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8β-Angeloyloxymaximilianin*

By William H. Watson† and Volker Zabel

FASTBIOS Laboratory, Department of Chemistry, Texas Christian University, Fort Worth, Texas 76129, *USA*

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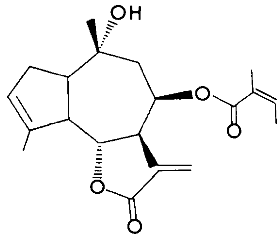
Abstract. 8β-Angeloyloxymaximilianin, $\Delta^{3,4},\Delta^{11,13}$-8β,10α-dihydroguaianolide 8-angelate, is a guaianolide-type sesquiterpene lactone isolated from *Helianthus maximiliani.* $C_{20}H_{26}O_5$, monoclinic, space group $P2_1$, $a = 10\cdot116\,(2)$, $b = 11\cdot979\,(2)$, $c = 7\cdot787\,(2)$ Å, $\beta = 92\cdot30\,(2)^\circ$, $V = 942\cdot8\,(3)$ Å^3, $Z = 2$, $d_c = 1\cdot22$ Mg m^{-3} and $\mu = 5\cdot9$ cm^{-1}. The structure was solved by direct methods and refined by full-matrix least-squares techniques (non-H atoms anisotropic, H atoms isotropic) to a final R of 0·056 for 1716 independent observed reflexions. The five- and seven-membered carbocyclic rings are *cis* fused while the lactone ring exhibits a *trans* ring juncture. The two five-membered rings are in flattened envelope conformations while the seven-membered ring can be described as a twist chair. An angelate side chain is found at C(8).

Introduction. *Helianthus* L. (Tribe Heliantheae, Family Compositae) is a genus of about 50 species which are native to North America. The genus has been a source of food and medicine for thousands of years to the inhabitants of North America (Heiser, 1976) and has become the second most important vegetable-oil source in the world (Putt, 1978). Surprisingly, little chemical work has been reported on this genus, and the genus is still not well understood systematically (Heiser, 1969). It is anticipated that a detailed phytochemical investigation will lead to a better understanding of the interspecific boundaries and the evolutionary interrelationships in the genus (Gershenzon, Ohno & Mabry, 1981). The expansion of cultivation of the main oil-producing sunflower species in the United States is limited by insect damage (Schulz, 1978). Many wild sunflower species appear to be resistant to insect predation; however, there is no obvious morphological feature in the resistant plants which might account for their resistance to insect attack. A number of terpenoid compounds have been implicated in plant defence mechanisms against insects (Mabry & Gill, 1979), and it is anticipated that resistance in wild sunflower species may be related to chemical composition. We would like to report the structure of 8β-angeloyloxymaximilianin (1). At present *H. maximiliani* is the only species of *Helianthus* known to produce guaianolide-type sesquiterpenoids (Gershenzon *et al.*, 1981).



(1)

Good single crystals of 8β-angeloyloxymaximilianin could be obtained from hot ethyl acetate solutions. A crystal of dimensions 0·35 × 0·6 × 0·35 mm was selected for X-ray analysis. All data were collected on a Syntex $P2_1$ diffractometer by the θ:2θ scanning technique using a variable scan speed, Cu $K\alpha$ radiation ($\lambda = 1\cdot54178$ Å) and a graphite monochromator. Room-temperature lattice parameters were refined by a least-squares procedure using 15 reflexions whose angles were measured by a centering routine associated with the diffractometer. Systematic absences were consistent with space group $P2_1$. A periodically monitored reflexion showed no significant change in intensity. Of the 1737 independent reflexions measured ($2\theta < 140^\circ$), 1716 had intensities greater than $2\sigma(I)$. Lorentz and polarization corrections were applied, but no absorption corrections were made.

The direct-methods program *MULTAN* 78 (Main, Lessinger, Woolfson, Germain & Declercq, 1978) was used to calculate phases for the $|E|$ values greater than 1·3. The phase set with the highest combined figure of merit was selected, and the E map calculated with these phases revealed the positions of all non-H atoms. After several cycles of least-squares refinement all H atoms except those associated with C(14) were located in a difference Fourier map. Five reflexions showing significant secondary extinction were omitted from further refinement. Full-matrix least-squares refinement converged to an R of 0·056 where $R = \sum||F_o| - |F_c||/\sum|F_o|$. The function minimized in the refinement

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[*] Angelic acid is (Z)-2-methylisocrotonic acid.

