$(C_6H_3OCH_3)_6(CH_2)_2S$

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Structure of a Triterpene Derivative from *Hebeloma* Species: 2α,3β-O-Isopropylideneanhydrocrustulinol,* C₃₃H₅₂O₅

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Abstract. $M_r = 528 \cdot 77$, triclinic, $P1$, $a = 17 \cdot 237$ (8), $b = 7 \cdot 287$ (5), $c = 6 \cdot 275$ (2) Å, $\alpha = 109 \cdot 52$ (2), $\beta = 89 \cdot 92$ (3), $\gamma = 99 \cdot 15$ (2)°, $V = 732 \cdot 3$ (7) Å³, $Z = 1$, $D_x = 1 \cdot 20$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0 \cdot 7107$ Å, $\mu = 0 \cdot 73$ cm⁻¹, $F(000) = 269 \cdot 00$, $T = 295$ K, $R = 0 \cdot 081$ for 1609 observed reflections. The title compound was obtained from a lanostane triterpene isolated from two *Hebeloma* species (Basidiomycetes). The overall stereochemistry of the lanostane nucleus was confirmed and the oxygenation pattern of the molecule shown. The five-, six- and seven-membered rings constituting the bicyclo[3.2.1]octane system adopt the half-chair, chair and boat conformations, respectively.

Introduction. The structure of a new cytotoxic triterpene (I) which was first isolated from *Hebeloma crustuliniforme* (Bull. ex Fr.) Quelét and *Hebeloma sinapizans* Fr. (Basidiomycetes) has already been proposed as 3β-acetyl-2α-(3-hydroxy-3-methyl)-glutarylcrustulinol on the basis of chemical and NMR, IR and mass-spectral evidence (De Bernardi, Fronza, Gianotti, Mellerio, Vidari & Vita Finzi, 1983).

As a part of the chemical work carried out to establish the oxygenation pattern of the molecule, particularly of ring *A* and of the side chain, including the characteristic hemiacetal ring, we prepared the title

compound (II) by hydrolysis of (I) followed by treatment with acetone and a catalytic amount of *p*-toluenesulfonic acid. X-ray diffraction analysis of (II) was undertaken to confirm the configuration of the C(24) centre and the structure of the 4,7,7-trisubstituted 6,8-dioxabicyclo[3.2.1]octane system.

(I)

(II)
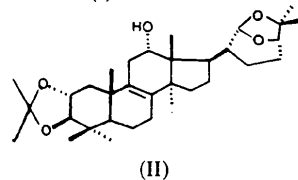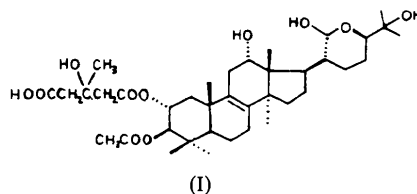
Experimental. Transparent colourless flat prisms grown from methanol–dichloromethane, single crystal 0·48 × 0·29 × 0·10 mm, Philips PW 1100 four-circle diffractometer, graphite-monochromatized Mo *K*α. Cell parameters by least squares based on 24 reflections in range $9 \cdot 2 \leq \theta \leq 18 \cdot 7°$. Intensities measured up to $2\theta = 44°$ (index range: $-18 \leq h \leq 18$, $-7 \leq k \leq 7$,

$0 \le l \le 6$), corrected for Lorentz and polarization effects and, semi-empirically, for absorption (North, Phillips & Mathews, 1968) with maximum correction factor 1·60. Three standard reflections monitored every 270 measurements with maximum intensity variation 2·1%; 1805 independent reflections collected with $\omega/2\theta$ scan technique, 196 $[I \le 3\sigma(I)]$ considered unobserved. Maximum value of $\sin\theta/\lambda$ 0·5271 Å^{-1}. Structure solved by direct methods (*RANTAN*, Yao Jia-xing, 1981); F magnitudes used in least-squares refinement. Out of 52 H atoms [coordinates calculated by geometrical considerations (*XANADU*, Roberts & Sheldrick, 1975)], only 31 H atoms, located on a difference density map, were included in the refinement with positions and B_{iso} factors fixed. Coordinates and anisotropic thermal parameters of non-H atoms refined by block-diagonal least squares; 341 independent parameters refined. Final $R = 0·081$, $wR = 0·101$, $w = 1/\sigma^2(F_{obs})$, $S = 8·60$; secondary-extinction final value 1·57 (8) ×10^{-2}. No significant peaks in final difference map, highest peak 0·21 e Å^{-3}, final value $\Delta/\sigma = 0·15$. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). All calculations performed on a Honeywell DPS 8/44.

