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Structure of an *ent*-Beyerene Diterpene

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Abstract. $C_{20}H_{32}O_3$, $M_r = 320{\cdot}48$, monoclinic, $P2_1$, $a = 17{\cdot}623\,(4)$, $b = 7{\cdot}429\,(1)$, $c = 7{\cdot}203\,(1)$ Å, $\beta = 100{\cdot}46\,(2)°$, $V = 927{\cdot}4\,(3)$ Å^3, $Z = 2$, $D_x = 1{\cdot}148$, D_m (flotation) $= 1{\cdot}142$ g cm^{-3}, $\lambda(\text{Cu } K\alpha) = 1{\cdot}54178$ Å, $\mu = 5{\cdot}566$ cm^{-1}, $F(000) = 352$, $T = 295$ K, $R = 0{\cdot}048$ for 1301 reflections. The molecule is a beyerene-type tetracyclic diterpene [9,11,17-trihydroxy-*ent*-beyer-15(16)-ene; *Chemical Abstracts* name (5*R*,8*R*,9*R*,10*R*,11*S*,13*S*)-13-(hydroxymethyl)-17-norkaur-15-ene-9,11-diol]. The molecule contains three *trans*-fused six-membered rings in slightly distorted chair conformations, a bridging ethylene moiety forming a five-membered ring in an envelope conformation and a seven-membered ring in a boat conformation. There are three relatively long C—C bonds of 1·569 (6), 1·572 (5), and 1·595 (5) Å which agree well with the values 1·562, 1·573 and 1·595 Å calculated by molecular-mechanics techniques. There is one C—C bond of 1·488 (9) Å which is statistically equivalent to the value in reference compounds but is 0·041 (9) Å shorter than the calculated value.

Introduction. As part of a chemotaxonomic study of the genus *Helianthus*, the terpenoid constituents of *Helianthus laciniatus* A. Gray were reinvestigated. A previous study of this species reported five partially characterized tetracyclic diterpenes (Ortega, Ayala, Guerrero & Romo de Vivar, 1972). Comparison of the physical properties of the *ent*-beyerene (1) indicated that it was not one of the compounds previously isolated. In order to confirm the substitution pattern and relative configuration based upon ^{1}H and ^{13}C NMR the structure was determined by X-ray diffraction. Also, the *ent*-beyerenes provide another opportunity to evaluate the use of molecular mechanics (MM) in reproducing natural-product structures and conformations.

Experimental. A colorless crystal of dimensions 0·52 × 0·41 × 0·31 mm, Syntex $P2_1$ diffractometer, θ:2θ scan, variable scan rate, $5{\cdot}1 \le 2\theta \le 114{\cdot}7°$, graphite-monochromated Cu $K\alpha$ radiation; lattice parameters from a least-squares refinement of 15 reflections ($12{\cdot}6 \le 2\theta \le 65{\cdot}6°$), angles measured by a centering routine associated with the diffractometer, systematic absences ($0k0$, $k = 2n + 1$) consistent with space group $P2_1$, Laue symmetry 2, a monitored reflection, 200, showed no significant change in intensity; 1409 independent reflections measured ($0 \le h \le 19$, $0 \le k \le 8$, $-7 \le l \le 7$) with 1312 intensities greater than $3\sigma(I)$, slow scan measurement of 54 equivalent reflections ($R_{\text{int}} = 0{\cdot}014$), Lorentz–polarization corrections applied, consideration of crystal shape, transmission factors and R_{int} resulted in neglect of absorption; direct methods (*MULTAN78*: Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) revealed the positions of all non-hydrogen atoms. Least-squares refinement followed by a difference Fourier synthesis