[†] To whom correspondence should be addressed.

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was $\sum w(|F_o| - |F_c|)^2$ where $w[= 1/\sigma^2(F_o)]$ was determined from counting statistics.

A final difference map showed no peak larger than $0{\cdot}2$ e Å^{-3}. Atomic scattering factors were calculated by the XRAY program (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) while the real and imaginary contributions to the anomalous dispersion were taken from *International Tables for X-ray Crystallography* (1974). Atomic positional parameters and U_{eq} values are given in Table 1 while interatomic distances, valence angles and torsion angles are given in Tables 2, 3 and 4, respectively.* Although the absolute

Table 1. *Final atomic coordinates* ($\times 10^4$, *for* H $\times 10^3$) *and isotropic thermal parameters* (Å^2 $\times 10^3$)

$$U_{eq} = (U_1U_2U_3)^{1/3}.$$

	x	y	z	U_{eq}/U
C(1)	3860 (2)	5686 (2)	8333 (3)	6·4 (1)
C(2)	3129 (4)	4768 (3)	9275 (5)	8·7 (2)
C(3)	2382 (3)	4171 (4)	7850 (6)	9·1 (2)
C(4)	2794 (2)	4406 (3)	6334 (5)	7·6 (2)
C(5)	3976 (2)	5190 (2)	6471 (3)	5·9 (1)
C(6)	5260 (2)	4561 (2)	6279 (2)	4·9 (1)
O(6)	5268 (1)	4000	4608 (2)	6·0 (1)
C(7)	6488 (2)	5308 (2)	6335 (2)	4·8 (1)
C(8)	7190 (2)	5278 (2)	8092 (2)	4·8 (1)
O(8)	7725 (1)	4149 (1)	8258 (2)	5·1 (1)
C(9)	6274 (3)	5470 (2)	9588 (3)	6·1 (1)
C(10)	5076 (2)	6235 (2)	9285 (3)	6·2 (1)
O(10)	5528 (2)	7175 (2)	8333 (2)	6·5 (1)
C(11)	7277 (2)	4910 (2)	4867 (3)	5·2 (1)
C(12)	6439 (2)	4107 (2)	3869 (2)	5·3 (1)
O(12)	6701 (2)	3589 (2)	2597 (2)	6·7 (1)
C(13)	8459 (3)	5194 (4)	4404 (4)	8·3 (1)
C(14)	2254 (3)	3941 (5)	4651 (7)	9·8 (3)
C(15)	4609 (4)	6627 (4)	11035 (4)	8·5 (2)
C(16)	8755 (2)	3983 (2)	9375 (2)	5·0 (1)
O(16)	9259 (2)	4726 (2)	10224 (2)	6·6 (1)
C(17)	9176 (2)	2796 (2)	9526 (3)	6·0 (1)
C(18)	9102 (3)	2062 (3)	8247 (4)	6·8 (1)
C(19)	8566 (4)	2217 (3)	6460 (5)	8·5 (2)
C(20)	9802 (4)	2509 (4)	11259 (5)	8·6 (2)
H(1)	316 (3)	622 (3)	833 (4)	5·3 (6)
H(2*a*)	232 (6)	514 (7)	1024 (9)	12·8 (21)
H(2*b*)	372 (6)	436 (9)	982 (10)	14·2 (23)
H(3)	160 (4)	365 (4)	817 (5)	7·5 (10)
H(5)	393 (3)	579 (3)	543 (4)	5·2 (6)
H(6)	525 (4)	403 (5)	721 (5)	8·2 (10)
H(7)	653 (5)	614 (5)	580 (6)	9·1 (11)
H(8)	789 (3)	586 (3)	821 (4)	5·7 (7)
H(9*a*)	591 (5)	477 (7)	992 (9)	11·1 (16)
H(9*b*)	680 (4)	587 (4)	1050 (5)	7·3 (8)
H(10)	474 (4)	772 (4)	814 (5)	7·9 (10)
H(13*a*)	880 (3)	487 (4)	343 (5)	6·8 (9)
H(13*b*)	889 (7)	556 (11)	536 (4)	15·5 (26)
H(15*a*)	533 (6)	692 (5)	1160 (8)	10·3 (14)
H(15*b*)	372 (5)	712 (5)	1088 (7)	9·8 (13)
H(15*c*)	432 (5)	598 (6)	1188 (8)	10·8 (14)
H(18)	946 (5)	131 (5)	853 (7)	10·5 (14)
H(19*a*)	885 (3)	314 (3)	597 (4)	6·7 (8)
H(19*b*)	755 (5)	204 (4)	644 (6)	8·2 (9)
H(19*c*)	870 (6)	153 (8)	550 (10)	12·2 (20)
H(20*a*)	919 (3)	282 (4)	1207 (5)	6·9 (8)
H(20*b*)	997 (4)	174 (4)	1120 (5)	7·5 (9)
H(20*c*)	1066 (5)	287 (4)	1153 (6)	8·1 (10)

