

There is a shortened intramolecular distance C(2)H...O = 2.883 Å [C(2)—H = 0.92, O...H = 2.29 Å, angle C(2)—H—O = 122°] which corresponds, according to the geometrical characteristics, to a weak CH...O hydrogen bond (Taylor & Kennard, 1982).

The projection of the crystal structure on the *yz* plane is given in Fig. 1. There are no contacts between separate molecules shorter than 3.5 Å within the crystal.

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## Structure of Gentiopiricin Hemihydrate: (–)-(5*R*,6*S*)-5-Ethenyl-6-(β-D-glucopyranosyloxy)-5,6-dihydro-1*H*,3*H*-pyrano[3,4-*c*]pyran-1-one Hemihydrate, C<sub>16</sub>H<sub>20</sub>O<sub>9</sub>·½H<sub>2</sub>O

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**Abstract.**  $M_r = 365.34$ , orthorhombic,  $P2_12_12_1$ ,  $a = 8.175$  (2),  $b = 12.810$  (2),  $c = 31.99$  (2) Å,  $U = 3350$  (1) Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 1.449$  g cm<sup>-3</sup>, Mo  $K\alpha$ ,  $\lambda = 0.71069$  Å,  $\mu = 0.77$  cm<sup>-1</sup>,  $F(000) = 1544$ ,  $T = 294$  K,  $R = 0.042$  for 1789 reflexions [ $I > 2.5\sigma(I)$ ]. There are two independent molecules (*A*, *B*) in the structure with different conformations of the δ-lactone ring of the secoiridoid moiety: half-chair (*A*) and nearly planar (*B*) [with mean torsion angle 4 (1)°]. Both molecules show a skew-boat conformation of the pyran ring. The β-glucose moieties are in the chair, <sup>4</sup>C<sub>1</sub>, conformation. Molecular packing is dominated by intermolecular hydrogen bonds between the water

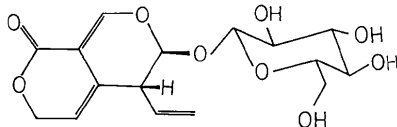
molecule and both sugar residues [O(31)—H...O(3')(A), 3.017 (7); O(31)—H...O(4')(B), 2.904 (7); O(4')(A)—H...O(31), 2.684 (7) Å], sugar–sugar [O(2')(A)—H...O(4')(A), 2.719 (6); O(6')(A)—H...O(2')(A), 2.731 (6); O(2')(B)—H...O(6')(B), 2.821 (7); O(4')(B)—H...O(3')B, 2.796 (7) Å], and sugar–secoiridoid moiety [O(3')(A)—H...O(11)(A), 2.745 (6); O(3')(B)—H...O(11)A, 2.716 (7) Å]. Molecules connected by hydrogen bonds form layers (in the *ab* plane), which are separated by ethenyl residues.

**Introduction.** Gentiopiricin (gentiopicroside) is one of the major secoiridoid glucoside constituents of plant drugs originating from the Gentianaceae and the principal glucoside in the roots of *Gentiana lutea* and the aerial parts of *Blackstonia perfoliata*. Although the

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isolation of this compound was described in 1862 (Kromayer), its structure and absolute configuration were elucidated only recently (Inouye, Ueda & Nakamura, 1970).



The present X-ray study was undertaken to obtain more stereochemical information on gentiopicrin. The configuration obtained by other methods (Inouye, Ueda & Nakamura, 1970) was confirmed.

Previously reported related X-ray studies are of an iridoid (Ballesia, Pagnoni, Trave, Andreotti, Bocelli & Sgarabotto, 1979), a secoiridoid (Kojić-Prodić, Spek, van der Sluis & Labadie, 1985) and conversion products of secoiridoid aglucones (Suhr, Arends & Jensen, 1978; Spek, Duisenberg, van der Sluis, van der Nat & Labadie, 1983).

