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Taurin from *Artemisia cretacea* Fiori,* $C_{15}H_{20}O_3$

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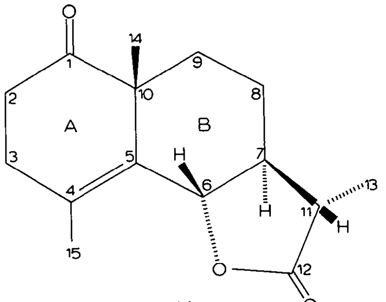
Abstract. $M_r = 248{\cdot}3$, m.p. 392–393 K, $[\alpha]_D^{25^\circ c} = +120^\circ$ [$CHCl_3$, $0{\cdot}1$ g dm^{-3}], orthorhombic, space group $P2_12_12_1$, $a = 11{\cdot}144$ (2), $b = 15{\cdot}222$ (3), $c = 16{\cdot}531$ (3) Å, $U = 2804$ (1) Å^3, $Z = 8$, $D_x = 1{\cdot}17$ Mg m^{-3}, λ(Mo $K\alpha$) = $0{\cdot}71069$ Å, $\mu = 0{\cdot}08$ mm^{-1}, $F(000) = 1072$, $T = 293$ K. Final $R = 0{\cdot}043$ for 1695 unique observed reflexions. The ring system is in the chair–half-chair conformation with C(14) on the β face. The lactone, *trans*-fused at C(6)—C(7), assumes an envelope conformation with C(11) at the flap and C(13) in the pseudo-equatorial position on the α face.

Introduction. Taurin is a spasmolitic (Villar & Zafra-Polo, 1981) sesquiterpene lactone isolated from various species of *Artemisia*, belonging to the section *Seriphidium* of this genus. The compound was isolated for the first time by Kechatova, Rybalko, Sheichenko & Tolstykh (1968) who proposed formula (I) without describing the configuration at C(11). Recently Serkerov & Aleskerova (1981) elucidated the complete stereochemistry of taurin (formula I) and proved it to be identical with the lactone (6β,7α,11βH)-1-oxoeudesm-4-en-6,12-olide previously described by Gonzales-Gonzales, Breton Funes & Stockel (1974).



(I)

Taurin has been recently isolated (G. Appendino, personal communication) from the aerial parts of *Artemisia caerulescens* L. subsp. *cretacea* Fiori and we studied its structure and conformation as a part of an extensive research program on sesquiterpenoids from Compositae.

Experimental. Specimens suitable for X-ray analysis obtained from ethyl acetate–ether as prismatic transparent crystals of fairly large size; for intensity collection crystal ground to an approximately spherical shape, $\bar{r} = \sim 0{\cdot}20$ mm, and sealed in a Lindemann-glass capillary filled with nitrogen since decomposition under X-rays had been observed. Nicolet *R*3 diffractometer, graphite-monochromatized Mo $K\alpha$ radiation. No appreciable decrease in intensity of a standard reflexion measured at intervals of 50 observations. Cell parameters obtained and refined using 25 reflexions, $12 \le 2\theta \le 33^\circ$. Intensities collected with ω-scan technique at variable speed: from 2° min^{-1} for the weakest to 20° min^{-1} for the strongest reflexions. Left and right backgrounds measured in stationary mode for same length of time as peak scan. Copper attenuator automatically inserted for 14 reflexions exceeding 60 000 counts s^{-1} on prescan; these reflexions, nevertheless, showed poor F_o *vs* F_c agreement and were left out from closing cycles of refinement. Reciprocal-lattice sphere explored up to $2\theta \le 40^\circ$, collecting two sets of *hkl* and $\bar{h}kl$ reflexions (h: −10–10, k: 0–20, l: 0–21). A trial to extend data collection up to $2\theta \le 56^\circ$ was interrupted since very few reflexions in this range had significant intensity. Total of 2641 reflexions measured and, after averaging the two octants ($R_{\rm int} = 0{\cdot}033$), 1716 reflexions with $I \ge 2\sigma(I)$ considered observed and corrected for background effects using the Nicolet (1980) system. Empirical absorption correction based on ψ-scan method (North, Phillips & Mathews, 1968) applied using five reflexions distributed over range $11 \le 2\theta \le 37^\circ$; applied absorption coefficients 1·00–1·14. *SHELXTL* (Sheldrick, 1981) used for all subsequent computations. Solution achieved with *RANTAN* (Yao Jia-xing, 1981) assigning random phases to 240 largest *E*'s (2993 triple-phase relationships). All 18 non-H atoms of one molecule and five atoms of the other located on *E* map showing best figures of merit; subsequent difference Fourier cycles located missing atoms. $R = 0{\cdot}166$ at end of isotropic refinement of non-H atoms which dropped to 0·103 on inserting H atoms in calculated positions. Final cycles run with anisotropic thermal parameters for non-H atoms; H atoms forced to ride on bonded C atoms using three different variable isotropic thermal

