

Fig. 1. Perspective view of the molecule with atom numbering. H atoms (omitted for clarity) are given the numbers of their bonding partners.

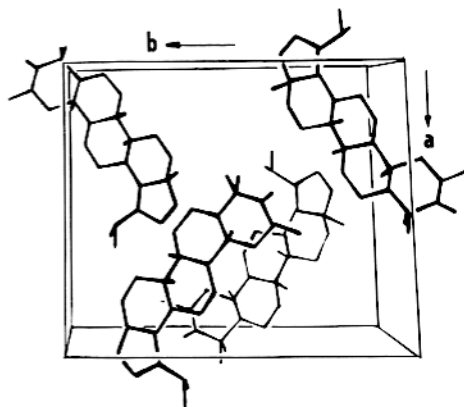


Fig. 2. The unit-cell contents viewed down the *c* axis.

3. Fig. 1 depicts a perspective view of the molecule together with the atom numbering. The unit-cell contents are shown in Fig. 2.

The general features of the structure are closely related to similar triterpenoid and steroid compounds (Cambridge Structural Database, 1986; Duax, Weeks & Rohrer, 1976). The C—C bond lengths average 1.543 (22) Å with only two typical bonds, C(8)—C(14) and C(17)—C(28), outside the  $2\sigma$  limit of the mean. Similarly, the mean C—C—C angle of 110.8 (3.7)° is exceeded by more than  $2\sigma$  in three cases, all involving C(18). In accordance with the proposed solution structure (Klinot, Buděšinský, Klinotová & Vystrčil, 1986), the *A*-ring conformation is very close to an ideal chair as reflected in the mean endocyclic torsion angle of  $\pm 52$  (2)°. The arrangement of the *B*, *C*, *D* and *E* rings is normal and corresponds to chair, chair, chair and distorted envelope, respectively, with all *trans* ring junctions.

A remarkable feature of the structure is a distinct bending of the triterpenoid skeleton which is apparent, for example, from the dihedral angle of 156.5° between the mean C(1)C(2)C(4)C(5) and C(13)C(15)C(16)C(18) planes. It seems likely that this effect is caused by

intramolecular constraints, since the crystal packing is very loose (with only four C...C contacts in the usual van der Waals range of 3.7 to 3.9 Å) and hence cannot be assumed to influence significantly the molecular geometry.

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### X-ray Structure of 6-Deoxymikanokryptin, a New Guaianolide from *Vernonia scorpioides* Pers: 3-Oxo-1 $\alpha$ ,7 $\alpha$ ,8 $\beta$ ,10 $\beta$ (H)-guaia-4(5),11(13)-dien-8,12-olide

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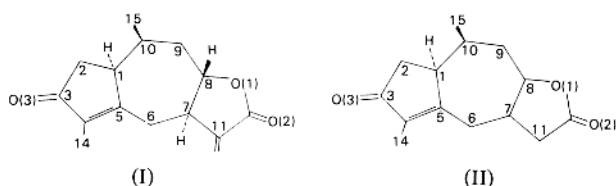
**Abstract.** C<sub>15</sub>H<sub>18</sub>O<sub>3</sub>, *M<sub>r</sub>* = 246.31, orthorhombic, *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, *a* = 10.800 (3), *b* = 9.685 (3), *c* =

12.704 (4) Å, *V* = 1329 Å<sup>3</sup>, *Z* = 4, *D<sub>m</sub>* = 1.24, *D<sub>x</sub>* = 1.232 Mg m<sup>-3</sup>,  $\lambda$ (Mo *K* $\alpha$ ) = 0.71069 Å,  $\mu$  = 0.049 mm<sup>-1</sup>, *F*(000) = 528, *T* = 295 K, *R* = 0.055 for 952 unique reflections with *I* > 3 $\sigma$ (*I*). The crystal

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structure consists of discrete molecules in which the seven-membered ring has a chair conformation as expected for the cycloheptane ring in mikanokryptins. The cyclopentene ring is planar and the  $\gamma$ -lactone ring, which is *trans* fused, has an envelope conformation.

**Introduction.** A study of the aerial parts of *Vernonia scorpioides* Pers collected in Rancho Grande, Maracay-Venezuela, yielded bitter colourless crystals, m.p. = 463–465 K [ $\alpha$ ]<sub>D</sub><sup>25°C</sup> = +217 (*c* 1.84), soluble in chloroform, ethyl acetate, ketone and insoluble in petroleum ether. Chemical and spectroscopic studies (UV, IR, NMR and MS) showed the compound to be an  $\alpha,\beta$ -unsaturated  $\gamma$ -lactone of the guaianolide type with molecular formula C<sub>15</sub>H<sub>18</sub>O<sub>3</sub>, supposed to be 6-deoxymikanokryptin (I), a compound not yet reported in the literature. Catalytic hydrogenation with PtO<sub>2</sub> (5%) yielded a compound similar to 11-demethylene-6-deoxymikanokryptin (II) that had been reported with tentative configuration at C(1) and C(10) (Herz, Srinivasan & Kalyanaraman, 1975) but spectroscopic comparison between the two derivatives was not conclusive.



