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THE CRYSTAL STRUCTURE OF AN OLEFINIC CYCLIC TRIMER OF LEVOGLUCOSENONE

THOMAS T. STEVENSON*,
Department of Botany, University of Washington, Seattle, Washington 98195 (U.S.A.)

RONALD E. STENKAMP, LYLE H. JENSEN,
Department of Biological Structure, University of Washington, Seattle, Washington 98195 (U.S.A.)

FRED SHAFIZADEH, AND RICHARD H. FURNEAUX
Wood Chemistry Laboratory, Department of Chemistry, University of Montana, Missoula, Montana 59812 (U.S.A.)

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ABSTRACT

A single-crystal, X-ray diffraction study has been performed on an olefinic cyclic trimer (**4**) of levoglucosenone. Crystals of **4** are orthorhombic with unit-cell parameters: $a = 1886.95$, $b = 1419.92$, and $c = 562.24$ pm; space group $P2_12_12_1$; $Z = 4$. Structure factors calculated from a low-resolution structure determination (based on three, low-order, centric reflections) yielded a starting set for a successful solution by direct methods. Refinement by least squares using 1291 reflections gave $R = 0.033$. The previously assigned chemical structure was found to be correct and the protons on the three asymmetric carbons were found to have an all-*cis* configuration, projecting from the same side of the molecule as their 1,6-anhydro bridges.

INTRODUCTION

The potential for obtaining useful chemicals *via* the pyrolysis of cellulosic materials has stimulated interest in the chemistry of pyrolysis products[1,2]. One such product, levoglucosenone (**1**, 1,6-anhydro-3,4-dideoxy-β-D-*glycero*-hex-3-enopyranos-2-ulose), has been of particular interest[3], as its ease of preparation and polyfunctional nature make it industrially attractive. Under aqueous conditions, levoglucosenone forms a dimer (**2**) and two cyclic trimers [one non-olefinic (**3**) and one olefinic (**4**)], and their chemical structures have been tentatively identified by spectroscopic methods[4,5]. The stereochemistry of three asymmetric carbon atoms in the central cyclohexene ring of **4** could not be determined, and an X-ray crystallographic study of **4** was therefore undertaken.

*Address correspondence to this author, at the Wood Chemistry Laboratory, University of Montana, Missoula, MT 59812, U.S.A.

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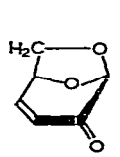

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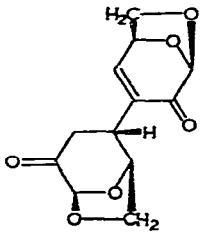

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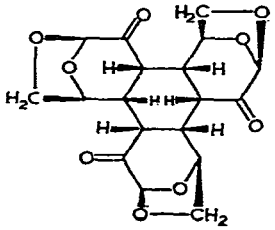

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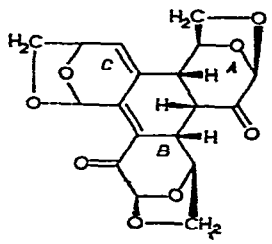

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RESULTS AND DISCUSSION

A stereochemical drawing of 4 from the X-ray data is shown in Fig. 1, and the atomic co-ordinates are listed in Table I*. This figure shows the three levoglucosenone residues (*A*, *B*, and *C*) forming a central cyclohexene ring and is consistent with