**Experimental.** Sample for data collection crystallized from 50% ethanol (*The Merck Index*, 1976). Intensities collected on Enraf-Nonius CAD-4F diffractometer,  $\omega/2\theta$  scan mode, Zr-filtered Mo  $K\alpha$  radiation; needle-shaped (0.125 × 0.125 × 1.00 mm) colourless transparent crystal; 2671 independent reflexions ( $0 < h < 9$ ,  $0 < k < 14$ ,  $0 < l < 35$ ), 1792 [ $I > 2.5\sigma(I)$ ] used in calculations; two reference reflexions (032, 016) showed variations <4% during 41 h of X-ray exposure time; cell constants by least squares from diffractometer settings of 25 reflexions in range  $7 < \theta < 12^\circ$ . Data corrected for Lorentz and polarization effects. Structure solved by *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) (based on 350 reflexions having  $|E| > 1.48$ ) revealing 45 atoms out of 51 in structure. Subsequent difference synthesis located remaining atoms. H atoms of hydroxyl groups in pyranose and ethenyl moieties of both molecules located in difference Fourier maps; other H atoms introduced at calculated positions and refined in riding mode on carrier atoms. A slack constraint (Sheldrick, 1976) applied on all ten O—H distances refined to 0.884 (2) Å. Least-squares minimizing of  $\sum w\Delta F^2$  with  $w = 1$ . A scale factor, atomic coordinates of non-H atoms and H atoms located from difference map, anisotropic parameters for non-H atoms and overall thermal parameter for H atoms refined. Max.  $\Delta/\sigma$  coordinates in final refinement cycle 0.3 [on  $y$  for C(6')(B)]; anisotropic thermal parameters in usual range; final  $R = 0.0417$ ,  $wR = 0.0424$ ,  $S = 1.43$ ; max. and min. residual densities 0.08 and  $-0.09 \text{ e } \text{Å}^{-3}$ ; scattering factors from Cromer & Mann (1968) and (for H) Stewart, Davidson & Simpson (1965). Calculations carried out on either an in-house DG Eclipse S/230 minicomputer using programs of the *ILIAS*

