$S = 1.091$
3209 reflections
205 parameters
H atoms: riding and rotating model

$(\Delta/\sigma)_{\max} = 0.004$
$\Delta\rho_{\max} = 1.403$ e Å^{-3}
$\Delta\rho_{\min} = -1.379$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Comparison of average geometric parameters (Å, °) of the mbts molecule in structures (1)–(5)*

Compound	(1)	(3)	(4)	(2)	(5)
N†	2	2	3	2	1
Se1—C2	1.817	1.851	1.857	1.859	1.880
S1—C2	1.723	1.713	1.721	1.723	1.711
S1—C9	1.738	1.738	1.740	1.744	1.754
C2—N3	1.349	1.335	1.334	1.336	1.317
N3—C4	1.406	1.402	1.399	1.393	1.413
N3—C10	1.443	1.465	1.482	1.470	1.497
C4—C5	1.391	1.393	1.382	1.385	1.390
C4—C9	1.393	1.383	1.394	1.389	1.386
C5—C6	1.379	1.377	1.371	1.389	1.367
C6—C7	1.394	1.365	1.380	1.401	1.392
C7—C8	1.387	1.381	1.378	1.377	1.373
C8—C9	1.370	1.381	1.392	1.391	1.390
C2—S1—C9	92.7	91.3	91.1	90.9	90.7
Se1—C2—S1	122.1	123.9	124.7	124.3	124.5
Se1—C2—N3	127.3	124.2	123.4	123.5	122.6
S1—C2—N3	110.5	111.9	111.9	112.3	112.9
C2—N3—C4	114.9	114.5	114.8	114.1	114.7
C2—N3—C10	123.1	123.1	123.3	124.1	123.9
C4—N3—C10	121.9	122.4	121.8	121.7	121.4
N3—C4—C5	127.3	127.3	127.3	126.7	128.0
N3—C4—C9	112.3	111.7	111.5	112.4	111.2
C5—C4—C9	120.4	121.0	121.2	120.9	120.8
C4—C5—C6	117.9	116.7	117.9	118.3	117.0
C5—C6—C7	121.7	122.4	121.2	120.6	122.4
C6—C7—C8	119.7	121.0	121.9	120.8	120.9
C7—C8—C9	118.9	117.7	117.3	118.4	117.0
S1—C9—C4	109.6	110.7	110.6	110.3	110.6
S1—C9—C8	129.1	128.8	128.8	128.8	127.6
C4—C9—C8	121.3	121.1	120.5	120.9	121.8

† *N* = number of independent structural mbts units.

Refinement on F^2 for all reflections except for 31 with very negative F^2 [$<-3\sigma(F^2)$] or flagged by us for potential systematic errors.

Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993).

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: AV1002). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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p-Nitrophenyl α-D-Mannopyranoside Ethanol Solvate

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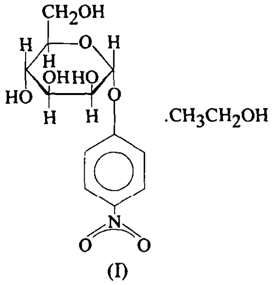
Abstract

The sugar moiety of the title compound, $C_{12}H_{15}NO_8.C_2H_6O$, has a $^4C_1$ conformation. The nitrophenyl group adopts a planar conformation. The glycosidic linkage is α. The angle between the 'best planes' through the saccharide and aglycon residues is 71.5 (1)°.

Comment

The ways in which the legume lectin Concanavalin A (Con A) binds to a series of saccharides consisting of a mannoside or glucoside group (saccharide residue) bonded to a second hydrophobic ring (aglycon residue) are currently being studied (Kanellopoulos *et al.*, 1996). The title compound, the methanol solvate of *p*-nitrophenyl α-D-mannopyranoside (α-PNM), (I), a member of the series, binds to Con A with a high affinity. Its precise molecular structure determination was necessary for modelling the Con A–saccharide complexes.



(I)

The crystal structure shows disorder; there is an ethanol molecule per asymmetric unit, which may adopt three different orientations, at approximately the same site, with relative occupancies of 43, 22 and 35%. The saccharide part of the molecule has a slightly distorted $^4C_1$ chair conformation (Stoddart, 1971), as measured by the Cremer & Pople (1975) parameters [Q = 0.528 (4), θ = 4.9 (5)° and φ = 76 (6)°]. The glycosidic linkage is confirmed to be α. The mean C—C bond length of the pyranose ring [1.529 (6) Å] and the mean C—O(hydroxyl) length [1.426 (5) Å] are similar to those observed in pyranose sugars (Jeffrey, 1990).

