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An Oxetanol Derived from Royleanone Methyl Ether†

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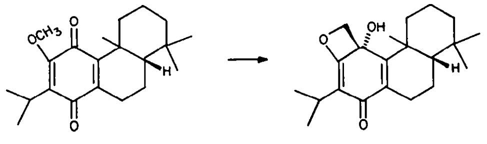
Abstract. $C_{21}H_{30}O_3$, derived from photolysis of royleanone methyl ether, monoclinic, $P2_1$, $a = 13\cdot228$ (2), $b = 7\cdot231$ (3), $c = 9\cdot947$ (3) Å, $\beta = 96\cdot04$ (3)°, $Z = 2$, $D_x = 1\cdot160$, $D_m = 1\cdot151$ g cm^{-3} (by flotation in a carbon tetrachloride/*n*-hexane mixture). The structure was solved by direct methods, and refined to a final R of 0·033 for 1688 observed reflexions. The molecule contains the oxetanol grouping and has strained stereochemistry. The molecules are linked by hydrogen bonds to form spirals along **b** that are not connected.

Introduction. Royleanone is a naturally occurring diterpenoid quinone and its methyl ether is (I).



(I) (II)

The photolysis of (I) was studied by Edwards & Ho (1978), and in benzene a compound was obtained which is quite different from those produced in acetic acid. On the basis of its formula, $C_{21}H_{30}O_3$, and the examination of its spectra and chemical reactions, they had assigned to it the structure (II), which contains an oxetanol grouping. The X-ray analysis has been carried out to investigate the strained molecular geometry of this unique product and to confirm the configuration of the OH group.

Colourless prismatic crystals, m.p. 161 °C, obtained from absolute methanol, were kindly supplied by Dr O. E. Edwards. The data were measured on a Picker diffractometer using Ni- filtered Cu radiation [$\lambda(K\alpha_1) = 1\cdot54050$, $\lambda(K\alpha_2) = 1\cdot54434$ Å], and a crystal fragment of dimensions 0·25 × 0·25 × 0·20 mm mounted along **a***. The unit-cell parameters were based on the angular settings of the 900, 040 and 006 reflexions and their equivalents, measured at 2θ and -2θ. The integrated intensities of the hkl and $hk\bar{l}$ reflexions with $2\theta < 130°$ were obtained with the θ–2θ scan method and the background was measured for 20 s at the upper 2θ limit of every reflexion. The 020 and 006 reflexions were used as standards for scaling purposes, and the intensities were corrected for background and the Lorentz and polarization effects. The absorption correction was considered negligible, $\mu(\mathrm{Cu}) = 5\cdot63$ cm^{-1}.

The structure was solved by application of the tangent formula (Karle & Hauptman, 1956), as described by Karle (1976). The starting set of phases consisted of three origin-defining ($81\bar{7}$, $90\bar{8}$, $\underline{0}$,0,11) and five additional reflexions ($81\bar{6}$, $70\bar{7}$, 228, $60\bar{2}$, 064). The phasing process was limited to the 252 reflexions with $|E| \geq 1\cdot40$. An E map evaluated with 250 of these reflexions ($R_{\mathrm{Karle}} = 0\cdot18$), revealed the locations of 19 non-hydrogen atoms, and the remaining atoms were located from subsequent difference maps.

The refinement was by block-diagonal least-squares calculation on the observed reflexions, minimizing $\Sigma\, w(|F_o| - |F_c|)^2$, where $w = 1/\{1 + [(|F_o| - 30)/30]^4\}$ and $0\cdot9 \leq |F_o| \leq 87\cdot2$. The thermal parameters were assumed to be anisotropic for C and O, and isotropic for H. The strongest reflexion (011) appeared to suffer from extinction and was excluded from the final stages

