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Two Eudesmanolide-Type Sesquiterpene Lactones from *Umbelliferae*

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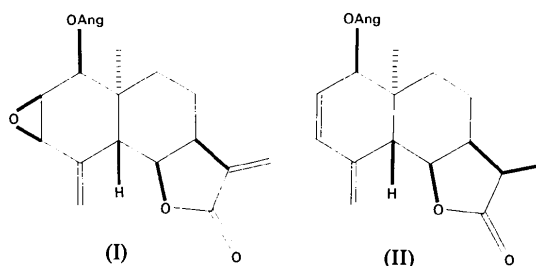
Abstract

(I) 1 β -Angeloyloxy-2 β ,3 β -epoxy-5 β H,7 α H-10 α -methyleudesma-4(15),11(13)-dien-6,12-olide; (II) 1 β -angeloyloxy-5 β H,6 α H,7 α H,11 α H-10 α -methyl-eudesma-2,4(15)-dien-6,12-olide. (I) and (II) are two closely related native eudesmanolides whose structures are based on the fundamental 5 β H,6 α H,7 α H,10 α CH₃-eudesman-6,12-olide skeleton. As regards molecular conformation, the largest difference between the two compounds is in the cyclohexane B ring which is of the rigid chair type in (I) and of the flexible boat type in (II).

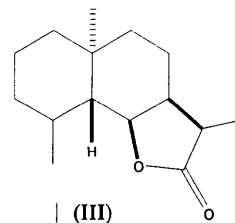
Comment

Spectroscopic (Holub & Buděšínský, 1986) and X-ray (Rychlewska, 1986) investigations of sesquiterpene lactones isolated from members of the *Umbelliferae* revealed that these compounds possess an inverted stereochemistry at some of the chiral centres, as compared with analogous species extracted from members of the *Compositae*, and led to the discovery of new stereostructural groups of natural sesquiterpene lactones. As a consequence, several previously established structures have been corrected, mostly on the basis of new interpretation of the ¹H NMR spectra (Holub & Buděšínský, 1986). Among eudesmanolides whose stereostructures have been revised were lactones isolated from *Ferula oopoda* (Boiss, et Bushe.) Boiss: badkhsinin (I),* obtained for the first time by Kirialov & Serkerov

(1966) and oopodin (II),* isolated for the first time by Serkerov (1969). The structures of the two lactones have been the subject of significant modifications over the years (Serkerov, 1971, 1972, 1980). We have undertaken X-ray investigations of these compounds in order to confirm unambiguously the most recent spectroscopic assignments (Holub & Buděšínský, 1986).



Fractional atomic coordinates and isotropic displacement coefficients for non-H atoms, bond lengths, bond angles and selected torsion angles involving non-H atoms are given in Tables 1–5. Figs. 1 and 2 give ORTEP (Johnson, 1965) drawings of (I) and (II), respectively. As seen from Figs. 1 and 2 and Tables 2, 4 and 5, the molecular structure of (I) and (II) consists of two *trans*-fused [at C(5)—C(10)] six-membered rings and a *cis*-fused [at C(6)—C(7)] five-membered γ -lactone. Both compounds investigated belong to a group of eudesmanolides represented by the basic stereostructure 5 β H,6 α H,7 α H,10 α CH₃-eudesman-6,12-olide (III) which exhibits enantiomeric stereochemistry at the place of fusion of the six-membered rings and at the site of the lactone closure, compared with eudesmanolides isolated from the members of the *Compositae*. In this respect our results support earlier spectroscopic assignments (Holub & Buděšínský, 1986).



The angeloyloxy substituent at C(1) is β in both compounds, as is the C(2)—C(3) epoxy group in (I). The C(13) methyl, present in (II), is β and not α , as recently suggested (Holub & Buděšínský, 1986).