Sesquiterpene lactones are known to have biological activity, and some guaianolides have antitumour and cytotoxic activities (Rodríguez, Towers & Mitchell, 1976). In order to ascertain the structure and secure the assignment of the stereochemistry of this compound an X-ray analysis was performed.

**Experimental.** Density determined by flotation in hexane-carbon tetrachloride. Colourless transparent parallelepiped crystal 0.45 × 0.30 × 0.20 mm. Automated four-circle Philips PW1100 diffractometer. Lattice parameters determined by least-squares procedure applied to the setting angles of 21 strong reflections in the range  $2 < \theta < 6^\circ$ . Intensity data up to  $(\sin \theta)/\lambda = 0.63 \text{ \AA}^{-1}$  in the range  $0 \leq h \leq 12$ ,  $0 \leq k \leq 11$ ,  $0 \leq l \leq 15$  measured with graphite-monochromated Mo K $\alpha$  radiation. Systematic absences proved the space group to be *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>. After Lp corrections the initial 1004 reflections were reduced to 952 unique data with  $I > 3\sigma(I)$ . Number of unobserved reflections: 52. 3 standard reflections, no variation in intensity. No corrections for absorption or extinction. Structure solved by direct methods (*MULTAN77*; Main, Lesinger, Woolfson, Germain & Declercq, 1977) with part of the geometry of the molecule taken into account. Structure refined by full-matrix least squares with

isotropic temperature factors for all non-H atoms converged to  $R = 0.116$ . All H atoms were placed in geometrically calculated positions and refined as rigid groups with the constraint C–H = 1.00 Å and one overall temperature factor. All non-H atoms were refined anisotropically. Final anisotropic–isotropic refinement converged to  $R = 0.055$  and  $wR = 0.058$ , with  $(\Delta/\sigma)_{\text{max}} = 0.003$ . The absolute configuration could not be determined since another run with two additional cycles having all positional parameters inverted converged to the same final  $R$ . Maximum and minimum heights in final difference Fourier synthesis were +0.25 and –0.29 e Å<sup>-3</sup>. Complex neutral atomic scattering factors from *International Tables for X-ray Crystallography* (1974). The function minimized was  $\sum_w (|F_o| - |F_c|)^2$  where  $w = 1/[\sigma^2(F_o) + gF_o^2]$  and  $g$  converged to 0.016016. All calculations performed with the *SHELX76* system (Sheldrick, 1976) on a Burroughs B5900 computer at the Universidad de Los Andes.

**Discussion.** Positional and isotropic thermal parameters and the resulting bond lengths and angles are given in Tables 1 and 2, respectively.\*

The crystal structure consists of discrete molecules of C<sub>15</sub>H<sub>18</sub>O<sub>3</sub> (Fig. 1) situated such that the mean plane of the cyclopentenone ring is almost perpendicular to the (100) plane (89.3°). The cyclopentenone ring is planar within one standard deviation while the *trans*-fused  $\gamma$ -lactone ring has an envelope conformation at C(8) with C(7), C(11), C(12) and O(1) approximately in the same plane. The seven-membered ring of mikanokryptin has a conformation that approximates more closely to a chair conformation than to a twist-chair form. The deoxycycloheptane chair conformation corresponds to that in which the smallest torsion angle in the ring is adjacent to the exocyclic double bond (Fig. 2). This conformer has been proposed to be the only point in conformational space accessible to the cycloheptane ring in mikanokryptin (Bovill, Guy, Sim, White & Herz, 1979).

A comparison between the mikanokryptin (Bovill, Guy, Sim, White & Herz, 1979) and 6-deoxymikanokryptin structures shows that similar bond lengths and angles are equal within standard deviations except the C(5)–C(6)–C(7) bond angle which is more obtuse in 6-deoxymikanokryptin than in mikanokryptin [115.9 (4) vs 112.6 (1)°]. This difference is probably due to the non-substituted C(6) in 6-deoxymikanokryptin.