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Table 1. *Fractional atomic coordinates* (× 10^4) *and* U_{eq} ($Å^2 \times 10^3$) *for non-hydrogen atoms*

	x	*y*	*z*	U_{eq}†
C(1)	8120 (2)	0883 (7)	7809 (6)	64
C(2)	8973 (3)	1254 (8)	8623 (8)	78
C(3)	9133 (3)	3221 (8)	8734 (8)	86
C(4)	8925 (2)	4236 (7)	6862 (7)	76
C(5)	8070 (2)	3773 (7)	5948 (6)	61
C(6)	7789 (2)	4701 (7)	4057 (6)	66
C(7)	6923 (2)	4613 (7)	3505 (5)	61
C(8)	6594 (2)	2698 (6)	3456 (5)	52
C(9)	6922 (2)	1644 (6)	5322 (5)	51
O(9)	6610 (2)	2564	6804 (3)	52
C(10)	7840 (2)	1741 (6)	5843 (6)	55
C(11)	6596 (2)	−304 (6)	5190 (5)	55
O(11)	6666 (2)	−947 (4)	7100 (3)	62
C(12)	5746 (2)	−464 (6)	4235 (5)	55
C(13)	5516 (2)	750 (7)	2504 (5)	53
C(14)	5712 (2)	2661 (6)	3191 (5)	50
C(15)	6687 (2)	1591 (7)	1722 (5)	62
C(16)	6093 (2)	529 (7)	1181 (5)	64
C(17)	4689 (2)	431 (7)	1524 (5)	62
O(17)	4146 (1)	833 (5)	2738 (3)	62
C(18)	9505 (3)	3810 (9)	5590 (9)	100
C(19)	8990 (3)	6232 (8)	7255 (9)	100
C(20)	8213 (2)	705 (8)	4404 (6)	70

† $U_{eq} = \frac{1}{3}[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aba^*b^*\cos\gamma + 2U_{13}aca^*c^*\cos\beta + 2U_{23}bcb^*c^*\cos\alpha]$.

revealed the positions of all hydrogen atoms; least-squares refinement (U_{iso} for H fixed at 0·06 Å^2, H positional parameters fixed) reduced *R* to 0·048, *wR* = 0·059, *S* = 3·04, $(\Delta/\sigma)_{avg}$ = 0·08, $(\Delta/\sigma)_{max}$ = 0·46; the largest positive or negative excursion in the final difference Fourier map was 0·19 e Å^{-3}; $\sum w(|F_o| - |F_c|)^2$ minimized, $w = 1/\sigma^2(F_o)$ from counting statistics; an isotropic extinction correction (Larson, 1970) introduced in last cycles of refinement refined to 0·33 (8); 304 parameters refined using 1312 reflections; H-atom parameters scaled to C—H = 1·08 and O—H = 1·00 Å for better comparison with MM calculations, all calculations, performed with *XRAY76* (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976); atomic scattering factors for C and O those of Cromer & Mann (1968), those for H from Stewart, Davidson & Simpson (1965), anomalous dispersion applied, no significant difference in *R* factor found for the two enantiomers.

Table 1 lists atomic positional parameters and U_{eq} values while Table 2 gives interatomic distances and valence angles.*

Discussion. Fig. 1 is an *ORTEP* drawing (Johnson, 1971) of the title compound (1). The stereochemistry has been assigned from biogenetic assumptions associated with the genus *Helianthus* (Pearce, Gershenzon & Mabry, 1986). The molecule can be described as a phenanthrene ring system with a bridging ethylene group. The three saturated *trans*-fused six-membered rings exhibit chair conformations. The bridging ethylene moiety forms a five-membered ring and a seven-membered ring. The five-membered ring is in an envelope conformation while the seven-membered ring is in the boat form (Toromanoff, 1980). The two *syn* methyl groups at C(4) and C(10), the three axial hydrogen atoms at C(2), C(6) and C(11), and the C(15) methylene sterically interact. The interactions between the C(20) hydrogen atoms and H(2*b*), H(18*b*), H(6*b*), H(11) and H(15) range from 2·01 (6) to 2·27 (6) Å. All other intramolecular contacts on the bottom face are greater than 2·30 Å while only one interaction on the top face is less than 2·30 Å, H(12*b*)···H(14*b*) = 2·17 (6) Å. This leads to a flattening of the torsion angles around ring *A*, 48·6–56·8°,

Table 2. *Interatomic distances* (Å), *valence angles* (°) *and selected torsion angles* (°)

