Acta Cryst. (1987). C**43**, 2362–2364

Structure of Olean-12(13)-en-3β-yl Acetate

By Knut Maartmann-Moe, Wendy Bicknell and George W. Francis

Department of Chemistry, University of Bergen, 5014 *Bergen, Norway*

(*Received* 7 *November* 1986; *accepted* 3 *August* 1987)

Abstract. β-Amyryl acetate, $C_{32}H_{52}O_2$, $M_r = 468{\cdot}8$, monoclinic, $P2_1$, $a = 7{\cdot}338$ (7), $b = 16{\cdot}466$ (6), $c = 11{\cdot}394$ (3) Å, $\beta = 92{\cdot}83$ (4)°, $V = 1375{\cdot}1$ Å^3, $Z = 2$, $D_x = 1{\cdot}13$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, $\mu = 0{\cdot}63$ cm^{-1}, $F(000) = 520$, 138 K, final $R = 0{\cdot}069$ for 140 independent reflections with $I > 2\sigma(I)$. The steroid rings *A, B, D* and *E* have chair conformations and ring *C* a symmetrical sofa conformation. Only the *D*/*E* ring junction is *cis*. The β face of the molecule is convex. The bond lengths and angles are in good agreement with those of β-amyrin analogues, apart from a shortening of bond lengths around C17.

Introduction. 3β-Hydroxyolean-12(13)-ene or β-amyrin occupies a central position in the chemistry of the triterpenes. It occurs both free and as simple esters in a wide variety of higher plants (De Mayo, 1959) and is the parent compound of innumerable oxygenated analogues (Connolly & Overton, 1972). It is thus surprising that while X-ray structure determinations have been carried out on a number of the more oxygenated analogues of β-amyrin (Hoge & Nordman, 1974; Roques, Druet & Comeau, 1978; Roques, Declercq & Germain, 1978; Roques, Comeau, Forme, Kahn & Andre, 1977; Mak, Chiang & Chang, 1982; Kitagawa *et al.*, 1982) the parent compound has not been so studied. Other relevant crystal structures that have been determined are those of simple α-amyrin esters (α-amyrin differs from β-amyrin only in the position of the C29 methyl group) and of methyl ursolate (α-amyrin-28-carboxylate) (Grynpas & Lindley, 1979; Paton & Paul, 1979). An authentic sample of β-amyryl acetate was isolated from mistletoe (*Viscum album* L.) by the procedure of Sakurai & Okumura (1971). Crystals were grown from ethanol.

Experimental. Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation. Crystal dimensions 0·04 × 0·07 × 0·14 mm. Temperature at crystal site 138 K. Cell parameters based on least-squares fit of 25 independent reflections with $2\theta > 20°$. Intensity data recorded using the ω-scan technique with a constant scan speed of 4° min^{-1}. Crystal orientation checked every 100 recordings. Three standard reflections measured every 2 h varied by less than 2%, variations were irregular with respect to time, intensity data were not corrected for decay. Lp correction, absorption ignored. 2239 independent reflections recorded ($2\theta < 48°$), $h = 0$ to 8, $k = 0$ to 18, $l = -12$ to 13, 832 with $I < 2{\cdot}0\sigma(I)$ regarded as unobserved. Structure solved by *MULTAN*80 (Main *et al.*, 1980). Full-matrix least-squares minimization of $\sum w(\Delta F)^2$, where $w^{-1} = \sigma^2(I)/4\mathrm{Lp}I$, $\sigma^2(I) = \sigma^2(I_c) + pI_c$, and $p = 0{\cdot}02$. Isotropic refinement, with H atoms placed geometrically (C—H = 0·95 Å), but not refined. Ratio of LS shift to e.s.d. <0·01. Difference Fourier map after the final LS iteration showed maximum residual electron density of 0·34 e Å^{-3}. The refinement converged to a conventional $R = 0{\cdot}069$, $wR = 0{\cdot}050$ and $S = 1{\cdot}48$.[*] The absolute configuration could not be determined from the data. Atomic scattering factors were from *International Tables for X-ray Crystallography* (1974). All computer programs used are part of the Enraf–Nonius *SDP-Plus* package (Frenz, 1983).

