and B(1) and B(2) lie close [max. deviation 0·101 (7) Å] to the mean planes, between which the dihedral angle is 68°. The bond angle at O(2), on the local twofold axis and bridging the B_{tet} atoms, is 110·2 (3)°, compared with 118·0 to 118·6 (3)° at the other bridging O atoms. The B—O bond lengths are 1·449 to 1·500 (5) Å (av. 1·475 Å) for B_{tet} and 1·356 to 1·385 (5) Å (av. 1·369 Å) for B_{trig}. These dimensions agree well with those reported in recent years for the same anion in $Mg[B_4O_5(OH)_4].7H_2O$ (Che'ng Wan & Ghose, 1977), $K_2Ca[B_4O_5(OH)_4]_2.8H_2O$ (Sokolova, Yamnova, Simonov & Belov, 1979), and $(NH_4)_2[B_4O_5(OH)_4].2H_2O$ (Janda, Heller & Pickardt, 1981). The H atoms lie at 0·88 to 1·04 Å from O and 0·87 to 1·01 Å from N (bond lengths were not refined). With the exception of N(4)—H(12) and N(5)—H(13), the *X*—H bonds are closely directed towards a non-bonded near neighbour of the parent atom, the *X*—H···*Y* angles ranging from 152 to 177°. The network of hydrogen bonds includes interanion bonds, O(1)···O(9), O(5)···O(2), and O(9)···O(5). Each terminal (OH) oxygen atom of the anion is the donor in one and the acceptor in one or two hydrogen bonds; each bridging O is the acceptor in one or two bonds; each water molecule is the acceptor in two and the donor in two bonds; and each N atom is the donor in one of two bonds.

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Structure of Decentapicrin A: (—)-(4a*S*)-6-[3′-*O*-(3-Hydroxybenzoyl)-*β*-D-glucopyranosyloxy]-5-vinyl-4,4aα,5*β*,6α-tetrahydro-1*H*,3*H*-pyrano[3,4-*c*]pyran-1-one, $C_{23}H_{26}O_{11}$

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Abstract. $M_r = 478·45$, orthorhombic, $P2_12_12_1$, $a = 5·8234\ (6)$, $b = 12·512\ (2)$, $c = 31·693\ (5)$ Å, $U = 2309·2\ (6)$ Å^3, $Z = 4$, $D_x = 1·376$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0·69$ cm^{-1}, $F(000) = 1008$, $T = 294$ K. $R = 0·052$ for 1088 observed reflexions. The δ-lactone and pyran rings of the secoiridoid moiety exhibit puckered conformations which can be approximated to an envelope shape with C(6) and C(9) serving as the flaps. The β-glucose moiety occurs in the chair, $^4C_1$, conformation. The molecular packing is dominated by intermolecular hydrogen bonds. A spiral chain is formed along **a** through the bifurcated hydrogen bonds between sugar and secoiridoid moieties [O(2′)—H···O(7), 3·00 (1) and O(2′)—H···O(11), 3·16 (1) Å]. Sugar – *m*-hydroxybenzoyl interactions take part in the formation of a double spiral along **b** [O(4″)—H···O(4′), 2·79 (1); O(6′)—H···O(1″), 2·75 (1) Å] and also in bridging the spirals running in the perpendicular directions (along **a** and **b**) [O(6′)—H···O(1″), 2·75 (1) Å]. Hydrogen bond O(6′)—H···O(4″), 3·19 (1) Å, is a part of the connexion along **a**. Sugar – sugar contact O(4′)—H···O(6′), 2·65 (1) Å, connects double spiral chains into a layer (*ab* plane).

