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Structure of Angiopteroside (4-*O*-*β*-D-Glucopyranosyl-L-*threo*-2-hexen-5-olide) Monohydrate, a Fern Glycoside from *Angiopteris lygodiifolia* Ros.

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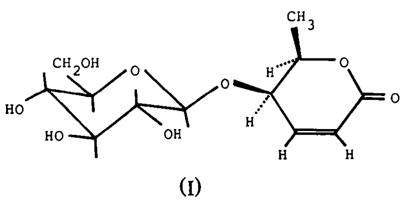
Abstract. $C_{12}H_{18}O_8.H_2O$ (isolated from the dried rhizome of *Angiopteris lygodiifolia* Ros.), orthorhombic, $P2_12_12_1$, $Z = 4$, $a = 9\cdot566$ (6), $b = 10\cdot502$ (4), $c = 14\cdot135$ (7) Å, $V = 1420\cdot0$ Å^3, $D_c = 1\cdot442$, $D_m = 1\cdot43$ Mg m^{-3}, μ(Cu $K\alpha$) = 1·088 mm^{-1}. The structure was determined using the direct method and refined by full-matrix least squares with anisotropic temperature factors for all non-hydrogen atoms to a final R of 0·038 for 1086 independent reflections. The conformation of the glucose residue is $^4C_1$ and that of the aglucone is close to a half-boat. The lactone group is roughly planar and exhibits the expected characteristics. Except for the bridging O and the ring O of the aglucone, all O atoms of the molecule are involved in hydrogen bonding. The conformations of the anomeric and bridge C—O bonds are such that one side of the molecule is nonpolar.

Introduction. Angiopteroside (I) was isolated from the dried rhizome of *Angiopteris lygodiifolia* Ros. (Marattiaceae), a common fern growing in tropical regions (Chen, 1981). Its diastereoisomer, osmundalin, has also been found in a number of *Osmunda* species (Hollenbeak & Kuehne, 1974). Although the carcinogenicity of both angiopteroside and osmundalin has not yet been established, some unsaturated lactones or their glycosides have been noted to be cytotoxic and antibiotic agents, *e.g.* ranunculin (Hill & Van Heyningen, 1951; Benn & Yelland, 1968), parasorbic acid (Reynolds, 1975), and tuliposide and parasorboside (Tschesche, Hoppe, Snatzke, Wulff & Fehlhaber, 1971). The present structure determination was undertaken to provide structural features of the Δ^2-pentenolide moiety and the conformation of the glycosidic bond.



(I)

Colourless needle crystals of angiopteroside were grown from chloroform–methanol. A single crystal 0·5 × 0·3 × 0·3 mm was used to collect 1086 independent reflections [$I > 2\sigma(I)$, $\sin\theta/\lambda < 0\cdot57$ Å^{-1}, total 1277] at room temperature on a Syntex $P\bar{1}$ auto-diffractometer with Ni-filtered Cu $K\alpha$ radiation. A θ–2θ scan technique with variable scan speed was employed. The cell dimensions were obtained by a least-squares fit to the setting angles of 15 reflections measured on the diffractometer. The intensity data were converted to structure factors after application of Lorentz–polarization and absorption corrections. Intensity data from azimuthal rotation about the two strong reflections, 202 and 404, were used for the absorption correction (North, Phillips & Mathews, 1968). No time-decay correction was made as the intensities of two check reflections remeasured periodically during data collection showed only random fluctuation (within 3%).

