

Search of the Cambridge Data Centre files shows only five other molecules that contain a C(Me)COOH group attached to a benzene ring. These compounds are listed in Table 4 together with selected dimensions. Three of these five structures contain intramolecular hydrogen bonds formed between two molecules over a centre of symmetry in an equivalent manner to (1). The conformation of the propionic acid moiety relative to the benzene ring can be described by a number of torsion angles. These are listed for all these molecules in Table 4. The C(13)–C(14)–C(16)–C(17) torsion angle varies considerably in the molecules, ranging from 82.4 (1)° in (1) to 158.2° in (6). However, there is more agreement in the position of the –CO₂H group relative to the phenyl ring measured either by the angle of intersection or by the C–C–C–O torsion angles, which fall within a 30° spread if sign variations are ignored. The considerable range of values for both these dimensions indicates that no particular conformation is favoured and that overall packing effects may well decide the exact molecular conformation.

We thank Mr A. W. Johans for his assistance with the crystallographic investigations.

References

- CASHIN, C. H., DAWSON, W. & KITCHEN, E. A. (1977). *J. Pharm. Pharmacol.* **29**, 330–336.
 CHATFIELD, D. H., CASHIN, C. H., KITCHEN, E. A. & GREEN, J. N. (1977). *J. Pharm. Pharmacol.* (1977). **29**, 371–377.
 DUNWELL, D. W., EVANS, D., HICKS, T. A., CASHIN, C. H. & KITCHEN, A. (1975). *J. Med. Chem.* **18**, 53–58.
 DUPONT, L., DIDEBERG, O., DIVE, G., GODFROID, J. J. & STEINER, E. (1982). *Acta Cryst.* **B38**, 2409–2415.
 FLIPPEN, J. L. & GILARDI, R. D. (1975). *Acta Cryst.* **B31**, 926–928.
 FOULON, M., BAERT, F., FOURET, R., BRIENNE, M. J. & JACQUES, J. (1979). *Acta Cryst.* **B35**, 2058–2062.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
 MCCONNELL, J. F. (1974). *Cryst. Struct. Commun.* **3**, 73–75.
 PEETERS, O. M., BLATON, N. M. & DE RANter, C. J. (1983). *Bull. Soc. Chim. Belg.* **92**, 191–199.
 SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

Acta Cryst. (1986). **C42**, 177–179

4-O-β-D-Galactopyranosyl-α-D-mannopyranose Hemioethanol Dihydrate

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(Received 20 June 1985; accepted 28 October 1985)

Abstract. C₁₂H₂₂O₁₁·½C₂H₆O·2H₂O, *M_r* = 401.4, tetragonal, *P*4₂,2, *a* = 9.2351 (13), *c* = 42.2158 (30) Å, *V* = 3600.46 Å³, *Z* = 8, *D_x* = 1.48 g cm⁻³, λ(Cu *Kα*) = 1.5418 Å, μ = 11.84 cm⁻¹, *F*(000) = 1720, *T* = 293 K, *R* = 0.0636 for 1999 observed reflections. The material was prepared by recrystallization from an ethanol/water mixture of a commercially prepared sample. The results have confirmed the disaccharide structure, showing two molecules of water per oligomer plus ethanol of crystallization.

Introduction. Great importance has been placed on carbohydrates which exhibit the properties of gelation because of their commercial applications. In this context, work on the structure of galactomannans, which form synergistic gels with other polysaccharides such as carrageenan (Dea & Morrison, 1975), is of interest. Thus, the crystal structure of any galactomanan oligomer is useful as a model for conformational analysis of the polymer. The present study has shown that the recrystallized compound is the free reducing disaccharide which contains ethanol of crystallization.