Discussion. The structure of β-amyryl acetate is in general terms close to those already found for the more oxygenated analogues of the β-amyrin series. Complete structural information is available for gymnemagenin (Hoge & Nordman, 1974), hederagenin (Roques, Druet & Comeau, 1978), 3β-acetoxyolean-12(13)-en-28β-oic acid (Roques, Declercq & Germain, 1978) and for

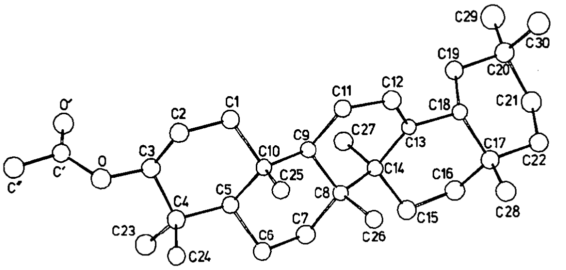

Fig. 1. *ORTEP* drawing (Johnson, 1965) of β-amyryl acetate. The atoms C3 and C10 lie in the plane of the paper while the vector C6–C10 makes an angle of 30° to the plane of the paper.

---

[*] Lists of structure factors, H-atom parameters and torsional angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44233 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0108-2701/87/122362-03$01.50

Table 1. *Non*-H-*atom fractional coordinates with e.s.d.'s in parentheses*

	x	*y*	*z*	$B_{\rm iso}$(Å^2)
O	0·6722 (6)	0·750	0·3068 (4)	2·2 (1)
O′	0·8834 (6)	0·7369 (3)	0·1732 (4)	2·3 (1)
C′	0·859 (1)	0·8624 (5)	0·2759 (7)	2·4 (2)
C″	0·808 (1)	0·7768 (4)	0·2454 (6)	1·9 (1)
C1	0·6325 (9)	0·5265 (5)	0·3665 (6)	1·8 (1)
C2	0·688 (1)	0·6150 (5)	0·3853 (6)	2·3 (2)
C3	0·610 (1)	0·6658 (4)	0·2858 (6)	1·9 (2)
C4	0·404 (1)	0·6666 (4)	0·2693 (6)	1·9 (1)
C5	0·3467 (9)	0·5746 (4)	0·2586 (6)	1·5 (1)
C6	0·1416 (9)	0·5614 (4)	0·2375 (6)	1·7 (1)
C7	0·104 (1)	0·4768 (5)	0·1876 (6)	2·0 (2)
C8	0·186 (1)	0·4076 (4)	0·2657 (6)	1·4 (1)
C9	0·3850 (9)	0·4276 (4)	0·3038 (6)	1·3 (1)
C10	0·4231 (9)	0·5143 (4)	0·3543 (6)	1·4 (1)
C11	0·4675 (9)	0·3595 (4)	0·3824 (6)	1·7 (1)
C12	0·397 (1)	0·2765 (5)	0·3510 (6)	1·9 (1)
C13	0·2678 (9)	0·2582 (4)	0·2712 (6)	1·3 (1)
C14	0·1843 (9)	0·3251 (4)	0·1937 (6)	1·4 (1)
C15	−0·013 (1)	0·3035 (4)	0·1452 (6)	2·0 (2)
C16	−0·045 (1)	0·2141 (5)	0·1194 (6)	2·2 (2)
C17	0·009 (1)	0·1582 (4)	0·2226 (6)	1·8 (1)
C18	0·2168 (9)	0·1694 (4)	0·2511 (6)	1·4 (1)
C19	0·334 (1)	0·1287 (5)	0·1595 (6)	1·9 (1)
C20	0·292 (1)	0·0388 (5)	0·1348 (6)	2·2 (2)
C21	0·086 (1)	0·0323 (5)	0·1026 (6)	2·3 (2)
C22	−0·0305 (9)	0·0695 (4)	0·1937 (6)	1·8 (2)
C23	0·311 (1)	0·7123 (4)	0·3673 (6)	1·8 (1)
C24	0·354 (1)	0·7103 (5)	0·1530 (6)	2·3 (2)
C25	0·3475 (9)	0·5295 (5)	0·4762 (6)	1·7 (1)
C26	0·067 (1)	0·3994 (5)	0·3740 (6)	1·8 (1)
C27	0·301 (1)	0·3304 (5)	0·0837 (6)	2·0 (2)
C28	−0·094 (1)	0·1795 (5)	0·3301 (6)	2·1 (2)
C29	0·401 (1)	0·0099 (5)	0·0325 (7)	3·2 (2)
C30	0·345 (1)	−0·0141 (5)	0·2423 (7)	2·8 (2)