The structure was solved by *MULTAN* (Germain, Main & Woolfson, 1971). All non-H atoms were

Table 1. *Fractional coordinates* (×10^4) *and equivalent isotropic thermal parameters for the non-hydrogen atoms*

	x	y	z	U_{eq}* (Å^2)
C(1)	8136 (4)	1813 (3)	−1542 (2)	0·166 (10)
C(2)	7493 (4)	502 (4)	−1412 (2)	0·179 (11)
C(3)	8056 (4)	−427 (3)	−2134 (2)	0·169 (10)
C(4)	7892 (4)	116 (5)	−3131 (2)	0·167 (6)
C(5)	8640 (4)	1401 (3)	−3163 (2)	0·177 (9)
C(6)	8631 (5)	2064 (4)	−4117 (3)	0·200 (10)
C(7)	7352 (4)	3902 (3)	1266 (3)	0·186 (10)
C(8)	8744 (4)	3389 (4)	1036 (3)	0·190 (10)
C(9)	9166 (4)	3286 (4)	139 (3)	0·187 (11)
C(10)	8232 (4)	3735 (3)	−652 (2)	0·175 (11)
C(11)	7276 (4)	4785 (4)	−314 (2)	0·188 (10)
C(12)	6119 (5)	5126 (5)	−984 (3)	0·217 (12)
O(1)	7398 (2)	2671 (2)	−969 (2)	0·173 (7)
O(2)	7830 (4)	128 (3)	−469 (2)	0·193 (8)
O(3)	7282 (3)	−1574 (2)	−2002 (2)	0·192 (8)
O(4)	8494 (3)	−763 (3)	−3768 (2)	0·184 (8)
O(6)	7282 (3)	2128 (3)	−4548 (2)	0·205 (8)
O(5)	7957 (3)	2243 (2)	−2494 (1)	0·173 (7)
O(7)	6824 (3)	3772 (3)	2045 (2)	0·186 (12)
O(8)	6606 (3)	4463 (2)	584 (2)	0·183 (8)
O(W)	5648 (4)	3568 (4)	−3352 (3)	0·250 (10)

* $U_{eq} = (U_1 U_2 U_3)^{1/3}$.

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Table 2. *Fractional coordinates* ($\times 10^3$) *and isotropic thermal parameters for the* H *atoms*

	x	y	z	B (Å^2)
H(1)	918 (5)	174 (5)	−140 (3)	1·8 (9)
H(2)	655 (6)	56 (4)	−148 (3)	2·0 (10)
H(3)	912 (5)	−58 (4)	−204 (3)	1·8 (9)
H(4)	686 (5)	33 (4)	−327 (3)	1·4 (9)
H(5)	961 (5)	126 (4)	−296 (3)	2·1 (9)
H(61)	900 (5)	296 (5)	−402 (3)	2·8 (11)
H(62)	928 (4)	158 (4)	−455 (3)	1·9 (9)
H(8)	936 (5)	308 (5)	154 (4)	3·2 (12)
H(9)	1008 (5)	290 (5)	1 (3)	2·2 (10)
H(10)	891 (4)	408 (4)	−119 (3)	2·1 (10)
H(11)	788 (5)	553 (5)	−25 (3)	1·9 (9)
H(121)	543 (5)	585 (5)	−66 (3)	3·5 (12)
H(122)	555 (5)	419 (5)	−111 (3)	3·4 (12)
H(123)	645 (6)	554 (5)	−147 (4)	3·1 (12)
H(O2)	779 (6)	−69 (5)	−29 (3)	3·1 (12)
H(O3)	762 (5)	−218 (5)	−231 (3)	2·2 (11)
H(O4)	813 (6)	−53 (5)	−427 (4)	3·5 (14)
H(O6)	662 (6)	250 (5)	−413 (3)	3·4 (12)
H(O*W*1)	615 (6)	377 (6)	−285 (5)	5·0 (18)
H(O*W*2)	522 (6)	294 (6)	−312 (4)	3·6 (15)

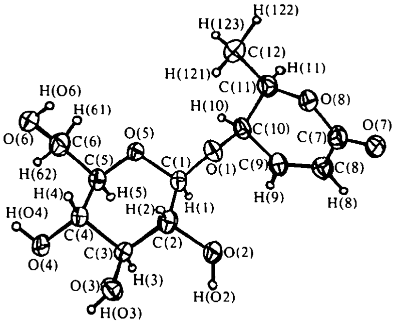

Fig. 1. A perspective view of the molecular structure with the atom-numbering scheme.