Experimental. Crystals prepared by slow evaporation from an ethanol/water mixture; crystal 0.2 × 0.2 × 0.25 mm, Enraf–Nonius CAD-4F diffractometer, Cu *Kα* radiation, cell dimensions calculated from θ measurements of 32 reflections. 6476 reflections measured, 2θ_{max} = 70°, *h* 0 to 8, *k* 0 to 11, *l* 0 to 52, data merged using *SHELX76* (Sheldrick, 1976) giving 2060 unique reflections, *R*_{int} = 0.0532, 1999 [*F* > 3σ(*F*)] used in analysis. As an intensity check the 5,5,18 reflection was used: average count 455.1 and σ (calculated from the distribution) = 63.0 (13.8%). No absorption correction applied. *MULTAN80* (Main *et al.*, 1980) used to solve structure and least-squares refinement carried out, with *SHELX*, for positional parameters and anisotropic thermal parameters for all non-H atoms; ∑*w*(Δ*F*)² minimized, *w* = 1/(σ²*F* + 0.001159*F*²); H atoms located from difference Fourier synthesis except for ethanolic H atoms but not refined; *R* = 0.0636, *wR* = 0.0940. In final cycle max. Δ/σ 0.084, av. 0.006; on final difference Fourier synthesis max. and min. electron densities 0.37 and –0.35 e Å⁻³; scattering factors from *International Tables for X-ray*

Crystallography (1974). Figures drawn with *PLUTO78* (Motherwell & Clegg, 1978).

Discussion. Fig. 1 shows the 4-*O*- β -D-galactopyranosyl- α -D-mannopyranose molecule with its labelling scheme. Fig. 2 is the packing diagram shown along the *a* axis. Atom coordinates and equivalent isotropic temperature factors are given in Table 1,* and bond lengths and angles in Table 2.

There are eight disaccharide molecules with sixteen associated water molecules (eight pairs) per unit cell, and four ethanol molecules occupying eight sites each with an occupancy of 0.46 (1).

In the *a*-axis projection two molecules overlap at the galactose residue where there is the possibility of an intermolecular hydrogen bond. All possible hydrogen bonds are shown in Table 3 (deposited).

* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates and Table 3 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42605 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

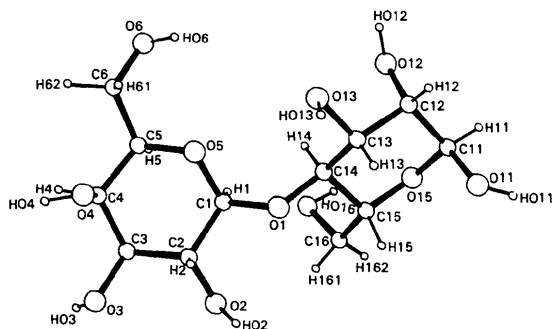


Fig. 1. View of the structure showing the numbering scheme.

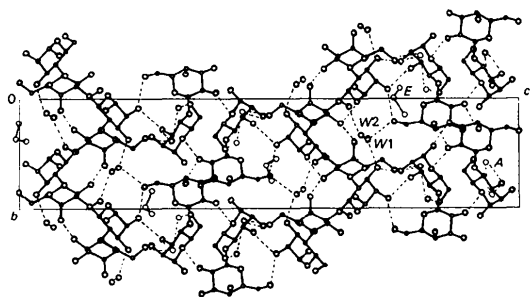


Fig. 2. *a*-axis-projection packing diagram showing the molecule from Fig. 1 (*A*), water molecules (*W1*) and (*W2*) and the ethanol position (*E*).

Table 1. Atom coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^4$)

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
C(1)	2873 (4)	170 (4)	8363 (1)	278
C(2)	3610 (5)	767 (4)	8656 (1)	304
C(3)	3848 (5)	2392 (4)	8626 (1)	320
C(4)	4586 (5)	2771 (5)	8320 (1)	398
C(5)	3765 (5)	2081 (4)	8053 (1)	361
C(6)	4454 (6)	2349 (5)	7744 (1)	493
C(11)	377 (5)	-4785 (4)	8089 (1)	319
C(12)	1531 (4)	-4225 (4)	7862 (1)	308
C(13)	2623 (4)	-3309 (4)	8044 (1)	276
C(14)	1841 (4)	-2098 (4)	8208 (1)	262
C(15)	684 (5)	-2739 (4)	8422 (1)	303
C(16)	-179 (6)	-1636 (5)	8595 (1)	430
O(1)	2868 (3)	-1330 (3)	8391 (1)	314
O(2)	2739 (3)	493 (4)	8916 (1)	396
O(3)	4718 (4)	2813 (3)	8885 (1)	438
O(4)	6042 (4)	2260 (4)	8309 (1)	542
O(5)	3689 (3)	534 (3)	8096 (1)	325
O(6)	3499 (5)	2034 (4)	7496 (1)	632
O(11)	1059 (3)	-5743 (3)	8286 (1)	388
O(12)	840 (3)	-3396 (4)	7631 (1)	364
O(13)	3700 (3)	-2770 (4)	7837 (1)	382
O(15)	-296 (3)	-3621 (3)	8246 (1)	297
O(16)	-742 (4)	-507 (4)	8405 (1)	528
O(<i>W1</i>)	6273 (6)	6164 (9)	8031 (2)	1475
O(<i>W2</i>)	6677 (9)	9178 (10)	8171 (2)	1670
CE(1)*	7490 (17)	9520 (17)	7500 (3)	673
CE(2)*	9073 (69)	10175 (40)	7463 (10)	2098
OE(2)*	9199 (26)	11478 (33)	7635 (5)	1915