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* (3*S*)-3α,5aβ,9-Trimethyl-3aα,5,5a,7,8,9bβ-hexahydronaphtho[1,2-*b*]furan-2,6(3*H*,4*H*)-dione.

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parameters for $-CH$, $-CH_2$ and $-CH_3$ groups whose values converged to 0·077 (4), 0·096 (3) and 0·123 (4) Å^2, respectively. Weighting scheme introduced in final cycles $w = 1/[\sigma^2(F_o) + GF_o^2]$, where σ is the standard deviation of F_o based on counting statistics and G was set equal to 0·001 in order to keep $\sum w(F_o - F_c)^2$ values as constant as possible over ranges of $\sin\theta/\lambda$ and $(F_o/F_{o\max})^{1/2}$. At convergence (average ratio of shifts to errors = 0·17) $wR = 0·046$; goodness of fit = 1·368 for the 1695 reflexions left for the refinement and 346 parameters. Highest peak in final difference map 0·21 e Å^{-3}.

Discussion. Table 1 lists the final parameters of the non-H atoms of the two molecules (I and II) in the asymmetric unit.*

Table 2 shows the bond distances and angles of the two molecules and Fig. 1 displays their *ORTEP*II (Johnson, 1970) drawings. The major difference between the two molecules is in the thermal vibration [mean $U_{eq} = 0·073$ and 0·084 Å^2 for molecules (I) and (II) respectively] which is visualized (Fig. 1) by the higher anisotropic character and the different orientation of the ellipsoids of molecule (II) with respect to (I). Nonetheless the geometry of the two molecules is identical within three times the e.s.d.'s (Table 2) excepting bonds C(11)—C(13) and C(10)—C(14) and a few angles involving mainly C(10).

In taurin the lactone ring, *trans*-fused at C(6)—C(7), assumes an envelope conformation with C(11) 0·47 (1) Å out of the mean plane through C(12), O(1), C(6), C(7) [r.m.s.d. = 0·12 (1) Å] in both molecules. The bridge-headed unsaturated decalin system shows a slightly distorted chair conformation in ring *B* and the half-chair conformation in ring *A* with C(2) above and C(1) below the mean plane through the other atoms. A similar chair–half-chair conformation has been found, for instance, in rosifoliol (Beagley, Pritchard, Ramage

Table 1. *Atom coordinates* (× 10^4) *and equivalent isotropic temperature factors* (Å^2 × 10^4)