* {3aS-[3 $\alpha\alpha$,5 $\alpha\alpha$,6 β (Z),6 $\alpha\alpha$,7 $\alpha\alpha$,8 $\alpha\beta$,8 $\beta\alpha$]}-Dodecahydro-5a-methyl-3,8-bis(methylene)-2-oxooxireno[6,7]naphtho[1,2-b]furan-6-yl 2-methyl-2-butenic acid ester

* {3R-[3 β ,3 $\alpha\alpha$,5 $\alpha\alpha$,6 β (Z),9 $\alpha\beta$,9 $\beta\alpha$]}-2,3,3a,4,5,5a,6,9,9a,9b-Decahydro-3,5a-dimethyl-9-methylene-2-oxonaphtho[1,2-b]furan-6-yl 2-methyl-2-butenic acid ester

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (\AA^2) for (I)
$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
C(1)	0.1368 (3)	-0.1900 (2)	-0.2617 (3)	0.0054 (1)
C(2)	0.0741 (4)	-0.1203 (3)	-0.3947 (3)	0.0062 (1)
C(3)	0.0925 (4)	-0.0152 (2)	-0.3710 (3)	0.0063 (1)
C(4)	0.1691 (4)	0.0234 (2)	-0.2136 (3)	0.0056 (1)
C(5)	0.2644 (3)	-0.0489 (2)	-0.0966 (3)	0.0051 (1)
C(6)	0.3161 (4)	-0.0055 (2)	0.0708 (3)	0.0059 (1)
C(7)	0.3787 (4)	-0.0767 (3)	0.2059 (3)	0.0064 (1)
C(8)	0.2817 (5)	-0.1727 (3)	0.1960 (3)	0.0070 (1)
C(9)	0.2553 (4)	-0.2144 (2)	0.0270 (3)	0.0066 (1)
C(10)	0.1589 (4)	-0.1435 (2)	-0.0971 (3)	0.0053 (1)
C(11)	0.5709 (4)	-0.0785 (3)	0.2065 (3)	0.0069 (1)
C(12)	0.6133 (5)	0.0143 (3)	0.1357 (3)	0.0068 (1)
C(13)	0.6873 (5)	-0.1461 (3)	0.2510 (4)	0.0095 (2)
C(14)	-0.0253 (4)	-0.1218 (3)	-0.0652 (4)	0.0070 (1)
C(15)	0.1446 (5)	0.1156 (3)	-0.1853 (4)	0.0080 (1)
C(16)	0.3017 (4)	-0.2890 (2)	-0.4058 (3)	0.0051 (1)
C(17)	0.4807 (3)	-0.3172 (2)	-0.4232 (3)	0.0052 (1)
C(18)	0.5110 (4)	-0.3844 (2)	-0.5264 (3)	0.0066 (1)
C(19)	0.3859 (5)	-0.4440 (3)	-0.6374 (5)	0.0091 (1)
C(20)	0.6274 (4)	-0.2643 (3)	-0.3202 (4)	0.0074 (1)
O(1)	0.3037 (2)	-0.2281 (2)	-0.2843 (2)	0.0054 (1)
O(2)	0.2086 (2)	-0.0680 (2)	-0.4560 (2)	0.0069 (1)
O(6)	0.4651 (3)	0.0584	0.0688 (2)	0.0067 (1)
O(12)	0.7539 (3)	0.0497 (2)	0.1322 (3)	0.0092 (1)
O(16)	0.1679 (3)	-0.3155 (2)	-0.4882 (2)	0.0070 (1)