Introduction. Decentapicrin A ($I_{3'}$), a natural acyl secoiridoid glucoside isolated from flower tops of *Centaurium littorale* (Gentianaceae) (van der Sluis & Labadie, 1981) and *Centaurium linariifolium* (Seoane, 1984), and detected in the fruits of *Centaurium chloodes* and *Centaurium scilloides* (van der Sluis &

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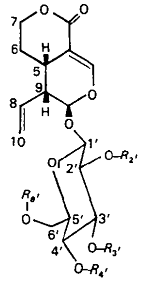
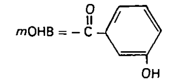
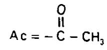
Labadie, 1984), proved to be of chemosystematical importance (van der Sluis & Labadie, 1984). The configuration was elucidated by means of mass, ^{1}H and ^{13}C NMR spectroscopical methods (van der Sluis & Labadie, 1981).



		$R_{2'}$	$R_{3'}$	$R_{4'}$	$R_{6'}$
I	Sweroside	H	H	H	H
$I_{2'a}$	Centapicrin	mOHB	Ac	H	H
$I_{2'}$	Desacetylcentapicrin	mOHB	H	H	H
$I_{3'}$	Decentapicrin A	H	mOHB	H	H
$I_{4'}$	Decentapicrin B	H	H	mOHB	H
$I_{6'}$	Decentapicrin C	H	H	H	mOHB





$\mathrm{Ac} = -\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$

Unlike the closely related centapicrin ($I_{2'a}$) and desacetylcentapicrin ($I_{2'}$), both esterified at C(2')—OH of the glucose moiety and accumulating in the fruits of *Centaurium erythraea,* decentapicrin A is only a weak bitter principle like sweroside (I) and decentapicrin B ($I_{4'}$) and C ($I_{6'}$) (van der Sluis & Labadie, 1981).

Only a few X-ray studies have been carried out on iridoids (Ballesia, Pagnoni, Trave, Andreetti, Bocelli & Sgarabotto, 1979) and on conversion products of secoiridoid aglucones (Suhr, Arends & Jensen, 1978; Spek, Duisenberg, van der Sluis, van der Nat & Labadie, 1983). In order to determine the conformation of decentapicrin A, an X-ray structure analysis was undertaken.

Experimental. Crystals of reasonable quality obtained by recrystallization from chloroform. Intensities collected on an Enraf–Nonius CAD-4F diffractometer, $\omega/2\theta$ scan mode ($\theta_{\max} = 23°$), Zr-filtered Mo $K\alpha$ radiation, aiming at a constant $\sigma(I)/I$ ratio of 0·01; crystal dimensions 0·075 × 0·125 × 0·625 mm; 1905 independent reflexions ($0 < h < 6$, $0 < k < 13$, $0 < l < 34$) of which 1088 [$I > 1{\cdot}5\sigma(I)$] used in calculations; one reference reflexion (019) showed variation <1% in intensity over 26 h of exposure time; cell constants derived by least squares from diffractometer settings of 18 reflexions. No correction for absorption. Structure solved by *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) (based on 286 reflexions having $E \geq 1{\cdot}43$) revealing 31 atoms out of 34 in the molecule. A subsequent difference synthesis located remaining atoms. The H atoms of four hydroxyl groups and three of the vinyl residue were located in a difference Fourier map; other H atoms were introduced at calculated positions and refined in the riding mode on their carrier atoms. Least-squares technique minimizing $\sum w\Delta F^2$ with $w = 1$ used. Scale factor, atomic coordinates of non-H atoms and of those H located from map [H(O2'), H(O4'), H(O6'), H(O4''), H(8), H(101), H(102)], anisotropic thermal parameters for non-H atoms and overall thermal parameters for H atoms were refined. The geometry of H(8) was poor during the refinement process and in the final cycles a constraint on the C(8)—H(8) distance was applied. $(\Delta/\sigma)_{\max}$ on coordinates in final refinement cycle 0·09 [for z of C(10)]; anisotropic thermal parameters in usual range; final $R = 0{\cdot}052$, $wR = 0{\cdot}053$, $S = 1{\cdot}47$; max. and min. residual densities 0·09 and $-0{\cdot}09$ e Å^{-3}; scattering factors from Cromer & Mann (1968) and (for H) Stewart, Davidson & Simpson (1965). Calculations carried out on the in-house DG-Eclipse S/230 minicomputer using programs of the *ILIAS* package [an adaptation and extension by ALS of the *SHELX*76 package (Sheldrick, 1976)], or the CDC-CYBER 175 of the University of Utrecht with programs of the *EUCLID* package (calculation of geometrical data and preparation of illustrations) including an extended version of the program *PLUTO* (Spek, 1982).