	x	y	z	U_{eq}*
O(1)	10079 (2)	1691 (1)	4344 (1)	64 (1)
O(2)	6130 (2)	457 (2)	2070 (2)	110 (1)
O(3)	10642 (3)	2239 (2)	5535 (2)	93 (1)
C(1)	7177 (3)	645 (2)	2191 (2)	74 (1)
C(2)	7978 (4)	979 (3)	1548 (2)	88 (2)
C(3)	8536 (4)	1841 (3)	1809 (2)	87 (2)
C(4)	9067 (3)	1823 (2)	2657 (2)	62 (1)
C(5)	8722 (3)	1222 (2)	3197 (2)	49 (1)
C(6)	9128 (3)	1114 (2)	4059 (2)	51 (1)
C(7)	8131 (3)	1251 (2)	4657 (2)	54 (1)
C(8)	7182 (3)	545 (2)	4551 (2)	70 (1)
C(9)	6723 (3)	585 (2)	3674 (2)	68 (1)
C(10)	7731 (3)	527 (2)	3030 (2)	57 (1)
C(11)	8835 (3)	1345 (2)	5441 (2)	66 (1)
C(12)	9936 (3)	1806 (2)	5158 (2)	67 (1)
C(13)	8212 (5)	1792 (3)	6150 (2)	98 (2)
C(14)	8268 (3)	−421 (2)	3002 (2)	72 (1)
C(15)	9961 (4)	2541 (3)	2791 (2)	86 (2)
O(1′)	5006 (2)	1093 (1)	−60 (2)	72 (1)
O(2′)	352 (3)	−328 (2)	1285 (3)	129 (2)
O(3′)	6274 (3)	2188 (2)	−296 (3)	143 (2)
C(1′)	1274 (4)	−432 (2)	908 (3)	82 (2)
C(2′)	1369 (4)	−1056 (3)	224 (3)	101 (2)
C(3′)	1698 (4)	−545 (3)	−512 (3)	95 (2)
C(4′)	2757 (3)	65 (2)	−401 (2)	59 (1)
C(5′)	3121 (3)	296 (2)	343 (2)	44 (1)
C(6′)	4154 (3)	867 (2)	572 (2)	49 (1)
C(7′)	3762 (3)	1744 (2)	910 (2)	60 (1)
C(8′)	3104 (4)	1581 (2)	1705 (2)	81 (1)
C(9′)	2061 (3)	948 (2)	1556 (2)	73 (1)
C(10′)	2418 (3)	79 (2)	1125 (2)	56 (1)
C(11′)	4933 (4)	2246 (2)	868 (3)	86 (2)
C(12′)	5498 (3)	1884 (3)	125 (3)	87 (2)
C(13′)	4850 (5)	3261 (3)	874 (4)	146 (3)
C(14′)	3122 (4)	−527 (2)	1697 (2)	79 (1)
C(15′)	3285 (4)	374 (3)	−1183 (2)	90 (2)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

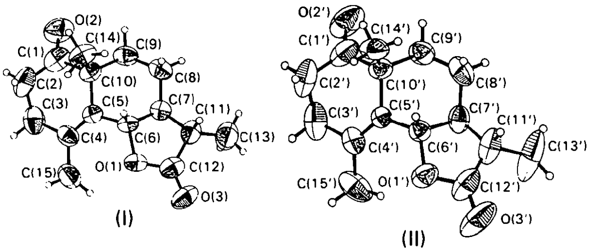

Fig. 1. *ORTEP*II projection, on the plane through C(5), C(7), C(8), of the two independent molecules of taurin. Thermal ellipsoids are drawn at the 50% probability level; the H atoms are represented by spheres of an arbitrary size.

Table 2. *Bond distances* (Å) *and angles* (°) *for the two independent molecules with e.s.d.'s in parentheses*