Table 1. *Fractional coordinates* (× 10^4) *of the* C *and* O *atoms*

	x	y	z
O(1)	−441 (1)	8995 (3)	4773 (2)
O(2)	732 (1)	3827 (3)	2478 (2)
O(3)	−756 (1)	5614 (3)	634 (2)
C(4)	348 (2)	5476 (5)	431 (2)
C(5)	609 (2)	5670 (4)	1990 (2)
C(6)	−476 (2)	6278 (4)	1923 (2)
C(7)	−917 (2)	7331 (4)	2777 (2)
C(8)	−163 (2)	8148 (4)	3801 (2)
C(9)	948 (2)	8115 (4)	3608 (2)
C(10)	1339 (2)	6985 (4)	2728 (2)
C(11)	2483 (2)	6839 (4)	2655 (2)
C(12)	2935 (2)	8799 (4)	2923 (2)
C(13)	2722 (2)	9438 (5)	4327 (3)
C(14)	1587 (2)	9482 (4)	4480 (3)
C(15)	2685 (2)	6207 (4)	1229 (3)
C(16)	3810 (2)	6327 (5)	1016 (3)
C(17)	4180 (2)	8289 (5)	1210 (3)
C(18)	4056 (2)	9091 (4)	2615 (3)
C(19)	−2019 (2)	7858 (5)	2758 (3)
C(20)	−2691 (2)	6605 (7)	1837 (4)
C(21)	−2192 (2)	9901 (6)	2419 (3)
C(22)	2897 (2)	5379 (5)	3701 (3)
C(23)	4860 (2)	8262 (5)	3683 (3)
C(24)	4264 (2)	11180 (5)	2557 (4)

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Table 2. *Fractional coordinates* (×10³) *and temperature factors of the hydrogen atoms with e.s.d.'s in parentheses*

	x	*y*	*z*	*B* (Å²)
H(2,1)	70 (2)	390 (4)	333 (2)	4·8 (0·6)
H(4,1)	55 (2)	654 (4)	−17 (2)	3·8 (0·6)
H(4,2)	57 (2)	426 (4)	2 (2)	5·1 (0·7)
H(12,1)	255 (2)	963 (3)	229 (2)	3·0 (0·5)
H(13,1)	306 (2)	1073 (4)	459 (2)	4·3 (0·6)
H(13,2)	308 (2)	846 (4)	504 (3)	6·0 (0·8)
H(14,1)	129 (2)	1074 (4)	430 (2)	5·0 (0·7)
H(14,2)	142 (2)	932 (4)	541 (3)	5·9 (0·7)
H(15,1)	227 (1)	717 (3)	58 (2)	2·4 (0·5)
H(15,2)	241 (2)	488 (4)	103 (2)	3·5 (0·5)
H(16,1)	391 (2)	591 (4)	11 (2)	5·3 (0·7)
H(16,2)	425 (2)	551 (5)	170 (3)	6·3 (0·8)
H(17,1)	378 (2)	907 (4)	46 (2)	3·6 (0·5)
H(17,2)	488 (2)	847 (3)	101 (2)	3·3 (0·5)
H(19,1)	−218 (1)	768 (3)	371 (2)	2·5 (0·5)
H(20,1)	−264 (2)	695 (5)	85 (3)	8·8 (1·0)
H(20,2)	−344 (2)	686 (5)	182 (3)	8·8 (1·0)
H(20,3)	−268 (3)	531 (6)	209 (3)	10·6 (1·1)
H(21,1)	−295 (2)	1029 (5)	253 (3)	7·9 (0·9)
H(21,2)	−212 (2)	1009 (5)	140 (3)	7·1 (0·8)
H(21,3)	−171 (2)	1070 (6)	298 (3)	9·8 (1·1)
H(22,1)	261 (2)	436 (4)	348 (2)	5·2 (0·7)
H(22,2)	372 (2)	522 (5)	379 (3)	7·5 (0·9)
H(22,3)	277 (2)	581 (5)	467 (3)	5·7 (0·7)
H(23,1)	482 (2)	869 (5)	469 (3)	8·0 (0·9)
H(23,2)	554 (2)	871 (5)	354 (3)	6·2 (0·7)
H(23,3)	489 (2)	682 (4)	362 (3)	6·0 (0·8)
H(24,1)	374 (2)	1184 (5)	190 (3)	9·6 (1·1)
H(24,2)	502 (2)	1137 (5)	217 (3)	6·6 (0·8)
H(24,3)	429 (2)	1183 (5)	353 (3)	9·0 (1·0)

of refinement. In the final cycle, $R = 0{\cdot}033$ and $R_w = 0{\cdot}029$ for the observed reflexions. The average and maximum shift/e.s.d. for all atoms were 0·10 and 0·64 respectively. The residual electron density in the final difference map was within −0·16 to 0·12 e Å^{-3}. The atomic parameters are listed in Tables 1 and 2.* The scattering factors were those of Hanson, Herman, Lea & Skillman (1964) for C and O, and of Stewart, Davidson & Simpson (1965) for H. All calculations were carried out with the NRC program system of Ahmed, Hall, Pippy & Huber (1973).