TABLE I

FRACTIONAL ATOMIC CO-ORDINATES[a] FOR 4

Atom	x	y	z	*Atom*	x	y	z
C-1*A*	3328(2)	4768(2)	6633(6)	C-4*C*	5490(2)	3903(3)	5042(7)
C-2*A*	3252(2)	3780(2)	5619(6)	C-5*C*	6025(2)	3284(3)	6255(7)
C-3*A*	3575(2)	3663(2)	3157(6)	C-6*C*	5797(2)	3127(3)	8818(7)
C-4*A*	4310(2)	4170(2)	3138(6)	O-1*C*	5263(1)	2405(2)	8564(4)
C-5*A*	4249(2)	5123(2)	4384(6)	O-5*C*	5980(1)	2349(2)	5349(5)
C-6*A*	3630(2)	5722(2)	3537(8)	H-1*A*	305(2)	484(2)	820(7)
O-1*A*	3046(1)	5436(1)	5030(5)	H-3*A*	323(1)	397(2)	210(5)
O-2*A*	2972(1)	3164(2)	6747(5)	H-4*A*	445(1)	432(2)	138(6)
O-5*A*	4054(1)	4961(1)	6856(4)	H-5*A*	473(1)	548(2)	436(6)
C-1*B*	3246(2)	0796(2)	3432(7)	H-6A_{endo}	349(2)	560(2)	193(7)
C-2*B*	3990(2)	1090(2)	4136(7)	H-6A_{exo}	372(2)	640(3)	387(7)
C-3*B*	4168(1)	2096(2)	3760(6)	H-1*B*	309(2)	019(3)	448(8)
C-4*B*	3653(2)	2662(2)	2212(6)	H-4*B*	386(1)	273(2)	071(6)
C-5*B*	2962(2)	2146(2)	1738(7)	H-5*B*	261(2)	261(2)	156(7)
C-6*B*	3024(3)	1410(3)	−0245(8)	H-6B_{endo}	341(3)	158(3)	−138(10)
O-1*B*	3247(1)	0577(2)	0957(5)	H-6B_{exo}	254(2)	139(3)	−075(8)
O-2*B*	4383(1)	0499(2)	4972(6)	H-1*C*	528(2)	135(2)	618(6)
O-5*B*	2774(1)	1539(2)	3724(5)	H-4*C*	561(2)	457(2)	506(6)
C-1*C*	5308(2)	2065(2)	6170(7)	H-5*C*	652(2)	349(2)	614(6)
C-2*C*	4742(2)	2537(2)	4667(6)	H-6C_{endo}	557(2)	377(3)	943(8)
C-3*C*	4876(1)	3548(2)	4290(6)	H-6C_{exo}	625(2)	290(3)	979(8)

[a] × 10^4 for C and O, × 10^3 for H (standard deviation in parentheses).

*Supplementary data: thermal parameters for hydrogen and non-hydrogen atoms (Table V), bond lengths and angles involving hydrogen atoms (Tables VI and VII), and a listing of observed and calculated structure factors (Table VIII) can be obtained from Elsevier Scientific Publishing Company, BBA Data Deposition, P.O. Box 1527, Amsterdam, The Netherlands. Reference should be made to No. BBA/DD/214 *Carbohydr. Res.*, 104 (1982) 11–19.

the chemical-structure determination[4]. The hydrogen atoms attached to the three asymmetric centers in question (C-3*A*, C-4*A*, and C-4*B*) were found to be all-*cis* and to project upward in the same direction as the 1,6-anhydride bridge of residue *B*. This results in a configuration where the pyranoid rings of residues *B* and *C* are roughly co-planar and that of residue *A* lies ~90° to this plane, with the anhydride bridge being *exo* to the rest of the molecule.

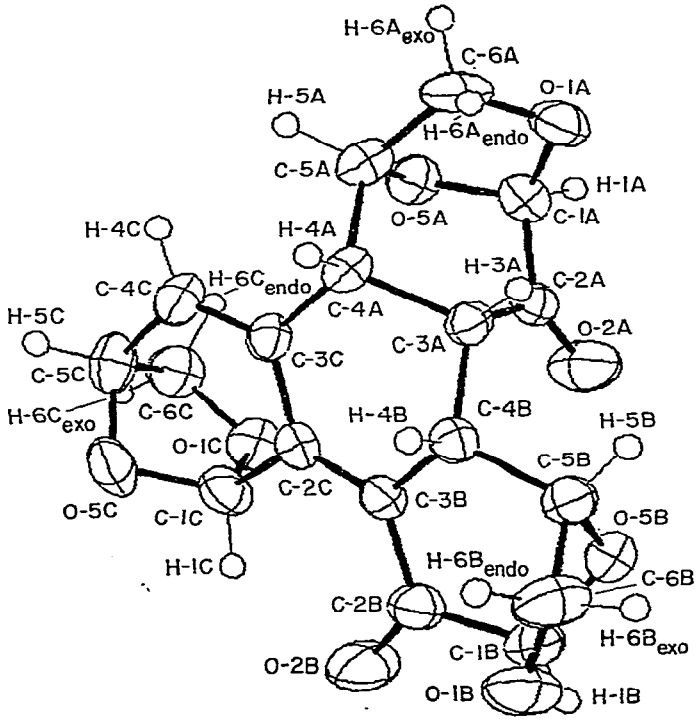

Fig. 1. ORTEP[6] drawing of **4** as viewed along the *z* axis. Thermal parameters for hydrogen atoms are not depicted.