Table 1. *Fractional atomic coordinates* (×10^4) *with e.s.d.'s in parentheses and equivalent isotropic temperature factors* (Å^2)

$$B_{eq} = \tfrac{4}{3}\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
C(1)	3225 (8)	4092 (21)	2512 (23)	4·06
C(2)	2381 (7)	3662 (21)	1627 (20)	3·15
C(3)	2029 (7)	1647 (20)	1188 (21)	3·22
C(4)	2377 (7)	122 (22)	−716 (21)	3·38
C(5)	3254 (7)	552 (20)	−39 (19)	2·76
C(6)	3746 (8)	−767 (21)	−1616 (22)	4·07
C(7)	4523 (8)	−787 (21)	−431 (22)	4·00
C(8)	4886 (8)	1249*	1192 (21)	3·22
C(9)	4525 (7)	2823 (18)	1748 (20)	2·87
C(10)	3704 (7)	2760 (20)	719 (20)	2·77
C(11)	4914 (8)	4804 (21)	3365 (23)	4·21
C(12)	5770 (7)	5117 (20)	4170 (19)	2·92
O(12)	5802 (5)	5443 (18)	6555*	4·45
C(13)	6187 (7)	3399 (21)	2775 (22)	3·06
C(14)	5659 (7)	1386 (21)	2439 (21)	3·14
C(15)	6193 (8)	−80 (21)	1291 (22)	3·98
C(16)	7014 (7)	875 (22)	2519 (22)	3·78
C(17)	6976 (7)	3112 (20)	3841 (20)	3·34
C(18)	6348 (7)	3702 (21)	446 (19)	3·36
C(19)	3831 (8)	3609 (21)	−1256 (21)	4·00
C(20)	7734 (7)	4461 (22)	3761 (21)	3·41
C(21)	7710 (7)	6670 (22)	4795 (21)	3·09
C(22)	8428 (7)	4050 (21)	4980 (22)	4·09
C(23)	8446 (7)	5088 (23)	7564 (23)	4·25
C(24)	8284 (8)	7152 (22)	8176 (21)	3·90
C(25)	8807 (8)	8550 (24)	7077 (25)	4·90
O(24)	7533 (5)	7098 (17)	7120 (16)	3·90
O(25)	8456 (6)	7799 (18)	4792 (17)	4·72
C(26)	9710 (8)	8334 (26)	7051 (30)	7·01
C(27)	8723 (8)	10739 (22)	8233 (27)	5·42
C(28)	2022 (8)	−2002 (22)	−778 (26)	5·38
C(29)	2176 (8)	231 (24)	−3054 (23)	4·84
C(30)	5465 (8)	1005 (21)	4699 (21)	4·09
C(31)	1087 (8)	3566 (24)	2499 (23)	4·84
C(32)	710 (9)	3274 (26)	4591 (26)	6·02
C(33)	624 (8)	4551 (25)	1302 (24)	5·57
O(2)	1865*	4698 (18)	3209 (17)	4·91
O(3)	1212 (6)	1668 (19)	914 (17)	4·84

* Coordinates selected to establish the origin.