Table 3. Fractional atomic coordinates and equivalent isotropic thermal parameters (\AA^2) for (II)
$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
C(1)	0.5282 (4)	0.2000 (5)	0.7872 (2)	0.0061 (1)
C(2)	0.3880 (4)	0.2514 (5)	0.7281 (2)	0.0068 (1)
C(3)	0.3890 (4)	0.2110 (5)	0.6471 (2)	0.0066 (1)
C(4)	0.5252 (4)	0.1129 (5)	0.6072 (2)	0.0059 (1)
C(5)	0.6642 (3)	0.0430 (5)	0.6657 (2)	0.0050 (1)
C(6)	0.8261 (3)	0.0040 (5)	0.6199 (2)	0.0052 (1)
C(7)	0.9794 (3)	-0.0159 (5)	0.6765 (2)	0.0053 (1)
C(8)	0.9282 (4)	-0.0694 (5)	0.7651 (2)	0.0062 (1)
C(9)	0.8271 (4)	0.0913 (6)	0.8026 (2)	0.0068 (1)
C(10)	0.6938 (4)	0.1730 (5)	0.7413 (2)	0.0056 (1)
C(11)	1.0820 (3)	-0.1632 (5)	0.6291 (2)	0.0058 (1)
C(12)	0.9532 (4)	-0.2713 (6)	0.5833 (2)	0.0061 (1)
C(13)	1.2053 (5)	-0.2797 (6)	0.6801 (2)	0.0086 (2)
C(14)	0.7477 (4)	0.3679 (5)	0.7113 (2)	0.0078 (1)
C(15)	0.5209 (5)	0.0840 (6)	0.5240 (2)	0.0082 (2)
C(16)	0.3746 (4)	0.0227 (5)	0.8879 (2)	0.0062 (1)
C(17)	0.3482 (4)	-0.1675 (6)	0.9223 (2)	0.0067 (1)
C(18)	0.2258 (5)	-0.2019 (7)	0.9738 (2)	0.0086 (1)
C(19)	0.0980 (5)	-0.0765 (7)	1.0060 (3)	0.0100 (2)
C(20)	0.4706 (6)	-0.3180 (6)	0.8952 (3)	0.0092 (2)
O(1)	0.4882 (2)	0.0197 (4)	0.8265 (1)	0.0062 (1)
O(6)	0.8087 (2)	-0.1771	0.5779 (1)	0.0062 (1)
O(12)	0.9650 (3)	-0.4243 (4)	0.5522 (1)	0.0084 (1)
O(16)	0.3075 (3)	0.1629 (5)	0.9100 (2)	0.0088 (1)

Table 2. Geometric parameters (\AA , $^\circ$) for (I)