The conjugated system of residues *B* and *C* in **4** is very nearly planar. The calculated, least-squares plane for the six sp^2-hybridized atoms in this system (Table II, plane I) shows that there are only minor deviations from planarity, and none greater than 5 pm. The atoms attached to the conjugated system deviate slightly from the plane, with C-4*B* lying 26 pm above the plane and C-1*C* 22pm below. While this is evidence for strain within the conjugated system, each sp^2-hydridized carbon atom is coplanar with the three atoms bonded to it (Table II, planes II–VII), despite the fact that individual bond-angles vary from 113 to 126° (Fig. 3).

The ^{1}H-n.m.r. resonance of the anomeric H-1*C* was shifted remarkably downfield (7.10 p.p.m.)[4], presumably due, in part, to the *peri*-effect which occurs in planar, polycyclic ketones when the proton is γ to the carbonyl group[7]. In the crystalline state, H-1*C* is very nearly coplanar with O-2*B*, C-2*B*, C-3*B*, C-2*C*, and C-1*C*, lying

TABLE II

SOME LEAST-SQUARES PLANES FOR **4**

Atom	*Plane*							
	I	*II*	*III*	*IV*	*V*	*VI*	*VII*	*VIII*
	Deviations of atoms from plane (pm)							
C-1*A*		0[a]						
C-2*A*		−1.1						
C-3*A*		0[a]						
C-4*A*	−4.9					0[a]		
O-2*A*		0[a]						
C-1*B*	−20.5		0[a]					
C-2*B*	−3.0[a]		0.6	0[a]				−7.1[a]
C-3*B*	4.9[a]		0[a]	−0.04	0[a]			2.4[a]
C-4*B*	26.2			0[a]				
O-2*B*	2.0[a]		0[a]					5.4[a]
C-1*C*	−22.4				0[a]			−3.2[a]
C-2*C*	−5.1[a]			0[a]	0.3	0[a]		2.6[a]
C-3*C*	−1.0[a]				0[a]	1.4	0[a]	
C-4*C*	2.2[a]					0[a]	4.9	
C-5*C*	0.5						0[a]	
H-1C								11.6
H-4C	−6.1						0[a]	
	Coefficients of equations for planes[b]							
m	8.071	16.582	6.190	9.921	9.762	7.518	8.106	9.496
n	−2.518	−3.515	−3.091	−3.479	−3.055	−2.731	−2.027	−2.521
r	−4.983	2.294	−5.168	−4.580	−4.657	−5.042	−5.013	−4.755
s	5.897	3.070	5.158	6.264	6.335	5.561	6.096	6.373

[a]An atom defining the plane. [b]$mx + ny + rz = s$.

only 12 pm above the least-squares plane defined by these five atoms (Table II, plane VIII).

Calculation of ring-puckering parameters[8] (Table III) and the use of a stereogram[9] revealed that the conformations of the three pyranoid rings differ, due to different hybridization states of the carbon atoms in the rings. Residue *A*, with only one sp^2-hybridized carbon atom, adopts the $^1C_4$ conformation with some distortion toward the $sofa_0$ conformation[10,11] (where 5 atoms are coplanar). This is common for 1,6-anhydro-β-D-hexopyranose compounds in which all members of the ring are sp^3-hybridized[9]. The pyranoid ring of residue *B* contains two adjacent sp^2-hybridized members that significantly flatten the ring and cause the adoption of a $sofa_0$ conformation with some distortion toward the $B_{3,0}$ form. The pyranoid ring of residue *C* also adopts a $sofa_0$ conformation, as would be expected for a six-membered ring with three adjacent trigonal atoms, but strain generated by the fused-ring system causes distortion toward the half-chair, $^1H_0$ conformation. The central cyclohexene ring also contains three sp^2-hybridized carbons and has a conformation very similar to that of residue *C*, between a half-chair ($^{4B}H_{3A}$) and a $sofa_{3A}$ conformation.

TABLE III

PUCKERING PARAMETERS FOR **4**

Residue	*Q (pm)*	*θ (°)*	*φ (°)*
A	64.8	161.0	174.1
B	65.5	115.8	178.8
C	59.6	128.3	190.4
D[a]	51.0	122.4	196.6
A[b]	41.8		40.4
B[b]	42.7		43.5
C[b]	44.4		51.0

[a]Central cyclohexene ring: C-3*A* is atom 1, C-4*B* atom 2, *etc.* [b]Five-membered anhydro-ring: C-1 is atom 1, O-5 atom 2, *etc.*

Similar calculations[8,12] show that unsaturation in the pyranoid rings has very little effect on the conformation of the anhydride rings. As shown in Table III, all three five-membered anhydro rings take on similar conformations lying between a twist (3 adjacent atoms coplanar, $^{C-5}T_{O-5}$, where $\phi = 54°$) and an envelope form (4 atoms coplanar, E_{O-5}, where $\phi = 36°$), with O-5 *exo* to the molecule. The anhydro ring of residue *A* favors the envelope form, whereas residue *C* has more twist character. All three conformations are similar to those observed for saturated 1,6-anhydropyranoses[13].