Discussion. The structure found for this oxetanol derivative confirms fully that assigned by Edwards & Ho (1978). It was not possible to determine crystallographically the absolute configuration, but it was established for royleanone by Edwards, Feniak & Los (1962) and the configuration of the molecule in this work is chosen in agreement with it.

The bond lengths and angles, not corrected for thermal vibration, are shown in Fig. 1. The $C(sp^3)$–$C(sp^3)$ values vary from 1·507 to 1·559 Å. The longest bonds, C(4)–C(5), C(11)–C(12) and C(12)–C(18), are associated with the fully substituted C atoms. The $C(sp^3)$–$C(sp^2)$ bonds vary from 1·493 to 1·527 Å. The C=C, C–OH, C=O bonds are in agreement with those given in *Molecular Structures and Dimensions* (1972). Of special interest is the O(3)–C(6) bond which is significantly shortened to 1·383 Å.

Preliminary IR and Raman spectra indicated unusual intensity patterns near 1620 and 1710 cm^{-1} and it was thought that it would be possible to correlate the X-ray results with these findings. However, in polar solvent (unpublished work by Dr P. R. Carey) both peaks in the Raman spectrum were somewhat broader showing that a complex coupling of double-bond vibrations exists.

The variations of the bond angles also testify to the presence of strain in rings *A* and *B*, and at the fusion of rings *B* and *C*.The fusion of the *C*/*D* rings is *trans*, as expected for a derivative of royleanone.

The C–H bonds vary from 0·85 to 1·12 Å, and the C–C–H and H–C–H angles from 95·5 to 119·0°.

Some mean planes, and the displacements of the

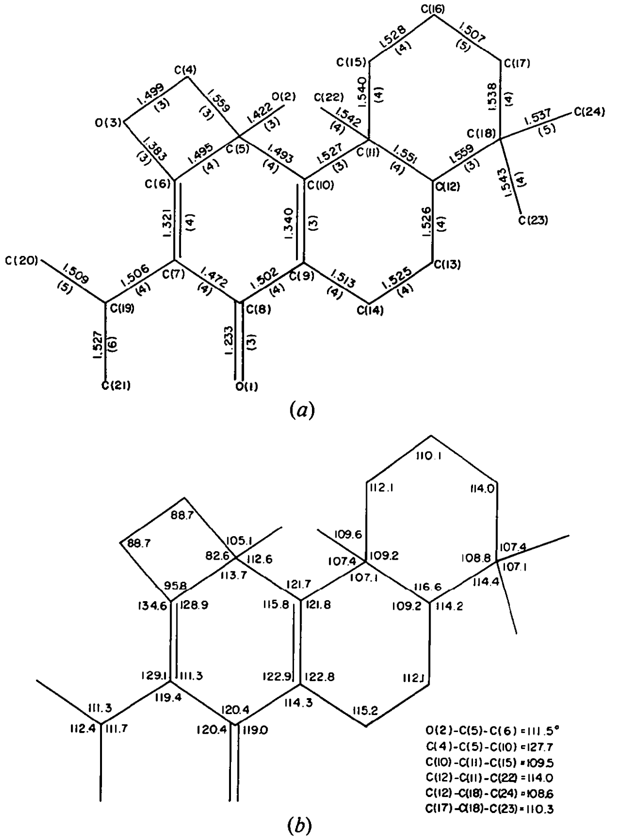

Fig. 1. (*a*) Bond lengths (Å) of oxetanol with their e.s.d.'s. (*b*) Valency angles (°) (the e.s.d. is ≤0·3°).

