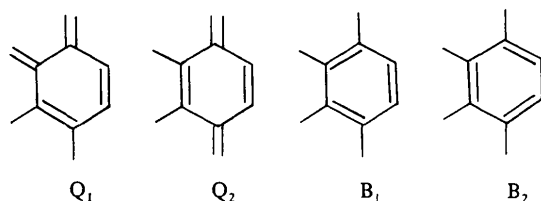


which there is no parameter for an NO₂ group twisted by more than 30°. This is, however, included in the Norrestam & Schepper set of data, and it was used for our analysis together with other angular parameters taken from Domenicano & Murray-Rust (1979). For this case $\sum |\Delta|_i = 5.4^\circ$. To our surprise the greatest deviation is for an angle at C(6), $\Delta_6 = 2.5^\circ$. This may be due to the short intermolecular contact C(6)···O(2'), equal to 3.3 Å. Similar non-additivities of substituent effect on endocyclic valence angles have been found for *p*-nitroaniline (Colapietro, Domenicano; Marciante & Portalone, 1982) and *p,N,N*-dimethylaminobenzoic acid (Anulewicz, Häfeling, Krygowski, Regelmann & Ritter, 1986) as a result of strong through resonance and for 2,4-dinitrobenzoic acid (Więckowski & Krygowski, 1985) and 2,5-dinitrobenzoic acid (Grabowski & Krygowski, 1985) as a result of overcrowding.

Bond-length deformations are analyzed by use of the HOSE model (Krygowski, Anulewicz & Kruszewski, 1983) in which four resonance structures have been taken into account.



Applying bond lengths corrected for libration the following contributions have been determined: $Q_1 = 19.9$, $Q_2 = 21.6$, $B_1 = 32.7$, and $B_2 = 25.8\%$. The

greater contribution of Q_2 compared with Q_1 is explained by the much lower twist angle of NO₂ at C(4) than at C(2), and hence the possibility of stronger through resonance between NMe₂ and NO₂ at C(4). Lower-than-expected values of B_2 and Q_2 may be explained by overcrowding in the C(2)–C(3) region leading to lengthening of the C(2)–C(3) bond. In the case when no through resonance is expected for 2,4-dinitrobenzoic acid (Więckowski & Krygowski, 1985) $B_1 = 33.9$, $B_2 = 39.7$, $Q_1 = 13.1$ and $Q_2 = 13.3\%$. The difference between these two systems is apparent, particularly in the comparison of $\sum_i Q_i$ values: 41.5 and 26.4%, respectively.

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Structure of an Oxidation Product of Echinocystic Acid*

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(Received 19 May 1986; accepted 8 July 1986)

Abstract. Methyl 3 β ,16 α -dihydroxy-12-oxo-13 α -oleanan-28-oate, C₃₁H₅₀O₅·2H₂O, $M_r = 538.7$, monoclinic, $P2_1$, $a = 12.795$ (2), $b = 6.904$ (1), $c = 16.427$ (2) Å, $\beta = 99.52$ (1)°, $V = 1431.1$ Å³, $Z = 2$, D_m (flotation in KI solution) = 1.23, $D_x =$

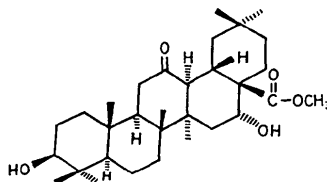
1.25 Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 0.093$ mm⁻¹, $F(000) = 592$, $T = 293$ K, $R = 0.078$ for 1999 observed reflections. All the rings have a 'chair' conformation with the hydroxyl group at C(16) in the α configuration. The molecules are held together by a network of hydrogen bonds involving O(1), O(3) and the two solvent water molecules. O(1)···WO(2) = 2.80 (1); O(3)···WO(1) = 2.85 (1), WO(1)···WO(2)

* NCL Communication No. 3932.