Discussion. Final atomic parameters are given in Table 1;* bond distances, angles, selected torsion angles describing the conformation of the molecule and hydrogen-bond geometry are listed in Table 2. A *PLUTO* drawing of the molecule with the atomic-numbering scheme is shown in Fig. 1. The molecular packing is illustrated in Fig. 2.

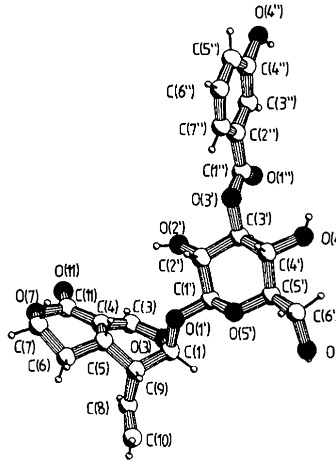


Fig. 1. A *PLUTO* drawing of the molecule with the atom numbering. The H atoms are named according to their carrier atoms. Their labels are omitted.

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* Lists of structure factors, anisotropic thermal parameters, coordinates of the H atoms, bond distances and angles involving H atoms, and bond distances and angles of the *m*-hydroxybenzoyl moiety have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39785 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Secoiridoid moiety. A δ-lactone ring fused to pyran forms the sweroside type of secoiridoid moiety. Bond distances deviating from standard values (required by the atom type and hybridization) are mostly influenced by the conjugation effect. The C—O bonds involving C(sp^2) are shorter than those with C(sp^3) and an asymmetry in bond lengths is present [C(1)—O(3), 1·44 (1); C(3)—O(3), 1·35 (1); C(7)—O(7), 1·43 (1);

Table 1. *Final atomic coordinates* (×10⁴) *and equivalent isotropic thermal parameters* (×10²) *for non*-H *atoms*

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a^*_i a^*_j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}(Å^2)
O(3)	2500 (11)	422 (5)	9021 (2)	5·5 (2)
O(7)	3035 (14)	1192 (6)	10494 (2)	8·4 (2)
O(11)	102 (13)	1788 (6)	10126 (3)	8·8 (2)
O(1′)	6302 (11)	986 (4)	8966 (2)	4·3 (2)
O(1″)	4011 (13)	5024 (6)	8043 (3)	9·2 (2)
O(2′)	4448 (11)	3094 (5)	8887 (2)	5·3 (2)
O(3′)	7203 (11)	4396 (4)	8345 (2)	4·5 (2)
O(4′)	8162 (12)	3292 (4)	7552 (2)	5·2 (2)
O(4″)	5232 (14)	8998 (5)	8003 (2)	6·6 (2)
O(5′)	8027 (11)	1163 (4)	8332 (2)	4·3 (2)
O(6′)	9484 (12)	90 (5)	7540 (2)	6·3 (2)
C(1)	4862 (17)	83 (7)	9002 (3)	4·3 (2)
C(3)	1798 (16)	848 (7)	9389 (3)	5·4 (2)
C(4)	3050 (16)	853 (7)	9751 (3)	4·7 (2)
C(5)	5357 (16)	358 (6)	9768 (3)	4·2 (2)
C(6)	5757 (18)	−88 (8)	10208 (3)	6·0 (2)
C(7)	5347 (19)	814 (9)	10512 (3)	7·7 (2)
C(8)	4222 (20)	−1486 (7)	9472 (3)	7·2 (2)
C(9)	5626 (16)	−465 (6)	9409 (3)	4·5 (2)
C(10)	5182 (25)	−2420 (10)	9443 (6)	11·5 (3)
C(11)	1992 (18)	1319 (8)	10123 (3)	6·2 (2)
C(1′)	6157 (15)	1522 (7)	8572 (3)	4·2 (2)
C(1″)	5824 (17)	5152 (8)	8203 (3)	5·3 (2)
C(2′)	6419 (15)	2707 (6)	8671 (2)	3·4 (2)
C(2″)	6790 (16)	6255 (7)	8292 (3)	3·9 (2)
C(3′)	6526 (17)	3304 (6)	8249 (2)	4·3 (2)
C(3″)	5506 (18)	7099 (6)	8128 (3)	4·8 (2)
C(4′)	8337 (16)	2840 (6)	7965 (3)	3·7 (2)
C(4″)	6385 (17)	8137 (7)	8164 (3)	4·7 (2)
C(5′)	8060 (16)	1639 (6)	7922 (3)	3·6 (2)
C(5″)	8464 (16)	8329 (7)	8368 (3)	5·0 (2)
C(6′)	9983 (17)	1137 (7)	7672 (3)	5·0 (2)
C(6″)	9637 (18)	7476 (7)	8528 (3)	5·8 (2)
C(7″)	8875 (17)	6430 (7)	8494 (3)	4·8 (2)