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

|				
C(1)–C(2)	1·51 (2)	C(13)–C(17)	1·59 (2)
C(1)–C(10)	1·55 (2)	C(13)–C(18)	1·57 (2)
C(2)–C(3)	1·43 (2)	C(14)–C(15)	1·52 (2)
C(2)–O(2)	1·43 (2)	C(14)–C(30)	1·56 (3)
C(3)–C(4)	1·53 (2)	C(15)–C(16)	1·55 (2)
C(3)–O(3)	1·42 (2)	C(16)–C(17)	1·57 (2)
C(4)–C(5)	1·52 (2)	C(17)–C(20)	1·52 (2)
C(4)–C(28)	1·56 (3)	C(20)–C(21)	1·53 (3)
C(4)–C(29)	1·54 (3)	C(20)–C(22)	1·54 (3)
C(5)–C(6)	1·50 (2)	C(21)–O(25)	1·41 (2)
C(5)–C(10)	1·58 (2)	C(21)–O(24)	1·43 (2)
C(6)–C(7)	1·54 (2)	C(22)–C(23)	1·54 (2)
C(7)–C(8)	1·53 (2)	C(23)–C(24)	1·50 (3)
C(8)–C(9)	1·34 (2)	C(24)–C(25)	1·58 (3)
C(8)–C(14)	1·52 (2)	C(24)–O(24)	1·44 (2)
C(9)–C(10)	1·54 (2)	C(25)–C(26)	1·59 (2)
C(9)–C(11)	1·51 (2)	C(25)–O(25)	1·45 (2)
C(10)–C(19)	1·56 (3)	C(25)–C(27)	1·55 (3)
C(11)–C(12)	1·52 (2)	C(31)–C(32)	1·53 (3)
C(12)–C(13)	1·55 (2)	C(31)–C(33)	1·50 (3)
C(12)–O(12)	1·43 (2)	C(31)–O(2)	1·44 (2)
C(13)–C(14)	1·55 (2)	C(31)–O(3)	1·46 (2)
C(2)–C(1)–C(10)	108·8 (1·1)	C(14)–C(13)–C(17)	101·1 (1·1)
C(1)–C(2)–O(2)	114·1 (1·0)	C(8)–C(14)–C(13)	110·1 (1·0)
C(1)–C(2)–C(3)	112·5 (1·2)	C(13)–C(14)–C(30)	113·6 (1·1)
C(3)–C(2)–O(2)	101·8 (1·1)	C(13)–C(14)–C(15)	102·6 (1·1)
C(2)–C(3)–O(3)	103·3 (1·2)	C(8)–C(14)–C(30)	107·9 (1·0)
C(2)–C(3)–C(4)	115·5 (1·2)	C(8)–C(14)–C(15)	117·7 (1·0)
C(4)–C(3)–O(3)	116·2 (1·1)	C(15)–C(14)–C(30)	104·9 (1·1)
C(3)–C(4)–C(29)	111·8 (1·2)	C(14)–C(15)–C(16)	104·4 (1·1)
C(3)–C(4)–C(28)	109·8 (1·1)	C(15)–C(16)–C(17)	106·9 (1·1)
C(3)–C(4)–C(5)	104·1 (1·0)	C(13)–C(17)–C(16)	102·3 (1·0)
C(28)–C(4)–C(29)	106·7 (1·2)	C(16)–C(17)–C(20)	112·2 (1·1)
C(5)–C(4)–C(29)	114·8 (1·1)	C(13)–C(17)–C(20)	118·4 (1·2)
C(5)–C(4)–C(28)	109·7 (1·1)	C(17)–C(20)–C(22)	111·4 (1·2)
C(4)–C(5)–C(10)	119·2 (1·1)	C(17)–C(20)–C(21)	115·1 (1·1)
C(4)–C(5)–C(6)	115·6 (1·1)	C(21)–C(20)–C(22)	107·0 (1·1)
C(6)–C(5)–C(10)	109·0 (1·0)	C(20)–C(21)–O(24)	108·4 (1·2)
C(5)–C(6)–C(7)	111·8 (1·1)	C(20)–C(21)–O(25)	110·9 (1·1)
C(6)–C(7)–C(8)	112·6 (1·1)	O(24)–C(21)–O(25)	106·2 (1·0)
C(7)–C(8)–C(14)	116·6 (0·8)	C(21)–O(25)–C(25)	108·3 (1·1)
C(7)–C(8)–C(9)	123·8 (1·0)	O(25)–C(25)–C(26)	110·2 (1·2)
C(9)–C(8)–C(14)	119·1 (0·8)	O(25)–C(25)–C(27)	110·6 (1·2)
C(8)–C(9)–C(11)	121·6 (1·1)	O(25)–C(25)–C(24)	100·6 (1·1)
C(8)–C(9)–C(10)	122·6 (1·1)	C(26)–C(25)–C(27)	110·0 (1·3)
C(10)–C(9)–C(11)	115·9 (1·1)	C(24)–C(25)–C(26)	113·3 (1·3)
C(5)–C(10)–C(9)	108·1 (1·1)	C(24)–C(25)–C(27)	111·8 (1·2)
C(1)–C(10)–C(9)	110·4 (1·0)	C(25)–C(24)–O(24)	98·0 (1·1)
C(1)–C(10)–C(5)	108·7 (1·0)	C(23)–C(24)–C(25)	116·7 (1·2)
C(9)–C(10)–C(19)	107·4 (1·0)	C(23)–C(24)–O(24)	108·7 (1·2)
C(5)–C(10)–C(19)	114·1 (1·0)	C(22)–C(23)–C(24)	112·1 (1·2)
C(1)–C(10)–C(19)	108·2 (1·1)	C(20)–C(22)–C(23)	111·7 (1·1)
C(9)–C(11)–C(12)	120·1 (1·2)	C(21)–O(24)–C(24)	102·1 (0·9)
C(11)–C(12)–O(12)	108·3 (9·9)	O(2)–C(31)–O(3)	105·2 (1·0)
C(11)–C(12)–C(13)	111·9 (1·1)	C(33)–C(31)–O(3)	109·3 (1·1)
C(13)–C(12)–O(12)	113·5 (1·0)	C(33)–C(31)–O(2)	110·6 (1·3)
C(12)–C(13)–C(18)	106·4 (1·1)	C(32)–C(31)–O(3)	109·7 (1·3)
C(12)–C(13)–C(17)	118·2 (1·0)	C(32)–C(31)–O(2)	107·4 (1·1)
C(12)–C(13)–C(14)	110·4 (1·0)	C(32)–C(31)–C(33)	114·2 (1·2)
C(17)–C(13)–C(18)	109·6 (1·0)	C(2)–O(2)–C(31)	105·6 (0·9)
C(14)–C(13)–C(18)	111·0 (1·1)	C(3)–O(3)–C(31)	105·0 (1·0)
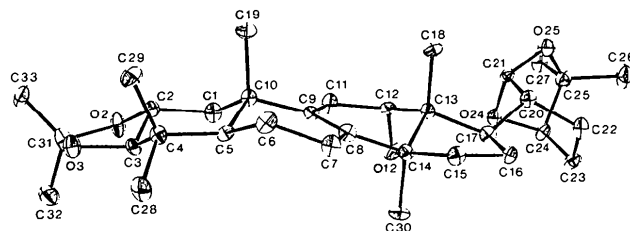
Fig. 1. *ORTEP* view (Johnson, 1965) of the molecule with the atom numbering. Thermal ellipsoids are drawn at the 20% probability level.