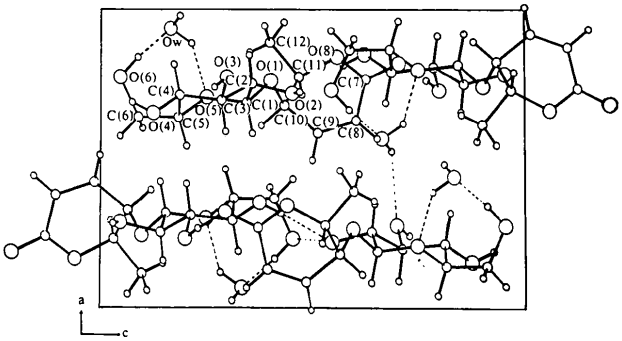

Fig. 2. A packing diagram (projection onto the *ac* plane). Dashed lines indicate hydrogen bonding.

located from an *E* map. Full-matrix isotropic least-squares refinement gave an *R* value of 0·154. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with the weighting scheme given by Stout & Jensen (1968). After three cycles of least-squares refinement with anisotropic thermal parameters for all non-H atoms, which gave an *R* value of 0·079, a difference Fourier synthesis revealed all the H atoms. The final refinement with anisotropic thermal parameters for non-H atoms and isotropic thermal parameters for H atoms led to $R = 0{\cdot}038$ and $R_w = 0{\cdot}045$, where $R = \sum \| F_o| - |F_c\| / \sum |F_o|$ and $R_w = \sum w(|F_o| - |F_c|)^2 / \sum wF_o^2$. The scattering factors were all taken from *International Tables for X-ray Crystallography* (1962).*

The final atomic coordinates are listed in Tables 1 and 2. A perspective view of the molecule with the atom-numbering scheme is shown in Fig. 1. Fig. 2 shows the crystal packing viewed along **b**.

Discussion. The bond distances and angles involving non-H atoms are given in Table 3. The bond lengths and angles of the glucose residue are within the range typically found in carbohydrates (Fries, Rao & Sundaralingam, 1971; Jeffrey, Pople & Radom, 1974). The C—C distances range from 1·511 to 1·529 Å [mean 1·521 (8) Å]. The exocyclic C—O distances, excluding the anomeric C—O bond, fall in the range 1·412–1·428 Å. The anomeric and bridge C—O bonds, 1·402 (4) and 1·444 (4) Å respectively, are similar to the corresponding bonds in cellobiose (Chu & Jeffrey, 1968).

Table 3. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

C(1)–C(2)	1·520 (5)	C(2)–C(3)	1·511 (5)
C(3)–C(4)	1·529 (4)	C(4)–C(5)	1·529 (5)
C(5)–C(6)	1·518 (5)	C(7)–C(8)	1·472 (5)
C(8)–C(9)	1·336 (5)	C(9)–C(10)	1·506 (5)
C(10)–C(11)	1·510 (5)	C(11)–C(12)	1·500 (6)
C(1)–O(1)	1·402 (4)	O(1)–C(10)	1·444 (4)
C(2)–O(2)	1·426 (4)	C(3)–O(3)	1·426 (5)
C(4)–O(4)	1·412 (4)	C(6)–O(6)	1·428 (6)
C(7)–O(7)	1·218 (4)	C(1)–O(5)	1·429 (4)
C(5)–O(5)	1·450 (4)	C(7)–O(8)	1·337 (4)
C(11)–O(8)	1·462 (4)		