The torsion angles of the pyranose ring are consistent with values reported for other saccharides, except for the angles about the C3—C4 and C4—C5 bonds [48.4 (4) and −48.4 (4)°, respectively], which are considerably smaller than those expected for a pyranose ring (Jeffrey, 1990). This is most probably related to the substitution at the O1 position and/or the particular crystal packing in this structure. The C-atom valence angles in the pyranose ring and the O5 valence angle, 115.0 (3)°, are in the range found in other carbohydrate structures (Jeffrey, 1990). The extracyclic torsion angle around the C5—C6 bond is also close to the expected value. The N1—C10 bond length of 1.440 (7) Å is similar to the value found in p-nitrophenol (Butt, Mackay & Topsom, 1987). The high anisotropy of the displacement parameters of the O7 and O8 atoms perhaps indicates rotational disorder of the nitro group, which was in fact observed in the crystal structure of the α-PNM–Con A complex (Kanellopoulos *et al.*, 1996). The conformation of the molecule in the crystal [C7—O1—C1—O5 81.4 (4) and C1—O1—C7—C8 164.8 (4)°] corresponds to a free-energy minimum, most probably the global one, as determined by semi-empirical energy calculations (*HYPERCHEM*; E. Mikros, personal communication). Moreover, the molecule adopts approximately the same crystal structure conformation as does its complex with Con A (Kanellopoulos *et al.*, 1996). The phenyl ring is planar and deviations of the C atoms are less than 0.013 (5) Å from the least-squares plane. The O1 atom and the O8—N1—O7 plane are almost coplanar with the phenyl ring [maximum deviation 0.086 (8) Å for the O8 atom].

The packing in the crystal is determined by a rather complex intermolecular network of hydrogen bonds, involving all O atoms of the hydroxyl groups, the O atoms of the disordered ethanol molecules (Table 2), as well as a large number of intermolecular van der Waals interactions.

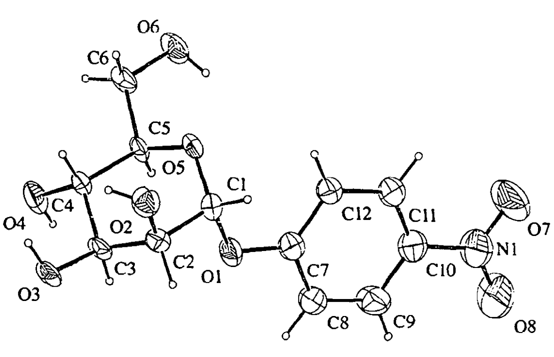


Fig. 1. The structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level and the disordered ethanol molecule is not shown.

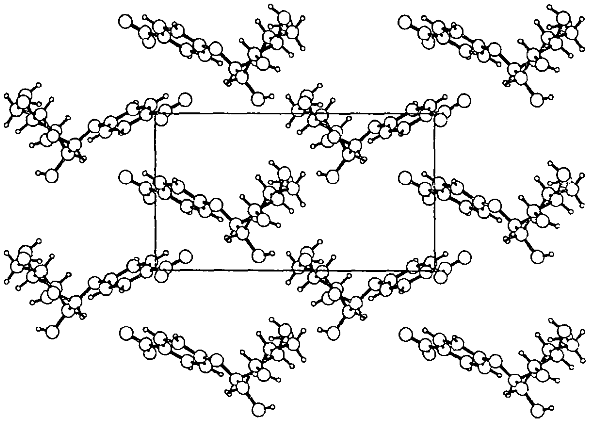


Fig. 2. A view of the crystal packing along the a axis. The disordered ethanol molecule and the hydrogen-bonding scheme have been omitted for clarity.

