417.

ROBERTS, P. & SHELDRICK, G. M. (1975). XANADU. Program for crystallographic calculations. Univ. of Cambridge, England.

SCHMALLE, H. W. (1986). Acta Cryst. In preparation.

SCHMALLE, H. W., JARCHOW, O. H. & HAUSEN, B. M. (1980). Acta Cryst. B36, 2450–2453.

SCHMALLE, H. W., KLUPSCH, S., JARCHOW, O. H., HAUSEN, B. M. & SCHULZ, K.-H. (1986). Acta Cryst. In preparation.

SCHMALLE, H. W., SCHOPPE, I., JARCHOW, O. H., HAUSEN, B. M. & SCHULZ, K.-H. (1986). Acta Cryst. In preparation.

SCHULTZ, A. G., GODFREY, J. D., ARNOLD, E. V. & CLARDY, J. (1979). J. Am. Chem. Soc. 101, 1276–1277.

SCHULZ, K. H., HAUSEN, B. M., WALLHÖFER, L. & SCHMIDT-LÖFFLER, P. (1975). Arch. Derm. Forsch. 251, 235–244.

SHELDRICK, G. M. (1976). SHELX76. Program for crystal structure determination. Univ. of Cambridge, England.

STAMPF, J.-L., BENEZRA, C., KLECAK, G., GELEICK, H., SCHULZ, K.-H. & HAUSEN, B. M. (1982). Contact Dermatitis, 8, 16–24.

STAMPF, J.-L., SCHLEWER, G., DUCOMBS, G., FOUSSEREAU, J. & BENEZRA, C. (1978). Br. J. Dermatol. 99, 163–169.

The Stereochemistry of the Major Epimer Formed on Reaction of Methyl 1-Methyl-6-oxo-2,4-cyclohexadiene-1-carboxylate with Dimethyl Acetylenedicarboxylate: Trimethyl endo-5-Methyl-6-oxobicyclo[2.2.2]octa-2,7-diene-2,3,exo-5-tricarboxylate

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Abstract. $C_{15}H_{16}O_7$, $M_r = 308\cdot3$, monoclinic, $I2/a$, $a = 19\cdot534$ (5), $b = 7\cdot213$ (5), $c = 21\cdot371$ (6) Å, $\beta = 101\cdot53$ (2)°, $U = 2950$ (4) Å^3, $Z = 8$, $D_x = 1\cdot39$ g cm^{-3}, Mo $K\bar{\alpha}$ radiation, $\lambda = 0\cdot71069$ Å, μ(Mo $K\bar{\alpha}$) = $1\cdot04$ cm^{-1}, $F(000) = 1296$, $T = 298$ K, $R = 0\cdot058$ for 1155 reflections with $I \geq 3\sigma(I)$. X-ray analysis indicates that dimethyl acetylenedicarboxylate reacts preferentially on the methyl face of methyl 1-methyl-6-oxo-2,4-cyclohexadiene-1-carboxylate to give trimethyl endo-5-methyl-6-oxobicyclo[2.2.2]octa-2,7-diene-2,3,exo-5-tricarboxylate. In the bicyclo[2.2.2]octadiene system, opposite bonds are very slightly twisted away from being eclipsed, with torsion angles about the C(2)=C(3) and C(7)=C(8) double bonds and bond C(5)—C(6) of $-2\cdot3$ (5), $1\cdot2$ (6) and $-1\cdot7$ (3)°, respectively. The two methoxycarbonyl groups are canted by $12\cdot4$ (7) and $79\cdot7$ (7)° with respect to the plane of the C(2)=C(3) double bond.

