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10-Fluoro-all-*trans*-α-retinal

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Abstract. $C_{20}H_{27}FO$, $M_r = 302.41$, monoclinic, $P2_1/c$, $a = 6.105$ (5), $b = 21.673$ (22), $c = 13.925$ (7) Å, $\beta = 96.66$ (5)°, $V = 1830$ (2) Å^3, $Z = 4$, $D_x = 1.10$, $D_m = 1.09$ (1) g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.68$ cm^{-1}, $F(000) = 656$, $T = 298$ K, $R = 0.062$, $wR = 0.046$ for 1797 unique observed reflections. The principal distortions in the polyene portion of the molecule can be seen in the angles opposite the methyl groups (119.9 and 121.7°, a steric effect) and that opposite fluorine (131.9°, an inductive effect). The hexene ring is in the half-chair form, and its double bond is not in conjugation with the all-*trans* chain.

Introduction. It is well known that the only action of light in vision is to isomerize the retinal molecule from the 11-*cis* to the all-*trans* configuration (Hubbard & Kropf, 1958; Hamanaka, Mitsui, Ashida & Kakudo, 1972). The 11-*cis* isomer can be obtained by direct irradiation of the all-*trans* isomer in alcohol solvents (Hubbard & Wald, 1952–1953; Brown & Wald, 1956). The zwitterionic intermediate (Liu, Denny, Grodowski & Asato, 1979) leading to the formation of the 11-*cis* isomer twists about the C(11)—C(12) double bond. Any substituent which destabilizes the zwitterionic intermediate should suppress the yield of the 11-*cis* isomer.
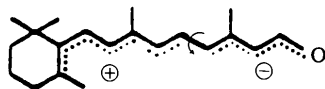
The title compound was prepared to test this hypothesis, and its crystal structure was determined to learn accurate geometry for molecular-modelling calculations on this reaction.

Experimental. Yellow colored crystals. Approximate parallelepiped: $0.6 \times 0.2 \times 0.3$ mm. D_m by flotation in aqueous NH_4Br. Data collected by a Syntex $P\bar{1}$

automated diffractometer, graphite-monochromated Mo $K\alpha$ radiation. Cell constants from 15 reflections with $6.2 < 2\theta < 22.0°$. No absorption correction. $2\theta_{max} = 50°$ ($0 \le h \le 7$, $0 \le k \le 25$, $-16 \le l \le 16$). Three check reflections ($\bar{2}0\bar{2}$, $\bar{1}50$, 014) measured after every 97 data points showed small fluctuations; corrections were made. 1797 of 3562 reflections with $I > 2\sigma(I)$ used in refinement. Lorentz–polarization correction applied. Non-H atoms were determined by *MULTAN*80 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Full-matrix least-squares refinement (Gantzel, Sparks & Trueblood, 1976) for non-H atoms with isotropic thermal parameters converged to $R = 0.151$. After the final anisotropic refinement of the complete structure (isotropic for H atoms): $R = 0.062$, $wR = 0.046$, $S = 1.83$, max. $\Delta/\sigma = 0.08$; $\sum w(F_o - |F_c|)^2$ minimized, $w = \sigma^{-2}(F)$, $p = 0.02$ (Peterson & Levy, 1957). No significant features in the final ΔF synthesis with max. $\Delta\rho = 0.22$ e Å^{-3}. Atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974).

Discussion. The structure of the title compound is presented in Fig. 1. The C(5)—C(6)—C(7)—C(8) torsion angle is +58.4° for the molecule shown in the figure. This torsion angle agrees with the theoretical angle (60°) based on the torsional potential calculated for the rotation of the cyclohexene ring about the C(6)—C(7) bond in the retinals (Honig, Warshel & Karplus, 1975). The double bond in the hexene ring is C(4)—C(5) (1.320 Å). The conjugated chain C(7)—O(21) has the all-*trans* configuration. The average single- and double-bond lengths in the conjugated chain are 1.437 and 1.320 Å respectively. The chain C(6)—O(21) is approximately planar (plane 1); C(10) shows the largest deviation (0.054 Å) from this least-squares plane. All atoms attached to this chain are also approximately in the same plane [largest deviation, F(22), 0.079 Å]. The measure of the in-plane bending in the polyene chain

