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Methyl (1*S*,5*S*,6*S*,7*R*)-6-Formyl-7-methyl-2,8-dioxabicyclo[3.3.1]non-3-ene-4-carboxylate

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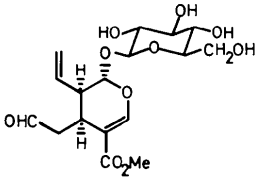
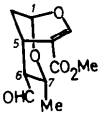
Abstract. $C_{11}H_{14}O_5$, M_r = 226·23, orthorhombic, $P2_12_12_1$, a = 8·116 (4), b = 9·684 (4), c = 13·998 (6) Å, U = 1102 Å^3, Z = 4, D_x = 1·364 Mg m^{-3}, μ(Mo $K\alpha$) = 0·1 mm^{-1}. Final R = 0·040 for 1572 unique observed reflexions. The X-ray structure resolves the ambiguity of NMR measurements. The saturated and unsaturated rings adopt chair and sofa conformations respectively.

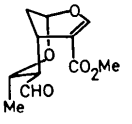
Introduction. The title compound was prepared from the natural product secologanin (I) *via* the action of β-glucosidase. Its proton NMR spectrum was consistent with either of two structures (II, III), which have different configurations at the C atoms bearing the methyl and formyl substituents; an X-ray structural investigation was undertaken to resolve this problem.



(I)



(II)



(III)

Prisms elongated along a were grown from diethyl ether/n-hexane. Data were collected to $2\theta_{max}$ = 50° on a Stoe STADI-2 diffractometer with monochromated Mo $K\alpha$ radiation and two crystals mounted respectively about a (layers 0–7, 1466 reflexions) and c (layers 0–12, 1733 reflexions). After Lp corrections, averaging equivalent reflexions gave 1797 unique reflexions, 1573 with $F > 4\sigma(F)$. Interlayer scale factors were obtained by least squares from equivalent reflexions from different layers; accurate cell constants were determined from ω angles of 279 strong reflexions.

The structure was solved by automated direct methods with *SHELXTL*; the best E map showed all the non-hydrogen atoms. Refinement proceeded to R = 0·13 (isotropic), 0·10 (anisotropic). In the final cycles a riding model was employed for H atoms [C–H 0·96 Å, H–C–H 109·5°, U(H) = 1·2 U(C)]. The final $R' = \sum w^{1/2}\Delta/\sum w^{1/2}|F_o|$ was 0·046, with a corresponding R = 0·040. A final difference map showed no peaks

Table 1. *Atom coordinates* (×10^4) *and isotropic temperature factors* (Å^2 × 10^3)

	x	y	z	U or U_{eq}
O(1)	5945 (2)	7141 (2)	6995 (1)	60 (1)*
C(2)	5384 (3)	8036 (3)	6328 (2)	47 (1)*
H(2)	4590	7699	5876	57
C(3)	5855 (3)	9359 (2)	6250 (2)	43 (1)*
C(4)	7071 (3)	9933 (3)	6950 (2)	47 (1)*
H(4)	6902	10912	6998	56
C(5)	6812 (4)	9171 (4)	7890 (2)	66 (1)*
H(5)	5709	9315	8116	77
H(5′)	7581	9497	8360	77
C(6)	7096 (3)	7677 (3)	7697 (2)	61 (1)*
H(6)	6908	7210	8292	73
O(7)	8714 (2)	7400 (2)	7413 (1)	54 (1)*
C(8)	9251 (3)	8130 (2)	6565 (1)	40 (1)*
H(8)	8673	7829	6004	47
C(9)	8882 (3)	9670 (2)	6635 (2)	42 (1)*
H(9)	9604	10043	7112	50
C(10)	9208 (3)	10384 (2)	5704 (2)	53 (1)*
H(10)	9310	11372	5713	63
O(11)	9350 (3)	9816 (3)	4956 (1)	76 (1)*
C(12)	11065 (3)	7828 (3)	6476 (2)	59 (1)*
H(12)	11472	8283	5914	72
H(12′)	11239	6851	6419	72
H(12″)	11642	8168	7027	72
C(13)	5180 (3)	10267 (2)	5512 (2)	45 (1)*
O(14)	5610 (3)	11447 (2)	5407 (2)	72 (1)*
O(15)	4018 (2)	9673 (2)	4973 (1)	59 (1)*
C(16)	3290 (4)	10529 (3)	4248 (2)	64 (1)*
H(16)	2519	9985	3888	76
H(16′)	4114	10894	3826	76
H(16″)	2719	11276	4554	76

* U_{eq} is ⅓ of the trace of the orthogonalized U matrix.