C(1)—C(2)	1.506 (4)	C(7)—C(11)	1.507 (4)
C(1)—C(10)	1.528 (4)	C(8)—C(9)	1.534 (4)
C(1)—O(1)	1.455 (3)	C(9)—C(10)	1.542 (4)
C(2)—C(3)	1.472 (5)	C(10)—C(14)	1.545 (5)
C(2)—O(2)	1.450 (4)	C(11)—C(12)	1.482 (6)
C(3)—C(4)	1.473 (4)	C(11)—C(13)	1.316 (5)
C(3)—O(2)	1.456 (4)	C(12)—O(6)	1.348 (4)
C(4)—C(5)	1.516 (4)	C(12)—O(12)	1.212 (5)
C(4)—C(15)	1.319 (5)	C(16)—C(17)	1.489 (4)
C(5)—C(6)	1.538 (4)	C(16)—O(1)	1.334 (4)
C(5)—C(10)	1.548 (4)	C(16)—O(16)	1.214 (4)
C(6)—C(7)	1.531 (4)	C(17)—C(18)	1.331 (4)
C(6)—O(6)	1.468 (4)	C(17)—C(20)	1.510 (4)
C(7)—C(8)	1.526 (6)	C(18)—C(19)	1.489 (5)
C(10)—C(1)—O(1)	108.3 (2)	C(5)—C(10)—C(9)	109.8 (2)
C(2)—C(1)—O(1)	108.4 (2)	C(1)—C(10)—C(9)	109.1 (2)
C(2)—C(1)—C(10)	113.2 (2)	C(1)—C(10)—C(5)	109.5 (2)
C(1)—C(2)—O(2)	115.4 (2)	C(9)—C(10)—C(14)	111.4 (2)
C(1)—C(2)—C(3)	121.2 (2)	C(5)—C(10)—C(14)	110.5 (2)
C(3)—C(2)—O(2)	59.8 (2)	C(1)—C(10)—C(14)	106.5 (2)
C(2)—C(3)—O(2)	59.4 (2)	C(7)—C(11)—C(13)	131.0 (3)
C(2)—C(3)—C(4)	119.9 (2)	C(7)—C(11)—C(12)	106.2 (3)
C(4)—C(3)—O(2)	116.5 (2)	C(12)—C(11)—C(13)	122.7 (3)
C(3)—C(4)—C(15)	118.0 (3)	C(11)—C(12)—O(12)	129.1 (3)
C(3)—C(4)—C(5)	115.9 (2)	C(11)—C(12)—O(6)	109.1 (3)
C(5)—C(4)—C(15)	126.1 (3)	O(6)—C(12)—O(12)	121.8 (3)
C(4)—C(5)—C(10)	110.8 (2)	O(1)—C(16)—O(16)	122.2 (3)
C(4)—C(5)—C(6)	112.0 (2)	C(17)—C(16)—O(16)	126.7 (3)
C(6)—C(5)—C(10)	112.8 (2)	C(17)—C(16)—O(1)	111.1 (2)
C(5)—C(6)—O(6)	107.8 (2)	C(16)—C(17)—C(20)	116.8 (2)
C(5)—C(6)—C(7)	116.5 (2)	C(16)—C(17)—C(18)	122.0 (2)
C(7)—C(6)—O(6)	104.2 (2)	C(18)—C(17)—C(20)	121.2 (3)
C(6)—C(7)—C(11)	101.7 (2)	C(17)—C(18)—C(19)	129.4 (3)
C(6)—C(7)—C(8)	115.3 (2)	C(1)—O(1)—C(16)	116.3 (2)
C(8)—C(7)—C(11)	118.3 (3)	C(2)—O(2)—C(3)	60.9 (2)
C(7)—C(8)—C(9)	111.3 (3)	C(6)—O(6)—C(12)	110.6 (2)
C(8)—C(9)—C(10)	112.1 (2)		

Table 4. Geometric parameters (\AA , $^\circ$) for (II)

C(1)—C(2)	1.501 (4)	C(8)—C(9)	1.540 (5)
C(1)—C(10)	1.540 (5)	C(9)—C(10)	1.552 (5)
C(1)—O(1)	1.479 (4)	C(10)—C(14)	1.548 (5)
C(2)—C(3)	1.320 (4)	C(11)—C(12)	1.478 (5)
C(3)—C(4)	1.457 (5)	C(11)—C(13)	1.522 (5)
C(4)—C(5)	1.527 (4)	C(12)—O(6)	1.347 (4)
C(4)—C(15)	1.338 (4)	C(12)—O(12)	1.213 (5)
C(5)—C(6)	1.527 (4)	C(16)—C(17)	1.492 (6)
C(5)—C(10)	1.539 (5)	C(16)—O(1)	1.347 (4)
C(6)—C(7)	1.520 (4)	C(16)—O(16)	1.200 (5)
C(6)—O(6)	1.472 (4)	C(17)—C(18)	1.313 (5)
C(7)—C(8)	1.522 (4)	C(17)—C(20)	1.531 (6)
C(7)—C(11)	1.547 (4)	C(18)—C(19)	1.466 (6)
C(10)—C(1)—O(1)	106.5 (3)	C(1)—C(10)—C(9)	110.1 (3)
C(2)—C(1)—O(1)	108.4 (2)	C(1)—C(10)—C(5)	108.8 (2)
C(2)—C(1)—C(10)	112.4 (3)	C(9)—C(10)—C(14)	110.1 (3)
C(1)—C(2)—C(3)	122.6 (3)	C(5)—C(10)—C(14)	110.7 (3)
C(2)—C(3)—C(4)	123.2 (3)	C(1)—C(10)—C(14)	106.2 (3)
C(3)—C(4)—C(15)	119.9 (3)	C(7)—C(11)—C(13)	117.8 (3)
C(3)—C(4)—C(5)	116.3 (3)	C(7)—C(11)—C(12)	103.1 (2)
C(5)—C(4)—C(15)	123.8 (3)	C(12)—C(11)—C(13)	114.6 (3)
C(4)—C(5)—C(10)	112.1 (2)	C(11)—C(12)—O(12)	128.4 (3)
C(4)—C(5)—C(6)	113.0 (3)	C(11)—C(12)—O(6)	111.2 (3)
C(6)—C(5)—C(10)	111.2 (2)	O(6)—C(12)—O(12)	120.4 (3)
C(5)—C(6)—O(6)	107.7 (2)	O(1)—C(16)—O(16)	122.6 (3)
C(5)—C(6)—C(7)	115.1 (2)	C(17)—C(16)—O(16)	126.8 (3)
C(7)—C(6)—O(6)	104.8 (2)	C(17)—C(16)—O(1)	110.6 (3)
C(6)—C(7)—C(11)	102.1 (2)	C(16)—C(17)—C(20)	116.9 (3)
C(6)—C(7)—C(8)	110.0 (2)	C(16)—C(17)—C(18)	120.9 (4)
C(8)—C(7)—C(11)	115.5 (3)	C(18)—C(17)—C(20)	122.2 (4)
C(7)—C(8)—C(9)	108.6 (3)	C(17)—C(18)—C(19)	129.6 (4)
C(8)—C(9)—C(10)	113.9 (3)	C(1)—O(1)—C(16)	116.5 (3)
C(5)—C(10)—C(9)	110.8 (3)	C(6)—O(6)—C(12)	110.0 (2)