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(Schenk, 1971) is $\Delta = a - b + c - d + e - f = 16\cdot4°$, where the angles a to f are hain angles associated with atoms C(8) to C(13); this indicates that this structure has less strain than all-*trans*-retinal (19·5°) (Simmons, Liu, Denny & Seff, 1981). The average bond angle along the conjugated chain is 126·2°; the bond angles opposite the C(19) and C(20) methyl groups are significantly decreased (121·7 and 119·9°) due to the steric effects of the methyl groups; the bond angle opposite the F(22) atom is markedly increased (131·9°) due to the inductive effect of fluorine. C(3) shows the largest deviation (0·045 Å) from the least-squares plane of C(3), C(4), C(5), C(6), and C(18) (plane 2). The deviations of C(1) (0·56 Å) and C(2) (0·13 Å) from this plane show that the cyclohexene ring is in the half-chair form. The average single-bond length in the ring is 1·510 Å. The angle between the plane of the chain [taken as the atoms C(6) to C(15)] and the plane of the ring [C(3) to C(6)] is 80·4°. The atomic positions with equivalent isotropic thermal parameters are given in Table 1.* The bond distances and angles of the non-H atoms are given in Table 2.

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, bond lengths and angles involving H atoms and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44861 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
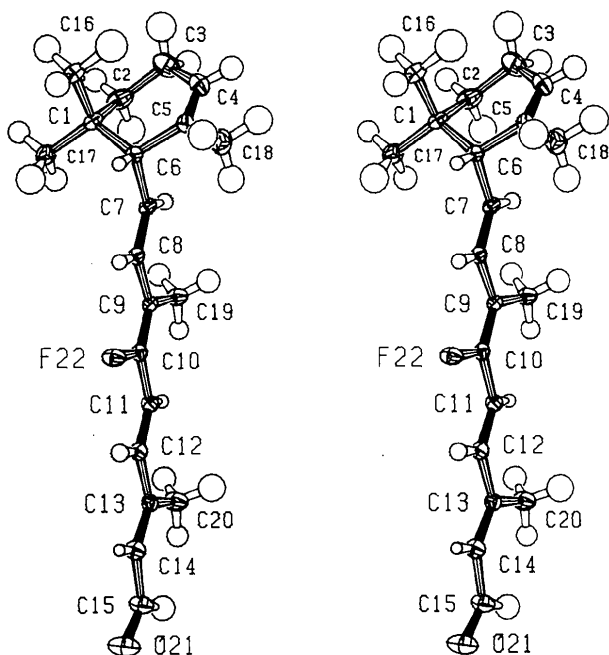

Fig. 1. A stereoview (Johnson, 1965) of the title compound drawn with ellipsoids of 15% probability. Double bonds have been drawn as solid lines.

Table 1. *Positional parameters, equivalent isotropic thermal parameters and their e.s.d.'s*

$B_{eq} = \frac{4}{3}[\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + \beta_{13}ac(\cos\beta)]$. E.s.d.'s in parentheses are in the units of the least-significant figure given for the corresponding parameter.