O(5)–C(1)–C(2)	110·6 (3)	O(5)–C(1)–O(1)	106·3 (3)
C(2)–C(1)–O(1)	108·0 (3)	C(1)–C(2)–C(3)	111·0 (3)
C(1)–C(2)–O(2)	105·8 (3)	C(3)–C(2)–O(2)	111·9 (3)
C(2)–C(3)–O(3)	105·7 (3)	C(2)–C(3)–C(4)	110·2 (3)
C(4)–C(3)–O(3)	112·4 (3)	C(3)–C(4)–C(5)	107·9 (2)
C(2)–C(4)–O(4)	107·6 (2)	C(5)–C(4)–O(4)	111·6 (3)
C(4)–C(5)–O(5)	107·9 (3)	C(4)–C(5)–C(6)	115·3 (3)
C(6)–C(5)–O(5)	107·3 (3)	C(5)–C(6)–O(6)	114·0 (3)
C(5)–O(5)–C(1)	111·5 (3)	C(1)–O(1)–C(10)	113·5 (3)
O(1)–C(10)–C(9)	108·5 (3)	O(1)–C(10)–C(11)	109·2 (3)
C(9)–C(10)–C(11)	110·7 (3)	C(8)–C(9)–C(10)	120·0 (4)
C(7)–C(8)–C(9)	120·8 (3)	O(8)–C(7)–C(8)	119·0 (3)
O(8)–C(7)–O(7)	118·6 (3)	C(8)–C(7)–O(7)	122·3 (3)
C(7)–O(8)–C(11)	119·6 (3)	C(10)–C(11)–C(12)	115·0 (3)
C(10)–C(11)–O(8)	111·8 (3)	O(8)–C(11)–C(12)	106·3 (3)

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36165 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. *Displacements* (Å) *from a least-squares plane*

Estimated errors are in parentheses. The equation of the plane is in the form: $lx + my + nz = p$, where x, y, z are fractional atomic coordinates and p is the distance of the plane from the unit-cell origin. Asterisks indicate atoms included in the calculation of the equation.

$$4{\cdot}083X + 9{\cdot}417Y + 1{\cdot}662Z = 6{\cdot}844\ (\chi^2 = 5554)$$

C(7)*	−0·043 (4)	C(8)*	0·090 (4)
C(9)*	−0·016 (2)	O(8)*	0·153 (4)
C(10)*	−0·074 (3)	O(7)*	−0·166 (4)
C(11)	0·581 (4)		

Table 6. *Hydrogen-bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

	O···O	H···O	∠O–H···O
O(*W*)–H(O*W*2)···O(3)$^{(b)}$	2·851 (5)	2·45 (6)	110 (5)
O(*W*)–H(O*W*1)···O(5)$^{(a)}$	2·879 (5)	2·41 (6)	113 (5)
O(5)–H(O6)···O(*W*)$^{(a)}$	2·755 (5)	1·82 (5)	165 (5)
O(2)–H(O2)···O(6)$^{(c)}$	2·705 (4)	1·84 (5)	161 (5)
O(4)–H(O4)···O(2)$^{(d)}$	2·798 (4)	1·98 (5)	175 (6)
O(3)–H(O3)···O(7)$^{(d)}$	2·806 (4)	1·98 (5)	171 (5)

Symmetry codes: (*a*) x, y, z; (*b*) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (*c*) $\frac{3}{2} - x, -y, \frac{1}{2} + z$; (*d*) $\frac{3}{2} - x, -y, -\frac{1}{2} + z$.

The unsaturated lactone group, C—C=C—C(=O)—O—C, is roughly planar (Table 4). The lengths of the asymmetric C—O bonds are unequal, 1·337 (4) and 1·462 (4) Å, with the shorter one being adjacent to the carbonyl group. This is a feature encountered in many lactones (Fridrichsons & Mathieson, 1962; Mathieson, 1963; Jeffrey, Rosenstein & Vlasse, 1967; Berman, Rosenstein & Southwick, 1971). C(7)—C(8) is only slightly longer than O(8)—C(11). In view of the rough planarity of the group, this suggests that there might be electron delocalization between the two adjacent double bonds, which increases the bond order of C(7)—C(8) and draws O(8) toward the carbonyl carbon.