The atoms marked with ′ belong to the pyranose moiety and those with ″ to the *m*-hydroxybenzoyl one.

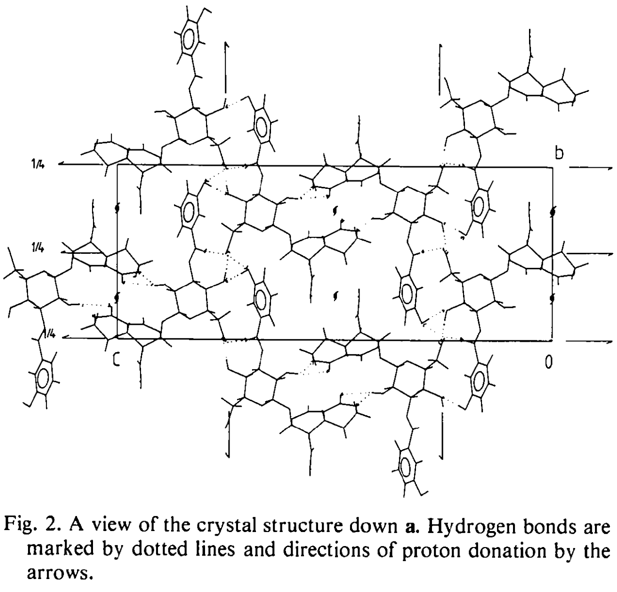

Fig. 2. A view of the crystal structure down **a**. Hydrogen bonds are marked by dotted lines and directions of proton donation by the arrows.

Table 2. *Bond distances* (Å), *bond angles* (°), *torsion angles* (°) *and hydrogen-bond geometry*

Secoiridoid moiety

C(1)–O(1′)	1·41 (1)	C(5)–C(9)	1·54 (1)
C(1)–O(3)	1·44 (1)	C(6)–C(7)	1·50 (1)
C(1)–C(9)	1·53 (1)	C(7)–O(7)	1·43 (1)
C(3)–O(3)	1·35 (1)	C(8)–C(9)	1·53 (1)
C(3)–C(4)	1·36 (1)	C(8)–C(10)	1·30 (2)
C(4)–C(5)	1·48 (1)	C(11)–O(7)	1·33 (1)
C(4)–C(11)	1·45 (1)	C(11)–O(11)	1·25 (1)
C(5)–C(6)	1·52 (1)		

O(1′)–C(1)–O(3)	109·6 (7)	C(5)–C(6)–C(7)	106·7 (8)
O(1′)–C(1)–C(9)	104·8 (7)	C(6)–C(7)–O(7)	111·9 (9)
O(3)–C(1)–C(9)	112·1 (7)	C(7)–O(7)–C(11)	120·2 (8)
O(3)–C(3)–C(4)	124·7 (8)	C(9)–C(8)–C(10)	121 (1)
C(1)–O(3)–C(3)	116·2 (7)	C(1)–C(9)–C(5)	107·0 (6)
C(3)–C(4)–C(5)	121·1 (8)	C(1)–C(9)–C(8)	109·2 (8)
C(3)–C(4)–C(11)	117·3 (9)	C(5)–C(9)–C(8)	114·0 (7)
C(5)–C(4)–C(11)	121·5 (8)	C(4)–C(11)–O(7)	118·4 (9)
C(4)–C(5)–C(6)	109·1 (7)	C(4)–C(11)–O(11)	124·7 (9)
C(4)–C(5)–C(9)	110·2 (7)	O(7)–C(11)–O(11)	116·8 (9)
C(6)–C(5)–C(9)	114·6 (7)		

