The Structure of 6-*O*-Acetyl-2,3,4-trideoxy-4-*C*-ethenyl-3-*C*-(methoxycarbonylmethyl)-α-D-lyxopyranose, C₁₃H₂₀O₆

By Serge Léger, Francine Belanger-Gariepy, Stephen Hanessian* and François Brisse*

Département de Chimie, Université de Montréal, CP 6210, Succ. A, Montréal, Québec, Canada H3C 3V1

Abstract. $M_r = 272 \cdot 30$, monoclinic, $C2$, $a = 21 \cdot 935$ (12), $b = 6 \cdot 110$ (5), $c = 11 \cdot 002$ (6) Å, $\beta = 107 \cdot 01$ (4)°, $V = 1410 \cdot 0$ Å³, $Z = 4$, $D_x = 1 \cdot 282$ Mg m⁻³, $\lambda(\text{Cu} K\bar{\alpha}) = 1 \cdot 54178$ Å, $\mu = 0 \cdot 82$ mm⁻¹, $F(000) = 584$, $T = 293$ K, $R = 0 \cdot 037$ for 984 reflections. The pyranose ring has the $^4C_1$ conformation. The primary acetate substituent is in the gt conformation, the ethenyl group is axial and the methoxycarbonylmethyl substituent is equatorial. The molecules are held in the crystal through hydrogen bonds between the anomeric hydroxyl and the ring oxygen to form helices extending in the **b** direction.

Introduction. In connection with a synthetic problem involving the utility of carbohydrate precursors in alkaloid synthesis (Hanessian, 1983), we have developed a sequential carbon–carbon bond-forming reaction which incorporates vinyl and methoxy-carbonylmethyl substituents on adjacent carbon atoms (Hanessian & Léger, 1983). The sequence involves the conjugate 1,4-attack of a mixed vinyl cuprate (Lipshutz, Wilhelm & Floyd, 1981) on a cyclic enone system (1) followed by quenching of the resulting enolate with methyl bromoacetate. The kinetically formed 'diaxial' product (2) can then be equilibrated by base-catalyzed epimerization of the methoxycarbonyl-methyl substituent adjacent to the carbonyl function. While spectroscopic evidence indicated that the desired sequence of events had indeed taken place, the necessity of an unambiguous proof was deemed important, particularly in view of the critical nature of the intermediate and its advanced position along the reaction scheme leading to the target. Crystalline material suitable for X-ray analysis was obtained after two additional transformations on the above-mentioned product to give the title compound (3).

Experimental. Clear crystal recrystallized from a diethyl ether/pentane mixture. Accurate cell dimensions from 25 reflections centered on the Nonius CAD–4 diffractometer, graphite-monochromatized Cu $K\bar{\alpha}$
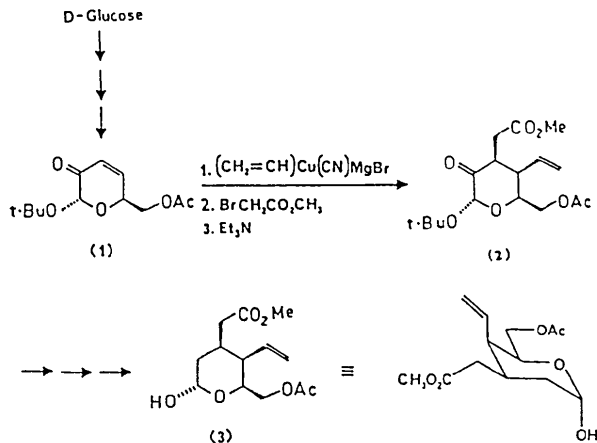
radiation, ω–2θ scan mode, scan range $\Delta\omega = (1 \cdot 00 + 0 \cdot 14 \tan\theta)°$, $\theta_{max} = 70°$ ($-26 \le h \le 25$, $0 \le k \le 7$, $0 \le l \le 13$), crystal size $0 \cdot 08 \times 0 \cdot 18 \times 0 \cdot 30$ mm; orientation monitored every 100 reflections, intensity checked every hour using three standard reflections (largest fluctuation of the standard 2%). 1476 independent reflections; 984 of them satisfying $I \ge 1 \cdot 96\sigma(I)$ retained for structure determination and refinement. Lp correction, no absorption correction, direct methods (*MULTAN*),† anisotropic block-diagonal least-squares refinement based on F. H atoms located on difference Fourier syntheses, refined isotropically. Final $R = 0 \cdot 037$, $R_w = 0 \cdot 041$, weights derived from counting statistics, $S = 1 \cdot 37$; for all measured reflections $R_w = 0 \cdot 058$. Maximum $(\Delta/\sigma) = 0 \cdot 35$, mean $(\Delta/\sigma) = 0 \cdot 06$, extreme values of the residual electron density on the final difference Fourier map $\pm 0 \cdot 18$ e Å⁻³. Scattering curves for O and C from Cromer & Mann (1968), for H from Stewart, Davidson & Simpson (1965).