Introduction. A key step in the syntheses of cedranoid sesquiterpenes that are being pursued in these laboratories is the photosensitized isomerization of bicyclo[2.2.2]octenones of type (4) to tricyclo-[3.2.1.0^{2,8}]octanones (5); compounds (4) were prepared

by selective hydrogenation of (3), the Diels–Alder adducts of 6,6-disubstituted 2,4-cyclohexadien-1-ones (1) with dimethyl acetylenedicarboxylate (2) (Yates & Stevens, 1981, 1982). Thus the relative stereochemistry at C(4) in (5) ($R \neq CH_3$) is dependent on the face selectivity in the Diels–Alder reaction. In that connection we have investigated the reaction of (1) ($R = CO_2CH_3$) with (2) and found that this gives a mixture of epimers (3) ($R = CO_2CH_3$) in a 3:1 ratio. This reaction has also been investigated recently by others (Schultz, Dittami, Lavieri, Salowey, Sundararaman & Szymula, 1984), who obtained a similar result. We report now on an X-ray crystallographic study of the structure of the major epimer formed on reaction of (1) ($R = CO_2CH_3$) with (2). The result is of importance not only in respect of the synthesis of cedranoid sesquiterpenes with $R \neq CH_3$ but also in the elucidation of the factors affecting face selectivity in the Diels–Alder reaction (Auksi & Yates, 1981).

(E = CO_2CH_3)
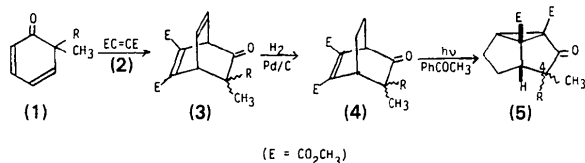
Experimental. Compound (1) ($R = CO_2Me$) was prepared by dehydrobromination of methyl 3,3-dibromo-1-methyl-2-oxocyclohexane-1-carboxylate with $LiBr/Li_2CO_3$ in dimethylformamide at 393 K. Reaction of this with (2) in boiling benzene for 50 h gave the epimeric adducts (3) ($R = CO_2Me$), which were separated by chromatography on silica gel. Crystallization of the major epimer from water gave clear colorless crystals as thin elongated plates, m.p. 370·6–371·6 K. Long thin plate of semi-dimensions 0·020 × 0·400 × 0·088 mm in a,b,c directions used throughout. Precession photographs to check crystal quality. Peak profiles somewhat broad. Further work on Enraf–Nonius CAD-4 diffractometer using graphite-monochromatized Mo $K\bar{\alpha}$ radiation. Unit-cell dimensions by least-squares fit of diffracting positions of 25 reflections ($7·0 < \theta < 16·4°$). Intensity data collected using ω–2θ scans over ω-scan ranges ($0·85 + 0·35 \tan\theta$)°. Scan rates conditional on information collected in prescans (at 10° min^{-1}) selected to give $I/\sigma(I) \geq 25$ within a max. scan time of 85 s. 3 standard reflections monitored every 9500 s of exposure time showed no significant losses in intensity over data collection period. Backgrounds by extending scan by 25% on either side of peak measured for half the time taken to collect the peak. 2746 reflections (exclusive of systematic absences) in quadrants h, k, $\pm l$ with $2\theta \leq 50°$ measured. Lorentz and polarization corrections applied to all reflections. 75 symmetry-equivalent reflections averaged [$R_{merge}(I) = 0·036$] and 392 reflec-

Table 1. *Final atomic positional* ($\times 10^4$; $\times 10^3$ *for* H *atoms) and thermal parameters with e.s.d.'s in parentheses*