C(3)–O(3)–C(1)–O(1′)	−75·4 (9)	O(3)–C(3)–C(4)–C(11)	−178·1 (8)
C(3)–O(3)–C(1)–C(9)	41 (1)	C(3)–C(4)–C(5)–C(6)	−148·0 (9)
C(1)–O(3)–C(3)–C(4)	−9 (1)	C(3)–C(4)–C(5)–C(9)	−21 (1)
C(11)–O(7)–C(7)–C(6)	−42 (1)	C(11)–C(4)–C(5)–C(6)	29 (1)
C(7)–O(7)–C(11)–O(11)	−170·4 (9)	C(5)–C(4)–C(11)–O(7)	−7 (1)
C(7)–O(7)–C(11)–C(4)	13 (1)	C(4)–C(5)–C(6)–C(7)	−54 (1)
O(3)–C(1)–C(9)–C(8)	63·2 (9)	C(9)–C(5)–C(6)–C(7)	−178·2 (8)
O(1′)–C(1)–C(9)–C(8)	−178·0 (7)	C(4)–C(5)–C(9)–C(1)	49·4 (9)
O(3)–C(3)–C(4)–C(5)	−1 (1)		

β-Glucopyranose moiety

C(1′)–O(1′)	1·42 (1)	C(3′)–C(4′)	1·50 (1)
C(1′)–O(5′)	1·40 (1)	C(4′)–O(4′)	1·43 (1)
C(1′)–C(2′)	1·52 (1)	C(4′)–C(5′)	1·52 (1)
C(2′)–O(2′)	1·42 (1)	C(5′)–O(5′)	1·43 (1)
C(2′)–C(3′)	1·53 (1)	C(5′)–C(6′)	1·51 (1)
C(3′)–O(3′)	1·45 (1)	C(6′)–O(6′)	1·41 (1)

O(1′)–C(1′)–C(2′)	105·9 (6)	C(3′)–O(3′)–C(1″)	116·0 (7)
O(1′)–C(1′)–O(5′)	106·3 (7)	C(3′)–C(4′)–O(4′)	110·2 (7)
C(2′)–C(1′)–O(5′)	110·2 (7)	C(3′)–C(4′)–C(5′)	111·3 (7)
C(1)–O(1′)–C(1′)	114·5 (6)	O(4′)–C(4′)–C(5′)	107·5 (6)
C(1′)–C(2′)–O(2′)	110·5 (7)	C(4′)–C(5′)–O(5′)	109·4 (6)
C(1′)–C(2′)–C(3′)	107·4 (6)	C(4′)–C(5′)–C(6′)	112·4 (7)
C(3′)–C(2′)–O(2′)	106·6 (7)	O(5′)–C(5′)–C(6′)	108·3 (7)
C(2′)–C(3′)–O(3′)	106·8 (6)	C(1′)–O(5′)–C(5′)	111·8 (6)
C(2′)–C(3′)–C(4′)	111·2 (7)	C(5′)–C(6′)–O(6′)	113·1 (8)
O(3′)–C(3′)–C(4′)	107·3 (7)		