The bond lengths and angles for **4** are shown in Figs. 2 and 3. The large angle formed by C-2*A*–C-3*A*–C-4*B* (117.3°) is associated with a long C-3*A*–C-4*A* bond of

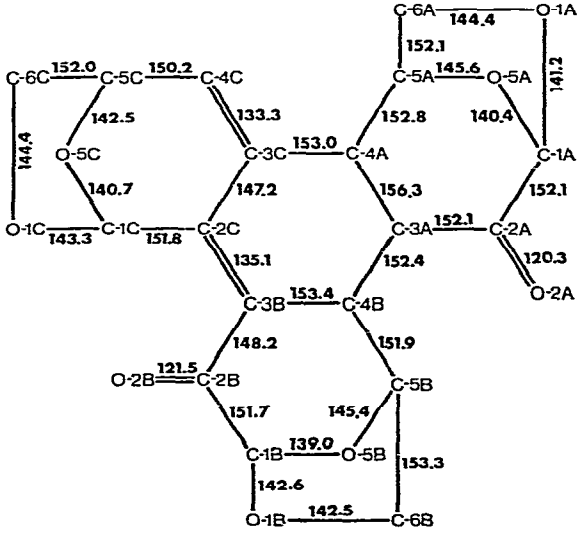

Fig. 2. Bond lengths (pm) for **4**. The standard deviations ranged from 0.4 to 0.6. Bond lengths involving H atoms are omitted.

156.3 pm. In the anhydro ring, bond angles are all smaller than those in an unstrained system, but are typical of those found in other 1,6-anhydropyranoses[14,15]. The O-5–C-5–C-6 and C-5–O-5–C-1 angles are all particularly small, as noted elsewhere[16]. The lengths of all C-H bonds ranged from 93 to 108 pm and bond angles involving hydrogen atoms varied from 100 to 117°, except those involving the vinylic H-4*C*, which were 114 and 125°.

In other 1,6-anhydropyranoses, the two inner C-1–O bonds of the C-5–O-5–C-1–O-1–C-6 bond-sequence are short and the outer two long, when compared to the average C–O bond[17–19]. This has been attributed to the "anomeric effect", in which "back-donation" of electron density from the oxygen lone-pair orbitals to the adjacent C–O σ^* orbitals result in slightly shorter bonds[20]. In **4**, when the C–O bond lengths are compared to the mean value (Table IV), it is apparent that only residue *A* shows the typical long-short-short-long sequence observed in other 1,6-anhydropyranoses. Residue *B* has one long outer-bond, followed by a short inner-bond, but the next two bonds are close to average in length. In residue *C*, the two C–O bonds on one side of C-1*C* are shorter than the mean, while those on the other side are longer. The presence of an extended π system running through the adjacent C-2 atoms may somehow be responsible for these differences, since, if the geometry is correct, the *p* orbital could also overlap with the unoccupied C–O σ^* orbital. Caution should be used here, however, since these bond-length differences are small.

EXPERIMENTAL

Crystals of **4** ($C_{18}H_{16}O_8$) were obtained[4] as fine, yellow needles. Weissenberg and precession photographs showed the crystals to be orthorhombic, space group

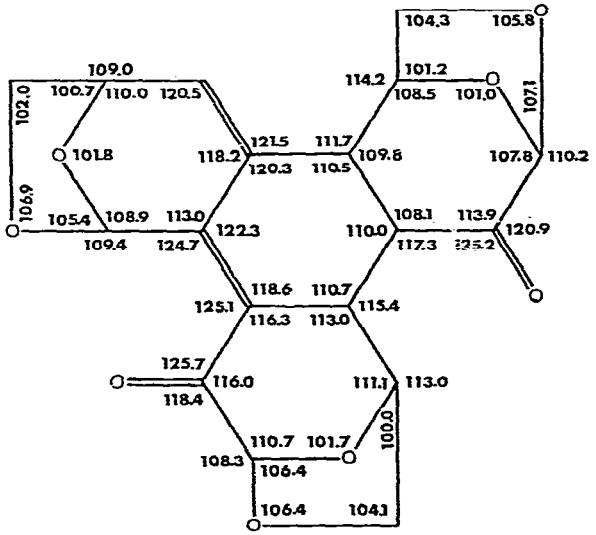

Fig. 3. Bond angles (degrees) for **4**. The standard deviations ranged from 0.2 to 0.3°. Bond angles involving H atoms are omitted.

