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The Structure of Gentiogenal: (±)-6-Methyl-1-oxo-3,4-dihydro-1*H*,6*H*-pyrano[3,4-*c*]pyran-5-carbaldehyde, $C_{10}H_{10}O_4$

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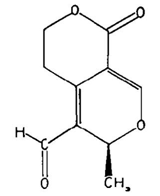
Abstract. $M_r = 194 \cdot 19$, monoclinic, $P2_1/c$, $a = 9 \cdot 368$ (5), $b = 8 \cdot 282$ (5), $c = 11 \cdot 969$ (4) Å, $\beta = 103 \cdot 71$ (4)°, $U = 902 \cdot 2$ (8) Å^3, $Z = 4$, $D_x = 1 \cdot 431$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0 \cdot 71069$ Å, $\mu = 1 \cdot 2$ cm^{-1}, $F(000) = 408$, $T = 295$ K, $R = 0 \cdot 0515$ for 1033 observed reflections [$I > 2 \cdot 5\,\sigma(\mathrm{I})$]. The two fused six-membered rings are significantly puckered.

Introduction. Gentiopicrin (gentiopicroside), one of the major secoiridoid glucoside constituents of plant drugs originating from the Gentianaceae, is fungitoxic against *Penicillium expansum* on silica-gel thin-layer plates but only in the presence of β-glucosidase (van der Sluis, van der Nat & Labadie, 1983). Hydrolysis of this glucoside with β-glucosidase yields the aglucone. Absorbed on silica gel this aglucone is rapidly converted into an unknown compound, which was given the name gentiogenal. This compound proved to be active against our test organism *Penicillium expansum* (van der Sluis, van der Nat, Labadie, Spek & Ikeshiro, 1983). Gentiogenal was isolated in large amounts from an extract of *Blackstonia perfoliata* (L.) Hudson (Gentianaceae), a plant species known to be rich in gentiopicrin. Attempts to elucidate the structure of gentiogenal by means of ^{1}H, ^{13}C NMR and mass spectrometry resulted in two postulated structures, compatible with the available data. A subsequent X-ray structure determination was undertaken to secure the structure unequivocally. One of the proposed structures turned out to be the correct one (van der Sluis, van der Nat, Labadie, Spek & Ikeshiro, 1983). The 8*S* enantiomer is shown in (I).



(I)

Experimental. Good crystals obtained by recrystallization from chloroform, yellow crystal, 1·0 × 0·5 × 0·25 mm, Enraf–Nonius CAD4F diffractometer, accurate cell parameters calculated from the setting angles of 20 reflections and checked on the diffractometer *via* rotation photographs about the three crystal axes, unique data set $(+h, +k, \pm l)$ up to $\theta = 27 \cdot 5°$ collected with the $\omega/2\theta$ scan technique, Zr-filtered Mo $K\alpha$ radiation, 2088 reflections scanned; four reference reflections ($\bar{1}2\bar{1}$; $1\bar{2}1$; $\bar{1}21$; $12\bar{1}$) measured every hour of X-ray exposure time showed fluctuations less than 2% from the mean, the three groups of four reference reflections did not indicate any decay during the deliberately fast data collection (2·3 h of X-ray exposure time) contrary to what was expected from previous experience with another crystal; correction for the usual factors, excluding negligible absorption effects, 1033 unique reflections with $I > 2 \cdot 5\,\sigma(I)$, direct methods, refined on F by full-matrix least-squares techniques, atoms located from difference Fourier; refined parameters included all positional parameters, anisotropic temperature factors for the non-hydrogen atoms and one overall temperature factor for the H

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atoms; the final values are given in Table 1.* Convergence reached at $R = 0\cdot0515$ $\{wR = 0\cdot056;\ w^{-1} = [\sigma^2(F) + 0\cdot0071F^2]/1\cdot31\}$, max shift/error = 1, residual density in the final difference Fourier map ranged from 0·19 to $-0\cdot20$ e Å^{-3}, scattering factors were those of Cromer & Mann (1968).

The calculations were carried out on either the CDC-Cyber175 of the University of Utrecht with programs *APOLLO* (data reduction and correction by A. L. Spek), *MULTAN*80 (Main *et al.*, 1980) and *EUCLID* [calculation of geometrical data and preparation of illustrations including an extended version of the program *PLUTO* (Spek, 1982)] or on the in-house DG-Eclipse S/230 minicomputer using the programs of the *ILIAS* package [an adaptation and extension (by ALS) of the *SHELX76* package (Sheldrick, 1976)].

Discussion. The unit cell contains a racemic mixture of four molecules of the title compound (Figs. 1 and 2). The bond distances and angles as given in Table 2 are within the commonly observed ranges. The structure includes the secoiridoid carbon skeleton, a taxonomic feature associated with the Gentianaceae. The crystal structure of the related gentiolactone has been reported previously (Suhr, Arends & Jensen, 1978). Both six-membered rings in the present structure are significantly puckered with average absolute torsion angles of 28·7 (4) and 17·4 (4)° and with C(7) and C(10) on the same side of the fused-ring skeleton. The imaginable *trans* isomer is not observed in this crystal structure. The double bond of the keto function is found to be essentially coplanar with the sp^2–sp^2 plane of the double bond it is attached to as may be seen from the torsion angle about C(1)—C(9) (Table 2).