|	x	y	z	B_{eq} or $B(Å^2)$*
O(1)	2121 (2)	728 (5)	2482 (2)	3·30 (7)
O(2)	1604 (2)	−1037 (6)	4219 (2)	5·5 (1)
O(3)	1476 (2)	−1909 (6)	3216 (2)	6·0 (1)
O(4)	3576 (2)	3777 (6)	4778 (2)	5·3 (1)
O(5)	4470 (2)	1787 (5)	4896 (2)	4·07 (8)
O(6)	4439 (2)	3988 (5)	3590 (2)	4·48 (9)
O(7)	4359 (2)	2230 (5)	2717 (2)	3·79 (8)
C(1)	2522 (2)	417 (6)	2969 (2)	2·4 (1)
C(2)	2330 (2)	452 (6)	3625 (2)	2·6 (1)
C(3)	2996 (3)	−95 (7)	4124 (2)	3·0 (1)
C(4)	3559 (2)	1308 (6)	4041 (2)	2·6 (1)
C(5)	3700 (2)	1345 (6)	3458 (2)	2·6 (1)
C(6)	3291 (3)	−73 (7)	3005 (2)	2·8 (1)
C(7)	3366 (3)	−1956 (7)	3325 (3)	3·5 (1)
C(8)	3224 (3)	−1978 (7)	3902 (3)	3·9 (1)
C(9)	1758 (3)	−987 (7)	3649 (2)	3·3 (1)
C(10)	1060 (4)	−2348 (11)	4306 (3)	7·1 (2)
C(11)	2055 (3)	2426 (7)	3744 (2)	3·5 (1)
C(12)	3867 (3)	2457 (7)	4598 (2)	3·2 (1)
C(13)	4791 (3)	2661 (11)	5489 (3)	6·4 (2)
C(14)	4199 (2)	2655 (7)	3274 (2)	3·0 (1)
C(15)	4820 (3)	3503 (10)	2478 (3)	5·3 (2)
H(31)	282 (3)	−15 (9)	456 (2)	6·5
H(61)	338 (3)	−4 (10)	256 (3)	6·5
H(71)	349 (3)	−295 (9)	305 (2)	6·5
H(81)	322 (3)	−299 (9)	417 (3)	6·5
H(101)	68 (3)	−225 (9)	392 (3)	6·5
H(102)	132 (3)	−325 (9)	428 (2)	6·5
H(103)	106 (3)	−211 (9)	478 (3)	6·5
H(111)	204 (3)	262 (9)	421 (3)	6·5
H(112)	160 (3)	263 (8)	344 (2)	6·5
H(113)	243 (3)	321 (9)	370 (2)	6·5
H(131)	514 (3)	189 (9)	564 (3)	6·5
H(132)	475 (3)	386 (9)	539 (2)	6·5
H(133)	438 (3)	308 (9)	574 (2)	6·5
H(151)	524 (3)	383 (9)	283 (2)	6·5
H(152)	493 (3)	305 (9)	209 (2)	6·5
H(153)	455 (3)	450 (9)	249 (3)	6·5

* Equivalent isotropic thermal parameter for the anisotropically refined atoms (all C and O) is defined as:

$$B_{eq} = \tfrac{4}{3} \Sigma_{ij} \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j.$$

tions with $F_{obs} = 0·0$ rejected to give final data set of 2192 reflections. Structure solution: direct methods (*MULTAN*11), least squares, Fourier and ΔF Fourier synthesis. Hydrogen atoms located in ΔF maps or placed in calculated positions with fixed thermal parameters ($U = 6·5 Å^2$). Full-matrix least-squares refinement (C and O anisotropic, all positional parameters refined – 247 variables) minimizing $\Sigma w \Delta F^2$ converged (max. $\Delta/\sigma = 0·22$) to final agreement indices $R = 0·058$ ($wR = 0·074$) for 1155 observed data with $I \geq 3\sigma(I)$. Weights given by $w = 4F^2\{\sigma^2(I) + (0·11F^2)^2\}^{-1}$ and, at convergence, S was 1·14 e. Most significant feature in final difference Fourier map was a peak of height 0·31 e Å^{-3} near (0·81 Å) C(3). Programs: Enraf–Nonius *SDP* package on a PDP 11/23 computer. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). The final atomic positional and thermal parameters are given in Table 1.*

Discussion. The molecular structure found (Fig. 1) establishes that the major epimer formed on reaction of (1) ($R = CO_2Me$) with (2) is the *endo*-5-methyl isomer with the configuration shown in (6). The preponderant formation of (6) is of considerable interest, since it implies preferred attack by (2) on the methyl face of (1) ($R = CO_2Me$), which is considered to be the more sterically hindered face, although the difference may be small (Ouellette, Rawn & Jreissaty, 1971). This suggests that there may be a repulsive interaction between (2) and the ester group of (1).
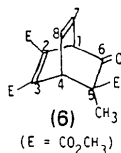
(6) CH_3

