

THE CRYSTAL STRUCTURE OF A SEPTANOSE* DERIVED FROM LEVOGLUCOSENONE

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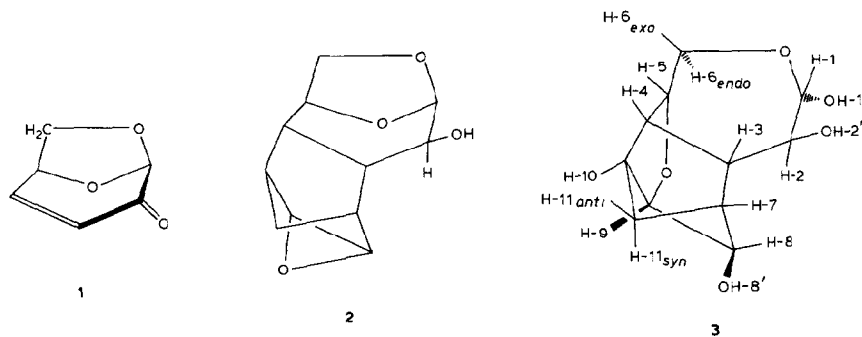
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ABSTRACT

A single-crystal, X-ray diffraction study was performed on a septanose* ($C_{11}H_{16}O_5$) derived from levoglucosenone. The crystals are monoclinic, with unit-cell parameters of $a = 1054.5$, $b = 832.4$, $c = 597.3$ pm, $\beta = 83.53^\circ$, space group $P2_1$, and $z = 2$. The structure was solved by direct methods, and refined by least squares to $R = 0.035$. The septanose ring adopts a boat conformation, with a furanoid and one cyclopentane ring in twist conformations, and another cyclopentane ring in an envelope conformation.

INTRODUCTION

Levoglucosenone (1; 1,6-anhydro-3,4-dideoxy- β -D-glycero-hex-3-eno-



*Systematic name: [2*R*-(2 α ,2 $\alpha\beta$,4 α ,4 $\alpha\beta$,5 β ,6 α ,8 $\alpha\beta$,8 β ,9*R**)]-decahydro-2,4-methano-1,7-dioxacyclopent[*cd*]azulene.

**Deceased October 1st, 1983.

pyranos-2-ulose) is readily obtained from the pyrolysis of acid-treated, cellulosic waste¹ (such as newsprint), and has been shown to undergo a wide range of chemical reactions², including intramolecular rearrangements³. Acid hydrolysis³ of the epoxide **2** (a cyclopentadiene adduct of levoglucosenone) yielded a single product (**3**) quantitatively. This compound was considered to be a triol on the basis of its ¹H-n.m.r. and i.r. spectra, and the observation that acetylation yielded a triacetate. However, the proton coupling-constants found in the ¹H-n.m.r. spectra of **3** and its triacetate were not consistent with a C-8,C-9 *trans*-diol. The crystal structure of **3** was ascertained in order to characterize its structure and conformation fully.

RESULTS AND DISCUSSION

A stereoscopic drawing of **3** is shown in Fig. 1, and atomic coordinates are listed in Table I*. The molecule consists of a norbornyl residue fused to a seven-membered heterocycle, and each is joined to a furanoid portion. The pyranoid and oxirane rings of **2** are cleaved in the formation of the furanoid ring of **3**; however, the mechanism of this transformation has not yet been fully elucidated.

Bond lengths and bond angles for **3** are respectively shown in Figs. 2 and 3. The standard deviations in the C–C and C–O bond-lengths range from 0.7 to 1.2 pm. The C-4–C-5 bond-length (150.6 pm) is significantly shorter than the mean C–C bond-length of 152.8(1.7) pm. Presumably, this shortening is associated with the strain exerted by the furanoid ring. The C–O bonds in the rings do not show a pattern the same as that observed in other septanoses^{4–6}, in which the C-1–O-6 has been found to be longer than the C-1–O-1 bond. In this molecule, the C-1–O-6 (140.0 pm) is much shorter than the C-1–O-1 (142.7 pm) and the other C–O bonds.