	x	y	z	$B_{eq}(\text{Å}^2)$
C(1)	0·3788 (6)	0·34601 (17)	0·6524 (3)	4·85 (9)
C(2)	0·1774 (10)	0·3873 (3)	0·6357 (5)	8·03 (15)
C(3)	0·2054 (14)	0·4409 (3)	0·5700 (6)	10·30 (20)
C(4)	0·3302 (11)	0·4243 (3)	0·4878 (5)	8·44 (15)
C(5)	0·4427 (8)	0·37272 (19)	0·4814 (3)	5·58 (10)
C(6)	0·4315 (6)	0·32180 (16)	0·5540 (3)	4·14 (8)
C(7)	0·2719 (7)	0·27339 (18)	0·5123 (3)	4·39 (9)
C(8)	0·3126 (7)	0·21480 (17)	0·4993 (3)	4·06 (8)
C(9)	0·1562 (6)	0·16899 (16)	0·45800 (22)	3·81 (8)
C(10)	0·2160 (6)	0·11144 (16)	0·44354 (24)	4·05 (8)
C(11)	0·0962 (7)	0·05962 (18)	0·4027 (3)	4·27 (9)
C(12)	0·1738 (7)	0·00380 (18)	0·3889 (3)	4·44 (9)
C(13)	0·0524 (6)	−0·04842 (18)	0·3466 (3)	4·44 (9)
C(14)	0·1539 (7)	−0·10205 (20)	0·3390 (3)	5·38 (10)
C(15)	0·0627 (10)	−0·15941 (22)	0·3016 (4)	6·84 (12)
C(16)	0·5749 (10)	0·3855 (3)	0·6972 (4)	7·21 (14)
C(17)	0·3447 (12)	0·2931 (3)	0·7204 (4)	7·07 (14)
C(18)	0·5742 (13)	0·3595 (3)	0·3987 (5)	8·41 (17)
C(19)	−0·0756 (7)	0·18957 (25)	0·4294 (4)	5·61 (11)
C(20)	−0·1890 (10)	−0·0402 (3)	0·3146 (6)	7·53 (15)
O(21)	0·1635 (5)	−0·20687 (14)	0·3023 (3)	9·59 (10)
F(22)	0·4345 (3)	0·09622 (8)	0·46959 (16)	5·91 (5)

Table 2. *Bond lengths (Å) and bond angles (°) of the non-H atoms with their e.s.d.'s in parentheses*

C(1)–C(2)	1·517 (7)	C(8)–C(9)	1·449 (5)
C(1)–C(6)	1·536 (5)	C(9)–C(10)	1·322 (5)
C(1)–C(16)	1·544 (7)	C(9)–C(19)	1·493 (6)
C(1)–C(17)	1·517 (7)	C(10)–C(11)	1·423 (5)
C(2)–C(3)	1·500 (10)	C(10)–F(22)	1·381 (4)
C(3)–C(4)	1·491 (11)	C(11)–C(12)	1·321 (6)
C(4)–C(5)	1·320 (7)	C(12)–C(13)	1·441 (6)
C(5)–C(6)	1·504 (6)	C(13)–C(14)	1·327 (6)
C(5)–C(18)	1·505 (8)	C(13)–C(20)	1·500 (7)
C(6)–C(7)	1·502 (5)	C(14)–C(15)	1·435 (7)
C(7)–C(8)	1·311 (6)	C(15)–O(21)	1·198 (6)
C(2)–C(1)–C(6)	108·3 (4)	C(6)–C(7)–C(8)	127·3 (4)
C(2)–C(1)–C(16)	108·2 (4)	C(7)–C(8)–C(9)	126·3 (4)
C(2)–C(1)–C(17)	112·0 (4)	C(8)–C(9)–C(10)	121·7 (3)
C(6)–C(1)–C(16)	108·5 (3)	C(8)–C(9)–C(19)	117·5 (3)
C(6)–C(1)–C(17)	110·9 (3)	C(10)–C(9)–C(19)	120·8 (4)
C(16)–C(1)–C(17)	108·8 (4)	C(9)–C(10)–C(11)	131·9 (4)
C(1)–C(2)–C(3)	113·8 (5)	C(9)–C(10)–F(22)	117·4 (3)
C(2)–C(3)–C(4)	112·6 (6)	C(11)–C(10)–F(22)	110·7 (3)
C(3)–C(4)–C(5)	125·0 (6)	C(10)–C(11)–C(12)	127·2 (4)
C(4)–C(5)–C(6)	120·7 (4)	C(11)–C(12)–C(13)	127·0 (4)
C(4)–C(5)–C(18)	122·7 (5)	C(12)–C(13)–C(14)	119·9 (4)
C(6)–C(5)–C(18)	116·4 (4)	C(12)–C(13)–C(20)	118·0 (4)
C(1)–C(6)–C(5)	112·3 (3)	C(14)–C(13)–C(20)	122·1 (4)
C(1)–C(6)–C(7)	112·9 (3)	C(13)–C(14)–C(15)	128·5 (4)
C(5)–C(6)–C(7)	109·3 (3)	C(14)–C(15)–O(21)	124·3 (5)