(E = CO_2CH_3)

In the bicyclo[2.2.2]octadiene system opposite bonds are very slightly twisted away from being eclipsed with torsion angles about C(1)—C(2)* and the two double bonds C(4)=C(5) and C(7)=C(8) of −1·7 (3), −2·3 (5) and 1·2 (6)°, respectively. Other internal torsion angles are in the ranges −50·3 (5) to −60·3 (5)° or 51·2 (5) to 60·0 (5)°. The double bond C(4)=C(5) is not affected by the two bulky substituents and has the same length [1·329 (7) Å] as C(7)=C(8) [1·317 (8) Å] (Table 2). These bond lengths are not significantly different from bond lengths observed (by both X-ray and electron diffraction) in related compounds containing bicyclo-[2.2.2]octene and octadiene skeletons (Hechtfischer, Steigemann & Hoppe, 1970; Yokozeki & Kuchitsu, 1971; Destro, Filippini, Gramaccioli & Simonetta, 1971; Vannerberg & Brasen, 1970).

Steric interactions between the methoxycarbonyl groups do, however, contribute to the increase in the angles C(5)=C(4)—C(12) and C(4)=C(5)—C(14) to

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* The crystallographic numbering system used to identify atoms as defined in Fig. 1 is used for consistency and clarity in the following discussion. The chemical system is given in (6).

128·1 (5) and 122·5 (5)°, respectively, the displacement of C(12) [by −0·029 (5) Å] and C(14) [by 0·066 (5) Å] out of the C(3)—C(4)=C(5)—C(6) plane and significant rotations of the mean planes of the methoxycarbonyl groups by 79·7° [C(12)] and 12·4° [C(14), e.s.d.'s *ca* 0·7°] about the C(4)—C(12) and C(5)—C(14) bonds. In the related compound bicyclo[2.2.2]octa-2,5-diene-2,3-dicarboxylic acid (Hechtfischer, Steigemann & Hoppe, 1970) intra- and intermolecular hydrogen-bonding interactions constrain the arrangements of the carboxylic acid groups and the average rotation about the C(sp^2)—C(O)OH bonds is *ca* 4·5° in one molecule and 18·6° in the other independent molecule. The C(sp^2)=C(sp^2)—C(O)OH angles in the two independent molecules [127·3 (2)– 131·1 (3)°] are, however, somewhat larger than those in the present molecule [122·5 (5) and 128·1 (5)°]. Similarly, the C(sp^2)—C(sp^2) bond lengths are

Table 2. *Selected bond lengths* (Å) *and bond angles* (°)

O(1)	C(1)	1·192 (5)	C(2)	C(3)	1·558 (7)
O(2)	C(9)	1·312 (7)	C(2)	C(9)	1·533 (7)
O(2)	C(10)	1·462 (8)	C(2)	C(11)	1·561 (7)
O(3)	C(9)	1·183 (6)	C(3)	C(4)	1·530 (7)
O(4)	C(12)	1·210 (6)	C(3)	C(8)	1·533 (8)
O(5)	C(12)	1·314 (6)	C(4)	C(5)	1·329 (7)
O(5)	C(13)	1·442 (8)	C(4)	C(12)	1·476 (7)
O(6)	C(14)	1·214 (6)	C(5)	C(6)	1·521 (7)
O(7)	C(14)	1·326 (6)	C(5)	C(14)	1·467 (7)
O(7)	C(15)	1·449 (8)	C(6)	C(7)	1·515 (8)
C(1)	C(2)	1·522 (7)	C(7)	C(8)	1·317 (8)
C(1)	C(6)	1·530 (7)			