	(1) obs	(1) calcd	(3) obs*		(3) calcd
C(1)—C(2)	1·536 (6)	1·535	1·518	1·536	1·533
C(1)—C(10)	1·550 (6)	1·555	1·553	1·539	1·550
C(2)—C(3)	1·488 (9)	1·529	1·507	1·503	1·532
C(3)—C(4)	1·530 (8)	1·548	1·546	1·544	1·552
C(4)—C(5)	1·569 (6)	1·562	1·553	1·534	1·564
C(5)—C(6)	1·526 (6)	1·540	1·504	1·516	1·542
C(5)—C(10)	1·562 (7)	1·567	1·564	1·581	1·561
C(6)—C(7)	1·508 (6)	1·532	1·527	1·518	1·533
C(7)—C(8)	1·534 (7)	1·532	1·509	1·526	1·531
C(8)—C(9)	1·572 (5)	1·564	1·545	1·552	1·552
C(8)—C(14)	1·531 (6)	1·556	1·529	1·545	1·552
C(8)—C(15)	1·529 (6)	1·514	1·504	1·518	1·511
C(9)—C(10)	1·595 (5)	1·593	1·558	1·557	1·570
C(9)—C(11)	1·553 (6)	1·563	1·554	1·505	1·549
C(11)—C(12)	1·534 (5)	1·549	1·519	1·514	1·544
C(12)—C(13)	1·532 (6)	1·537	1·551	1·525	1·542
C(13)—C(14)	1·522 (7)	1·542	1·543	1·486	1·543
C(13)—C(16)	1·524 (6)	1·533	1·507	1·516	1·509
C(13)—C(17)	1·518 (5)	1·533	–	–	–
C(15)—C(16)	1·312 (6)	1·338	1·315	1·317	1·339
C(4)—C(18)	1·524 (8)	1·556			
C(4)—C(19)	1·510 (8)	1·544			
C(10)—C(20)	1·532 (7)	1·545			
C(9)—O(9)	1·456 (5)	1·425			
C(11)—O(11)	1·440 (4)	1·417			
C(17)—O(17)	1·439 (5)	1·415			

C(2)—C(1)—C(10)	113·7 (4)	C(8)—C(9)—C(11)	109·7 (3)
C(1)—C(2)—C(3)	111·1 (4)	O(9)—C(9)—C(11)	107·3 (3)
C(2)—C(3)—C(4)	115·1 (5)	O(9)—C(9)—C(10)	108·0 (3)
C(3)—C(4)—C(5)	108·7 (4)	C(1)—C(10)—C(5)	108·4 (3)
C(4)—C(5)—C(10)	116·9 (4)	C(5)—C(10)—C(9)	107·4 (4)
C(6)—C(5)—C(10)	110·7 (3)	C(9)—C(11)—C(12)	114·8 (3)
C(5)—C(6)—C(7)	111·4 (4)	C(9)—C(11)—O(11)	106·5 (3)
C(6)—C(7)—C(8)	113·9 (4)	O(11)—C(11)—C(12)	108·1 (3)
C(7)—C(8)—C(9)	111·3 (3)	C(11)—C(12)—C(13)	114·3 (3)
C(7)—C(8)—C(14)	112·9 (4)	C(12)—C(13)—C(14)	105·9 (3)
C(7)—C(8)—C(15)	115·0 (4)	C(12)—C(13)—C(16)	109·7 (3)
C(9)—C(8)—C(15)	110·7 (4)	C(14)—C(13)—C(16)	99·6 (3)
C(9)—C(8)—C(14)	107·8 (4)	C(8)—C(14)—C(13)	102·9 (3)
C(14)—C(8)—C(15)	98·3 (3)	C(8)—C(15)—C(16)	111·6 (4)
C(8)—C(9)—O(9)	105·4 (3)	C(13)—C(16)—C(15)	109·6 (4)
C(8)—C(9)—C(10)	112·1 (3)		

* Standard deviations 0·006–0·010.