TABLE IV

C–O BOND-LENGTH VARIATIONS IN **4**

Residue	*Difference from mean C–O bond-distance*[a]			
	C-5------*O-5*------*C-1*------*O-1*------*C-6*			
A	+2.9	−2.3	−1.5	+1.7
B	+2.7	−3.7	−0.1	−0.2
C	−0.2	−2.0	+0.6	+1.7

[a]Mean C–O length is 142.7 pm.

$P2_12_12_1$ (systematic absences at $h00$, $0k0$, and $00l$ when h, k, or l is odd), with $Z = 4$. Cell parameters were found to be a = 1886.95 (24), b = 1419.92 (12), and c = 562.24 (6) pm, ρ_{calc} = 1.59, and ρ_{meas} = 1.54. Intensity data were collected from a single crystal measuring ~0.13 × 0.05 × 0.83 mm. The intensities of 1334 unique reflections were measured to a maximum of 2θ of 120° (CuK_α- radiation), using a computer-controlled, four-circle diffractometer. Absorption and decomposition corrections were found to be unnecessary; however, correction for coincidence loss was made, based on 70 reflections collected with a reduced beam intensity.

Initial attempts to determine a phase set by direct methods with MULTAN[21] and GENTAN[22] were unsuccessful. To increase the power of MULTAN, reflections of known phases were determined in the following manner. Three zonal reflections with high F_{rel}, E > 1.2, and low $\sin\theta/\lambda$ (0 1 1, 2 0 1, and 1 3 0) were chosen as origin-determining reflections. An F_0 map of very low resolution was calculated in 3 dimensions based solely on these 3 reflections, for which phases could be assigned arbitrarily to be 90°. The resulting map gave only one area of high electron density per asymmetric unit. Although a narrow band of density joined individual molecules, the three lobes of the molecule were visible. Seventeen atoms derived from a model of residues *B* and *C* were fitted into two of the lobes with the orientation determined by a previously calculated Patterson map, and 9 carbon atoms were added in the region of high electron density believed to be residue *A*. The observed structure factors were then scaled to the calculated structure factors for all reflections, based on the 26-atom model. A comparison of the observed and calculated structure factors yielded six low-order, zonal reflections with high E values (>1.2), $F_o > 50$, and $F_c > 0.5 \times F_o$, including the 3 originally chosen to fix the origin. Since zonal reflections in $P2_12_12_1$ are centrosymmetric (*i.e.*, either A or B = 0), their calculated phases had a high probability of being correct. MULTAN was then run using a starting set consisting of the three origin-defining reflections, three zonal reflections (1 6 0, 2 3 0, and 0 2 1) of known phase with weights equal to 0.9, six additional, zonal reflections with permutable phases, and one general reflection (9 9 1) chosen to fix the enantiomorph. This resulted in a strong convergence map and 128 phase sets were generated. Two of these were equal (the initial phase of 9 9 1 making no difference) and had figures of merit far superior to any other set. The E map from one of these sets re-

vealed the location of all 26 non-hydrogen atoms. The sign of all z co-ordinates was changed to make this model conform to the known D configuration of its precursor, cellulose, yielding $R\{\sum||F_o| - |F_c||/\sum|F_o|\}$ equal to 0.19.

Upon re-examining the phase determination[23], it was found that, on tangent refinement, MULTAN had altered the phases of two of the origin-determining reflections. Presumably, transgressions had occurred early in the phase-determining procedure, but this did not prevent MULTAN from converging on the correct structure.

The refinement proceeded routinely, using CRYLSQ, the least-squares program of the X-ray system[24]. With 3 cycles of least squares, R decreased to 0.07, and a Fourier-difference map revealed the positions of all 16 hydrogen atoms. Anisotropic thermal parameters for carbon and oxygen atoms and isotropic thermal parameters for hydrogen atoms were included in the refinement. Weights of $1/\sigma(F_o)$ were applied, and the final model gave $R = 0.033$ with all shift/errors <0.4, based on 1291 unique reflections with $F_o^2 > 2\sigma(F_o^2)$. At this point, the Fourier-difference map showed no density greater than 2×10^{-7} e-/pm^3, and the isotropic thermal parameters (U) for all hydrogen atoms averaged 554 (217) pm where the temperature factor is of the form $\exp[-2\pi^2(Uh^2a^{*2} + Uk^2b^{*2} + Ul^2c^{*2})]$.

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