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= 2.88 (1) Å (symmetry $x, y, 1+z$). O(1)··WO(1) = 2.78 (1), WO(1)··WO(2) = 2.93 (1) Å (symmetry $1-x, \frac{1}{2}+y, 1-z$).

Introduction. In a study of the epoxidation of pentacyclic triterpenes, echinocystic acid 3,16-diacetate bromolactone* (White & Noller, 1939) was refluxed with 10% methanolic NaOH for one hour to obtain echinocystic acid methyl ester 12 β -13 β epoxide. This bromolactone on treatment with 10% methanolic NaOH for a longer time gave an isomeric diol (title compound, I). The PMR spectrum of this compound indicated that the C(3)-hydroxyl is unchanged while the other at C(16) is now equatorial but still adjacent to the methylene group. The spectral data were also consistent with a 16 β -OH isomer or a 13 α ,16 α -epoxy 12 β -OH derivative of the epoxide. We report here the complete structure and conformation of this compound.



(I)

Experimental. Crystal approx. 0.35 × 0.20 × 0.90 mm, Nonius CAD-4F-11M diffractometer, graphite-monochromated Mo K α radiation, $\omega/2\theta$ scan mode, scan speed 1° min⁻¹, $\theta < 23.5^\circ$, h 0 to 14, k 0 to 7, l -18 to 18, 2323 unique reflections collected, 1999 judged significant ($|F_o| > 3\sigma|F_o|$), lattice parameters from 23 reflections ($15 < 2\theta < 33^\circ$), three standard reflections ($3\bar{1}\bar{5}$; $4\bar{1}\bar{4}$; $60\bar{7}$) every 3600 s, 4% variation in intensity. No correction for absorption. Structure solved by direct methods using MULTAN78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Least-squares refinement (on F) in large blocks, using anisotropic thermal parameters (isotropic thermal parameters for H atoms, initial H positions calculated by stereochemistry); convergence at $R = 0.078$, $wR = 0.074$, $S = 1.72$, $\sum w(|F_o| - |F_c|)^2$ minimized, $w = (6.0 + 1.0|F_o| + 0.028|F_o|^2)^{-1}$. $(\Delta/\sigma)_{\max} = 0.1$, final $\Delta\rho$ excursions $< 10.3 e \text{ \AA}^{-3}$. No correction for secondary extinction. The high value of R is due to the poor quality of the crystal. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Program LALS (Gantzel, Sparks & Trueblood, 1961) for refinement.

Discussion. The atomic parameters with their e.s.d.'s and equivalent isotropic temperature factors are given

* 3 β ,16 α -Diacetyloxyoleanan-28-oic acid 12 α -bromo-13-hydroxy- γ -lactone.

Table 1. Fractional atomic coordinates ($\times 10^4$) with their standard deviations in parentheses and equivalent values of the isotropic temperature factor coefficients