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33249 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Mean planes and atomic displacements*

(*a*) Parameters for the planes $lX + mY + nZ = p$, where X, Y, Z are orthogonal coordinates in Å

	l	m	n	p
Ring *A*	0·1668	0·9595	−0·2271	3·6793
Ring *B*	0·0524	0·7538	−0·6550	2·1249
Ring *C*	−0·0363	0·6775	−0·7346	1·3434
Ring *D*	−0·1902	0·6406	−0·7439	1·2818
O(1)···O(3)	0·1291	0·8419	−0·5240	2·8546
C=O	−0·0262	0·8565	−0·5155	3·1541

(*b*) Deviations from the mean planes (Å)

Ring *A*		Ring *B*		Ring *C*	
O(3)	−0·104	C(6)	0·007	C(9)	−0·020
C(4)	0·092	C(7)	−0·007	C(10)	0·042
C(5)	−0·093	C(9)	0·006	C(11)	−0·031
C(6)	0·105	C(10)	−0·007	C(13)	0·021
		C(5)*	−0·292	C(14)	−0·012
		C(8)*	−0·178	C(12)*	0·713

Ring *D*		O(1)···O(3)		C=O	
C(12)	−0·037	O(1)	0·007	C(7)	0·009
C(15)	0·037	C(8)	0·056	C(8)	−0·029
C(16)	−0·037	C(7)	−0·024	C(9)	0·009
C(18)	0·036	C(6)	−0·136	O(1)	0·011
C(11)*	−0·639	O(3)	0·096		
C(17)*	0·639	C(5)*	−0·357		

* Atoms excluded from the mean-plane calculation.

atoms from them are listed in Table 3. The torsion angles within the rings are presented in Fig. 2 where the signs are according to the convention of the IUPAC–IUB Commission on Biochemical Nomenclature (1970). None of the rings is planar. The average torsion angle in ring *A* is 15·4°. Ring *B* has a very flattened boat form with C(5) and C(8) displaced from the plane of the double bonds by 0·29 and 0·18 Å respectively. Ring *C* adopts the bent-chair II*b* form (Hendrickson, 1961) with five of its atoms within −0·03 to +0·04 Å from their mean plane, while C(12) is 0·71 Å from that plane. Ring *C* can also be described as having the envelope or half-boat form with the puckering parameters q_2 = 0·41 Å, q_3 = 0·33 Å, Q = 0·52 Å, φ_2 = −7·5° and θ = 50·7° (Cremer & Pople, 1975). Ring *D* has a slightly twisted chair form. The conjugated chain O(1)=C(8)–C(7)=C(6)–O(3) is far from planar. The results show the greatest puckering at C(6) which is in agreement with the existing strain caused by the *A*/*B* fusion. Some strain is also indicated in the carbonyl group which deviates significantly from planarity.

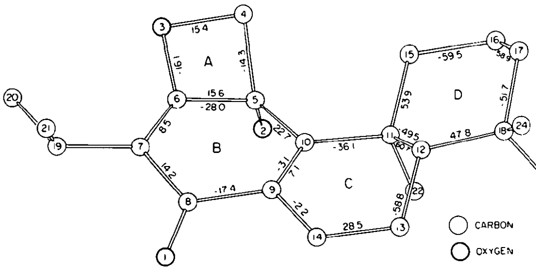

Fig. 2. Torsion angles (°).

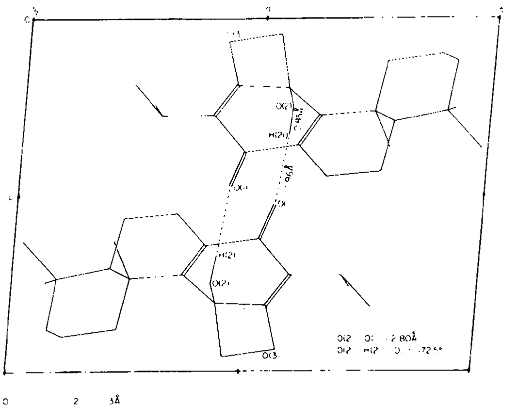

Fig. 3. Projection along the *b* axis showing the hydrogen bonds.

The molecules are linked by hydrogen bonds forming a continuous spiral along **b**. The hydrogen-bonding parameters are shown in Fig. 3. There are no other contacts shorter than the sums of the appropriate van der Waals radii.

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