---

* To whom correspondence should be addressed.

Table 1. *Fractional atomic coordinates for the substituted* α-D-*lyxopyranose molecule* ($\times 10^4$ *for* O *and* C, $\times 10^3$ *for* H), U_{eq} (Å^2, $\times 10^4$ *for* C *and* O), U_{iso} (Å^2, $\times 10^3$ *for* H)

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a^*_i a^*_j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}/U_{iso}
O(1)	2200 (1)	1226 (5)	3288 (2)	549 (9)
O(2)	3525 (1)	4065 (5)	306 (2)	640 (11)
O(3)	3643 (1)	7674 (6)	200 (3)	848 (14)
O(4)	4966 (1)	2370 (7)	7492 (3)	1046 (15)
O(5)	2923 (1)	3478	4734 (2)	432 (8)
O(6)	4056 (1)	1160 (5)	6204 (2)	527 (8)
C(1)	2324 (1)	3358 (7)	3766 (3)	467 (12)
C(2)	2316 (2)	4877 (7)	2684 (3)	505 (13)
C(3)	2880 (1)	4535 (6)	2157 (3)	426 (12)
C(4)	3514 (1)	4540 (6)	3239 (3)	412 (12)
C(5)	3462 (1)	2970 (6)	4286 (3)	404 (11)
C(6)	4047 (2)	3063 (6)	5421 (3)	492 (13)
C(7)	4564 (1)	1005 (8)	7239 (3)	584 (14)
C(8)	4559 (2)	−1048 (9)	7962 (4)	701 (17)
C(9)	3727 (2)	6783 (7)	3746 (3)	501 (14)
C(10)	4265 (2)	7680 (8)	3743 (4)	721 (18)
C(11)	2864 (2)	6239 (8)	1136 (3)	566 (14)
C(12)	3385 (2)	6123 (8)	512 (3)	572 (14)
C(13)	4001 (2)	3739 (10)	−344 (4)	833 (21)
H(O1)	214 (1)	42 (7)	382 (3)	75 (12)
H(1)	198 (1)	390 (6)	422 (3)	52 (9)
H(3)	284 (1)	318 (5)	186 (2)	32 (8)
H(4)	383 (1)	407 (5)	287 (3)	40 (8)
H(5)	341 (1)	156 (5)	390 (2)	32 (8)
H(9)	343 (1)	759 (7)	411 (3)	69 (11)
H(21)	190 (2)	461 (7)	199 (3)	76 (11)
H(22)	232 (1)	628 (6)	293 (3)	61 (10)
H(61)	444 (1)	310 (6)	511 (3)	64 (11)
H(62)	404 (1)	429 (6)	591 (3)	52 (9)
H(81)	423 (2)	−116 (10)	833 (4)	128 (17)
H(82)	449 (2)	−244 (10)	737 (5)	136 (18)
H(83)	497 (2)	−135 (10)	862 (5)	134 (17)
H(101)	443 (2)	900 (8)	409 (3)	101 (14)
H(102)	453 (2)	678 (8)	335 (4)	107 (15)
H(111)	286 (1)	755 (7)	142 (3)	65 (11)
H(112)	245 (1)	631 (6)	45 (3)	52 (9)
H(131)	382 (2)	420 (11)	−118 (4)	130 (17)
H(132)	441 (2)	471 (9)	14 (4)	107 (15)
H(133)	416 (2)	213 (11)	−18 (5)	162 (21)