The crystal structure of p-nitrophenyl α-D-mannopyranoside hemihydrate has recently been reported (Fernandez-Castaño & Foces-Foces, 1996). This compound crystallizes in the same space group, $P2_1$, with two molecules per asymmetric unit and cell parameters a = 17.797 (3), b = 10.2594 (6), c = 7.4438 (5) Å and β = 98.44 (1)°. A water molecule links the two independent molecules in the asymmetric unit through O—H···O hydrogen bonds. While the geometry (bond lengths and angles) of the molecule is similar in both structures, its conformation is slightly different [torsion angles C7—O1—C1—O5 81.4 (4) and C1—O1—C7—C8 164.8 (4)° in α-PNM ethanol solvate; Ci7—Oi1—Ci1—Oi5 59.6 (6) and 61.4 (6)° and Ci1—Oi1—Ci7—Ci12 −171.1 (6) and −146.1 (5)° for the two independent molecules (i = 1, 2) in p-nitrophenyl α-D-mannopyranoside hemihydrate]. The differences perhaps reflect the effect of the solvent. A comparison of the geometry of α-PNM ethanol solvate (this study) with α-PNM hemihydrate (Fernandez-Castaño & Foces-Foces, 1996) and other mannose derivatives obtained from the Cambridge Structural Database (Allen *et al.*, 1991), *e.g.* MEMANP (Gatehouse & Poppleton, 1970) and MEMANP11 (Jeffrey, McMullan & Takagi, 1977), reveals the following: the endocyclic C5—O5 and O5—C1 bond lengths of 1.438 (5) and 1.387 (5) Å (Table 1), respectively, are significantly different in the *p*-nitro-substituted saccharides [C*i*5—O*i*5 1.455 (6) and 1.453 (6) Å (*i* = 1, 2), and O*i*5—C*i*1 1.400 (7) and 1.401 (6) Å (*i* = 1, 2) in α-PNM hemihydrate; Fernandez-Castaño & Foces-Foces, 1996], with the shorter bond close to the anomeric C1 atom. This effect has also been observed in several other *p*-nitropyranose compounds (Fernandez-Castaño & Foces-Foces, 1996, and references therein), and in other glycosidic substituted molecules, *e.g.* sucrose (Brown & Levy, 1963). Furthermore, the C1—O1 glycosidic bond, 1.422 (5) Å, does not show the characteristic anomeric shortening observed in the free sugar (Berman, Chu & Jeffrey, 1967), while the length of the O1—C7 bond of 1.369 (6) Å [corresponding bond lengths in α-PNM hemihydrate are 1.356 (6) and 1.361 (6) Å] suggests a partial double-bond character. This probably reflects the resonance of the glycosidic O-atom lone pairs with the aromatic ring, in agreement with values observed in several enol esters (Allen *et al.*, 1987). These differences probably arise from the *p*-nitrophenyl substitution at the glycosidic O1 atom.

Experimental

Crystals of the title compound (Sigma Chemical Company) were prepared by slow evaporation from ethanol solutions at room temperature. As they were unstable in air, they were mounted into capillaries in equilibrium with ethanol vapour.

Crystal data

$C_{12}H_{15}NO_8.C_2H_6O$
$M_r = 347.32$
Monoclinic
$P2_1$
$a = 7.290\ (3)$ Å
$b = 7.926\ (3)$ Å
$c = 14.654\ (4)$ Å
$\beta = 92.94\ (7)°$
$V = 845.6\ (5)$ Å^3
$Z = 2$
$D_x = 1.364$ Mg m^{-3}
$D_m = 1.33$ Mg m^{-3}
D_m measured by flotation

Cu $K\alpha$ radiation
$\lambda = 1.54180$ Å
Cell parameters from 22 reflections
$\theta = 20–40°$
$\mu = 0.989$ mm^{-1}
$T = 293\ (2)$ K
Needle
0.8 × 0.5 × 0.2 mm
White

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega–2\theta$ scans
Absorption correction: none
2321 measured reflections
2147 independent reflections
2036 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.0463$
$\theta_{\max} = 60°$
$h = 0 \rightarrow 8$
$k = -8 \rightarrow 8$
$l = -16 \rightarrow 16$
3 standard reflections every 100 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0647$
$wR(F^2) = 0.1767$
$S = 1.084$
2133 reflections
226 parameters
H atoms refined isotropically
$w = 1/[\sigma^2(F_o^2) + (0.1379P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.014$
$\Delta\rho_{\max} = 0.407$ e Å^{-3}
$\Delta\rho_{\min} = -0.357$ e Å^{-3}

Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.005 (2)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: Flack (1983)
Flack parameter = −0.2 (4)