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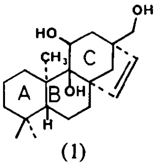
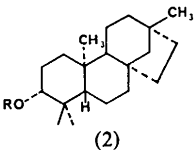
* Lists of H-atom coordinates, anisotropic thermal parameters, selected torsion angles and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43152 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

compared with the normal chair values of 56° (Bucourt, 1974). The torsion angles around ring *B*, 49·9–60·7°, and ring *C*, 39·2–75·8°, show the effects of the bridging ethylene group fused at C(8) and C(13). There is an intramolecular hydrogen bond between O(9) and O(11); O(9)···O(11) = 2·618 (4) Å, H(O9)···O(11) = 2·05 (4) Å; O(9)—H(O9)···O(11) = 130·7 (8)°.

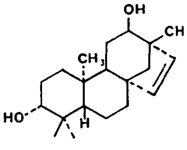
There are some interesting bond-length variations in the molecule. Unfortunately, only a few beyerene-type terpene crystal structures have been reported and most exhibit large standard deviations. This is due partially to the difficulties encountered in obtaining good single crystals. Compounds (2) (Hanson, McLaughlin & Sim, 1972) and (3) (Delgado, Romo de Vivar, Ortega, Cardenas & Schlemper, 1983) provide reference structures; however, the standard deviations are 0·013–0·019 in (2) and 0·006–0·010 Å in (3). Compound (3) has the same skeleton as (1) but the hydroxyl at C(9) is absent. Compound (2) does not have the double bond at C(15)—C(16) and introduces different strains and steric requirements. Compounds (4) and (5) (Murakami, Tanaka, Iida & Iitaka, 1981) have the opposite stereochemistry at C(8) but have an axial hydroxyl group at C(9). The lower portion of the molecules can be compared with the beyeranes. MM calculations (Allinger & Yuh, 1980) were used to derive isolated-molecule conformations for compounds (1) and (3).



(1)



(2)



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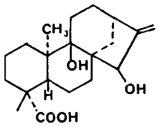

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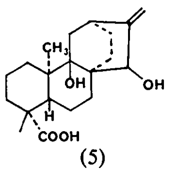

(5)

In the title compound (1) the observed C(2)—C(3) distance is unusually short while the C(4)—C(5), C(8)—C(9), and C(9)—C(10) distances are long compared with similar bonds in six-membered-ring tricyclic terpenes. It is of interest to see if these deviations are reproduced by the MM calculations. There are two independent molecules per cell for compounds (3) and (5), and the values used in this discussion are the average values and average deviations.

The C(4)—C(5) distances in compounds (1)–(5) are 1·569 (6), 1·580 (12), 1·543 (9), 1·542 (9) and 1·579 (1) Å, respectively. The MM calculated values for (1) and (3) are 1·562 and 1·564 Å, respectively. The values found for (1), (2) and (5) compare well with the calculated values. Although (3) and (4) are of normal length, the large deviations make them statistically equivalent to the calculated values. The calculated value of about 1·563 Å probably represents a best estimate of this distance.

The observed C(8)—C(9) distances in the five molecules are 1·572 (5), 1·594 (13), 1·549 (3), 1·582 (7) and 1·570 (6) Å with calculated values for (1) and (3) of 1·569 and 1·552 Å. These values for the C(9)—C(10) distances are 1·595 (5), 1·56 (12), 1·557 (1), 1·595 (7) and 1·590 (4) Å with calculated values for (1) and (3) of 1·593 and 1·570 Å. The values for (1) are calculated to be larger than the corresponding distances in (3). This is related to the axial hydroxyl group at C(9) and to some extent the hydroxyl at C(11). Compounds (4) and (5) have axial hydroxyl groups at C(9) and have bond lengths comparable with (1). The standard deviations in (2) are too large for comparison. The distances in (3) are consistent with MM calculations. The MM distances again appear to be good estimates for these molecules.