Table 1. Final atomic coordinates and equivalent isotropic thermal parameters

Molecule A	x	y	z	$U_{eq}(\text{Å}^2)^\dagger$
O(3)	0.3817 (5)	0.0066 (3)	0.9051 (1)	0.042 (1)
O(7)	0.9452 (5)	0.0235 (4)	0.8684 (1)	0.049 (1)
O(11)	0.8750 (6)	-0.0201 (4)	0.9323 (1)	0.059 (1)
O(1')	0.3854 (5)	0.1787 (3)	0.8818 (1)	0.033 (1)
O(2')	0.5482 (5)	0.2607 (4)	0.9520 (1)	0.044 (1)
O(3')	0.3920 (5)	0.4351 (4)	0.9890 (1)	0.047 (1)
O(4')	0.0419 (5)	0.4068 (3)	0.9958 (1)	0.040 (1)
O(5')	0.1500 (5)	0.2628 (3)	0.9000 (1)	0.033 (1)
O(6')	-0.1972 (5)	0.2440 (4)	0.8971 (1)	0.047 (1)
C(1)	0.3446 (7)	0.0773 (5)	0.8708 (2)	0.039 (1)
C(3)	0.5447 (8)	-0.0080 (5)	0.9125 (2)	0.035 (1)
C(4)	0.6601 (7)	0.0170 (5)	0.8851 (2)	0.033 (1)
C(5)	0.6226 (7)	0.0522 (4)	0.8427 (2)	0.032 (1)
C(6)	0.7390 (8)	0.0825 (5)	0.8174 (2)	0.039 (1)
C(7)	0.9140 (7)	0.0821 (6)	0.8304 (2)	0.044 (1)
C(8)	0.3861 (9)	-0.0590 (5)	0.8172 (2)	0.052 (2)
C(9)	0.4407 (7)	0.0474 (5)	0.8322 (2)	0.033 (1)
C(10)	0.475 (1)	-0.1387 (6)	0.8088 (2)	0.058 (2)
C(11)	0.8306 (8)	0.0066 (5)	0.8973 (2)	0.044 (1)
C(1')	0.2955 (7)	0.2187 (5)	0.9162 (2)	0.034 (1)
C(2')	0.3982 (7)	0.3022 (5)	0.9375 (2)	0.034 (1)
C(3')	0.3013 (7)	0.3500 (5)	0.9728 (2)	0.036 (1)
C(4')	0.1303 (7)	0.3843 (5)	0.9584 (2)	0.032 (1)
C(5')	0.0465 (7)	0.2963 (5)	0.9337 (2)	0.033 (1)
C(6')	-0.1130 (8)	0.3302 (5)	0.9149 (2)	0.037 (1)
Molecule B				
O(3)	-0.0210 (5)	0.1184 (3)	0.7180 (1)	0.043 (1)
O(7)	0.5068 (6)	-0.0368 (4)	0.7029 (2)	0.068 (1)
O(11)	0.4843 (6)	0.1179 (4)	0.7318 (2)	0.070 (1)
O(1')	-0.0373 (5)	0.0683 (3)	0.6484 (1)	0.039 (1)
O(2')	0.1205 (6)	0.2516 (4)	0.6149 (2)	0.054 (1)
O(3')	-0.0076 (6)	0.3047 (4)	0.5339 (1)	0.047 (1)
O(4')	-0.3495 (6)	0.3036 (4)	0.5303 (1)	0.049 (1)
O(5')	-0.2668 (5)	0.1109 (3)	0.6125 (1)	0.038 (1)
O(6')	-0.6120 (6)	0.1125 (5)	0.6152 (2)	0.077 (1)
C(1)	-0.0858 (8)	0.0430 (5)	0.6889 (2)	0.038 (1)
C(3)	0.1452 (8)	0.1157 (5)	0.7237 (2)	0.041 (1)
C(4)	0.2343 (8)	0.0328 (5)	0.7138 (2)	0.035 (1)
C(5)	0.1653 (8)	-0.0635 (5)	0.6979 (2)	0.038 (1)
C(6)	0.262 (1)	-0.1410 (6)	0.6868 (2)	0.059 (2)
C(7)	0.440 (1)	-0.1363 (7)	0.6896 (3)	0.076 (2)
C(8)	-0.0921 (9)	-0.1004 (6)	0.7405 (2)	0.054 (2)
C(9)	-0.0218 (8)	-0.0670 (5)	0.6981 (2)	0.044 (1)
C(10)	-0.012 (1)	-0.1443 (5)	0.7704 (2)	0.055 (2)
C(11)	0.4161 (8)	0.0425 (6)	0.7170 (2)	0.051 (2)
C(1')	-0.1207 (7)	0.1527 (5)	0.6300 (2)	0.035 (1)
C(2')	-0.0113 (8)	0.1976 (5)	0.5963 (2)	0.041 (1)
C(3')	-0.1049 (7)	0.2727 (5)	0.5684 (2)	0.035 (1)
C(4')	-0.2640 (7)	0.2256 (5)	0.5530 (2)	0.034 (1)
C(5')	-0.3600 (8)	0.1874 (5)	0.5902 (2)	0.039 (1)
C(6')	-0.5216 (8)	0.1362 (6)	0.5784 (2)	0.052 (2)
Water molecule				
O(31)	0.2468 (6)	0.0014 (5)	0.0054 (2)	0.069 (1)

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

package [an adaptation and extension by ALS of *SHELX76* (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 *PLUTO* (Spek, 1982)].

**Discussion.** Final atomic parameters are given in Table 1.\* Bond distances and angles (with the exceptions of

\* Table 4 together with lists of structure factors, anisotropic thermal parameters, coordinates of the H atoms and bond distances and angles involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39983 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond distances (Å) and angles (°) for non-hydrogen atoms