As far as the molecular conformation is concerned, the two molecules differ considerably. In (I), both six-membered rings adopt conformations which can be derived from a rigid chair form of cyclohex-

ane; however, both rings are significantly flattened. The Cremer & Pople (1975) total puckering amplitudes for rings *A* and *B* amount to 0.500 (3) and 0.519 (3) \AA , respectively, and may be compared with the value of 0.63 \AA quoted by these authors for an ideal cyclohexane. The flattening of the *A* ring takes place at the β -*cis*-fusion with the epoxide, and the

Table 5. Selected torsion angles ($^{\circ}$) for (I) and (II)

	Compound (I)	Compound (II)
Six-membered ring A		
C(2)—C(1)—C(10)—C(5)	-49.2 (3)	-49.8 (4)
C(10)—C(1)—C(2)—C(3)	19.9 (4)	23.6 (5)
C(1)—C(2)—C(3)—C(4)	-1.7 (4)	0.1 (5)
C(2)—C(3)—C(4)—C(5)	14.6 (4)	4.9 (5)
C(3)—C(4)—C(5)—C(6)	-171.6 (2)	-160.0 (3)
C(4)—C(5)—C(10)—C(1)	62.3 (3)	54.9 (3)
Six-membered ring B		
C(6)—C(5)—C(10)—C(9)	-51.6 (3)	-56.3 (4)
C(10)—C(5)—C(6)—C(7)	41.9 (3)	37.3 (4)
C(5)—C(6)—C(7)—C(8)	-38.8 (4)	22.9 (4)
C(6)—C(7)—C(8)—C(9)	45.1 (4)	-64.8 (3)
C(7)—C(8)—C(9)—C(10)	-56.8 (4)	45.1 (4)
C(8)—C(9)—C(10)—C(5)	60.2 (3)	14.3 (4)
γ-Lactone ring		
C(7)—C(6)—O(6)—C(12)	22.9 (3)	-18.4 (3)
O(6)—C(6)—C(7)—C(11)	-28.1 (3)	27.9 (3)
C(6)—C(7)—C(11)—C(12)	24.4 (3)	-27.6 (3)
C(7)—C(11)—C(12)—O(6)	-11.7 (4)	18.1 (3)
C(11)—C(12)—O(6)—C(6)	-7.3 (3)	-0.2 (3)