$$B_{eq} = \frac{1}{3}(B_{11}a^2 + B_{22}b^2 + B_{33}c^2 + B_{13}ac\cos\beta).$$

	x	y	z	$B_{eq}(\text{\AA}^2)$
O(1)	6135 (4)	2993	6595 (3)	2.96
O(2)	10394 (4)	4441 (11)	11056 (3)	4.25
O(3)	7200 (4)	698 (8)	13462 (3)	2.93
O(4)	7426 (5)	6352 (8)	13315 (3)	3.78
O(5)	7675 (4)	4307 (9)	14376 (3)	3.66
WO(1)	5202 (4)	1034 (9)	4021 (3)	3.90
WO(2)	5861 (5)	-362 (10)	-4338 (4)	4.72
C(1)	7873 (6)	4358 (12)	8573 (4)	2.57
C(2)	7247 (6)	4529 (11)	7708 (4)	2.60
C(3)	6677 (5)	2695 (11)	7406 (4)	2.30
C(4)	5956 (5)	1913 (11)	8003 (4)	1.95
C(5)	6619 (5)	1790 (10)	8878 (4)	2.00
C(6)	6055 (5)	835 (12)	9520 (4)	2.48
C(7)	6850 (6)	314 (12)	10277 (4)	2.71
C(8)	7437 (5)	2095 (10)	10728 (4)	1.90
C(9)	7942 (5)	3173 (10)	10040 (4)	1.70
C(10)	7190 (6)	3709 (10)	9228 (4)	2.03
C(11)	8590 (5)	4902 (10)	10450 (4)	2.37
C(12)	9415 (5)	4234 (11)	11069 (4)	2.21
C(13)	9130 (5)	3039 (11)	11812 (4)	1.86
C(14)	8321 (5)	1435 (10)	11438 (4)	1.78
C(15)	7879 (5)	497 (10)	12181 (4)	2.12
C(16)	7506 (5)	1847 (11)	12806 (4)	2.24
C(17)	8377 (5)	3334 (11)	13180 (4)	2.12
C(18)	8813 (5)	4460 (11)	12473 (4)	2.10
C(19)	9717 (5)	5787 (11)	12849 (4)	2.24
C(20)	10582 (5)	4992 (11)	13502 (4)	2.56
C(21)	10064 (6)	3880 (13)	14154 (4)	2.86
C(22)	9259 (5)	2431 (11)	13777 (4)	2.18
C(23)	5613 (6)	-155 (12)	7708 (4)	3.01
C(24)	4923 (5)	3087 (13)	7919 (4)	3.19
C(25)	6404 (6)	5390 (11)	9331 (5)	2.92
C(26)	6578 (5)	3320 (12)	11036 (4)	2.65
C(27)	9039 (6)	-183 (11)	11144 (5)	2.81
C(28)	7765 (5)	4892 (12)	13610 (4)	2.54
C(29)	11373 (6)	3624 (14)	13164 (5)	3.82
C(30)	11226 (6)	6705 (13)	13930 (5)	3.50
C(31)	7035 (8)	5624 (15)	14808 (5)	4.73

in Table 1. Bond lengths and angles involving the non-hydrogen atoms are given in Table 2.* Fig. 1 gives a perspective view of the molecule. All the rings have chair conformations. The X-ray study confirms the presence of hydroxyl groups at C(3) and at C(16) [C(3)-O(1) = 1.411 (8), C(16)-O(3) = 1.444 (9) Å], and a carbonyl group at C(12) [C(12)-O(2) = 1.265 (8) Å]. There are distortions in bond lengths owing to the presence of axial substituents as in the structure of gymnemagenin [(3 β ,4 α ,16 β ,21 β ,22 α)-olean-12-ene-3-,16,21,22,23,28-hexol] (Hoge & Nordman, 1974); in particular, the C(11)-C(12) distance of 1.416 (9) and C(12)-O(2) of 1.265 (8) Å indicate delocalization. The α configuration of the 16-hydroxyl group and the chair-chair conformation of the molecule are particularly interesting. Because the 17 β -CH₂OH derivative of echinocystic acid forms an acetonide with the 16-OH, the 16-OH of echinocystic acid and all

* Lists of structure factors, anisotropic thermal parameters, torsion angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43268 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

related triterpenes were claimed to have β configuration (Segal & Taube, 1973). As an acetate group was found to migrate readily from the 17 β -CH₂OH group to the 16 α -OH group, a boat conformation was envisaged for the *D,E* rings of the molecule (Baigent, Hansens & Lewis, 1976). However, a recent X-ray crystallographic structure determination of the rigid and more planar molecule, echinocystic acid diacetate bromolactone, showed that the 16-hydroxyl group is α -oriented and all the rings are in the chair-chair conformation (Carlisle, Lindley & Perales, 1976). In this case the molecule is held very rigidly by the γ -lactone across the rings, but in more flexible molecules such as friedelin (Laing, Burke-Laing, Bartho & Weeks, 1977) and some of its hydroxylated derivatives which have the *D,E* rings *cis*-fused and have considerable non-bonded interactions between bulky groups, more than one ring of the