The standard deviations in the bond angles for the non-hydrogen atoms range from 0.4 to 0.6°. Differences from ideal tetrahedral values are observed throughout the molecule. Six of the seven bond angles in the seven-membered ring are considerably larger than 109.5°. The existence of internal angles consistently larger than the ideal tetrahedral value has also been observed in other septanose structures^{4–7}. It has been suggested that a characteristic of septanose rings is an average value for the internal angles involving the even-numbered carbon atoms which is significantly greater than that found for the odd-numbered carbon atoms⁴. However, the mean of the internal angles involving the even-numbered carbon atoms of the septanose ring of **3** (112.8°) is significantly lower than that for the odd-numbered atoms (115.9°). The internal angles of the furanoid ring and the two cyclopentane rings are all less than the ideal, tetrahedral value, as has been found for dioxolane rings fused to a septanose structure⁴. Unusually small bond-angles of 94.7 and 97.9° were observed in the five-membered rings of **3**.

*Supplementary data: Hydrogen and non-hydrogen thermal parameters (Table IV) and observed and calculated structure factors (Table V) can be obtained from Elsevier Science Publishers B.V., BBA Deposition, P.O. Box 1527, Amsterdam, The Netherlands. Reference should be made to No. BBA/DD/278/*Carbohydr. Res.*, 129 (1984) 55–61.

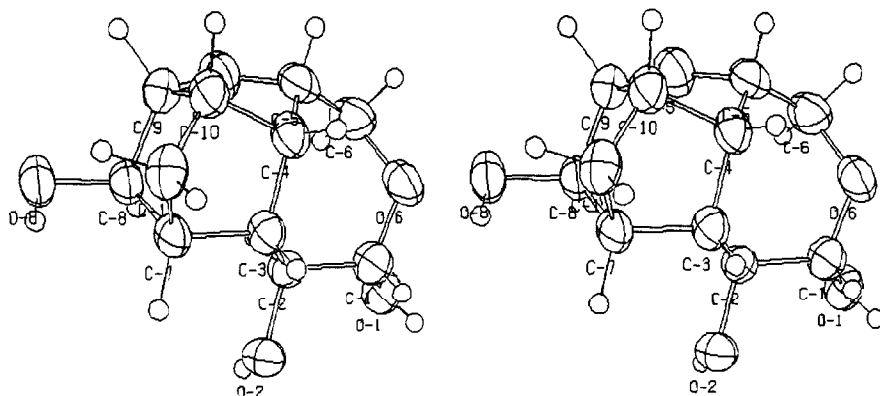
Fig. 1. Stereoview¹¹ of **3** from the X-ray data.

TABLE I

FRACTIONAL ATOMIC COORDINATES^a FOR **3**

Atom	x	y	z	Atom	x	y	z
C-1	3382(5)	1268	3994(11)	H-1	340(4)	125(6)	554(8)
C-2	3735(4)	-390(10)	3100(10)	H-2	377(3)	-39(5)	130(7)
C-3	2839(5)	-1673(9)	4159(10)	H-3	290(4)	-170(6)	582(8)
C-4	1401(5)	-1473(10)	3884(10)	H-4	96(4)	-114(7)	516(8)
C-5	1082(5)	-474(11)	1925(11)	H-5	21(5)	-42(7)	198(9)
C-6	1635(6)	1214(11)	1688(12)	H-6 _{exo}	96(6)	208(9)	167(9)
C-7	3141(5)	-3415(9)	3316(9)	H-6 _{endo}	235(5)	126(7)	43(8)
C-8	3039(5)	-3504(9)	811(9)	H-7	404(7)	-377(11)	409(13)
C-9	1624(5)	-3088(9)	718(10)	H-8	373(5)	-268(8)	-22(10)
C-10	1036(5)	-3174(10)	3162(10)	H-9	100(5)	-383(8)	-35(9)
C-11	1913(6)	-4283(11)	4266(11)	H-10	6(6)	-329(8)	301(9)
O-1	4229(4)	2425(8)	2880(8)	H-11 _{syn}	183(5)	-543(8)	361(10)
O-2	5005(3)	-771(8)	3673(7)	H-11 _{anti}	185(5)	-432(8)	586(9)
O-5	1517(3)	-1424(9)	-26(6)	H-1'	447(9)	292(12)	384(17)
O-8	3296(3)	-5112(9)	-54(7)	H-2'	566(7)	-46(12)	229(13)
O-6	2114(3)	1684(9)	3782(7)	H-8'	353(9)	-557(13)	130(17)

^a × 10⁴ for C and O, and × 10³ for H atoms (standard deviation in parentheses).