Table 1. *Selected geometric parameters (Å, °)*

O1—C7	1.369 (6)	O7—N1	1.231 (8)
O1—C1	1.422 (5)	O8—N1	1.188 (7)
O2—C2	1.412 (6)	N1—C10	1.440 (7)
O3—C3	1.434 (5)	C1—C2	1.533 (6)
O4—C4	1.434 (5)	C2—C3	1.512 (6)
O5—C1	1.387 (5)	C3—C4	1.530 (6)
O5—C5	1.438 (5)	C4—C5	1.540 (5)
O6—C6	1.429 (5)	C5—C6	1.496 (6)
C7—O1—C1	117.8 (3)	O3—C3—C4	110.7 (3)
C1—O5—C5	115.0 (3)	C2—C3—C4	111.7 (3)
O5—C1—O1	113.0 (3)	O4—C4—C3	108.1 (3)
O5—C1—C2	111.4 (3)	O4—C4—C5	109.1 (3)
O1—C1—C2	106.2 (3)	C3—C4—C5	111.3 (3)
O2—C2—C3	112.6 (3)	O5—C5—C6	106.0 (3)
O2—C2—C1	107.3 (3)	O5—C5—C4	111.9 (3)
C3—C2—C1	110.2 (4)	C6—C5—C4	110.2 (3)
O3—C3—C2	108.5 (3)	O6—C6—C5	111.5 (3)
C7—O1—C1—O5	81.4 (4)	C1—O1—C7—C12	−15.6 (6)
C7—O1—C1—C2	−156.1 (4)	O8—N1—C10—C11	178.1 (7)
O5—C5—C6—O6	64.8 (4)	O7—N1—C10—C11	0.4 (11)
C4—C5—C6—O6	−173.9 (4)	O8—N1—C10—C9	−1.6 (11)
C1—O1—C7—C8	164.8 (4)	O7—N1—C10—C9	−179.3 (8)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2A···O3	0.820 (4)	2.437 (4)	2.786 (4)	106.8 (3)
O2—H2A···O4$^{\rm i}$	0.820 (4)	2.330 (4)	3.128 (4)	164.2 (4)
O2—H2A···O6$^{\rm ii}$	0.820 (4)	2.383 (4)	2.747 (4)	107.8 (3)
O3—H3A···O4$^{\rm i}$	0.819 (8)	2.066 (8)	2.835 (4)	156.2 (7)
O6—H6A···O3$^{\rm iii}$	0.821 (7)	2.429 (5)	2.818 (5)	110.0 (4)
O6—H6A···O5	0.821 (7)	2.477 (5)	2.819 (5)	106.2 (4)
O4—H4A···O50$^{\rm iv}$	0.890 (9)	1.85 (2)	2.68 (2)	152.3 (9)
O4—H4A···O60$^{\rm iv}$	0.890 (9)	1.97 (3)	2.85 (3)	165.7 (10)
O4—H4A···O70$^{\rm iv}$	0.890 (9)	2.043 (19)	2.79 (2)	140.8 (8)

Symmetry codes: (i) $-x, y-\frac{1}{2}, 1-z$; (ii) $1-x, y-\frac{1}{2}, 1-z$; (iii) $1+x, y, z$; (iv) $x, 1+y, z$.

Difference Fourier maps revealed an ethanol solvent molecule per asymmetric unit which adopts three different orientations, at approximately the same site. All atoms of the ethanol molecule of the same orientation were given the same site-occupation factor (s.o.f.). The sum of the s.o.f.'s in all three orientations was constrained to have a value of 1. Simultaneously, the isotropic displacement parameters of each atom in each orientation of the ethanol molecule were set to be equal. Hydroxyl H atoms of the pyranose ring were first located from difference Fourier maps and then left to refine riding on the bonded atom with their $U_{\rm iso}$ fixed at $1.2U_{\rm eq}$ of the attached atom. All other H atoms were calculated to fit the geometry and their isotropic displacement parameters constrained to be the same and refined to 0.028 Å^2. The absolute configuration of the molecule was not determined since it was known from the synthesis and was assigned according to the configurational angles given by Cano *et al.* (1985). Calculation of the Flack absolute structure parameter χ and its e.s.d. [−0.2 (4); Flack, 1983] further suggests that the refined absolute structure is correct.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *CAD*-4 *Software*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *PLUTON* (Spek, 1991) and *PLATON* (Spek, 1990). Software used to prepare material for publication: *SHELXL*93.

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: SK1000). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Clerodane Diterpene with Antibacterial Activity from *Ajuga lupulina*

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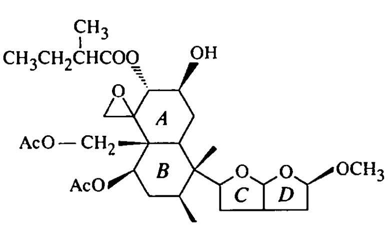
Abstract

The structure of a new diterpene, $C_{30}H_{46}O_{11}$, with antibacterial activity against *Pseudomonas aeruginose* and *Escherichia coli*, isolated from the fresh whole plants of *Ajuga lupulina* (Labiatae) was established to be 2β-hydroxy-2-methylbutanoyl-3α-lupulin (3-deoxy-14,15-dihydro-2-hydroxy-15-methoxycaryoptinol 2-methylbutanoate), by means of X-ray crystallographic analysis. The present study confirms that the two six-membered rings are in ideal chair conformations.

Comment

As part of our ongoing research on diterpenoid compounds with antibacterial activity from *Ajuga lupulina* (Labiatae), a new clerodane diterpene, (I), with potential antibacterial activity against *Pseudomonas aeruginose* and *Escherichia coli*, was isolated from the fresh whole plants of *Ajuga lupulina*. In order to establish its structure, the X-ray analysis was undertaken. The results of the present study are in agreement with the structural elucidation based on spectroscopic data.



(I)

In rings *A* and *B*, the mean values of the valence angles (109.8 and 111.6°) are close to that of 111.6° for the chair form of cyclohexane obtained by Hendrickson (1967) from strain-energy minimization calculations. Rings *C* and *D* of the tetrahydrofurofuran