Molecule A		Molecule B		Molecule A		Molecule B	
O(3)—C(1)	1.457 (7)	1.442 (7)	C(1)—O(3)—C(3)	114.7 (5)	115.7 (5)		
O(3)—C(3)	1.367 (7)	1.371 (8)	C(7)—O(7)—C(11)	122.8 (5)	124.1 (6)		
O(7)—C(7)	1.453 (8)	1.45 (1)	C(1)—O(1')—C(1'')	114.3 (4)	115.5 (5)		
O(7)—C(11)	1.333 (8)	1.337 (9)	C(1')—O(5')—C(5'')	109.9 (4)	112.7 (5)		
O(11)—C(11)	1.226 (8)	1.211 (9)	O(3)—C(1)—O(1'')	109.9 (5)	109.9 (5)		
O(1')—C(1)	1.387 (7)	1.392 (7)	O(3)—C(1)—C(9)	110.5 (5)	111.5 (5)		
O(1'')—C(1')	1.419 (7)	1.408 (7)	O(1'')—C(1)—C(9)	108.7 (5)	107.1 (5)		
O(2')—C(2')	1.414 (7)	1.412 (8)	O(3)—C(3)—C(4)	123.1 (5)	122.2 (6)		
O(3')—C(3')	1.417 (8)	1.421 (7)	C(3)—C(4)—C(5)	122.6 (6)	123.5 (6)		
O(4')—C(4')	1.429 (7)	1.418 (7)	C(3)—C(4)—C(11)	118.7 (6)	117.6 (6)		
O(5')—C(5')	1.415 (7)	1.423 (7)	C(5)—C(4)—C(11)	118.6 (5)	118.8 (6)		
O(5'')—C(5'')	1.435 (7)	1.432 (7)	C(4)—C(5)—C(6)	120.8 (6)	120.2 (6)		
O(6')—C(6')	1.420 (8)	1.422 (9)	C(4)—C(5)—C(9)	113.4 (5)	114.4 (5)		
C(1)—C(9)	1.513 (8)	1.532 (9)	C(6)—C(5)—C(9)	125.8 (5)	125.4 (6)		
C(3)—C(4)	1.327 (9)	1.326 (9)	C(5)—C(6)—C(7)	121.8 (6)	123.4 (7)		
C(4)—C(5)	1.460 (8)	1.449 (9)	O(7)—C(7)—C(6)	113.8 (5)	115.4 (7)		
C(4)—C(11)	1.454 (9)	1.495 (9)	C(9)—C(8)—C(10)	128.0 (7)	125.8 (7)		
C(5)—C(6)	1.308 (9)	1.32 (1)	C(1)—C(9)—C(5)	108.4 (5)	108.3 (5)		
C(5)—C(9)	1.526 (8)	1.53 (1)	C(1)—C(9)—C(8)	109.5 (5)	107.3 (5)		
C(6)—C(7)	1.489 (9)	1.46 (1)	C(5)—C(9)—C(8)	113.3 (5)	112.7 (5)		
C(8)—C(9)	1.511 (9)	1.53 (1)	O(7)—C(11)—O(11)	118.1 (6)	118.9 (6)		
C(8)—C(10)	1.28 (1)	1.29 (1)	O(7)—C(11)—C(4)	118.2 (6)	117.7 (6)		
C(1')—C(2')	1.520 (9)	1.515 (9)	O(11)—C(11)—C(4)	123.7 (6)	123.4 (7)		
C(2')—C(3')	1.510 (9)	1.518 (9)	O(1'')—C(1'')—O(5'')	107.2 (5)	106.4 (5)		
C(3')—C(4')	1.536 (8)	1.518 (8)	O(1'')—C(1'')—C(2'')	108.4 (5)	107.7 (5)		
C(4')—C(5')	1.538 (8)	1.508 (8)	O(5'')—C(1'')—C(2'')	110.3 (5)	111.0 (5)		
C(5')—C(6')	1.500 (9)	1.522 (9)	O(2'')—C(2'')—C(1'')	111.2 (5)	109.7 (5)		
			O(2'')—C(2'')—C(3'')	111.2 (5)	108.8 (5)		
			C(1'')—C(2'')—C(3'')	109.3 (5)	111.1 (5)		
			O(3'')—C(3'')—C(2'')	108.2 (5)	110.9 (5)		
			O(3'')—C(3'')—C(4'')	111.5 (5)	110.0 (5)		
			C(2'')—C(3'')—C(4'')	111.6 (5)	111.8 (5)		
			O(4'')—C(4'')—C(3'')	105.4 (4)	108.0 (5)		
			O(4'')—C(4'')—C(5'')	110.7 (5)	112.1 (5)		
			C(3'')—C(4'')—C(5'')	110.5 (5)	108.5 (5)		
			O(5'')—C(5'')—C(4'')	110.0 (5)	109.8 (5)		
			O(5'')—C(5'')—C(6'')	107.4 (5)	106.9 (5)		
			C(4'')—C(5'')—C(6'')	112.4 (5)	113.3 (5)		
			O(6'')—C(6'')—C(5'')	110.9 (5)	109.7 (5)		

Table 3. Selected torsion angles (°)