The torsion angles of the septanose ring of **3** are given in Table II. Theoretical values for the ideal boat-form of cycloheptane⁸ are also listed. By comparison, the septanoid ring of **3** can be seen to be in a boat form with the pseudo-plane of symmetry passing through C-2. For septanose derivatives, a twist-chair has been reported^{4,6,7} more frequently than a boat conformation⁵.

The torsion angles for the furanoid and two cyclopentane rings are listed in Table III. The furanoid ring is in a twist form, with C-5-O-5-C-9 forming a plane from which C-4 and C-10 are displaced on opposite sides. An ideal, twist form would have the torsional angles C-4-C-5-O-5-C-9 and C-5-O-5-C-9-C-10 equal in sign and magnitude⁷. Because they differ in magnitude (20.3 and 8.7°, respec-

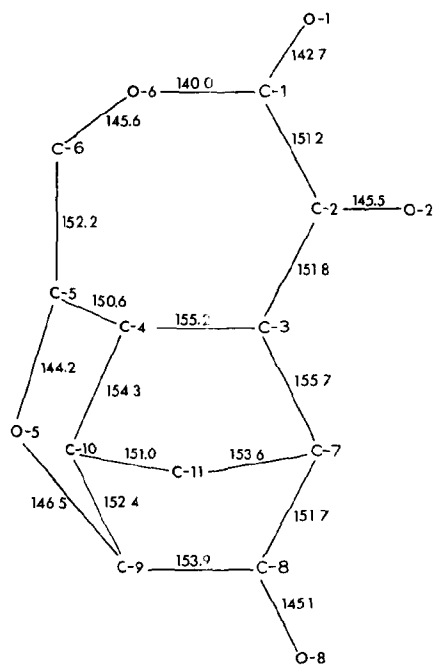


Fig. 2. Bond lengths (pm) for 3. Bond lengths involving hydrogen atoms are not included.

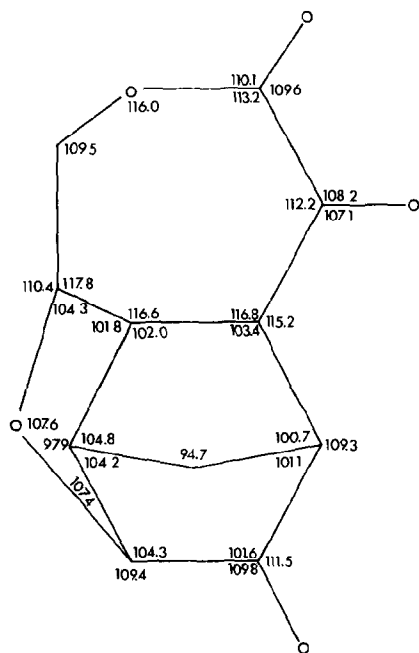


Fig. 3. Bond angles (degrees) for 3. Angles involving hydrogen atoms are not included.

TABLE II

TORSION ANGLES (DEGREES) OF THE SEPTANOSE RING OF **3** AND THOSE CALCULATED⁸ FOR THE BOAT CONFORMATION OF CYCLOHEPTANE

<i>Bond</i>	<i>Observed for 3</i>	<i>Calculated for cycloheptane⁸</i>
C-1-C-2	-54.6	-57.5
C-2-C-3	58.2	57.5
C-3-C-4	23.4	30.9
C-4-C-5	-53.7	-69.9
C-5-C-6	-14.8	0
C-6-O-6	88.4	69.9
O-6-C-1	-40.7	-30.9