\* Lists of anisotropic thermal parameters, H-atom coordinates refined as rigid groups, mean-plane calculations, torsion angles and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44214 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic positional parameters ( $\times 10^4$ ) and isotropic temperature factors ( $\text{\AA}^2 \times 10^3$ ) with e.s.d.'s in parentheses

	x	y	z	$U_{eq}^*$
C(1)	8587 (4)	-446 (5)	5178 (3)	50
C(2)	7245 (4)	-105 (6)	5436 (5)	68
C(3)	7265 (4)	1219 (5)	6060 (4)	58
C(4)	8563 (4)	1543 (5)	6275 (3)	49
C(5)	9304 (4)	649 (4)	5774 (3)	44
C(6)	10690 (4)	705 (5)	5837 (4)	53
C(7)	11380 (4)	-435 (5)	5261 (3)	46
C(8)	11173 (4)	-456 (4)	4077 (3)	45
C(9)	10057 (4)	-1248 (5)	3706 (3)	55
C(10)	8842 (4)	-533 (4)	3976 (4)	52
C(11)	12777 (4)	-329 (5)	5333 (4)	52
C(12)	13252 (4)	-904 (5)	4330 (4)	54
C(13)	13493 (5)	210 (8)	6055 (4)	75
C(M1)	8935 (5)	2732 (6)	6960 (4)	66
C(M2)	8691 (5)	884 (6)	3445 (4)	69
O(1)	12302 (3)	-1100 (4)	3651 (3)	57
O(2)	14302 (3)	-1177 (4)	4084 (3)	71
O(3)	6363 (3)	1862 (4)	6344 (3)	73

$$* U_{eq} = (U_{11} + U_{22} + U_{33})/3.$$

Table 2. Bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) with e.s.d.'s in parentheses

C(1)—C(2)	1.523 (7)	C(7)—C(8)	1.521 (6)
C(1)—C(5)	1.516 (6)	C(7)—C(11)	1.515 (6)
C(1)—C(10)	1.554 (7)	C(8)—C(9)	1.505 (6)
C(2)—C(3)	1.508 (8)	C(8)—O(1)	1.473 (5)
C(3)—C(4)	1.462 (7)	C(9)—C(10)	1.523 (7)
C(3)—O(3)	1.211 (6)	C(10)—C(M2)	1.537 (8)
C(4)—C(5)	1.340 (6)	C(11)—C(12)	1.482 (7)
C(4)—C(M1)	1.498 (7)	C(11)—C(13)	1.309 (7)
C(5)—C(6)	1.500 (6)	C(12)—O(1)	1.354 (6)
C(6)—C(7)	1.520 (6)	C(12)—O(2)	1.205 (6)
C(2)—C(1)—C(5)	103.1 (4)	C(8)—C(7)—C(11)	101.9 (3)
C(2)—C(1)—C(10)	113.1 (4)	C(7)—C(8)—C(9)	115.8 (4)
C(5)—C(1)—C(10)	116.0 (4)	O(1)—C(8)—C(7)	104.3 (4)
C(1)—C(2)—C(3)	106.5 (4)	O(1)—C(8)—C(9)	109.4 (3)
C(2)—C(3)—C(4)	107.2 (4)	C(8)—C(9)—C(10)	112.8 (4)
C(2)—C(3)—O(3)	125.6 (5)	C(1)—C(10)—C(9)	113.5 (4)
O(3)—C(3)—C(4)	127.3 (5)	C(1)—C(10)—C(M2)	111.4 (4)
C(3)—C(4)—C(5)	110.2 (4)	C(9)—C(10)—C(M2)	113.5 (4)
C(3)—C(4)—C(M1)	122.0 (4)	C(7)—C(11)—C(12)	105.6 (4)
C(5)—C(4)—C(M1)	127.8 (4)	C(7)—C(11)—C(13)	131.1 (4)
C(1)—C(5)—C(4)	112.6 (4)	C(12)—C(11)—C(13)	123.2 (4)
C(1)—C(5)—C(6)	124.2 (4)	O(1)—C(12)—C(11)	109.7 (4)
C(4)—C(5)—C(6)	123.2 (4)	O(1)—C(12)—O(2)	121.1 (5)
C(5)—C(6)—C(7)	115.9 (4)	O(2)—C(12)—C(11)	129.2 (5)
C(6)—C(7)—C(8)	114.4 (4)	C(8)—O(1)—C(12)	109.5 (3)
C(6)—C(7)—C(11)	114.2 (4)		

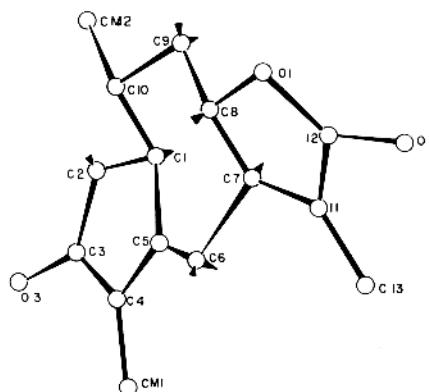


Fig. 1. Perspective view of 6-deoxymikanokryptin showing the atomic labelling.

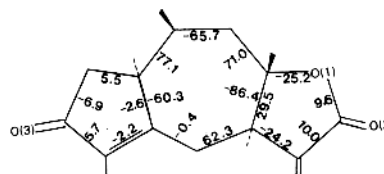


Fig. 2. Torsion angles ( $^\circ$ ). E.s.d.'s are in the range 0.3–0.6 $^\circ$ .

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