The investigations were supported in part by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Advancement of Pure Research (ZWO).

Table 1. *Final coordinates and equivalent isotropic thermal parameters*

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

	x	y	z	$U_{\rm eq}$ (Å^2)
O(1)	0·3735 (3)	0·1321 (3)	0·6086 (2)	0·0635 (7)
O(2)	0·2087 (2)	0·6540 (3)	0·5586 (2)	0·0581 (7)
O(3)	0·4019 (3)	0·3375 (3)	0·8158 (2)	0·0749 (7)
O(4)	0·0036 (3)	0·4547 (3)	0·2367 (2)	0·0680 (7)
C(1)	0·0576 (3)	0·3666 (4)	0·3169 (2)	0·0504 (8)
C(2)	0·2760 (4)	0·5497 (4)	0·6383 (3)	0·0526 (8)
C(3)	0·3573 (3)	0·2899 (4)	0·7193 (3)	0·0524 (8)
C(4)	0·2843 (3)	0·3896 (4)	0·6213 (2)	0·0412 (7)
C(5)	0·2042 (3)	0·3220 (3)	0·5130 (2)	0·0391 (7)
C(6)	0·1906 (3)	0·1414 (4)	0·5144 (2)	0·0478 (8)
C(7)	0·3357 (4)	0·0733 (4)	0·5809 (3)	0·0585 (8)
C(8)	0·1794 (4)	0·6016 (4)	0·4376 (3)	0·0490 (8)
C(9)	0·1468 (3)	0·4229 (3)	0·4257 (2)	0·0386 (7)
C(10)	0·3078 (4)	0·6512 (4)	0·3915 (3)	0·0680 (9)
H(11)	0·043 (2)	0·250 (2)	0·308 (1)	0·067 (2)
H(21)	0·320 (2)	0·589 (2)	0·713 (2)	0·067 (2)
H(61)	0·102 (2)	0·118 (2)	0·549 (2)	0·067 (2)
H(62)	0·160 (2)	0·097 (2)	0·440 (2)	0·067 (2)
H(71)	0·417 (2)	0·105 (2)	0·545 (2)	0·067 (2)
H(72)	0·331 (2)	−0·041 (2)	0·591 (2)	0·067 (2)
H(81)	0·086 (2)	0·668 (2)	0·403 (2)	0·067 (2)
H(101)	0·390 (2)	0·599 (2)	0·430 (2)	0·067 (2)
H(102)	0·321 (2)	0·773 (2)	0·399 (2)	0·067 (2)
H(103)	0·274 (2)	0·633 (2)	0·310 (2)	0·067 (2)

Table 2. *Relevant data on the geometry of gentiogenal*

Bond distances (Å)

O(1)—C(3)	1·346 (4)	C(4)—C(5)	1·447 (4)	C(6)—H(62)	0·94 (2)
O(1)—C(7)	1·453 (4)	C(5)—C(6)	1·501 (4)	C(7)—H(71)	0·99 (2)
O(2)—C(2)	1·330 (4)	C(5)—C(9)	1·347 (4)	C(7)—H(72)	0·96 (2)
O(2)—C(8)	1·474 (4)	C(6)—C(7)	1·513 (5)	C(8)—H(81)	1·03 (2)
O(3)—C(3)	1·199 (4)	C(8)—C(10)	1·495 (5)	C(10)—H(101)	0·90 (2)
O(4)—C(1)	1·216 (4)	C(8)—C(9)	1·511 (4)	C(10)—H(102)	1·01 (2)
C(1)—C(9)	1·448 (4)	C(1)—H(11)	0·98 (2)	C(10)—H(103)	0·96 (2)
C(2)—C(4)	1·347 (5)	C(2)—H(21)	0·95 (2)		
C(3)—C(4)	1·464 (5)	C(6)—H(61)	1·03 (2)		

Bond angles (°)

C(3)—O(1)—C(7)	119·5 (3)	C(6)—C(5)—C(9)	127·4 (3)
C(2)—O(2)—C(8)	117·3 (3)	C(4)—C(5)—C(9)	118·8 (3)
O(4)—C(1)—C(9)	124·1 (3)	C(5)—C(6)—C(7)	108·0 (3)
O(2)—C(2)—C(4)	124·5 (3)	O(1)—C(7)—C(6)	111·5 (3)
O(3)—C(3)—C(4)	125·2 (3)	C(9)—C(8)—C(10)	113·4 (3)
O(1)—C(3)—C(4)	116·9 (3)	O(2)—C(8)—C(9)	111·6 (2)
O(1)—C(3)—O(3)	117·9 (3)	O(2)—C(8)—C(10)	107·7 (3)
C(2)—C(4)—C(3)	117·8 (3)	C(1)—C(9)—C(8)	117·4 (3)
C(3)—C(4)—C(5)	123·0 (3)	C(5)—C(9)—C(8)	120·0 (3)
C(2)—C(4)—C(5)	118·7 (3)	C(1)—C(9)—C(5)	122·5 (3)
C(4)—C(5)—C(6)	113·7 (3)		