The absolute configuration of the molecule was not determined in the present analysis. Nevertheless, it has been suggested, from the negative Cotton effect at 273 nm in its circular dichroic spectra and the coupling constant of ^{1}H NMR spectra, that it has the relative stereochemistry shown in Fig. 1 (Chen, 1981). The conformation of the pyranoid ring is a $^4C_1$ chair. The Cremer & Pople (1975) puckering parameters and endocyclic torsional angles are shown in Table 5. The total puckering amplitude, $Q = 0{\cdot}597$ Å, is greater than that of the pyranoid ring in sucrose and is close to the value for an ideal cyclohexane chair (Cremer & Pople, 1975). φ_2 is −64·8°, which indicates that the distortion is in the direction of a twist-boat. The conformation of the hydroxymethyl group is *gauche–gauche* with torsional angles C(4)—C(5)—C(6)—O(6) = 48·9 (4)° and O(5)—C(5)—C(6)—O(6) = −71·4 (4)°.

Table 5. *Torsional angles and Cremer–Pople puckering parameters with e.s.d.'s in parentheses*

(*a*) Torsional angles (°)

O(5)–C(1)–C(2)–C(3)	53·9 (4)	C(7)–C(8)–C(9)–C(10)	1·9 (6)
C(1)–C(2)–C(3)–C(4)	−52·7 (4)	C(8)–C(9)–C(10)–C(11)	27·5 (5)
C(2)–C(3)–C(4)–C(5)	56·8 (4)	C(9)–C(10)–C(11)–O(8)	−47·4 (4)
C(3)–C(4)–C(5)–O(5)	−62·2 (3)	C(10)–C(11)–O(8)–C(7)	41·9 (4)
C(4)–C(5)–O(5)–C(1)	65·7 (3)	C(11)–O(8)–C(7)–C(8)	−12·2 (5)
C(5)–O(5)–C(1)–C(2)	−61·2 (4)	O(8)–C(7)–C(8)–C(9)	−11·2 (6)

(*b*) Puckering parameters [calculated according to Cremer & Pople (1975)]. The sequences are O(5), C(1), C(2), C(3), C(4), C(5) for the glucose residue and O(8), C(7), C(8), C(9), C(10), C(11) for the lactone ring.

Glucose residue		Unsaturated lactone ring	
$q_2 = 0{\cdot}071$ Å	$\varphi_2 = -64{\cdot}8°$	$q_2 = 0{\cdot}355$ Å	$\varphi_2 = -77{\cdot}4°$
$q_3 = 0{\cdot}593$	$\theta = 6{\cdot}8$	$q_3 = 0{\cdot}187$	$\theta = 62{\cdot}2$
$Q = 0{\cdot}597$		$Q = 0{\cdot}401$	

The conformation of the aglucone is close to a half-boat due to the presence of the unsaturated lactone group. The 'spherical polar set' of puckering parameters have the values $\theta = 62{\cdot}2°$ and $\varphi = -77{\cdot}4°$. The out-of-plane deviation of C(11) from the plane of the lactone group is 0·581 (4) Å (Table 4).

The twists about the bridge bonds C(1)—O(1) and O(1)—C(10) are highly asymmetrical with φ_1 and φ_2 being −90·2 (3) and 162·4 (3)°, respectively, as compared with a fully extended conformation in a carbohydrate (φ_1 and φ_2 close to −110 and 110° respectively) (Fries, Rao & Sundaralingam, 1971). The twists generate a nonpolar surface on one side of the molecule such that no H bonds are formed among molecules in the **b** direction.

A list of H-bond distances and angles about H is given in Table 6. There are no intramolecular H bonds and none are bifurcated. The mean O···O distance is 2·80 (6) Å. Except for O(1) and O(8), all O atoms are involved in H bonding.

The molecules are oriented in the cell with their long axes parallel to the twofold screw axes in the **c** direction (Fig. 2). The water molecules are embedded between molecular planes parallel to the *bc* plane. There are no H bonds between the molecules related by the twofold screw symmetry in the **b** direction. The packing thus appears to be governed by van der Waals interactions in one direction and H bonding in the others.

I thank Professor C. M. Chen for providing the crystal for the study.

References

Benn, M. H. & Yelland, L. J. (1968). *Can. J. Chem.* **46**, 729–732.