	Molecule A	Molecule B
<b>Secoiridoid moieties</b>		
C(3)—O(3)—C(1)—O(1')	-70.0 (6)	-69.3 (6)
C(3)—O(3)—C(1)—C(9)	49.9 (6)	49.4 (7)
C(1)—O(3)—C(3)—C(4)	-16.4 (8)	-19.6 (8)
C(1)—O(7)—C(7)—C(6)	-24.5 (8)	9 (1)
C(7)—O(7)—C(11)—O(11)	-162.3 (6)	171.5 (7)
C(7)—O(7)—C(11)—C(4)	20.0 (9)	-8 (1)
O(3)—C(1)—C(9)—C(8)	64.8 (6)	66.4 (7)
O(1'')—C(1)—C(9)—C(8)	-174.6 (5)	-173.4 (5)
O(3)—C(3)—C(4)—C(5)	-6.7 (9)	-3 (1)
O(3)—C(3)—C(4)—C(11)	174.8 (6)	173.5 (6)
C(3)—C(4)—C(5)—C(6)	175.6 (6)	176.6 (7)
C(3)—C(4)—C(5)—C(9)	-5.4 (8)	-6.9 (9)
C(11)—C(4)—C(5)—C(6)	-6.0 (9)	0.6 (9)
C(5)—C(4)—C(11)—O(7)	-4.1 (9)	3.3 (9)
C(4)—C(5)—C(6)—C(7)	0.4 (9)	0 (1)
C(9)—C(5)—C(6)—C(7)	-178.5 (6)	-176.1 (7)
C(10)—C(8)—C(9)—C(1)	-128.5 (8)	-134.6 (8)
<b>β-Glucopyranose moieties</b>		
C(1'')—O(1'')—C(1)—C(9)	176.3 (5)	163.1 (5)
C(1'')—O(1'')—C(1)—O(3)	-62.7 (6)	-75.6 (6)
O(1'')—C(1'')—C(2'')—C(3'')	177.0 (5)	167.4 (5)
O(5'')—C(1'')—C(2'')—O(2'')	-177.0 (5)	171.6 (5)
O(5'')—C(1'')—C(2'')—C(3'')	59.9 (6)	51.3 (7)
O(2'')—C(2'')—C(3'')—C(4'')	-173.7 (5)	-170.6 (5)
C(1'')—C(2'')—C(3'')—O(3'')	-173.6 (5)	-172.9 (5)
C(1'')—C(2'')—C(3'')—C(4'')	-50.6 (7)	-49.8 (7)
O(3'')—C(3'')—C(4'')—C(5'')	169.6 (5)	177.1 (5)
C(2'')—C(3'')—C(4'')—O(4'')	168.1 (5)	175.1 (5)
C(2'')—C(3'')—C(4'')—C(5'')	48.5 (7)	53.4 (6)
O(4'')—C(4'')—C(5'')—O(5'')	-170.5 (5)	-178.5 (5)
O(4'')—C(4'')—C(5'')—C(6'')	70.0 (6)	62.0 (7)
C(3'')—C(4'')—C(5'')—O(5'')	-54.1 (6)	-59.4 (6)
C(3'')—C(4'')—C(5'')—C(6'')	-173.6 (5)	-178.8 (5)
C(5'')—O(5'')—C(1'')—C(2'')	-67.5 (6)	-59.4 (6)
C(4'')—C(5'')—C(6'')—O(6'')	-172.3 (5)	-173.9 (5)
C(1'')—O(5'')—C(5'')—C(4'')	64.1 (6)	64.1 (6)
C(1'')—O(5'')—C(5'')—C(6'')	-173.3 (5)	-172.6 (5)

those at OH groups) in both conformers are comparable within  $3\sigma$  (Table 2). Selected torsion angles describing the conformation of the molecule are listed in Table 3. During the structure determination of this natural product the enantiomer with the D-glucopyranose moiety was selected. Hydrogen-bond geometry is given in Table 4.\* A *PLUTO* drawing of the molecules with the atomic numbering scheme is shown in Fig. 1. The molecular packing is illustrated in Fig. 2.

\* See deposition footnote.