The C(2)—C(3) distances in the five compounds are 1·488 (9), 1·505 (13), 1·505 (2), 1·549 (10) and 1·517 (2) Å with calculated values for (1) and (3) of 1·529 and 1·532 Å. The values for compounds (2), (3) and (5) are smaller than the calculated values but are statistically equivalent to them. The value for compound (4) is larger but also is statistically equivalent to the calculated values. The value for (1) of 1·488 (9) Å is statistically equivalent to the average of (2), (3) and (5); however, it is significantly shorter than the calculated value. It would appear that the ideal value for this distance might be in the 1·505–1·520 Å range with the calculated value being statistically equivalent

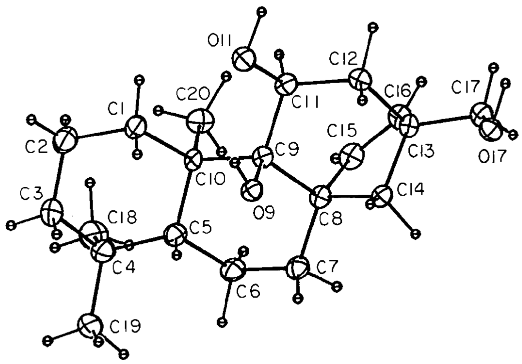

Fig. 1. *ORTEP* drawing (Johnson, 1971) of the title compound. Thermal ellipsoids are drawn at the 35% probability level. H atoms are represented by spheres of arbitrary size.

but high and the observed value for (1) being statistically equivalent but low. Although some modification of MM parameters might be needed better to approximate this distance, nevertheless the calculated values are useful in analyzing observed bond-length variations.

The three hydroxyl groups participate in hydrogen bonding. In addition to the intramolecular hydrogen bond between O(9) and O(11) there are intermolecular hydrogen bonds involving O(11) and O(17): O(17)···O(9)($1-x$, $\frac{1}{2}+y$, $1-z$) = 2·818 (4) Å, H(O17)···O(9) = 1·71 (4) Å, O(17)–H(O17)···O(9) = 177·5 (8)°; O(11)···O(17)($1-x$, $\frac{1}{2}+y$, $1-z$) = 2·801 (5) Å, H(O11)···O(17) = 1·75 (4) Å, O(11)–H(O11)···O(17) = 171·5 (7)°.

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Structure of 1,1a,4,5,6,8,9,9a-Octahydro-3-methoxy-1,1,2-trimethyl-(1a*S*-*trans*)-7*H*-cyclopropa[3,4]cyclohept[1,2-*e*]inden-7-one

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Abstract. $C_{19}H_{24}O_2$, $M_r = 284·40$, monoclinic, $P2_1$, $a = 15·522$ (3), $b = 5·196$ (1), $c = 10·332$ (1) Å, $\beta = 107·67$ (1)°, $V = 793·9$ (4) Å^3, $Z = 2$, $D_x = 1·19$ g cm^{-3}, λ(Cu $K\alpha$) = 1·54184 Å, $\mu = 5·54$ cm^{-1}, $F(000) = 308$, $T = 297$ K, final $R = 0·043$ for 1548 unique observed reflections. Of interest in this structure is the novel *trans* ring junction between the three- and seven-membered rings. This stereochemical arrangement causes the carbonyl moiety and the cycloheptane ring to be twisted out of the plane of the aromatic ring. The cyclopropane is also twisted out of the plane of the aromatic system.

Introduction. The title compound was prepared as part of a program directed toward the total synthesis of jatropholones A and B (Smith, Liverton, Hrib, Sivaramakrishnan & Winzenberg, 1985), two architecturally novel diterpenes isolated from *Jatropha gossypiifolia* L. (Euphorbiaceae), the plant that also yields jatrophone and the hydroxyjatrophones A–C (Smith, 1984). An X-ray crystal determination was undertaken to define unambiguously the structure and relative stereochemistry of this substance. Of particular interest was the stereochemistry of the cyclopropane–cycloheptane ring fusion.

Experimental. Clear colorless crystal (0·30 × 0·20 × 0·15 mm), m.p. 397–398 K, $[\alpha]_D^{20\,°C} = +225°$(0·052 g/100 ml in $CHCl_3$, 1 dm); Enraf–Nonius CAD-4 dif-

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* Camille and Henry Dreyfus Teacher-Scholar, 1978–1983; National Institutes of Health (National Cancer Institute) Career Development Award, 1980–1985.

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