Table 2. *Selected structural data for β-amyryl acetate*

Bond lengths are given in Å, bond angles and dihedral angles in degrees. E.s.d.'s are in parentheses.

C Nos.	Bond length	C Nos.	Bond angle	C Nos.	Dihedral angle
1–2	1·526 (9)	10–1–2	113·3 (6)	10–1–2–3	−57·2
2–3	1·499 (8)	1–2–3	109·7 (5)	1–2–3–4	60·4
3–4	1·519 (8)	2–3–4	116·1 (5)	2–3–4–5	−54·5
4–5	1·575 (8)	3–4–5	105·1 (5)	3–4–5–10	50·7
5–10	1·558 (8)	4–5–10	118·3 (5)	4–5–10–1	−50·6
10–1	1·550 (8)	5–10–1	107·5 (5)	2–1–10–5	51·6
5–6	1·528 (8)	10–5–6	109·7 (5)	10–5–6–7	−64·0
6–7	1·524 (8)	5–6–7	110·3 (6)	5–6–7–8	56·4
7–8	1·548 (9)	6–7–8	113·7 (5)	6–7–8–9	−46·9
8–9	1·537 (8)	7–8–9	109·9 (5)	7–8–9–10	48·3
9–10	1·559 (8)	8–9–10	116·8 (5)	8–9–10–5	−55·3
		9–10–5	105·9 (5)	6–5–10–9	61·1
		14–8–9	108·3 (5)	14–8–9–11	−60·4
9–11	1·540 (8)	8–9–11	110·4 (5)	8–9–11–12	33·4
11–12	1·498 (9)	9–11–12	113·8 (5)	9–11–12–13	−4·7
12–13	1·316 (8)	11–12–13	127·1 (6)	11–12–13–14	4·5
13–14	1·522 (8)	12–13–14	119·4 (6)	12–13–14–8	−31·5
14–8	1·586 (8)	13–14–8	109·1 (5)	9–8–14–13	59·1
		18–13–14	121·2 (5)	18–13–14–15	30·1
14–15	1·563 (8)	13–14–15	112·3 (5)	13–14–15–16	−33·9
15–16	1·517 (9)	14–15–16	114·9 (6)	14–15–16–17	52·6
16–17	1·529 (9)	15–16–17	113·8 (5)	15–16–17–18	−61·3
17–18	1·558 (9)	16–17–18	107·5 (5)	16–17–18–13	53·6
18–13	1·523 (8)	17–18–13	112·1 (5)	14–13–18–17	−41·5
		22–17–18	109·4 (5)	22–17–18–19	47·8
18–19	1·540 (8)	17–18–19	112·5 (5)	17–18–19–20	−52·8
19–20	1·536 (9)	18–19–20	115·4 (5)	18–19–20–21	53·6
20–21	1·539 (8)	19–20–21	107·4 (5)	19–20–21–22	−53·9
21–22	1·508 (8)	20–21–22	113·0 (6)	20–21–22–17	56·4
22–17	1·521 (9)	21–22–17	115·6 (6)	18–17–22–21	−51·0
C–C(methyl) bonds			Interannular dihedral angles		
4–23	1·534 (9)		Junction *A–B*	4–5–10–9	−166·0
4–24	1·536 (9)			6–5–10–1	176·5
10–25	1·541 (8)				
8–26	1·555 (8)		Junction *B–C*	7–8–9–11	179·5
14–27	1·556 (8)			14–8–9–10	168·4
17–28	1·512 (9)				
20–29	1·523 (9)		Junction *C–D*	18–13–14–8	153·9
20–30	1·536 (9)			12–13–14–15	−155·3
			Junction *D–E*	16–17–18–19	−74·0
				22–17–18–13	175·4