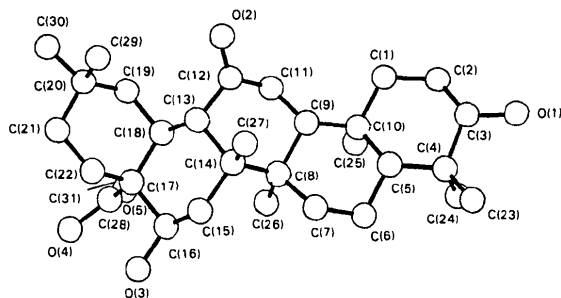


Fig. 1. A perspective view of the molecule (excluding the water molecules), showing atomic numbering.

pentacyclic triterpene is found to exist in a boat conformation (Masaki, Niwa & Kikuchi, 1975; Rogers, Williams, Joshi, Kamat & Vishwanathan, 1974). In the present study, owing to the *cis* fusion of the *C,D* and *D,E* rings, the molecule has a zigzag form and there are considerable non-bonded interactions between the bulky groups, with all the rings in the chair-chair conformation.

The molecules are held together by a network of hydrogen bonds involving the hydroxyl groups at O(1) and O(3) and the water molecules *WO*(1) and *WO*(2). Three hydrogen bonds are formed with the translated molecule along the 'c' axis [O(1)···*WO*(2) = 2.80 (1), O(3)···*WO*(1) = 2.85 (1), *WO*(1)···*WO*(2) = 2.88 (1) Å; symmetry operation $x, y, 1 + z$]. The symmetry-related molecules also form two other hydrogen bonds [O(1)···*WO*(1) = 2.78 (1), *WO*(1)···*WO*(2) = 2.93 (1) Å; symmetry operation $1 - x, \frac{1}{2} + y, 1 - z$].

Table 2. Intramolecular bond lengths (Å) and angles (°) with their standard deviations in parentheses