Torsion angles (°)

C(5)—C(9)—C(1)—O(4)	179·6 (3)	C(2)—O(2)—C(8)—C(9)	33·8 (4)
C(3)—O(1)—C(7)—C(6)	−45·0 (4)	C(1)—C(9)—C(8)—C(10)	−84·1 (4)

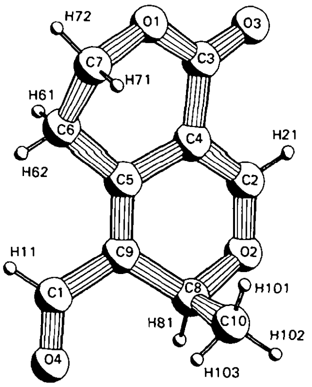

Fig. 1. Drawing of one of the two observed optical enantiomers (*S*), illustrating the stereochemistry and adopted numbering scheme.

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* Lists of structure factors, anisotropic thermal parameters and bond angles involving hydrogen have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38459 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

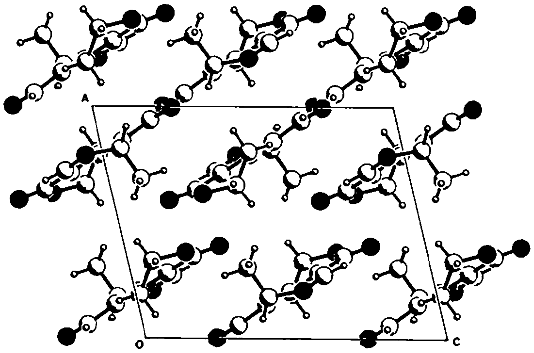

Fig. 2. Projection of the crystal structure down the *b* axis. Oxygen atoms are represented as black spheres.

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Structure of 1,1,3,3-Tetraisopropyl-1,3-disiloxanediol, $C_{12}H_{30}O_3Si_2$

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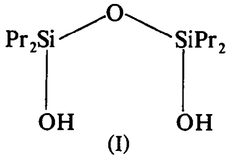
Abstract. $M_r = 278\cdot5$, triclinic, $P\bar{1}$, $a = 8\cdot968\,(1)$, $b = 9\cdot008\,(1)$, $c = 21\cdot898\,(3)$ Å, $\alpha = 82\cdot21\,(1)$, $\beta = 89\cdot69\,(1)$, $\gamma = 85\cdot08\,(1)°$, $U = 1746\cdot2$ Å^3, $Z = 4$, $D_x = 1\cdot059$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0\cdot71069$ Å, $\mu = 0\cdot19$ mm^{-1}, $F(000) = 616$, $T = 291$ K, $R = 0\cdot045$ for 4662 observed reflections. The two crystallographically independent molecules have mean Si—O(Si) and Si—O(H) bond lengths of 1·639 (2) and 1·619 (2) Å and a mean Si—O—Si angle of 164·1 (2)°. Molecules are linked together by hydrogen bonds, to form chains parallel to the *b* axis.

Introduction. Hydrolysis of Pr_2SiF_2 (Pr = isopropyl) with KOH (Klingebiel, 1983) yields the title compound (I) and the six-membered ring siloxane $(Pr_2SiO)_3$, a homologue of the *tert*-butyl compound $(Bu_2SiO)_3$, the structure of which has been reported (Clegg, 1982).



(I)

Experimental. Crystals obtained from *n*-hexane and mounted in capillaries, 0·5 × 0·45 × 0·25 mm, Stoe–Siemens AED diffractometer, unit-cell parameters refined from 2θ angles for 50 reflections centred at $\pm\omega$ $(20 < 2\theta < 25°)$, intensities measured for 6124 reflections with $2\theta < 50°$ and $h \geq 0$, real-time profile-fitting (Clegg, 1981), no significant intensity variation for three standard reflections; no absorption correction, 6124 unique reflections (no equivalents measured), 4662 with $F > 4\sigma(F)$; structure solved by automatic multisolution direct methods, blocked-cascade refinement on F, $w^{-1} = \sigma^2(F) + 0\cdot0005F^2$, alkyl H atoms constrained to give C—H = 0·96 Å, H—C—H = 109·5°, $U(\text{H}) = 1\cdot2U_{\text{eq}}(\text{C})$, hydroxyl H atoms refined freely with isotropic U, anisotropic thermal parameters for all non-H atoms, no extinction correction, 371 parameters, $R = 0\cdot045$, $wR = 0\cdot054$, slope of normal probability plot = 1·32, max. shift/e.s.d. = 0·2, mean = 0·04, largest peak in final difference map = 0·27 e Å^{-3}, largest hole = −0·24 e Å^{-3}, scattering factors from *International Tables for X-ray Crystallography* (1974), programs used: *SHELXTL* (Sheldrick, 1978), diffractometer control program by WC.

Discussion. Atomic coordinates and bond lengths are given in Tables 1 and 2 respectively.* The two

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* Tables of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38469 (31 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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