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Structure of [2*S*-(2α,2a*β*,4α,4a*β*,5α,8α,8a*β*,8b*β*,10*R**)]-2,2a,3,4,4a,5,6,8,8a,8b-Decahydro-5,8-epoxy-2,4-methano-1,7-dioxacyclopent[*cd*]azulen-10-ol Monohydrate, $C_{11}H_{14}O_4.H_2O$, a Pentacyclic Alcohol Prepared from Levoglucosenone

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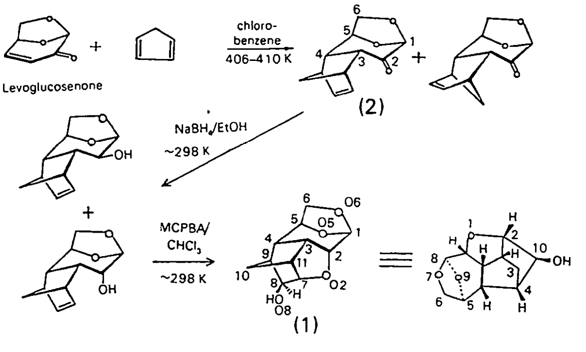
Abstract. $M_r = 228{\cdot}3$, orthorhombic, $P2_12_12_1$, $a = 7{\cdot}832$ (1), $b = 21{\cdot}985$ (2), $c = 6{\cdot}115$ (1) Å, $V = 1053$ Å^3, $D_x = 1{\cdot}439$ g cm^{-3}, $Z = 4$, graphite-monochromated Mo $K\bar{\alpha}$ radiation, $\lambda = 0{\cdot}71069$ Å, $\mu = 1{\cdot}06$ cm^{-1}, $F(000) = 488$, $T = 294$ K, $R(F) = 0{\cdot}036$ for 1241 reflections and 210 variables. There are no unusual bond lengths or angles. Ring torsion angles show that the geometry of the parent 1,6-anhydrohexopyranose system has not been significantly perturbed.

Introduction. A program in this laboratory (Horton & Takagi, 1982; compare Horton, Machinami & Takagi, 1983) is concerned with the preparation of functionalized, optically pure carbocycles by Diels–Alder reaction of dienes with readily available, unsaturated sugar derivatives. To this end, we have studied the Diels–Alder reaction between cyclopentadiene and 1,6-anhydro-3,4-dideoxy-*β*-D-*glycero*-hex-3-en-2-one (levoglucosenone, Bhaté & Horton, 1982, 1983). The various transformations leading to the title pentacyclic alcohol (1) are shown in scheme (1).† We undertook an X-ray diffraction study of (1) with the objective of providing independent proof of the stereochemistry of the Diels–Alder reaction.



Scheme (1)

Experimental. Clear, colorless, hexagonal prismatic rods crystallized from 95% ethanol. D_m not determined. Crystal: 0·42 × 0·39 × 0·45 mm. Precession photographs: *mmm* symmetry with systematic absences *h*00 for *h* odd, 0*k*0 for *k* odd, and 00*l* for *l* odd. Syntex $P\bar{1}$ diffractometer. Unit cell: least squares on 27 reflections, $20 < 2\theta < 30°$. Intensity measurements by θ–2θ scans, 2 to 12° min^{-1} in 2θ, 1·0° below $K\alpha_1$ to 1·2° above $K\alpha_2$, background/scan time = 0·5, graphite-monochromated Mo $K\alpha$ radiation, 1434 unique reflections $(+h, +k, +l)$, $4 < 2\theta < 55°$. Six standards every 100 reflections, no decay evident. Instability constant $p = 0{\cdot}02$, used in $\sigma_I^2 = R^2(S + t^2B) + p^2I^2$, $I = R(S - tB)$. Structure solved by *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980): two four-atom fragments recycled into *MULTAN* to obtain all C and O positions. Water molecule also present. Isotropic least-squares refinement with *SHELX*76 (Sheldrick, 1976), $R = 0{\cdot}12$. After anisotropic refinement all H atoms located from a $\Delta\rho$ map. Final cycle of anisotropic least squares on F, H atoms refined isotropically: the usual f values [Stewart, Davidson & Simpson (1965) for H, *International Tables for X-ray Crystallography* (1974) for C and O], $1/\sigma^2(F)$ weights, inclusion rule $F_o^2 > 2\sigma(F_o^2)$, 1241 contributing F's, 210 variables, $R = 0{\cdot}036$, $R_w = 0{\cdot}037$, $S = 2{\cdot}05$, final $\Delta\rho_{\max} = 0{\cdot}20$ e Å^{-3}, $(\Delta/\sigma)_{\max} = 0{\cdot}10$. No correction made for anomalous dispersion or absorption. Isotropic-extinction parameter included, $x = 1{\cdot}11$ (6) $\times 10^{-6}$, where $F_c' = F_c[1 - (xF_c^2)/\sin\theta]$.