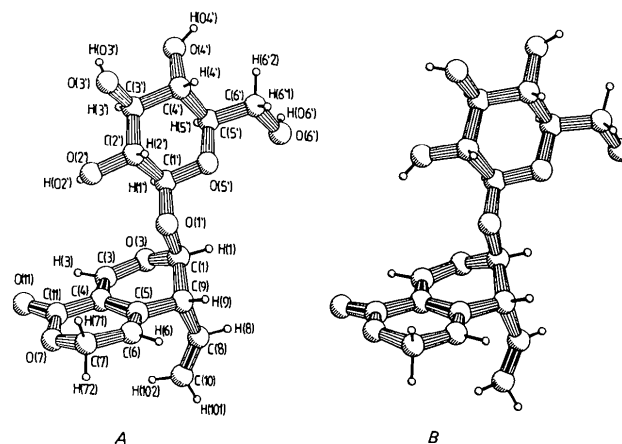


Fig. 1. A *PLUTO* drawing of the two independent gentiopicrotin molecules (*A* and *B*) and numbering scheme. Double bonds are indicated.

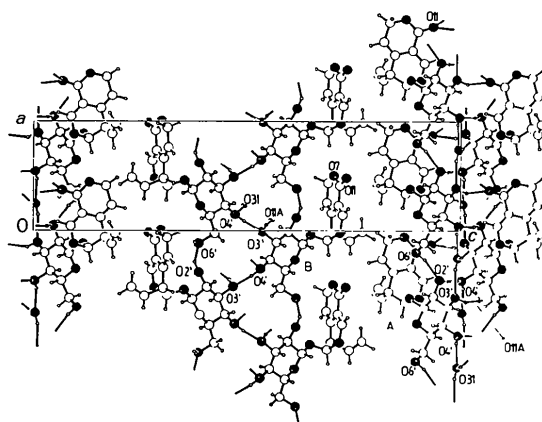


Fig. 2. Projection of the structure down *b* illustrating the packing and hydrogen bonding. Oxygen atoms are indicated as black spheres. Spirals of *A* and *B* molecules are at  $y = \frac{1}{4}$ ,  $z = 1$  and  $\frac{1}{2}$  respectively are shown. Similar spirals of *A* and *B* molecules are at  $y = \frac{3}{4}$ ,  $z = \frac{1}{2}$  and 1 respectively, resulting in a two-dimensional hydrogen-bonded layer structure (*ab* plane).

*Secoiridoid moieties.* A secondary structure of iridoid with opening of the cyclopentane ring results in a secoiridoid skeleton. Bond distances in both secoiridoid moieties deviating from standard values are mostly influenced by conjugation effects. The endocyclic C—O bonds with adjacent C( $sp^2$ ) are considerably shorter [O(3)—C(3), 1.367 (7)(A), 1.371 (8)(B); O(7)—C(11), 1.333 (8)(A), 1.337 (9)(B) Å] than those involving C( $sp^3$ ) [O(3)—C(1), 1.457 (7)(A), 1.442 (7)(B); O(7)—C(7), 1.453 (8)(A), 1.45 (1)(B) Å]. The C—O bond lengths of the glycosidic linkage correspond to a single C—O bond. The large bond angles at O(7) [122.8 (5)(A), 124.1 (6)(B)°] are related to the  $\delta$ -lactone ring geometry (Kojić-Prodić, Spek, van der Sluis & Labadie, 1985, and references therein). The  $\delta$ -lactone ring of conformer *A* exhibits a half-chair conformation whereas that of *B* is planar. The displacements of atoms O(7)(A) [−0.13 (1) Å] and C(7)(A) [0.11 (1) Å] (from the least-squares plane through the  $\delta$ -lactone ring) are in agreement with a symmetrical half-chair conformation. The results of a Cremer & Pople (1975) ring-puckering analysis [for the sequence O(7), C(7), C(6), C(5), C(4), C(11) in molecule *A*] are  $Q = 0.185$  (6) Å,  $\theta = 63$  (2),  $\varphi = 22$  (2)°. The C(7) atom deviates 0.36 (1) Å from the plane through the atoms O(7), O(11), C(4), C(5), C(11). Of all the oxygen atoms in the secoiridoid moieties, only atom O(11) of the lactone group in conformer *A* is involved in hydrogen bonds. The  $\delta$ -lactone ring of molecule *B* is planar with mean torsion angle 4 (1)°. The lactone group does not deviate significantly from planarity with puckering-analysis parameters (Cremer & Pople, 1975)  $Q = 0.062$  (7) Å,  $\theta = 123$  (7),  $\varphi = 187$  (9)°. The pyran rings of both molecules show a skew-boat conformation; the parameters of puckering analysis [for the sequence O(3), C(1), C(9), C(5), C(4), C(3)], are  $Q = 0.488$  (6)(A), 0.457 (7)(B) Å;  $\theta = 124.6$  (7)(A), 127.9(B);  $\varphi = 261.0$  (8)(A), 259 (1)(B)°. The two fused rings of the secoiridoid moieties make dihedral angles of 10.2 (3)(A) and 11.5 (3)(B)°. The ethenyl groups [attached at C(9)] of both conformers are not folded over the pyran rings; they show an extended conformation [O(1′)—C(1)—C(9)—C(8), −174.6 (5)(A), −173.4 (5)(B)°]. The same type of conformation around the C(1)—C(9) bond is observed in the structure of decentapicrin A (Kojić-Prodić, Spek, van der Sluis & Labadie, 1985) with torsion angle −178.0 (7)°. However, the relative orientation of the ethenyl moieties around the C(8)—C(9) bond is different from that observed in decentapicrin A. The values of torsion angles for the atom sequence C(10)—C(8)—C(9)—C(1) are −128.5 (8)(A) and −134.6 (8)(B) in gentiopicrin hemihydrate, and 112 (1)° in decentapicrin A. The conformation around the glycosidic bonds is defined by the torsion angles 176.3 (5)(A) and 163.1 (5)(B)° for the atom sequence C(1′)—O(1′)—C(1)—C(9).