Table 2. *Interatomic distances* (Å)

C(1)–C(2)	1·529 (5)	C(8)–C(9)	1·535 (3)
C(1)–C(5)	1·575 (4)	O(8)–C(16)	1·345 (2)
C(1)–C(10)	1·557 (3)	C(9)–C(10)	1·530 (4)
C(2)–C(3)	1·499 (6)	C(10)–O(10)	1·433 (3)
C(3)–C(4)	1·298 (6)	C(10)–C(15)	1·534 (4)
C(4)–C(5)	1·521 (4)	C(11)–C(12)	1·482 (3)
C(4)–C(14)	1·506 (6)	C(11)–C(13)	1·308 (4)
C(5)–C(6)	1·514 (3)	C(12)–O(12)	1·207 (3)
C(6)–O(6)	1·465 (2)	C(16)–O(16)	1·209 (3)
C(6)–C(7)	1·531 (3)	C(16)–C(17)	1·488 (4)
O(6)–C(12)	1·344 (2)	C(17)–C(18)	1·329 (4)
C(7)–C(8)	1·517 (3)	C(17)–C(20)	1·506 (4)
C(7)–C(11)	1·498 (3)	C(18)–C(19)	1·485 (5)
C(8)–O(8)	1·461 (3)		

Table 3. *Valence angles* (°)

C(2)C(1)C(5)	103·0 (2)	C(8)O(8)C(16)	117·9 (2)
C(2)C(1)C(10)	117·6 (2)	C(8)C(9)C(10)	118·1 (2)
C(5)C(1)C(10)	120·7 (2)	C(1)C(10)C(9)	115·2 (2)
C(1)C(2)C(3)	103·2 (3)	C(1)C(10)O(10)	110·4 (2)
C(2)C(3)C(4)	113·5 (3)	C(1)C(10)C(15)	106·7 (2)
C(3)C(4)C(5)	110·5 (3)	C(9)C(10)O(10)	106·4 (2)
C(3)C(4)C(14)	126·3 (3)	C(9)C(10)C(15)	108·5 (2)
C(5)C(4)C(14)	123·1 (3)	O(10)C(10)C(15)	109·6 (2)
C(1)C(5)C(4)	102·1 (2)	C(7)C(11)C(12)	107·3 (2)
C(1)C(5)C(6)	112·0 (2)	C(7)C(11)C(13)	130·4 (2)
C(4)C(5)C(6)	111·2 (2)	C(12)C(11)C(13)	122·3 (2)
C(5)C(6)O(6)	110·6 (1)	O(6)C(12)C(11)	109·4 (2)
C(5)C(6)C(7)	113·9 (2)	O(6)C(12)O(12)	122·0 (2)
O(6)C(6)C(7)	105·1 (1)	C(11)C(12)O(12)	128·6 (2)
C(6)O(6)C(12)	111·9 (1)	O(8)C(16)O(16)	123·0 (2)
C(6)C(7)C(8)	111·2 (2)	O(8)C(16)C(17)	113·8 (2)
C(6)C(7)C(11)	104·4 (2)	O(16)C(16)C(17)	123·2 (2)
C(8)C(7)C(11)	115·9 (2)	C(16)C(17)C(18)	124·5 (2)
C(7)C(8)O(8)	105·1 (1)	C(16)C(17)C(20)	113·4 (2)
C(7)C(8)C(9)	113·9 (2)	C(18)C(17)C(20)	122·0 (3)
O(8)C(8)C(9)	107·7 (2)	C(17)C(18)C(19)	128·9 (3)