Discussion. Fig. 1 is an *ORTEP* drawing (Johnson, 1965) of the molecule of alcohol (1), and Table 1 lists the final atomic coordinates and the estimated standard deviations.‡ The bond lengths and the valence angles given in Table 2 are all within the range expected for this type of compound. The molecular arrangement in the unit cell is shown stereoscopically in Fig. 2.

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† The atom numbering used in this paper is based on the standard carbohydrate nomenclature and is shown in formulas (1) and (2). As no suitable terminology that retains the carbohydrate antecedents for such fused-ring derivatives as (1) has yet been developed, the Ring Index name for (1) has been given in the title of this paper, and the numbering for this name is given in the formula to the right of the perspective formula for (1).

‡ Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38769 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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The configuration at C(3) and C(4) of adduct (2) (see scheme 1) was determined from stereochemical arguments, from evidence of chemical transformations, and from ^{1}H NMR data (Shafizadeh & Ward, 1981). These results are now unambiguously affirmed and extended by this crystal structure determination for the derived alcohol (1).

Table 1. *Final positional and thermal parameters for* (1)

	x	*y*.	*z*	*B*(Å^2)*
C(1)	0·38116 (35)	0·93859 (11)	0·35693 (44)	3·70
C(2)	0·56827 (34)	0·95563 (10)	0·35972 (44)	3·69
C(3)	0·66753 (34)	0·92706 (10)	0·54503 (39)	3·34
C(4)	0·59697 (30)	0·86375 (11)	0·61283 (37)	3·14
C(5)	0·40630 (30)	0·85976 (11)	0·58044 (39)	3·28
C(6)	0·31296 (35)	0·90963 (13)	0·70486 (44)	4·11
C(7)	0·77925 (32)	0·89293 (10)	0·21759 (40)	3·33
C(8)	0·71530 (32)	0·82693 (10)	0·24862 (38)	2·99
C(9)	0·71859 (33)	0·81963 (11)	0·49688 (42)	3·51
C(10)	0·88944 (35)	0·85005 (15)	0·54906 (49)	4·57
C(11)	0·84230 (33)	0·91052 (12)	0·44512 (42)	3·95
O(2)	0·64639 (26)	0·93460 (7)	0·16049 (26)	4·10
O(5)	0·36309 (19)	0·87471 (7)	0·35745 (26)	3·35
O(6)	0·30174 (26)	0·95897 (8)	0·55235 (31)	4·46
O(8)	0·83592 (22)	0·78643 (8)	0·14846 (35)	4·46
O(9)†	0·17472 (31)	0·80394 (10)	0·05451 (39)	5·16
H(1)	0·3248 (39)	0·9561 (13)	0·2362 (48)	4·79
H(2)	0·5774 (27)	0·9985 (11)	0·3675 (37)	3·31
H(3)	0·6670 (36)	0·9520 (13)	0·6702 (48)	4·92
H(4)	0·6195 (35)	0·8586 (12)	0·7709 (45)	4·37
H(5)	0·3629 (30)	0·8227 (10)	0·6062 (40)	3·25
H(6-*endo*)	0·3724 (36)	0·9237 (12)	0·8389 (50)	4·80
H(6-*exo*)	0·2032 (39)	0·8975 (12)	0·7550 (46)	5·03
H(7)	0·8645 (32)	0·8952 (10)	0·1009 (38)	3·58
H(8)	0·6046 (30)	0·8210 (9)	0·1803 (36)	2·49
H(9)	0·6971 (31)	0·7772 (11)	0·5414 (38)	3·80
H(10-*endo*)	0·9238 (43)	0·8523 (16)	0·7101 (58)	6·71
H(10-*exo*)	0·9882 (38)	0·8274 (12)	0·4799 (43)	4·53
H(11)	0·9294 (32)	0·9412 (11)	0·4485 (43)	3·73
H(O8)	0·7826 (37)	0·7586 (12)	0·0884 (42)	5·02
H′(O9)	0·0602 (49)	0·8017 (16)	0·0887 (60)	7·45
H″(O9)	0·2231 (56)	0·8188 (18)	0·1454 (80)	8·83

* For the non-hydrogen atoms, the equivalent isotropic *B* value is reported with $B_{\rm eq} = \frac{4}{3}(a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33})$.