* Atoms of ethanol molecule; refined site-occupation factor 0.46 (1).

Table 2. Bond distances (\AA) and angles ($^\circ$)

C(1)–C(2)	1.515 (5)	C(11)–C(12)	1.522 (5)
C(2)–C(3)	1.522 (5)	C(12)–C(13)	1.523 (5)
C(3)–C(4)	1.502 (5)	C(13)–C(14)	1.500 (5)
C(4)–C(5)	1.499 (6)	C(14)–C(15)	1.521 (5)
C(5)–C(6)	1.475 (6)	C(15)–C(16)	1.484 (6)
C(1)–O(1)	1.390 (5)	C(11)–O(11)	1.369 (5)
C(2)–O(2)	1.386 (5)	C(12)–O(12)	1.394 (5)
C(3)–O(3)	1.412 (4)	C(13)–O(13)	1.415 (4)
C(4)–O(4)	1.425 (6)	C(14)–O(1)	1.415 (4)
C(5)–O(5)	1.442 (5)	C(15)–O(15)	1.428 (5)
C(1)–O(5)	1.398 (4)	C(11)–O(15)	1.408 (5)
C(6)–O(6)	1.399 (7)	C(16)–O(16)	1.414 (6)
O(1)–C(1)–C(2)	107.2 (3)	O(11)–C(11)–C(12)	106.2 (3)
O(5)–C(1)–C(2)	109.2 (3)	O(15)–C(11)–C(12)	110.2 (3)
O(5)–C(1)–O(1)	108.0 (3)	O(15)–C(11)–O(11)	114.2 (3)
C(3)–C(2)–C(1)	110.8 (3)	C(13)–C(12)–C(11)	109.7 (3)
O(2)–C(2)–C(1)	108.6 (3)	O(12)–C(12)–C(11)	107.8 (3)
O(2)–C(2)–C(3)	109.3 (3)	O(12)–C(12)–C(13)	110.5 (3)
C(4)–C(3)–C(2)	111.6 (3)	C(14)–C(13)–C(12)	109.1 (3)
O(3)–C(3)–C(2)	106.8 (3)	O(13)–C(13)–C(12)	110.5 (3)
O(3)–C(3)–C(4)	110.1 (4)	O(13)–C(13)–C(14)	111.2 (3)
C(5)–C(4)–C(3)	108.4 (4)	C(15)–C(14)–C(13)	108.9 (3)
O(4)–C(4)–C(3)	112.2 (4)	O(1)–C(14)–C(13)	107.6 (3)
O(4)–C(4)–C(5)	108.2 (4)	O(1)–C(14)–C(15)	109.9 (3)
C(6)–C(5)–C(4)	112.0 (4)	C(16)–C(15)–C(14)	113.7 (3)
O(5)–C(5)–C(4)	110.6 (3)	O(15)–C(15)–C(14)	110.8 (3)
O(5)–C(5)–C(6)	107.4 (3)	O(15)–C(15)–C(16)	107.9 (4)
O(6)–C(6)–C(5)	110.9 (4)	O(16)–C(16)–C(15)	115.2 (3)
C(1)–O(1)–C(14)	117.1 (3)		