3β,16β-dimethoxyolean-12(13)-en-28(21)β-olide (Roques *et al.*, 1977), and may be used as a basis for detailed comparison with the results obtained in the present study. While our work does not allow determination of the absolute configuration, Fig. 1 shows an *ORTEP* (Johnson, 1965) representation of the accepted configuration for β-amyryl acetate. Final fractional atomic coordinates for non-H atoms are given in Table 1; selected structural data are provided in Table 2. The rings *A, B, C* and *D* form the main plane of the molecule. Ring *E*, as a result of the *D/E cis* junction, and the C3 acetate group lie almost perpendicular to this plane. Rings *A, B, D* and *E* have chair conformations, in contrast with the symmetrical sofa conformation of ring *C*. The β face of the molecule is convex and steric interaction between the C25 and C26 methyl groups is thus reduced. The molecule in the configuration shown is slightly skewed in a clockwise direction when viewed from ring *A* along the main plane.

Bond lengths in β-amyryl acetate are in the range 1·2–1·6 Å. Here as in the oxygenated analogues, the longest bonds are associated with the most substituted termini: C5—C10, C9—C10, C17—C18, C8—C26, C14—C15 and C14—C27 have bond lengths between 1·555 and 1·565 Å while exceptionally long distances are observed for C4—C5 1·575 and C8—C14 1·586 Å. The C12=C13 double bond is of a normal length. Short bond lengths for C2—C3 and C11—C12 are typical for the system and these bonds have lengths of 1·499 and 1·498 Å respectively in β-amyryl acetate.

The main change observed in going from the oxygenated analogues to β-amyryl acetate is a reduction of some bond lengths in the neighbourhood of C17: C16—C17 1·529, C17—C22 1·521 and C21—C22 1·508 Å. These changes are readily explained by the lack of supernumerary O atoms on the periphery of ring *E* in β-amyryl acetate. The structure of ring *E* in the title compound represents a starting point for the future evaluation of the effects of substitution in this part of the ring system.

The observed bond angles are in good agreement with those found in the β-amyrin analogues; in particular the results accord well with those for gymnemagenin (Hoge & Nordman, 1974) which like β-amyryl acetate lacks the C28 carboxyl group.

The expected differences in ring *E* are found when this structure is compared with that of α-amyryl acetate (Grynpas & Lindley, 1979) where one of the methyl groups carried on C20 in β-amyryl acetate is moved to C19. The endocyclic bond angles at C19 and C21 are greater and that at C20 is smaller, and the C18—C19 and C19—C20 bond lengths are shorter in β- than in α-amyryl acetate. The two structures are otherwise very similar, although a shorter C12—C13 bond length, 1·316 as against 1·334 Å, and a larger C11—C12—C13—C14 dihedral angle, 4·5 as against 0·3°, are found for β- than for α-amyryl acetate.

A parallel structural determination of α-amyryl acetate was carried out and gave results in good agreement with those previously published (Grynpas & Lindley, 1979).

References

CONNOLLY, J. D. & OVERTON, K. H. (1972). *Chemistry of Terpenes and Terpenoids*, edited by A. A. NEWMAN, pp. 207–287. London: Academic Press.

DE MAYO, P. (1959). *The Chemistry of Natural Products*. Vol. III. *The Higher Terpenoids*, edited by K. W. BENTLEY, p. 156. London: Interscience.

FRENZ, B. A. (1983). *Enraf–Nonius Structure Determination Package; SDP Users Guide*, version of 6 January 1983. Enraf–Nonius, Delft, The Netherlands.

GRYNPAS, M. & LINDLEY, P. F. (1979). *J. Cryst. Mol. Struct.* **9**, 199–217.

HOGE, R. & NORDMAN, C. E. (1974). *Acta Cryst.* B**30**, 1435–1440.

International Tables for X-ray Crystallography (1974). Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA.