C(1′)–O(1′)–C(1)–C(9)	169·9 (7)	C(2′)–C(3′)–C(4′)–C(5′)	51·6 (9)
C(1′)–O(1′)–C(1)–O(3)	−69·6 (8)	C(2′)–C(3′)–O(3′)–C(1″)	−125·2 (8)
O(1′)–C(1′)–C(2′)–C(3′)	174·2 (7)	C(4′)–C(3′)–O(3′)–C(1″)	115·5 (8)
O(5′)–C(1′)–C(2′)–O(2′)	175·5 (6)	O(4′)–C(4′)–C(5′)–C(6′)	64·6 (9)
O(5′)–C(1′)–C(2′)–C(3′)	59·6 (9)	C(3′)–C(4′)–C(5′)–O(5′)	−54·3 (9)
O(2′)–C(2′)–C(3′)–C(4′)	−171·2 (7)	C(3′)–C(4′)–C(5′)–C(6′)	−174·6 (7)
C(1′)–C(2′)–C(3′)–O(3′)	−169·6 (7)	C(4′)–C(5′)–C(6′)–O(6′)	−165·2 (7)
C(1′)–C(2′)–C(3′)–C(4′)	−52·8 (9)	C(1′)–O(5′)–C(5′)–C(4′)	62·3 (9)
O(3′)–C(3′)–C(4′)–C(5′)	168·1 (6)	C(5′)–O(5′)–C(1′)–C(2′)	−66·4 (8)
C(2′)–C(3′)–C(4′)–O(4′)	170·8 (7)		

Hydrogen-bond geometry

D–H···*A*	*D*···*A*	*D*–H	H···*A*	*D*–H···*A*
O(4″)–H(O4″)···O(4′^{i})	2·79 (1)Å	0·90 (5)Å	1·89 (5)Å	175 (5)°
O(2′)–H(O2′)···O(7^{ii})	3·00 (1)	0·86 (7)	2·41 (5)	127 (4)
O(2′)–H(O2′)···O(11^{ii})	3·16 (1)	0·86 (7)	2·31 (7)	169 (4)
O(4′)–H(O4′)···O(6′^{iii})	2·65 (1)	0·81 (5)	1·85 (4)	171 (6)
O(6′)–H(O6′)···O(1″^{iv})	2·75 (1)	1·01 (3)	2·03 (7)	126 (6)
O(6′)–H(O6′)···O(4″^{v})	3·19 (1)	1·01 (3)	2·46 (6)	128 (6)

Symmetry code: (i) $1-x$, $\frac{1}{2}+y$, $\frac{3}{2}-z$; (ii) $\frac{1}{2}+x$, $\frac{1}{2}-y$, $2-z$; (iii) $2-x$, $\frac{1}{2}+y$, $\frac{3}{2}-z$; (iv) $1-x$, $-\frac{1}{2}+y$, $\frac{3}{2}-z$; (v) x, $y-1$, z.

C(11)—O(7), 1·33 (1) Å]. The longer C—O bonds of the endocyclic type do not show any difference from the exocyclic one [C(1)—O(1′), 1·41 (1) Å]. The analogous bonds of the lactone group in the secoiridoid dilactone gentiolactone (Suhr *et al.*, 1978) are comparable to these values. The large endocyclic C—O(7)—C angle [120·2 (8)°] associated with δ-lactones can be compared with the values found in gentiogenal [119·5 (3)°] (Spek *et al.*, 1983), gentiolactone [118·9, 123·2 (molecule *A*); 118·4, 121·3° (molecule *B*)] (Suhr *et al.*, 1978), and other δ-lactones, *e.g.* *cis*-10-methyl-1-oxadecalin-2,5-dione [123·8 (2)°] (Dubourg, Roques & Guy, 1979). The C(7) atom is displaced 0·28 (1) Å from the plane through the atoms C(4), O(7), C(11). The smallest ring torsion angle of −7 (1)° is about C(4)—C(11) which on both sides involves C(sp^2). The torsion angles about two contiguous bonds are 13 (1) and 29 (1)°. Other angles ranging from 48 (1) to 63 (1)° illustrate the puckered conformation (Table 2). The participation of both lactone O atoms in the hydrogen bonds (Table 2) and the ring fusion influence the ring puckering. The least-squares planes of the two fused rings of the secoiridoid moiety make a dihedral angle of 4·1 (4)°. The values of the Cremer & Pople (1975) ring-puckering analysis [for the sequence O(7), C(7), C(6), C(5), C(4), C(11)] are $\theta = 47$ (1), $\varphi = 111$ (1)°, $Q = 0{\cdot}51$ (1) Å. The pyran ring conformation is of a similar type to that of the δ-lactone ring. The largest cyclic torsion angles are about the bonds of C(9) [−60·7 (9), 49·4 (9)°]. The parameters of the ring-puckering analysis (Cremer & Pople, 1975) [for the sequence O(3), C(1), C(9), C(5), C(4), C(3)] are $\theta = 129$ (1), $\varphi = 285$ (1)°, $Q = 0{\cdot}50$ (1) Å. Both rings exhibit a similar type of conformation being between a half-chair and an envelope. It can also be approximated to an envelope shape with C(6) and C(9) as the flaps (Fig. 1). The vinyl group attached at C(9) is not folded over the pyran ring; it shows an extended conformation [O(1′)—C(1)—C(9)—C(8), −178·0 (7)°]. The conformation around the O(1′) glycosidic bond is defined by the torsion angle 169·9 (7)° for the atom sequence C(1′)—O(1′)—C(1)—C(9).