*$\beta$ -D-Glucopyranose moieties.* Both  $\beta$ -D-glucopyranose moieties reveal the geometry typical of  $\beta$ -anomers (Jeffrey & Takagi, 1977). The difference in the two endocyclic C—O bonds of both conformers is within the limits of  $3\sigma$  [C(1′)—O(5′), 1.415 (7)(A), 1.423 (7)(B); C(5′)—O(5′), 1.435 (7)(A), 1.432 (7)(B) Å]. The anomeric C—O bonds in both molecules [C(1′)—O(1′), 1.419 (7)(A), 1.408 (7)(B) Å] do not differ from the endocyclic ones. Bond angles at endocyclic oxygen atoms O(5′) are 109.9 (4)(A) and 112.7 (5)(B)°; the exocyclic bond angles O—C—O are 107.2 (5)(A) and 106.4 (5)(B)°. The values of both types of angles are somewhat smaller than in the  $\alpha$ -anomers in general (Arnott & Scott, 1972). The values of the C—O bond lengths involving hydroxyl groups fall in a narrow range, differing by  $2\sigma$  (Table 2). All hydroxyl groups are involved in intermolecular hydrogen bonds. Some of them exhibit both donor and acceptor functions [O(2′), O(3′), O(4′)(A); O(2′), O(4′)(B)], whereas O(6′)(A) and O(2′)(B) serve as donors and O(6′)(B) as acceptor only. Both  $\beta$ -glucopyranose moieties occur in the  ${}^4C_1$  conformation; the endocyclic torsion angles range from 48.5 (7) to 67.5 (6)° in *A* and from 49.8 (7) to 64.1 (6)° in *B*. These values are also in agreement with general observations that  $\beta$ -anomers are more puckered than  $\alpha$  ones, having a range of torsion angles from 52 to 70° (Jeffrey & Takagi, 1977). The values of the ring torsion angles in both molecules correspond to those observed in  $\beta$ -maltose monohydrate (Gress & Jeffrey, 1977). Cremer & Pople (1975) puckering parameters are:  $Q = 0.581$  (6)(A), 0.563 (6)(B) Å;  $\theta = 8.4$  (6)(A), 6.6 (6)(B);  $\varphi = 19$  (4)(A), 305 (5)(B)°.

*Molecular packing.* Intermolecular hydrogen bonds (Fig. 2) acting between sugar moieties of *A* [O(2′)(A)—H...O(4′)(A); O(6′)(A)—H...O(2′)(A)] and between those of *B* [O(4′)(B)—H...O(3′)(B)] form spirals in the *a* direction. An interaction between the sugar moiety of *B* and the secoiridoid residue of *A* *via* carbonyl O(11)(A) of the lactone group [O(3′)(B)—H...O(11)(A)] connects the *A*—*A* and *B*—*B* spirals. A hydrogen bond between the sugar and secoiridoid moieties of *A* [O(3′)(A)—H...O(11)(A)] joins them into a spiral along *a*. The water molecule completes a two-dimensional hydrogen-bond network connecting sugar rings of *A* in the *a* direction [O(31)—H(311)...O(3′)(A); O(4′)(A)—H...O(31)] and those of *B* [O(31)—H(312)...O(4′)(B)] in the *b* direction. The layers formed in the *ab* plane are separated by ethenyl residues (Fig. 2).