Discussion. Atomic coordinates and equivalent isotropic temperature factors of non-H atoms are reported in Table 1;* bond lengths and angles (*PARST,* Nardelli, 1983) are given in Table 2 and agree well with generally accepted values. Fig. 1 is a computer-generated perspective drawing of the final X-ray model of the title compound, H atoms are omitted for clarity.

The X-ray crystallographic study of (II) confirmed the oxygenation pattern of the molecule and the overall relative stereochemistry of the lanostane nucleus; assuming that the chiral centres of (II) have the same configuration as the natural (+)-lanosterol, the configuration of C(24) is *R*.

Rings *A–C* adopt the chair, half-chair and 1,2-diplanar conformations, respectively (Bucourt, 1974), though they are somewhat deformed. Ring *A* is slightly flattened, probably to relieve the severe 1,3-diaxial methyl–methyl interaction and to allow the formation of the 1,3-dioxolane ring. In ring *B* C(5) is -0.61 (2) and C(6) 0.15 (2) Å out of the mean plane through C(7)C(8)C(9)C(10), whereas in ring *C* C(12) is 0.33 (2) and C(13) 0.85 (2) Å above the mean plane through C(8)C(9)C(11)C(14). The cyclopentane ring *D* is closer to the 'half-chair' than to the 'envelope' form, C(13) is 0.36 (2) and C(14) -0.40 (2) Å out of the mean plane through the other three atoms.

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and least-squares-planes' data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42242 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

As far as the conformations of the heterocyclic rings are concerned, the 1,3-dioxolane ring is in an almost perfect half-chair conformation, whereas the five-, six- and seven-membered rings constituting the bicyclo-|3.2.1|octane system adopt the half-chair, chair and boat conformations, respectively.

The largest distortion is suffered by the seven-membered ring to relieve the otherwise intolerable repulsive interaction between the axial H(22) and one of the geminal methyls at C(25).

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Retronecine and Heliotridine, C₈H₁₃NO₂: Diastereoisomeric Pyrrolizidine Necine Bases

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Abstract. $M_r = 155.20$, orthorhombic, $P2_12_12_1$, $Z = 4$, $\lambda(\text{Mo } K\bar{\alpha}) = 0.71069$ Å, $F(000) = 336$, $T = 298$ K. Retronecine: $a = 7.944$ (4), $b = 8.536$ (5), $c = 12.062$ (6) Å, $V = 817.9$ (7) Å³, $D_m = 1.25$, $D_x = 1.26$ g cm⁻³, $\mu = 0.54$ cm⁻¹. Heliotridine: $a = 11.904$ (2), $b = 7.620$ (1), $c = 8.800$ (1) Å, $V = 798.2$ (2) Å³, $D_m = 1.32$, $D_x = 1.29$ g cm⁻³, $\mu = 0.55$ cm⁻¹. Final $R = 0.040$ and 0.038 for 825 and 1328 observed reflections for retronecine and heliotridine respectively. The ring system in retronecine (I) is *exo*- and in heliotridine (II) *endo*-puckered. In both structures O(1) and O(2) are in an antiparallel conformation. There are no unusual bond distances or angles. The intermolecular distances N(4)···O(2) for (I) (2.69) and for (II) (2.72 Å) indicate the existence of hydrogen bonding.

Introduction. The pyrrolizidine alkaloids have attracted a great deal of attention, primarily because of their causative effects in the heavy loss of livestock in many

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