Table 2. *Bond distances* (Å) *and angles* (°) *in the substituted* α-D-*lyxopyranose molecule*

	This work	(1)		This work
C(1)–C(2)	1·506 (5)	1·523 (8)	C(3)–C(11)	1·524 (5)
C(2)–C(3)	1·526 (5)	1·521 (7)	C(4)–C(9)	1·502 (5)
C(3)–C(4)	1·544 (5)	1·523 (9)	C(7)–C(8)	1·487 (7)
C(4)–C(5)	1·529 (5)	1·525 (8)	C(9)–C(10)	1·302 (6)
C(1)–O(5)	1·431 (4)	1·414 (9)*	C(11)–C(12)	1·497 (5)
C(5)–O(5)	1·442 (4)	1·436 (9)*	C(7)–O(6)	1·343 (4)
C(5)–C(6)	1·507 (5)	1·514 (9)	C(7)–O(4)	1·186 (6)
C(6)–O(6)	1·444 (5)	1·427 (8)	C(12)–O(3)	1·204 (6)
C(1)–O(1)	1·401 (5)	1·415 (9)*	C(12)–O(2)	1·330 (6)
			C(13)–O(2)	1·442 (5)
C(1)–C(2)–C(3)	113·1 (3)	110·5 (13)	C(2)–C(3)–C(11)	109·9 (3)
C(2)–C(3)–C(4)	110·8 (3)	110·5 (14)	C(4)–C(3)–C(11)	112·9 (3)
C(3)–C(4)–C(5)	109·3 (3)	110·3 (14)	C(3)–C(4)–C(9)	113·6 (3)
C(4)–C(5)–O(5)	111·8 (3)	110·0 (13)	C(5)–C(4)–C(9)	112·1 (3)
C(5)–O(5)–C(1)	113·6 (2)	114·0 (4)	C(6)–O(6)–C(7)	115·2 (3)
O(5)–C(1)–C(2)	110·7 (3)	109·2 (11)	O(6)–C(7)–O(4)	121·6 (4)
			C(8)–C(7)–O(4)	126·1 (4)
C(2)–C(1)–O(1)	108·7 (3)	108·4 (19)	O(6)–C(7)–C(8)	112·3 (3)
O(1)–C(1)–O(5)	111·2 (3)	111·6 (9)	C(4)–C(9)–C(10)	124·5 (4)
C(4)–C(5)–C(6)	111·6 (3)	112·7 (14)	C(3)–C(11)–C(12)	116·7 (3)
O(5)–C(5)–C(6)	107·0 (3)	106·9 (5)	C(11)–C(12)–O(3)	125·4 (4)
C(5)–C(6)–O(6)	108·9 (3)	111·8 (12)	O(2)–C(12)–O(3)	123·0 (4)
			C(11)–C(12)–O(2)	111·6 (3)
			C(12)–O(2)–C(13)	116·9 (3)

(1) Standard residue, Arnott & Scott (1972).

* Theoretical values for the α-anomer (Jeffrey, Pople & Radom, 1974) are C(1)–O(5) = 1·421, C(5)–O(5) = 1·444 and C(1)–O(1) = 1·417 Å.