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>0.18 e Å^{-3}. Atom coordinates are given in Table 1, with derived parameters in Table 2 and Fig. 1.*

Discussion. The structure determination shows that the product adopts structure (II). The saturated ring thus possesses the chair conformation [maximum deviation from ideal torsion angles (Bucourt & Hainaut, 1965) is 7·5°]. Its substituents are equatorial. The junction between the saturated and unsaturated rings is diaxial; the latter ring adopts the sofa conformation (maximum torsion-angle deviation 5·3°).

The absolute configuration could not be deduced from the crystallographic data; the configuration given here is consistent with the known configuration of secologanin (Battersby, Burnett & Parsons, 1969) and the assumed reaction mechanism (Tietze & Uzar, to be published).

There are no unusually short non-bonded distances.

We thank the Fonds der Chemischen Industrie for financial assistance. The program *SHELXTL* was written by GMS.

* Lists of structure factors, torsion angles and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35576 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond lengths* (Å) *and angles* (°)

C(2)–O(1)	1·353 (4)	C(2)–C(3)	1·341 (4)
C(3)–C(4)	1·497 (4)	C(4)–C(5)	1·523 (5)
C(4)–C(9)	1·556 (4)	C(5)–C(6)	1·490 (6)
C(6)–O(1)	1·452 (4)	C(6)–O(7)	1·398 (4)
C(8)–O(7)	1·449 (4)	C(8)–C(9)	1·524 (4)
C(10)–C(9)	1·499 (4)	C(10)–O(11)	1·188 (4)
C(12)–C(8)	1·507 (5)	C(13)–C(3)	1·464 (4)
C(13)–O(14)	1·204 (4)	C(13)–O(15)	1·338 (4)
C(16)–O(15)	1·438 (4)		

C(2)–O(1)–C(6)	117·1 (3)	O(1)–C(2)–C(3)	124·9 (3)
C(2)–C(3)–C(4)	119·3 (3)	C(2)–C(3)–C(13)	121·6 (3)
C(4)–C(3)–C(13)	119·0 (3)	C(3)–C(4)–C(5)	107·1 (3)
C(3)–C(4)–C(9)	112·1 (3)	C(5)–C(4)–C(9)	107·2 (3)
C(4)–C(5)–C(6)	107·0 (3)	O(1)–C(6)–C(5)	111·7 (3)
O(1)–C(6)–O(7)	110·1 (3)	C(5)–C(6)–O(7)	112·5 (4)
C(6)–O(7)–C(8)	114·9 (3)	O(7)–C(8)–C(9)	111·5 (3)
O(7)–C(8)–C(12)	105·5 (3)	C(9)–C(8)–C(12)	112·8 (3)
C(4)–C(9)–C(8)	111·4 (3)	C(4)–C(9)–C(10)	109·7 (3)
C(8)–C(9)–C(10)	111·2 (3)	C(9)–C(10)–O(11)	124·7 (3)
C(3)–C(13)–O(14)	123·3 (3)	C(3)–C(13)–O(15)	113·8 (3)
O(14)–C(13)–O(15)	122·9 (3)	C(13)–O(15)–C(16)	116·1 (3)

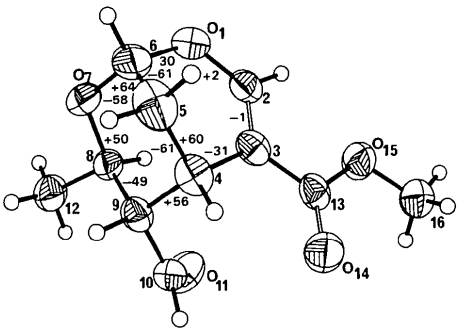

Fig. 1. The molecule of the title compound, showing the atom labelling and the ring torsion angles (to nearest degree). Torsion-angle e.s.d.'s were all $<0.5°$. *N.B.* The labelling does not correspond to the IUPAC numbering of the title.

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(6a*RS*,9*RS*,10a*RS*)-4-Bromo-1-methoxy-6,6,9-trimethyl-6a,7,8,9,10,10a-hexahydro-6*H*-dibenzo[*b*,*d*]pyran

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Abstract. $C_{17}H_{23}BrO_2$, $M_r = 339.28$, triclinic, $P\bar{1}$, $a = 7.378$ (4), $b = 9.740$ (5), $c = 11.406$ (6) Å, $\alpha = 80.83$ (4), $\beta = 81.26$ (4), $\gamma = 81.88$ (4)°, $U = 794.0$ Å^3, $Z = 2$, $D_x = 1.419$ Mg m^{-3}, $\mu = 2.6$ mm^{-1}. Final $R = 0.064$ for 1323 independent reflexions. The substitution pattern, which could not be unambiguously inferred from chemical or spectroscopic evidence, has been determined.

Introduction. The title compound (II) was synthesized from the cannabinoid analogue (I) (von Kiedrowski & Tietze, unpublished). A crystal structure determination

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