	Molecule (I)	Molecule (II)		Molecule (I)	Molecule (II)		Molecule (I)	Molecule (II)		Molecule (I)	Molecule (II)
O(1)—C(6)	1·455 (4)	1·454 (4)	C(1)—C(10)	1·529 (5)	1·536 (6)	C(5)—C(6)	1·505 (4)	1·491 (4)	C(8)—C(9)	1·538 (5)	1·529 (5)
O(1)—C(12)	1·366 (4)	1·357 (4)	C(2)—C(3)	1·515 (6)	1·491 (7)	C(5)—C(10)	1·553 (4)	1·547 (4)	C(9)—C(10)	1·550 (5)	1·554 (5)
O(2)—C(1)	1·218 (5)	1·212 (5)	C(3)—C(4)	1·521 (5)	1·512 (5)	C(6)—C(7)	1·501 (4)	1·512 (4)	C(10)—C(14)	1·562 (4)	1·536 (5)
O(3)—C(12)	1·202 (4)	1·203 (5)	C(4)—C(5)	1·336 (4)	1·342 (4)	C(7)—C(8)	1·518 (5)	1·525 (5)	C(11)—C(12)	1·489 (5)	1·487 (6)
C(1)—C(2)	1·478 (5)	1·480 (6)	C(4)—C(15)	1·495 (5)	1·496 (5)	C(7)—C(11)	1·522 (4)	1·514 (5)	C(11)—C(13)	1·522 (5)	1·548 (5)
C(6)—O(1)—C(12)	108·1 (2)	108·1 (3)	C(5)—C(4)—C(15)	126·4 (3)	126·2 (3)	C(6)—C(7)—C(11)	101·1 (3)	100·4 (3)	C(5)—C(10)—C(14)	111·2 (3)	112·5 (3)
O(2)—C(1)—C(2)	122·8 (4)	122·5 (4)	C(4)—C(5)—C(6)	128·4 (3)	128·3 (3)	C(8)—C(7)—C(11)	121·7 (3)	122·4 (3)	C(9)—C(10)—C(14)	110·5 (3)	111·1 (3)
O(2)—C(1)—C(10)	120·6 (3)	121·1 (4)	C(4)—C(5)—C(10)	123·5 (3)	123·8 (3)	C(7)—C(8)—C(9)	108·2 (3)	109·3 (3)	C(7)—C(11)—C(12)	101·6 (3)	102·4 (3)
C(2)—C(1)—C(10)	116·7 (3)	116·4 (3)	C(6)—C(5)—C(10)	108·0 (2)	107·6 (2)	C(8)—C(9)—C(10)	113·8 (3)	114·5 (3)	C(7)—C(11)—C(13)	117·5 (3)	116·9 (3)
C(1)—C(2)—C(3)	110·0 (3)	107·8 (3)	O(1)—C(6)—C(5)	117·3 (2)	117·4 (2)	C(1)—C(10)—C(5)	111·6 (3)	109·4 (3)	C(12)—C(11)—C(13)	114·0 (3)	113·6 (4)
C(2)—C(3)—C(4)	114·0 (3)	114·3 (4)	O(1)—C(6)—C(7)	104·0 (2)	104·2 (2)	C(1)—C(10)—C(9)	108·9 (3)	109·0 (3)	O(1)—C(12)—O(3)	120·4 (3)	120·1 (4)
C(3)—C(4)—C(5)	121·1 (3)	120·6 (3)	C(5)—C(6)—C(7)	112·7 (2)	112·7 (3)	C(5)—C(10)—C(9)	110·7 (3)	109·3 (2)	O(1)—C(12)—C(11)	110·2 (3)	110·3 (3)
C(3)—C(4)—C(15)	112·5 (3)	113·2 (3)	C(6)—C(7)—C(8)	109·9 (3)	108·2 (3)	C(1)—C(10)—C(14)	103·7 (3)	105·3 (3)	O(3)—C(12)—C(11)	129·4 (3)	129·8 (4)

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38572 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Selected torsion angles* (°); *e.s.d.'s* 0·3–0·4°