C(1)–C(2)	1.516 (9)	C(1)–C(10)	1.560 (10)
C(2)–C(3)	1.504 (11)	C(3)–C(4)	1.550 (9)
C(3)–O(1)	1.411 (8)	C(4)–C(5)	1.546 (9)
C(4)–C(23)	1.548 (11)	C(4)–C(24)	1.537 (10)
C(5)–C(6)	1.523 (10)	C(5)–C(10)	1.575 (10)
C(6)–C(7)	1.514 (10)	C(7)–C(8)	1.562 (10)
C(8)–C(9)	1.579 (9)	C(8)–C(14)	1.553 (9)
C(8)–C(26)	1.538 (10)	C(9)–C(10)	1.555 (9)
C(9)–C(11)	1.543 (10)	C(10)–C(25)	1.563 (11)
C(11)–C(12)	1.416 (9)	C(12)–C(13)	1.565 (10)
C(12)–O(2)	1.265 (8)	C(13)–C(14)	1.570 (10)
C(13)–C(18)	1.566 (10)	C(14)–C(15)	1.567 (9)
C(14)–C(27)	1.572 (10)	C(15)–C(16)	1.520 (10)
C(16)–C(17)	1.564 (10)	C(16)–O(3)	1.444 (9)
C(17)–C(18)	1.574 (10)	C(17)–C(22)	1.502 (10)
C(17)–C(28)	1.567 (10)	C(18)–C(19)	1.524 (10)
C(19)–C(20)	1.512 (9)	C(20)–C(21)	1.552 (10)
C(20)–C(29)	1.553 (11)	C(20)–C(30)	1.543 (11)
C(21)–C(22)	1.495 (11)	C(28)–O(4)	1.170 (10)
C(28)–O(5)	1.344 (8)	O(5)–C(31)	1.481 (11)
C(2)–C(1)–C(10)	113.6 (6)	C(1)–C(2)–C(3)	113.3 (6)
C(2)–C(3)–C(4)	113.0 (6)	C(2)–C(3)–O(1)	108.9 (5)
C(4)–C(3)–O(1)	113.4 (5)	C(3)–C(4)–C(5)	108.4 (5)
C(3)–C(4)–C(23)	106.9 (6)	C(3)–C(4)–C(24)	110.7 (6)
C(5)–C(4)–C(23)	108.9 (6)	C(5)–C(4)–C(24)	116.3 (6)
C(23)–C(4)–C(24)	105.3 (6)	C(4)–C(5)–C(6)	114.7 (6)
C(4)–C(5)–C(10)	116.3 (5)	C(6)–C(5)–C(10)	110.8 (5)
C(5)–C(6)–C(7)	109.9 (6)	C(6)–C(7)–C(8)	114.0 (6)
C(7)–C(8)–C(9)	104.7 (5)	C(7)–C(8)–C(14)	111.0 (5)
C(7)–C(8)–C(26)	106.0 (5)	C(9)–C(8)–C(14)	110.0 (5)
C(9)–C(8)–C(26)	112.1 (5)	C(14)–C(8)–C(26)	112.7 (5)
C(8)–C(9)–C(10)	117.2 (5)	C(8)–C(9)–C(11)	107.8 (5)
C(10)–C(9)–C(11)	113.7 (5)	C(1)–C(10)–C(5)	105.6 (6)
C(1)–C(10)–C(9)	108.8 (6)	C(1)–C(10)–C(25)	107.7 (6)
C(5)–C(10)–C(9)	107.3 (5)	C(5)–C(10)–C(25)	113.4 (6)
C(9)–C(10)–C(25)	113.7 (6)	C(9)–C(11)–C(12)	110.1 (6)
C(11)–C(12)–C(13)	119.3 (6)	C(11)–C(12)–O(2)	125.0 (6)
C(13)–C(12)–O(2)	115.6 (6)	C(12)–C(13)–C(14)	106.9 (5)
C(12)–C(13)–C(18)	109.3 (5)	C(14)–C(13)–C(18)	118.9 (6)
C(8)–C(14)–C(13)	116.0 (5)	C(8)–C(14)–C(15)	113.2 (5)
C(8)–C(14)–C(27)	111.6 (6)	C(13)–C(14)–C(15)	106.6 (5)
C(13)–C(14)–C(27)	103.9 (5)	C(15)–C(14)–C(27)	104.5 (5)
C(14)–C(15)–C(16)	117.8 (6)	C(15)–C(16)–C(17)	112.7 (6)
C(15)–C(16)–O(3)	108.8 (5)	C(17)–C(16)–O(3)	109.3 (5)
C(16)–C(17)–C(18)	110.5 (5)	C(16)–C(17)–C(22)	113.2 (6)
C(16)–C(17)–C(28)	104.5 (5)	C(18)–C(17)–C(22)	111.6 (6)
C(18)–C(17)–C(28)	104.9 (5)	C(22)–C(17)–C(28)	111.6 (6)
C(13)–C(18)–C(17)	111.5 (5)	C(13)–C(18)–C(19)	113.0 (6)
C(17)–C(18)–C(19)	109.7 (5)	C(18)–C(19)–C(20)	119.1 (6)
C(19)–C(20)–C(21)	108.9 (6)	C(19)–C(20)–C(29)	114.2 (6)
C(19)–C(20)–C(30)	108.6 (6)	C(21)–C(20)–C(29)	108.9 (6)
C(21)–C(20)–C(30)	108.8 (6)	C(29)–C(20)–C(30)	107.4 (6)
C(20)–C(21)–C(22)	112.9 (6)	C(17)–C(22)–C(21)	112.6 (6)
C(17)–C(28)–O(4)	125.7 (7)	C(17)–C(28)–O(5)	110.0 (6)
O(4)–C(28)–O(5)	124.3 (7)	C(28)–O(5)–C(31)	113.8 (6)

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