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*Acta Cryst.* (1985). **C41**, 802–804

### Structure of 3-Acetyl-4-hydroxy-6-phenyl-2-pyrone, C<sub>13</sub>H<sub>10</sub>O<sub>4</sub>

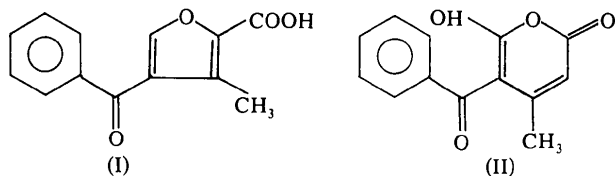
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(Received 28 August 1984; accepted 2 January 1985)

**Abstract.**  $M_r = 230.21$ , m.p.  $\sim 443$  K, monoclinic,  $P2_1/c$ ,  $a = 5.558$  (5),  $b = 24.301$  (5),  $c = 7.982$  (3) Å,  $\beta = 92.22$  (5)°,  $V = 1077$  (1) Å<sup>3</sup>,  $Z = 4$ ,  $D_m$ (floatation) = 1.423,  $D_x = 1.420$  g cm<sup>-3</sup>, Mo  $K\alpha$  radiation,  $\lambda = 0.7107$  Å,  $\mu = 1.36$  cm<sup>-1</sup>,  $F(000) = 480$ ,  $T = 293$  K,  $R = 0.051$  for 1008 observed reflections. The O of the acetyl group of the pyrone ring is hydrogen-bonded to the O of the hydroxyl group of the same molecule. This intramolecular hydrogen bond, though very strong [O...O 2.464 (7) Å], is asymmetrical. There are no unusual bond lengths or angles.

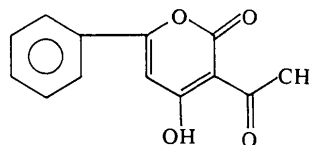
**Introduction.** C<sub>13</sub>H<sub>10</sub>O<sub>4</sub> is a plant product isolated from *Pogostemon heyneanus* Benth-Sym. (Purushothaman, Sarada & Connolly, 1984). The compound was supplied by Dr Purushothaman of Captain Srinivasamurti Research Institute for Ayurveda and Siddha. It has been reported to have 70% regression against methylcholanthrene-induced fibrosarcoma (Purushothaman, Sarada & Connolly, 1984). The present study was undertaken to establish the chemical structure, the following having been suggested:



\* Contribution No. 660.

0108-2701/85/050802-03\$01.50

However, the structure arrived at from single-crystal X-ray studies is:



which also agrees with spectroscopic results.

**Experimental.** Pale-yellow rectangular crystals (from ethyl acetate). Crystal  $0.7 \times 0.3 \times 0.3$  mm. Nonius CAD-4 diffractometer, monochromatic Mo  $K\alpha$ . 1528 independent reflections with  $2\theta \leq 48^\circ$ ; 1008 with  $I \geq 3\sigma(I)$ . Two standard reflections ( $\bar{3}62$  and  $\bar{2}8\bar{2}$ ), maximum variation in intensity 2.6%. 18 reflections with  $9 < \theta < 16^\circ$  for lattice-parameter measurement and refinement. Max.  $h = 6$ , max.  $k = 26$ , max.  $l = 8$ , min.  $l = -8$ . Lp correction, no absorption correction. Structure solution by *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Anisotropic block-diagonal least-squares refinement on  $F$  (Shiono, 1968) for non-hydrogen atoms; H atoms fixed geometrically and checked by  $\Delta F$  synthesis and isotropic refinement. Final  $R = 0.051$ ,  $wR = 0.083$  for 194 parameters, goodness of fit 0.50. Cruickshank's weighting scheme (Cruickshank, Bujosa, Lovell & Truter, 1961). Final  $\Delta F$  map had no peak  $> 0.3$  e Å<sup>-3</sup>.  $(\Delta/\sigma)_{\max} = 0.5$ ,  $(\Delta/\sigma)_{\text{mean}} = 0.2$ . No correction for secondary extinction. Scattering factors for non-

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