Berman, H. M., Rosenstein, R. D. & Southwick, J. (1971). *Acta Cryst.* B**27**, 7–10.

Chen, C. M. (1981). To be published.

Chu, S. S. C. & Jeffrey, G. A. (1968). *Acta Cryst.* B**24**, 830–838.

Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

Fridrichsons, J. & Mathieson, A. McL. (1962). *Acta Cryst.* **15**, 119–128.

Fries, D. C., Rao, S. T. & Sundaralingam, M. (1971). *Acta Cryst.* B**27**, 994–1005.

Germain, G., Main, P. & Woolfson, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

Hill, R. & Van Heyningen, R. (1951). *Biochem. J.* **49**, 332–337.

Hollenbeak, K. H. & Kuehne, M. E. (1974). *Tetrahedron*, **30**, 2307–2316.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

Jeffrey, G. A., Pople, J. A. & Radom, L. (1974). *Carbohydr. Res.* **38**, 81–95.

Jeffrey, G. A., Rosenstein, R. D. & Vlasse, M. (1967). *Acta Cryst.* **22**, 725–733.

Mathieson, A. McL. (1963). *Tetrahedron Lett.* **2**, 81–84.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Reynolds, T. (1975). *Chem. Ind.* (*London*), **19**, 603–605.

Stout, G. H. & Jensen, L. H. (1968). *X-ray Structure Determination*, p. 457. London: Macmillan.

Tschesche, R., Hoppe, H.-J., Snatzke, G., Wulff, G. & Fehlhaber, H.-W. (1971). *Chem. Ber.* **104**, 1420–1428.

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Acetamide Hemihydrochloride, by Neutron Diffraction at 120 K

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Abstract. $C_2H_5NO.\frac{1}{2}HCl$, monoclinic, $P2_1/c$, $Z = 4$, $a = 6{\cdot}291\ (6)$, $b = 8{\cdot}300\ (7)$, $c = 7{\cdot}931\ (8)$ Å, $\beta = 113{\cdot}43\ (4)°$, $V = 380{\cdot}0$ Å^3, $D_c = 1{\cdot}35$ Mg m^{-3}. $R = 0{\cdot}038$, $R_w = 0{\cdot}023$ for 882 reflexions. Room-temperature X-ray work has verified [Muir & Speakman (1979). *J. Chem. Res.* (*M*), pp. 3401–3424; (*S*), p. 277] the crystallographically symmetrical cation $[C_2H_5NO\cdots H\cdots ONC_2H_5]^+$ and found $O\cdots O$ to be 2·451 (1) Å. Low-temperature neutron diffraction work now finds 2·426 (3) Å, which is significantly shorter. Inter- and intramolecular vibrations have also been analysed.

Introduction. Carboxylic acids, H*X*, often form acid salts of compositions such as *MX*.H*X*, where *M* is a univalent metal. Some have structures of type *A* (Speakman, 1972): they have crystallographically symmetrical XHX^- anions embodying 'very short' OHO bonds (*e.g.* Bacon, Walker & Speakman, 1977). Organic bases, *B*, sometimes form analogous, type *A* basic salts, such as the chloride $BHB^+.Cl^-$ with a similarly symmetrical cation. The simplest example, and the first to be discovered, is acetamide hemihydrochloride (AHHCl). This compound is properly represented by the formula $[C_2H_5NO\cdots H\cdots ONC_2H_5]^+.Cl^-$, with each ion centred on a point of inversion, as was found by diffraction work with X-rays (Hughes & Takei, 1955) and with neutrons (Peterson & Worsham, 1959). Details of these early analyses were never published.

The preparation of AHHCl from aqueous solution was described by Muir & Speakman (1979). Crystals large enough for neutron diffraction (ND) work are hard to grow because, in acid solution, acetamide is rapidly decomposed to acetic acid and ammonium chloride. However, some large single crystals of moderate quality were grown at Oslo. Pieces cut from these were studied on the D9 diffractometer at the ILL, Grenoble. Two sets of data were collected. They led to almost identical atomic coordinates. We preferred the

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