Glucopyranose moiety. During the structure determination of this natural compound the enantiomer with the D-glucopyranose moiety was selected. The C—C bond distances are in the range 1·50 (1)–1·53 (1) Å. The endo- and exocyclic C—O bonds, with differences in the range of 3σ, are comparable (Table 2). The crystal quality prevents a more accurate structure determination which might reveal some specialities of the molecular geometry, particularly of the anomeric bond. The endocyclic angle C—O—C of 111·8 (6)° is smaller than the exocyclic ones carrying the bulky substituents [C(1′)—O(1′)—C(1), 114·5 (6); C(3′)—O(3′)—C(1″), 116·0 (7)°]. The angles involving ring C atoms range from 107·4 (6) to 111·3 (7)°. The values of exocyclic angles involving C and O atoms are scattered in a somewhat larger range [105·9 (6)–110·5 (7)°]. The O(4′) and O(6′) hydroxyl groups participate in hydrogen bonding, as both donors and acceptors, whereas O(2′) serves as a donor only. The β-D-glucopyranose moiety exhibits the characteristic chair, $^4C_1$, conformation. The values of the ring torsion angles are in agreement with the values found in the β-glucopyranose residue of β-maltose monohydrate (Gress & Jeffrey, 1977). Deviations from the least-squares plane [O(5′), C(2′), C(3′), C(5′)] of C(4′) [0·64 (1) Å] and C(1′) [−0·70 (1) Å] also give evidence for the almost symmetrical $^4C_1$ conformation. The Cremer & Pople (1975) criteria give values for the puckering parameters [$\theta = 5{\cdot}7$ (8), $\varphi = 38$ (1)°, $Q = 0{\cdot}580$ (9) Å] which correspond to the chair conformation. The ring substituents are in equatorial positions (Table 2). The conformation around the O(3′) glycosidic bond is defined by the torsion angle −175·8 (7)° for the atom sequence C(3′)—O(3′)—C(1″)—C(2″).

m-Hydroxybenzoyl moiety.* Bond distances in the benzene ring do not reveal any peculiarity. The C=O bonds of the benzoyl ester group and lactone group (secoiridoid moiety) are comparable [C(11)—O(11), 1·25 (1); C(1″)—O(1″), 1·18 (1) Å] within 4σ. Both are involved in hydrogen bonds with pyranose residues. The hydroxyl O(4″) is coplanar with the benzene ring.