TABLE III

TORSION ANGLES (DEGREES) OF THE FURANOID AND CYCLOPENTANE RINGS OF **3**

<i>Ring</i>	<i>Bond</i>	<i>Observed for 3</i>
Furanoid	C-4-C-5	-41.0
	C-5-O-5	20.3
	O-5-C-9	8.7
	C-9-C-10	-32.7
	C-10-C-4	43.9
Cyclopentane (A)	C-3-C-4	5.7
	C-4-C-10	30.1
	C-10-C-11	-53.2
	C-11-C-7	55.4
	C-7-C-3	-38.6
Cyclopentane (B)	C-8-C-9	-11.9
	C-9-C-10	-24.2
	C-10-C-11	49.1
	C-11-C-7	-57.0
	C-7-C-8	43.2

tively), the furanoid ring of **3** adopts a distorted, twist conformation. The cyclopentane ring (B) is also in a distorted, twist conformation, with C-7 and C-11 displaced on opposite sides of the plane defined by C-8-C-9-C-10. The cyclopentane ring (A), which is fused directly to the septanoid ring, adopts a slightly distorted, envelope conformation. An ideal envelope would contain one torsion angle of 0°, whereas distortion causes the smallest torsion angle in this cyclopentane ring to be 5.7°.

Hydrogen bonds stabilize the crystal structure parallel to the crystallographic, *b* and *c* directions. Interactions between O-1 and O-8 in molecules related by translation along *y* tie the crystal together in that direction. The hydrogen bond between O-1 and O-8 has an O-O separation of 294 pm and involves the proton on O-8. The O-H-O angle is 147°, which, combined with the O-O distance, makes this a relatively weak hydrogen-bond. Molecules related by the two-fold screw axes

are joined by hydrogen bonds between O-2 and O-1 (O–O distance = 274 pm; O-1–H-1–O-2 angle = 176°) and O-2 and O-8 (O–O distance = 271 pm; O-2–H-2–O-8 angle = 176°). These electrostatic interactions lace the molecules together in layers along *b* and *c*, and Van der Waals interactions must account for the crystal stabilization along the *a* direction.

EXPERIMENTAL

Compound **3** was prepared from **2** by hydrolysis³ in sulfuric acid–water. Needle-like crystals of **3**, m.p. 158–160°, were obtained by slow evaporation of a solution in acetone.

X-Ray structure determination. — X-Ray-diffraction photographs of crystals of **3** showed them to be monoclinic, space group $P2_1$ (OkO reflections present for $k = 2n$), $z = 2$. X-Ray-diffraction data were collected from a single crystal ($0.23 \times 0.07 \times 0.47$ mm) on a computer-controlled, four-circle diffractometer. Least-squares refinement of the unit-cell parameters against twelve centered reflections yielded values of $a = 1054.5(4)$ pm, $b = 832.4(3)$ pm, $c = 597.3(2)$ pm, $\beta = 83.53(3)^\circ$. Data were collected in the $\omega - 2\theta$ mode, scan width 1.0° , scan rate $2^\circ/\text{min}$, $\text{CuK}\alpha$, $\lambda = 154.18$ pm, maximum $2\theta = 110^\circ$, with 10-s backgrounds measured on both sides of each reflection. Five standard reflections measured periodically throughout the data collection indicated no deterioration of the crystal in the X-ray beam, and multiple measurements of a $\chi = 90^\circ$ reflection showed no need for an absorption correction. Three reflections (1,0,1; 0,2,0; 1,1,0) overflowed the counting electronics and were omitted from the data set.

The structure was solved by using the direct-methods program GENTAN⁹ and was completed and refined by using the XTAL80¹⁰ and XRAY76¹¹ crystallographic programs. Atomic coordinates and anisotropic temperature-factors were refined for the carbon and oxygen atoms. All of the hydrogen atoms were located in difference electron-density maps, and their positional and isotropic thermal-parameters were refined. Weights of $1/\sigma$ were applied in the refinement. The refinement converged to an R ($= \Sigma||F_o| - |F_c||/\Sigma|F_o|$) of 0.035 and a weighted R of 0.042 for 681 reflections with $F_o > 4\sigma(F_o)$. There were 20 reflections with $F_o < 4\sigma(F_o)$. The maximum shift/error in the last refinement cycle was 0.095.

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