† O(9) is the oxygen atom of the water molecule.

Table 2. *Valence angles* (°) *and bond lengths* (Å) *in alcohol* (1)

C(2)–C(1)–O(5)	110·1 (2)	C(5)–C(6)–O(6)	104·4 (2)
O(6)–C(1)–O(5)	105·6 (2)	C(6)–O(6)–C(1)	106·4 (2)
O(6)–C(1)–C(2)	109·7 (2)	C(2)–O(2)–C(7)	108·0 (2)
C(1)–C(2)–C(3)	113·8 (2)	O(2)–C(7)–C(8)	113·3 (2)
C(1)–C(2)–O(2)	108·8 (2)	O(2)–C(7)–C(11)	107·2 (2)
C(3)–C(2)–O(2)	106·4 (2)	C(8)–C(7)–C(11)	103·3 (2)
C(2)–C(3)–C(11)	104·9 (2)	C(7)–C(8)–O(8)	108·5 (2)
C(2)–C(3)–C(4)	112·9 (2)	C(7)–C(8)–C(9)	102·4 (2)
C(4)–C(3)–C(11)	102·1 (2)	O(8)–C(8)–C(9)	110·4 (2)
C(3)–C(4)–C(5)	111·7 (2)	C(8)–C(9)–C(10)	100·2 (2)
C(3)–C(4)–C(9)	102·9 (2)	C(8)–C(9)–C(4)	112·5 (2)
C(5)–C(4)–C(9)	121·2 (2)	C(4)–C(9)–C(10)	99·8 (2)
C(4)–C(5)–C(6)	111·6 (2)	C(9)–C(10)–C(11)	94·8 (2)
C(4)–C(5)–O(5)	110·1 (2)	C(10)–C(11)–C(3)	104·8 (2)
O(5)–C(5)–C(6)	101·3 (2)	C(10)–C(11)–C(7)	103·8 (2)
C(1)–O(5)–C(5)	101·8 (2)	C(3)–C(11)–C(7)	97·7 (2)

C(1)–O(6)	1·420 (3)	C(1)–O(5)	1·411 (3)
C(1)–C(2)	1·513 (4)	C(2)–C(3)	1·511 (4)
C(3)–C(4)	1·554 (3)	C(4)–C(5)	1·509 (3)
C(5)–O(5)	1·443 (3)	C(5)–C(6)	1·522 (4)
C(6)–O(6)	1·433 (3)	C(2)–O(2)	1·440 (3)
O(2)–C(7)	1·430 (3)	C(7)–C(11)	1·526 (3)
C(3)–C(11)	1·542 (4)	C(10)–C(11)	1·519 (4)
C(4)–C(9)	1·533 (4)	C(9)–C(10)	1·530 (4)
C(8)–C(9)	1·527 (3)	C(7)–C(8)	1·547 (3)
C(8)–O(8)	1·436 (3)		

The ring torsion angles for (1) are within the range of values determined for 1,6-anhydroaldohexopyranoses, showing that, despite the presence of the bicyclo[2.2.1]heptane system and the five-membered cyclic ether structure, the geometry of the parent 1,6-anhydrohexopyranose system is not significantly perturbed. Small differences, however, are evident. Thus, there is near total eclipsing of the O(6)–C(1) and C(5)–C(6) bonds [torsion angle 0·4 (3)°]. This deviation is also reflected in the torsion angles O(6)–C(6)–C(5)–O(5) [−26·4 (2)°] and O(5)–C(1)–O(6)–C(6) [26·9 (3)°].

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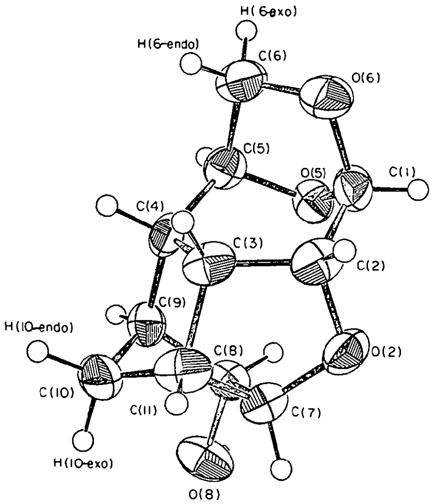

Fig. 1. *ORTEP* drawing of alcohol (1). Non-hydrogen atoms have been drawn with 50% probability thermal ellipsoids. The H atoms have been drawn artificially small, and are labeled according to the attached atoms.