Table 4. *Selected torsion angles* (°)

1–5–6–7	−68·7 (2)	8–9–10–1	80·2 (3)
5–6–7–8	100·0 (2)	9–10–1–5	−59·9 (3)
6–7–8–9	−49·6 (2)	10–1–5–6	41·3 (3)
7–8–9–10	−31·9 (3)	8–9–10–15	−160·4 (3)
1–2–3–4	15·2 (4)	6–7–11–12	8·5 (2)
2–3–4–5	2·7 (4)	7–11–12–O(6)	−0·3 (2)
3–4–5–1	−18·8 (3)	11–12–O(6)–6	−8·8 (2)
4–5–1–2	26·6 (3)	12–O(6)–6–7	14·0 (2)
5–1–2–3	−25·2 (3)	O(6)–6–7–11	−13·1 (2)
1–5–4–14	164·1 (3)	6–O(6)–12–O(12)	170·5 (2)
2–3–4–14	179·7 (3)	7–11–12–O(12)	−179·5 (2)
3–2–1–10	−160·7 (3)	O(12)–12–11–13	2·8 (3)
2–1–15–O(10)	−171·9 (3)	8–O(8)–16–17	176·6 (3)
10–9–8–O(8)	−148·1 (3)	O(8)–16–17–19	32·7 (3)
9–8–O(8)–16	−80·7 (3)	O(8)–16–17–20	−151·7 (3)
8–O(8)–16–O(16)	−0·8 (3)	16–17–18–19	−2·4 (4)
O(16)–16–17–20	25·7 (4)	20–17–18–19	−177·7 (4)
O(16)–16–17–18	−149·9 (4)		

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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 36606 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

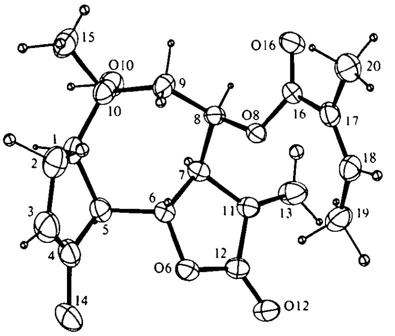

Fig. 1. *ORTEP* drawing of 8β-angeloyloxymaximilianin. Thermal ellipsoids are drawn at the 35% probability level. H atoms are represented by spheres of arbitrary size.

configuration was not established by this investigation, it is believed to be that shown in Fig. 1 (Fischer, Olivier & Fischer, 1979), and all refinements were based upon this assignment.

Discussion. Fig. 1 is an *ORTEP* drawing (Johnson, 1971) of 8β-angeloyloxymaximilianin. Cycloheptane rings can exist in boat and chair forms (C_s symmetry) and may undergo pseudorotation with twist forms (C_2 symmetry) being the most stable in each series (Hendrickson, 1961). The seven-membered ring in most guaianolide-type sesquiterpenoids most closely approximates the C twist-chair conformation although there are considerable deviations from this ideal form (Hendrickson, 1963; McPhail & Sim, 1973). The sum ($\sum$) of the absolute values of the sums of symmetry-related torsion angles has been used as a measure of deviation from the ideal form. The $\sum$ value for C_2 symmetry of the chair series is 47° for 8β-angeloyloxymaximilianin which may be compared with the ideal twist-chair value of 0° (Hendrickson, 1961) and the 19–60° observed for a series of guaianolide-type sesquiterpenoids (McPhail & Sim, 1973). The average valency angle in cycloheptane rings of the above series ranges from 114·5–115·9° which is consistent with the 115° value found for 8β-angeloyloxymaximilianin. The cyclopentene ring exhibits an envelope conformation while the α,β-unsaturated γ-lactone can be described as a flattened envelope.

The side chain at C(8) is composed of two planar segments rotated from coplanarity by a twist about the C(16)–C(17) bond, O(8)C(16)C(17)C(18) 32·7 (3)°. An intermolecular hydrogen bond is formed between the hydroxyl at C(10) and the O(12) keto oxygen, O(10)···O(12) ($1-x$, $\frac{1}{2}+y$, $1-z$) 2·889 (3), H(10)···O(12) 1·86 (4) and O(10)–H(10) 1·04 (4) Å.

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