	Molecule (I)	Molecule (II)		Molecule (I)	Molecule (II)		Molecule (I)	Molecule (II)
C(12)–O(1)–C(6)–C(5)	151·4	151·6	C(3)–C(4)–C(5)–C(10)	−2·7	−8·6	C(6)–C(7)–C(8)–C(9)	−57·9	−56·2
C(12)–O(1)–C(6)–C(7)	26·1	26·3	C(4)–C(5)–C(6)–O(1)	−4·6	−11·3	C(11)–C(7)–C(8)–C(9)	−175·5	−171·8
C(6)–O(1)–C(12)–O(3)	177·7	176·6	C(4)–C(5)–C(6)–C(7)	116·2	109·7	C(6)–C(7)–C(11)–C(12)	34·8	34·3
C(6)–O(1)–C(12)–C(11)	−3·1	−3·6	C(10)–C(5)–C(6)–O(1)	178·7	174·8	C(8)–C(7)–C(11)–C(12)	156·7	153·8
O(2)–C(1)–C(2)–C(3)	125·5	119·6	C(10)–C(5)–C(6)–C(7)	−60·4	−64·2	C(7)–C(8)–C(9)–C(10)	54·0	53·1
C(10)–C(1)–C(2)–C(3)	−55·5	−61·0	C(4)–C(5)–C(10)–C(1)	−2·3	0·2	C(8)–C(9)–C(10)–C(1)	−175·7	−172·1
O(2)–C(1)–C(10)–C(5)	−148·5	−144·8	C(4)–C(5)–C(10)–C(9)	−123·8	−119·1	C(8)–C(9)–C(10)–C(5)	−52·6	−52·5
O(2)–C(1)–C(10)–C(9)	−26·0	−25·2	C(6)–C(5)–C(10)–C(1)	174·5	174·4	C(7)–C(11)–C(12)–O(1)	−20·7	−20·3
C(2)–C(1)–C(10)–C(5)	32·5	35·8	C(6)–C(5)–C(10)–C(9)	53·0	55·0	C(7)–C(11)–C(12)–O(3)	158·5	159·4
C(2)–C(1)–C(10)–C(9)	155·0	155·4	O(1)–C(6)–C(7)–C(8)	−167·4	−166·6	C(13)–C(11)–C(12)–O(3)	31·0	32·4
C(1)–C(2)–C(3)–C(4)	48·2	50·0	O(1)–C(6)–C(7)–C(11)	−37·6	−37·2	C(13)–C(11)–C(7)–C(6)	159·9	159·1
C(2)–C(3)–C(4)–C(5)	−20·9	−17·8	C(5)–C(6)–C(7)–C(8)	64·5	65·2	C(13)–C(11)–C(7)–C(8)	−78·2	−81·4
C(3)–C(4)–C(5)–C(6)	−178·8	178·4	C(5)–C(6)–C(7)–C(11)	−165·8	−165·5	O(3)–C(12)–O(1)–C(6)	177·7	176·6

& Southwell, 1982). Atom C(14) is on the *β* and C(13) on the α face in the pseudo-equatorial position; this latter position, in the case of the C(6) *trans*-eudesmanolides, is the more stable conformationally (White & Sim, 1973). The mean values of the different C—C bond types, averaged over the two molecules, are: $\langle C_{sp^3}–C_{sp^3}\rangle = 1·527\ (4)$, $\langle C_{sp^2}–C_{sp^3}\rangle = 1·508\ (4)$, $\langle C_{sp^2}–C_{sp^2}\rangle = 1·339\ (4)$ Å. It is worth noting that bond C(5)—C(10) (Table 2) of the $C_{sp^2}–C_{sp^3}$ type, is strained, being significantly longer than the average; this bond is even longer in erivanin (Rychlewska, Holub, Bloszyk & Drozdz, 1982): 1·566 (7) Å. As pointed out by El-Feraly, Chan & Benigni (1979), the presence of an endocyclic double bond causes distortions in a six-membered ring. In ring *A* of taurin this is evidenced by the value of angle C(2)C(3)C(4), 114·1 (3)°, which is significantly larger than the corresponding angle in erivanin, 110·3 (5)°, where an exocyclic double bond is present instead.

The torsion angle C(3)C(4)C(5)C(6) is −178·8 (3) and 178·4 (3)° in molecules (I) and (II) respectively (Table 3), indicating an almost unstrained double bond. The endocyclic torsion angles of ring *B* compare well with those of erivanin (Rychlewska *et al.*, 1982) indicating that the presence of the C(4)=C(5) bond does not greatly affect this ring. In fact the mean value of the endocyclic torsion angles of this ring, averaged over the two molecules, is 56·4 (3)°, nearly identical to the value, 55·9°, found in cyclohexane by electron-diffraction studies (Geise, Buys & Mijlhoff, 1971). The presence of the endocyclic double bond, which forces ring *A* of taurin to assume the half-chair conformation, does not allow a comparison with the other eudesmanolides studied so far by X-ray analysis (Fischer, Olivier & Fischer, 1979).

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