Hydrogen bonds and molecular packing. The molecular packing is dominated by a three-dimensional hydrogen-bonding system (Table 2, Fig. 2). Three of the four hydroxyl groups in the molecule exhibit both donor and acceptor functions. The only exception is the pyranose O(2′) group acting as a donor only, in the bifurcated hydrogen bond. The pyranose O(6′) is also involved in a bifurcated hydrogen-bond system. The bifurcated type of hydrogen bond was analysed according to the criteria described by Newton, Jeffrey & Takagi (1979). The ring O(3) of the secoiridoid moiety and the pyranose ring O(5′) are not involved in hydrogen bonds. The bifurcated hydrogen bonds between the pyranose O(2′)—H and two O atoms of the lactone group in the secoiridoid moiety [O(2′)—H···O(7), 3·00 (1); O(2′)—H···O(11), 3·16 (1) Å] connecting two pyranose and two secoiridoid moieties, form a basic loop of the spiral running along a crystallographic twofold screw axis parallel to **a**. The inner part of the spiral is a hydrophilic area [O(3), O(7), O(11), O(2′)]. The bifurcated hydrogen bond of the pyranose donor O(6′)—H group and the hydroxyl O(4″) group of the *m*-hydroxybenzoyl residue [O(6′)—H···O(4″), 3·19 (1) Å] together with O(4″)—H···O(4′), 2·79 (1) Å, joins molecules into a double spiral along 2_1 axes running parallel to **b**. The other part of this bifurcated bond acts *via* the keto O(1″) atom of

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* See deposition footnote.

the *m*-hydroxybenzoyl ester group [O(6′)–H···O(1″), 2·75 (1) Å]; it contributes in the formation of a double spiral along **b** and also serves as a bridge between spirals running in perpendicular directions (**a**,**b**). The space left between these spirals is occupied by vinyl groups of the secoiridoid moieties and forms with the 'non-oxygen' part of the *m*-hydroxybenzoyl residue a hydrophobic region. Hydrophobic and hydrophilic regions alternate along **b**. The strongest interaction occurring between the double spiral chains [O(4′)–H···O(6′), 2·65 (1) Å] connects them into waved layers with an amplitude in the **a** direction. The short non-hydrogen-bonding interactions involving the C=O part of the lactone group of the secoiridoid moiety [O(11)···H(71), 2·35 (1); O(11)···H(O2′), 2·31 (1) Å] and O(4″) of the *m*-hydroxybenzoyl residue [O(4″)···H(1), 2·43 (1) Å] complete the three-dimensional packing. These interactions are permitted by the conformation of the molecule; the dihedral angles between the pyranose–secoiridoid and pyranose – *m*-hydroxybenzoyl moieties are 59·7 (4) and 89·7 (4)° respectively.

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The Structures of (Dimethylaminopropyl)phenothiazine Drugs and Their Metabolites. II. Chlorpromazine Sulphoxide, $C_{17}H_{19}ClN_2OS$, at 120 K

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Abstract. $M_r = 334\cdot7$, orthorhombic, *Pbca*, $a = 10\cdot357\ (1)$, $b = 14\cdot090\ (2)$, $c = 23\cdot585\ (4)$ Å, $V = 3442\ (1)$ Å^3, $Z = 8$, $D_m = 1\cdot290$, $D_x = 1\cdot292\ (1)$ g cm^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1\cdot5418$ Å, $\mu = 30\cdot6$ cm^{-1}, $F(000) = 1408$, room temperature, $R = 0\cdot067$ for 2144 contributing reflections; $a = 10\cdot210\ (2)$, $b = 13\cdot961\ (2)$, $c = 23\cdot441\ (3)$ Å, $V = 3341\ (1)$ Å^3, $D_x = 1\cdot331\ (1)$ g cm^{-3}, $\mu = 32\cdot1$ cm^{-1}, $T = 120$ K, $R = 0\cdot051$ for 2634 contributing reflections. Only the results at 120 K are reported. The sulphoxide O atom lies in a boat-axial conformation, and the solid-state conformation of the N(10) side chain is different from that of chlorpromazine.

Introduction. 2-Chloro-10-(3-dimethylaminopropyl)-phenothiazine 5-oxide (chlorpromazine sulphoxide, CPZSO) is one of the major metabolites of chlorpromazine (CPZ) in man (Salzman, Moran & Brodie, 1955). Pharmacokinetic studies in psychiatric patients have demonstrated that it may reach blood

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