Of particular interest with disaccharides of this type is the conformation around the glycosidic linkage. In this case the respective φ and ψ angles [defined as $\varphi = \text{O5}(i)-\text{C1}(i)-\text{O4}(i-1)-\text{C4}(i-1)$ and $\psi = \text{C1}(i)-\text{O4}(i)-\text{C4}(i-1)-\text{C3}(i-1)$ from IUPAC-IUB Joint Commission on Biochemical Nomenclature (1983)] are $-83.23(41)$ and $131.70(35)^\circ$ with a glycosidic angle [C(1)—O(1)—C(14)] of $117.1(3)^\circ$. It has been suggested by Perez & Marchessault (1978) that the *exo*-anomeric effect is important in the conformational analysis of polysaccharides. This effect occurs when there are sequences of atoms with alternating polarity and having free electron pairs. A sequence such as this is found in the disaccharide between the ring oxygen, O(5), and the ring carbon, C(14), *via* C(1) and O(1). This phenomenon is thought to give a conformational bias to the dihedral values related to rotation about the glycosidic linkage. With the occurrence of an intramolecular hydrogen bond, the values of φ and ψ normally lie in a very narrow range for a selection of disaccharides of this type, *e.g.* the values found for mannobiose (Sheldrick, Mackie & Akrigg, 1984) are -96.1 and 95.1° for φ and ψ with a glycosidic angle of 114.8° . However, when free of this restriction, instead of the larger range of φ and ψ angles that would be expected, φ still appears to be limited to a range of 30° , whereas ψ varies by as much as 100° . Therefore, it would appear that for all oligosaccharides, φ is limited to a narrow range, whilst ψ will only be restricted in compounds with intramolecular hydrogen bonds. An example of this is β -maltose (Gress & Jeffrey, 1977) which has no hydrogen bond and $\varphi = 121.7^\circ$ and

$\psi = 132.8^\circ$, with this latter value corresponding to the value in this study. In conclusion, 4-*O*- β -D-galactopyranosyl- α -D-mannose fits the general trend of having a biased conformation of dihedral angles due to the *exo*-anomeric effect which has been shown to exist in many other oligosaccharide crystal structures.

We thank the University of Leeds Computing Service for the provision of computing facilities.

References

- DEA, I. C. M. & MORRISON, A. (1975). *Adv. Carbohydr. Chem. Biochem.* **31**, 241–308.
- GRESS, M. E. & JEFFREY, G. A. (1977). *Acta Cryst.* **B33**, 2490–2495.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- IUPAC-IUB JOINT COMMISSION ON BIOCHEMICAL NOMENCLATURE (1983). *Eur. J. Biochem.* **131**, 1–7.
- MAIN, P., FISKE, S., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO78*. Program for drawing molecular and crystal structures. Univ. of Cambridge, England.
- PEREZ, S. & MARCHESSAULT, R. H. (1978). *Carbohydr. Res.* **65**, 114–120.
- SHELDRIK, B., MACKIE, W. & AKRIGG, D. (1984). *Carbohydr. Res.* **132**, 1–6.
- SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

Acta Cryst. (1986). **C42**, 179–181

A Bis(anisyl)cyclohexanone: A Non-Macrocyclic Model for Some Features of Spherand Structures

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(Received 18 June 1985; accepted 2 October 1985)

Abstract. *cis*-2,6-Bis(2-methoxyphenyl)cyclohexan-1-one, $\text{C}_{20}\text{H}_{22}\text{O}_3$, $M_r = 310.4$, orthorhombic, $P2_12_12_1$, $a = 9.364(1)$, $b = 7.865(1)$, $c = 23.219(5)$ Å, $V = 1710.0$ Å³, $Z = 4$, $D_m = 1.23$, $D_x = 1.21$ g cm⁻³, $\lambda(\text{Mo K}\alpha) = 0.7107$ Å, $\mu = 0.74$ cm⁻¹, $F(000) = 664$,

$T = 295$ K, $R = 0.057$ for 1445 unique observed reflections with $I > \sigma(I)$. The methoxy O and C atoms in this structure are nearly coplanar with the aromatic rings to which they are attached and the rings themselves are planar rather than folded, quite in contrast to the situation in the related macrocyclic spherands and hemispherands containing similar rings.

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