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Structures of cis-4-(2'-Methoxyphenyl)- (1) and trans-4-(3'-Methoxy-4'-hydroxyphenyl)-2-hydroxy-2-methyl-3,4-dihydro-2H,5H-pyrano[3,2-c][1]benzopyran-5-one (2)

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Abstract. Derivatives of 2-methyl-2H,5H-pyrano[3,2-c]-[1]benzopyran-5-one. Racemic *cis*-2-hydroxy-4-(2'-methoxyphenyl) (1), $C_{20}H_{18}O_5$, $M_r = 338.4$, triclinic, P$\bar{1}$, $a = 7.445$ (3), $b = 7.729$ (3), $c = 15.550$ (4) Å, $\alpha = 96.66$ (2), $\beta = 97.04$ (2), $\gamma = 107.49$ (3)°, $V = 835.9$ (5) Å^3, $Z = 2$, $D_x = 1.344$ g cm^{-3}, λ(Mo Kα) = 0.71073 Å, $\mu = 0.902$ cm^{-1}, $F(000) = 356$, $T = 293$ K, final $R = 0.0540$ for 3724 observations. The *cis* hemiketal of 2'-methoxywarfarin contains a dihydropyran ring in a half-chair conformation. The axial 2-hydroxy group is hydrogen-bonded to a neighboring coumarin carbonyl oxygen, O···O 2.755 (1) Å. Racemic *trans*-2-hydroxy-4-(3'-methoxy-4'-hydroxyphenyl) (2), $C_{20}H_{18}O_6$, $M_r = 354.4$, monoclinic, P$2_1/n$, $a = 10.581$ (2), $b = 9.954$ (7), $c = 16.360$ (8) Å, $\beta = 101.61$ (3)°, $V = 1687.7$ (15) Å^3, $Z = 4$, $D_x = 1.395$ g cm^{-3}, λ(Mo Kα) = 0.71073 Å, $\mu = 0.966$ cm^{-1}, $F(000) = 744$, $T = 293$ K, final $R = 0.0415$ for 2416 observations. The *trans* hemiketal of 3'-methoxy-4'-hydroxywarfarin contains a dihydropyran ring in a near half-chair conformation. Several intermolecular H bonds occur, O···O 2.865 (2), 3.104 (2) and 2.783 (2) Å, between hydroxyl groups and hydroxyl and carbonyl groups of neighboring molecules.

Introduction. As part of a study of the conformation of dihydropyran near its minimum-energy form, a series of crystalline warfarin analogs have been prepared. The present study describes the structures of two substituted 4-aryl derivatives of 2-hydroxy-2-methyl-3,4-dihydro-2H,5H-pyrano[3,2-c][1]benzopyran-5-one.
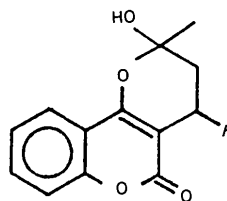
(1) R = o-(OCH₃)C₆H₄–

(2) R = m-(OCH₃)-p-(OH)C₆H₃–

While these compounds exist in a dynamic solution equilibrium between two diastereomeric hemiketals and the intermediate keto form, they crystallize as cyclic hemiketals with axial hydroxyls. The resulting dihydropyran ring may adopt any accessible conformation.

Experimental. Warfarin derivatives are synthesized generally by Michael-type addition of unsaturated ketones to 4-hydroxycoumarin (Ikawa, Stahmann & Link, 1944), and recrystallized from aqueous acetone, m.p. (1) 464–465, (2) 451–454 K. D_m's were not measured. Crystallographic specimens: (1) 0.2 × 0.35 × 0.35 mm; (2) 0.2 × 0.33 × 0.4 mm were chosen for data collection on a CAD-4 diffractometer. Intensities were collected to $2\theta = 57°$ (*h* and *k*: −10 to