C(9)	O(2)	C(10)	116·3 (5)	C(4)	C(5)	C(6)	113·7 (4)
C(12)	O(5)	C(13)	117·1 (5)	C(4)	C(5)	C(14)	122·5 (5)
C(14)	O(7)	C(15)	116·4 (5)	C(6)	C(5)	C(14)	123·7 (5)
O(1)	C(1)	C(2)	124·1 (5)	C(1)	C(6)	C(5)	105·2 (4)
O(1)	C(1)	C(6)	123·7 (5)	C(1)	C(6)	C(7)	103·6 (4)
C(2)	C(1)	C(6)	112·2 (4)	C(5)	C(6)	C(7)	108·9 (4)
C(1)	C(2)	C(3)	107·4 (4)	C(6)	C(7)	C(8)	114·5 (5)
C(1)	C(2)	C(9)	109·6 (4)	C(3)	C(8)	C(7)	114·0 (5)
C(1)	C(2)	C(11)	108·7 (4)	O(2)	C(9)	O(3)	123·6 (5)
C(3)	C(2)	C(9)	108·7 (4)	O(2)	C(9)	C(2)	110·7 (5)
C(3)	C(2)	C(11)	112·8 (4)	O(3)	C(9)	C(2)	125·7 (5)
C(9)	C(2)	C(11)	109·6 (4)	O(4)	C(12)	O(5)	124·6 (5)
C(2)	C(3)	C(4)	106·0 (4)	O(4)	C(12)	C(4)	123·8 (5)
C(2)	C(3)	C(8)	105·6 (4)	O(5)	C(12)	C(4)	111·5 (5)
C(4)	C(3)	C(8)	106·9 (4)	O(6)	C(14)	O(7)	123·5 (5)
C(3)	C(4)	C(5)	114·1 (4)	O(6)	C(14)	C(5)	124·4 (5)
C(3)	C(4)	C(12)	117·7 (4)	O(7)	C(14)	C(5)	112·4 (5)
C(5)	C(4)	C(12)	128·1 (5)				

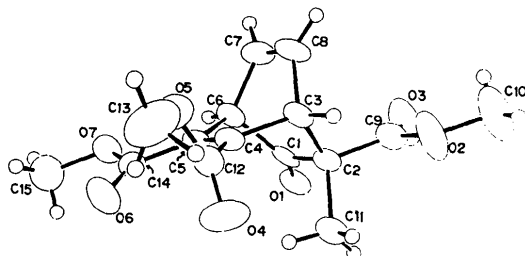Numbers in parentheses are e.s.d's in the least significant digits.

Fig. 1. *ORTEP* view of the molecule showing the numbering scheme used in the crystallographic refinements. Thermal ellipsoids are drawn at the 50% probability level. All hydrogen atoms are drawn with uniform isotropic thermal parameters.
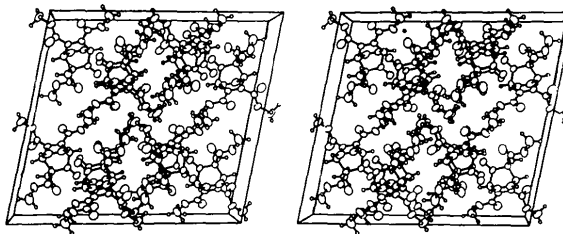
Fig. 2. Stereoscopic view down **b** of the crystal packing; **a** is down and **c** is along the top of the figure.

1·344 (4) and 1·349 (4) Å (substituted), 1·331 (4) and 1·351 (5) Å (unsubstituted) in the two independent molecules compared to 1·329 (7) Å (substituted) and 1·317 (8) Å (unsubstituted) in the present molecule.

Other bond lengths and bond angles in the present compound are comparable to those observed in the systems referenced above. The most significant intermolecular contact in the present molecule is a possible hydrogen bond $O(1)\cdots H(71)$ ($\frac{1}{2} - x$, $-\frac{1}{2} - y$, $\frac{1}{2} - z$) of length 2·49 (7) Å [$C(1)-O(1)\cdots H(71) = 115$ (1)°; $C(7)-H(71)\cdots O(1) = 135$ (5)°]. All other $O\cdots H$ contacts are >2·70 (6) Å in length. A view of the crystal packing is given in Fig. 2.