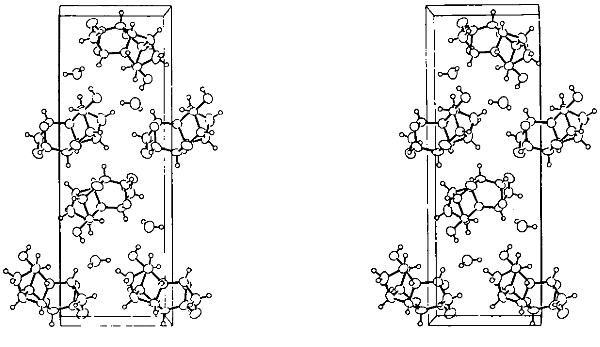

Fig. 2. Stereoscopic view of the unit cell for alcohol (1). The origin is in the lower left corner with the positive *a* axis horizontal and to the right, the positive *b* axis vertical, and the positive *c* axis in the direction toward the viewer.

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Crispatine Monohydrate, $C_{16}H_{23}NO_5.H_2O$, a Pyrrolizidine Alkaloid

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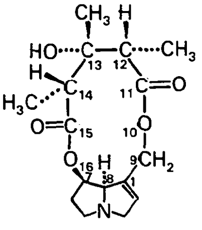
Abstract. $M_r = 327{\cdot}4$, triclinic, $P1$, $a = 5{\cdot}670\,(1)$, $b = 8{\cdot}020\,(1)$, $c = 9{\cdot}943\,(1)$ Å, $\alpha = 91{\cdot}25\,(1)$, $\beta = 103{\cdot}03\,(1)$, $\gamma = 106{\cdot}81\,(1)°$, $U = 419{\cdot}9\,(1)$ Å^3, $Z = 1$, $D_x = 1{\cdot}295$ Mg m^{-3}, $\lambda(\mathrm{Cu}\,K\alpha) = 1{\cdot}5418$ Å, $\mu = 0{\cdot}73$ mm^{-1}, $F(000) = 176$, $T = 291$ K. Final $R = 0{\cdot}037$ for 1367 observed terms. The conformation of the 11-membered macroring is similar to that observed in the related alkaloids, monocrotaline and fulvine. The hydroxyl substituent forms an intramolecular hydrogen bond with the carbonyl O of the secondary ester and forms an intermolecular hydrogen bond with the water molecule.

Introduction. Crispatine (I; stereochemistry of esterifying acid determined herein) has been isolated together with fulvine and monocrotaline from *Crotalaria crispata* (family Leguminosae). The alkaloid hydrolyses to retronecine and crispatic acid (Culvenor & Smith, 1963). The almost identical NMR spectra of fulvinic and crispatic acids and their lack of detectable optical activity led to the conclusion that the two acids were the symmetrical diastereoisomers of 3-hydroxy-2,3,4-trimethylglutaric acid. This conclusion was confirmed and the relative configuration established by synthesis of the diastereoisomers by Matsumoto, Fukui & Edwards (1973). The X-ray structure of fulvine has been determined by Sussman & Wodak (1973), leaving two possible structures for crispatine, the C(13)-epimer (I) of fulvine and the C(12),C(14)-epimer which would result if the crispatic acid were incorporated the other way in the macrocyclic ring. This present X-ray study defines the stereochemistry of crispatine and provides further conformational detail in the series of hepatotoxic pyrrolizidine alkaloids.



(I)

Experimental. Crystals grown from aqueous methanol; as they proved to be unstable in air, crystal *ca* 0·39 × 0·25 × 0·37 mm sealed in a thin-walled Lindemann-glass tube. Rigaku-AFC diffractometer, Cu $K\alpha$ radiation, graphite-crystal monochromator. Cell parameters determined by least squares from 2θ values measured for 25 strong reflections. Integrated intensities recorded by an ω–2θ scan, 2θ scan rate 2° min^{-1}, scan range $(\Delta\omega)$ $1{\cdot}2° + 0{\cdot}5°\tan\theta$, 10s stationary background counts. Three reference reflections monitored every 50 reflections showed no significant variation in intensity during data collection. $2\theta_{\max} = 130°$. Range of hkl: 0–6, −9–9, −11–10. 1406