Discussion. The final coordinates and equivalent U_{iso} values are given in Table 1.* The atomic numbering is shown in Fig. 1 and the molecular conformation in Fig. 2. The bond distances and angles are listed in Table 2. The values observed for the α-D-lyxopyranose molecule conform to those tabulated by Arnott & Scott (1972) for a standard glucose residue. All C—H bonds are within 0·86 (4) to 1·08 (4) Å, average 0·94 (4) Å. The O(1)—H(O1) bond is 0·81 (4) Å long and the angle C(1)—O(1)—H(O1) is 111 (3)°. The pyranose ring has the ${}^4C_1$ conformation. The endocyclic torsion angles have an average of 54·4° although the extreme values are C(2)—C(3)—C(4)—C(5) = 50·2 (4) and C(4)—C(5)—O(5)—C(1) = 60·2 (4)°.

The conformation of the acetate at C(6) is characterized by the torsion angles $\chi 5$ = O(5)—C(5)—C(6)—O(6) = 73·6 (2)° and $\theta 6$ = C(5)—C(6)—O(6)—C(7) = 178·4 (3)°. According to the terminology proposed by Sundaralingam (1968), the conformation of the C(6)

* Lists of structure factors, anisotropic thermal parameters and torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39542 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
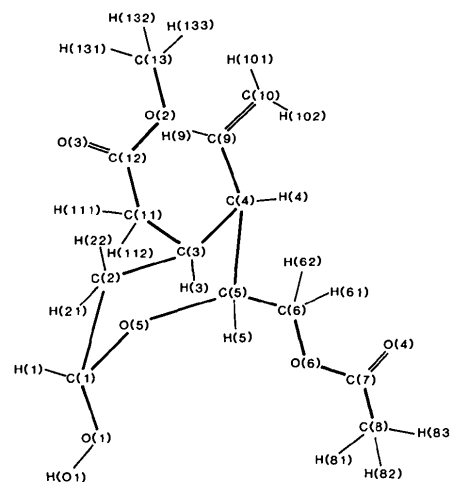

Fig. 1. Schematic representation of the molecule and atomic numbering.
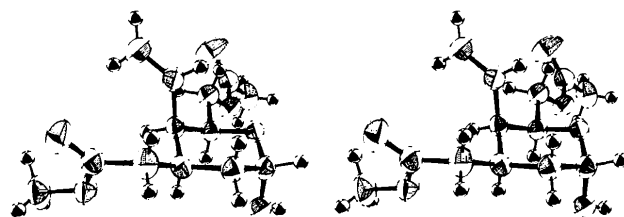

Fig. 2. Stereoview of the substituted α-D-lyxopyranose molecule.

acetate is *gt*. The dihedral angle between the plane formed by O(5),C(2),C(3),C(5) and the acetyl group formed by O(4),O(6),C(7),C(8) is 67 (1)°.

The methoxycarbonylmethyl substituent is in an equatorial position. Its conformation is described by C(2)–C(3)–C(11)–C(12) = –179·6 (3), C(4)–C(3)–C(11)–C(12) = 56·3 (4) and C(3)–C(11)–C(12)–O(2) = 39·3 (5)°. The group of atoms O(2),O(3),-C(12),C(13) is planar and is inclined at 68 (1)° from the plane formed by O(5),C(2),C(3),C(5).

The ethenyl group is attached at C(4) in an axial position. The atoms C(4),C(9),C(10),H(9),H(101) and H(102) are coplanar. This plane is at 93 (2)° from the pyranose mean plane [O(5),C(2),C(3),C(5)].

In the crystal the molecules are held by hydrogen bonds between the anomeric hydroxyl O(1)–H(O1) and the ring oxygen O(5) where O(1)–H(O1) = 0·81 (4), H(O1)···O(5′) = 2·02 (4), O(1)···O(5′) = 2·823 (3) Å, O(1)–H(O1)···O(5′) = 174 (4)°, and O(5′) is related to O(5) by ($\frac{1}{2}$–x, –$\frac{1}{2}$–y, 2–z). This hydrogen bond is comparable to those observed in α-DL-fucopyranose, 2·804 (3) Å (Longchambon & Gillier-Pandraud, 1977), α-D-glycopyranose, 2·849 (2) Å (Brown & Levy, 1979), and α-D-talopyranose, 2·844 (2) Å (Ohanessian, Avenel, Kanters & Smits, 1977).

for collecting the diffracted intensities on the Nonius CAD-4 diffractometer.