References

AUKSI, H. & YATES, P. (1981). Can. J. Chem. **59**, 2510–2517.
DESTRO, R., FILIPPINI, G., GRAMACCIOLI, C. M. & SIMONETTA, M. (1971). Acta Cryst. B**27**, 2023–2028.
HECHTFISCHER, S., STEIGEMANN, W. & HOPPE, W. (1970). Acta Cryst. B**26**, 1713–1722.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
KARLSSON, B., PILOTTI, A.-M. & WIEHAGER, A.-C. (1973). Acta Chem. Scand. **27**, 2945–2954, 2955–2964.
OUELLETTE, R. J., RAWN, J. D. & JREISSATY, S. N. (1971). J. Am. Chem. Soc. **93**, 7117–7118.
SCHULTZ, A. G., DITTAMI, J. P., LAVIERI, F. P., SALOWEY, C., SUNDARARAMAN, P. & SZYMULA, M. B. (1984). J. Org. Chem. **49**, 4429–4440.
VANNERBERG, N. G. & BRASEN, S. (1970). Acta Chem. Scand. **24**, 1894–1902.
YATES, P. & STEVENS, K. E. (1981). Tetrahedron, **37**, 4401–4410.
YATES, P. & STEVENS, K. E. (1982). Can. J. Chem. **60**, 825–834.
YOKOZEKI, A. & KUCHITSU, K. (1971). Bull. Chem. Soc. Jpn, **44**, 1783–1788.

Structure of All-*trans*-3,4-didehydroretinal (Retinal₂)

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Abstract. $C_{20}H_{26}O$, $M_r = 282\cdot4$, monoclinic, $P2_1/c$, $a = 15\cdot054$ (8), $b = 8\cdot105$ (3), $c = 18\cdot417$ (10) Å, $\beta = 127\cdot01$ (3)°, $V = 1794$ (1) Å³, $Z = 4$, $D_x = 1\cdot046$ Mg m⁻³, $\lambda(\text{Cu } K\bar{\alpha}) = 1\cdot5418$ Å, $\mu = 0\cdot44$ mm⁻¹, $F(000) = 616$, $T = 302$ K. Final $R = 0\cdot052$ for 2115 unique significant reflections. Except for the chemical and structural differences between the rings, all-*trans*-3,4-didehydroretinal (or retinal₂) and all-*trans*-retinal are nearly isomorphous. It is found that the distance between the center of the ring and the aldehydic carbon is 12·3 Å for both all-*trans*-retinal₂ and retinal. This distance exceeds the longitudinal restriction of the binding zone of bovine opsin, which explains why the *in vitro* pigment yields for both are too low to measure.

Introduction. Several studies have recently explored the relationship between the structural properties of retinal isomers (1) and homologues and their *in vitro* rates of pigment formation with bovine opsin (Matsumoto & Yoshizawa, 1978; Daemen, 1978; Matsumoto, Liu,

Simmons & Seff, 1980; Liu, Matsumoto, Kini, Asato, Denny, Kropf & DeGrip, 1984; Liu & Asato, 1984). On the basis of these results, a longitudinal restriction of the binding cavity of opsin was postulated: low recombination rates occur when the distance between the center of the trimethylcyclohexenyl ring and the reacting aldehydic C(15) atom (see Fig. 1) is above or below a particular optimum range, ca 10·1–10·9 Å (Matsumoto et al., 1980; Liu, Matsumoto, Kini, Asato, Denny, Kropf & DeGrip, 1984). What is surprising, however, is the lack of information about retinal₂ isomers and homologues, even though the 11-*cis* isomer, (2), is the only other visual chromophore (besides 11-*cis*-retinal) known in naturally occurring systems to form a pigment known as porphyropsin (Wald, 1953; Bridges, 1972).

(1) All-*trans*-retinal   (2) 11-*cis*-Retinal₂   (3) All-*trans*-retinal₂
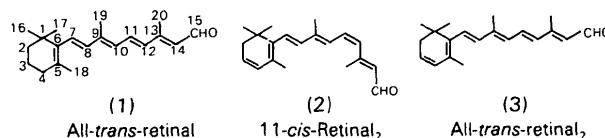
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