KITAGAWA, I., YOSHIKAWA, M., WANG, H. K., SAITO, M., TOSIRISUK, V., FUJIWARA, T. & TOMITA, K. (1982). *Chem. Pharm. Bull.* **30**, 2294–2297.

MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN*80. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.

MAK, T. C. W., CHIANG, T.-C. & CHANG, H.-M. (1982). *J. Chem. Soc. Chem. Commun.* pp. 785–786.

PATON, W. F. & PAUL, I. C. (1979). *Cryst. Struct. Commun.* **8**, 207–211.

ROQUES, R., COMEAU, L., FOURME, R., KAHN, R. & ANDRE, D. (1977). *Acta Cryst.* B**33**, 1682–1687.

ROQUES, R., DECLERCQ, J.-P. & GERMAIN, G. (1978). *Acta Cryst.* B**34**, 2367–2370.

ROQUES, R., DRUET, D. & COMEAU, L. C. (1978). *Acta Cryst.* B**34**, 1634–1639.

SAKURAI, A. & OKUMURA, Y. (1971). *Rep. Fac. Sci. Shizuoka Univ.* **6**, 63–69.

Acta Cryst. (1987). C**43**, 2364–2366

syn-8,*syn*-13-Bis(benzoyloxy)heptacyclo[7.6.0.0^{2,7}.0^{4,14}.0^{5,12}.0^{6,10}.0^{11,15}]pentadecan-3-one

BY JUDITH L. FLIPPEN-ANDERSON, RICHARD GILARDI AND CLIFFORD GEORGE

Laboratory for the Structure of Matter, Naval Research Laboratory, Washington, DC 20375, *USA*

ALAN P. MARCHAND

Department of Chemistry, North Texas State University, Box 5068, *Denton, TX* 76203–5068, *USA*

AND ARTHUR D. EARLYWINE

Department of Chemistry, University of Oklahoma, 620 *Parrington Oval, Norman, OK* 73019, *USA*

(*Received 5 March* 1987; *accepted* 14 *July* 1987)

Abstract. $C_{29}H_{24}O_5$, $M_r = 452{\cdot}52$, monoclinic, $I2/a$ (non-standard setting of $C2/c$), $a = 7{\cdot}979\,(2)$, $b = 21{\cdot}209\,(6)$, $c = 12{\cdot}614\,(4)$ Å, $\beta = 90{\cdot}49\,(2)°$, $V = 2134{\cdot}7\,(10)$ Å^3, $Z = 4$, $D_x = 1{\cdot}408$ Mg m^{-3}, $\lambda(\mathrm{Cu}\,K\alpha) = 1{\cdot}54178$ Å, $\mu = 0{\cdot}73$ mm^{-1}, $F(000) = 952$, $T = 295$ K, final $R = 0{\cdot}068$, $wR = 0{\cdot}062$ for 1012 observed reflections. The cage system exhibits a great deal of strain shown in both the bond lengths and angles. Of the 20 C—C—C angles in the cage moiety five are significantly larger than normal [ave. = 115·3 (4)°] and 13 are significantly smaller than normal [ave. = 101·8 (4)°]. The internal angle at C(8) at 95·4 (4)° is extremely small. Molecular-mechanics calculations predicted the angle strain but not the unusual bond lengths.

Introduction. In a recent study of the thermal reaction of (pentacarbonyl)iron with 7-(benzoyloxy)norbornadiene, a novel cage ketone, $C_{29}H_{24}O_5$ (1), was isolated as a minor reaction product (0·4% yield; Marchand, Earlywine & Heeg, 1986). Examination of its proton and ^{13}C NMR spectra indicated the absence of olefinic absorptions. In addition, the proton noise-decoupled ^{13}C NMR spectrum of (1) displays only 13 signals, a result which suggests that this compound possesses twofold symmetry. On the basis of spectral information available at that time, structure (1*a*) was assigned tentatively to this compound (Marchand, Earlywine & Heeg, 1986), although it was recognized that IR and NMR spectral information was not sufficient to determine its structure uniquely. It was not

0108-2701/87/122364-03$01.50