References

Ahmed, F. R., Hall, S. R., Pippy, M. E. & Huber, C. P. (1973). *NRC Crystallographic Computer Programs for the IBM/360.* Accession Nos. 133–147 in *J. Appl. Cryst.* **6**, 309–346.
Arnott, S. & Scott, W. E. (1972). *J. Chem. Soc. Perkin Trans. 2*, pp. 324–335.
Brown, G. M. & Levy, H. A. (1979). *Acta Cryst.* B**35**, 656–659.
Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* A**24**, 321–324.
Doedens, R. J. & Ibers, J. A. (1967). *Inorg. Chem.* **6**, 204–210.
Hanessian, S. (1983). *Total Synthesis of Natural Products: The 'Chiron' Approach,* edited by J. E. Baldwin. Oxford: Pergamon Press.
Hanessian, S. & Léger, S. (1983). Unpublished results.
Jeffrey, G. A., Pople, J. A. & Radom, L. (1974). *Carbohydr. Res.* **38**, 81–95.
Johnson, C. K. (1965). *ORTEP.* Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
Lipshutz, B. H., Wilhelm, R. S. & Floyd, D. M. (1981). *J. Am. Chem. Soc.* **103**, 7672–7674.
Longchambon, F. & Gillier-Pandraud, H. (1977). *Acta Cryst.* B**33**, 2094–2097.
Main, P., Hull, S. E., Lessinger, L., Germain, G., Declercq, J. P. & Woolfson, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.
Ohanessian, J., Avenel, D., Kanters, J. A. & Smits, D. (1977). *Acta Cryst.* B**33**, 1063–1066.
Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
Sundaralingam, M. (1968). *Biopolymers,* **6**, 189–213.

5,7-Dimethoxy-1-indanone, $C_{11}H_{12}O_3$

By M. P. Gupta,* A. T. H. Lenstra and H. J. Geise†

University of Antwerp (UIA), Department of Chemistry, Universiteitsplein 1, B-2610 Wilrijk, Belgium

Abstract. $M_r = 190\cdot2$, monoclinic, $P2_1/n$, $a = 8\cdot695$ (2), $b = 9\cdot782$ (1), $c = 11\cdot189$ (2) Å, $\beta = 90\cdot68$ (3)°, $V = 951\cdot6$ (5) Å³, $Z = 4$, $D_m = 1\cdot34$, $D_x = 1\cdot327$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0\cdot71069$ Å, $\mu = 0\cdot105$ mm⁻¹, $F(000) = 400$, room temperature, $R_w = 0\cdot042$ for 1417 observed [$I > 2\sigma(I)$] reflections. The molecular geometry is normal with the aromatic ring quite planar, but not the five-membered ring. The latter is close to a C_s conformation with the pseudo-mirror plane through C=O and the middle of the C(3)–C(9)
bond. The fragments H₃C–O–C(aryl)–C(aryl) have a staggered synperiplanar conformation.

Introduction. The crystal structure analysis of the title compound (Fig. 1) was undertaken to establish the disposition and conformation of the two methoxy groups *vis à vis* the aromatic ring. A private communication from the Cambridge Structural Database had indicated an earlier determination (Gupta & Ram, 1979) to be incorrect, inasmuch as the packing of the molecules showed very short contacts of the nature of polymeric linkages and this is chemically unacceptable. The present work is, therefore, a new determination.

* Permanent address: Department of Physics, University of Ranchi, Ranchi-834008, India.
† Author to whom correspondence should be addressed.

0108-2701/84/111846-03$01.50   © 1984 International Union of Crystallography