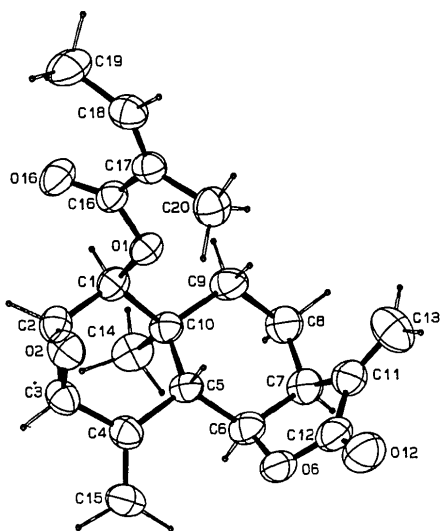


Fig. 1. A perspective view of the molecule of badkhisinin (I) with atom-numbering scheme.

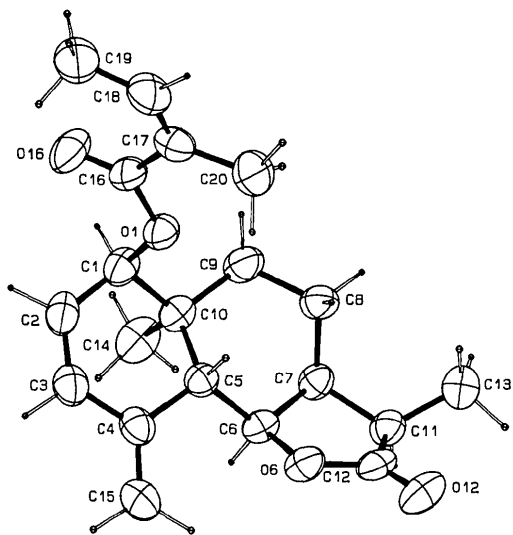


Fig. 2. A perspective view of the molecule of oopodin (II) with atom-numbering scheme.

ring approximates a $5\beta, 10\alpha$ half chair. The flattening of the *B* ring, required to accommodate the β -*cis*-fused γ -lactone, is accomplished not only by the closing of the junction torsion angle [$38.8(4)^{\circ}$], but also by the valence-angle deformation [$C(5)-C(6)-C(7)$ $116.5(2)$, $C(6)-C(7)-C(8)$ $115.3(2)^{\circ}$]. The conformation of the *B* ring can best be described as intermediate between 9β sofa and $9\beta, 10\alpha$ half chair. The γ -lactone is puckered [the Cremer & Pople (1975) puckering amplitude for this ring is $0.280(3)$ Å] and its conformation approximates a $6\alpha, 7\beta$ half chair. The lactone-chromophore torsion angle [$C(13)-C(11)-C(12)-O(12)$ $-13.8(6)^{\circ}$] is paired in sign to that at the place of fusion of the γ -lactone with the homocycle [$O(6)-C(6)-C(7)-C(11)$ $-28.1(3)^{\circ}$], a result in agreement with the general relationship between the signs of these angles for α -methylene- γ -lactones (Fischer, Olivier & Fischer, 1979).

The chair-type conformation of the *B* ring combined with the axial orientation of the $C(10)$ α -methyl and with the β -*cis*-fusion of the γ -lactone, forces $C(7)-C(11)$ to be axial and $C(6)-O(6)$ to be equatorial. As a result, the exomethylene- γ -lactone is, according to the notation proposed by Samek (1978), of the less preferred pseudo-rotational type *S* [$H(7)-C(7)$ and $C(6)-O(6)$ synclinal, the corresponding torsion angle being 92°]. The axial orientation of the $C(7)-C(11)$ bond seems generally less stable, but has been reported in natural sesquiterpene lactones callitrin, callitrisin and dihydrocallitrisin (Brecknell & Carman, 1979) and in 5-epitelekin (Appendino, Calleri, Chiari & Viterbo, 1984).

In (II), the cyclohexene *A* ring approaches a flattened sofa conformation with the $C(10)$ atom being out of the ring plane and directed towards the α face of the molecule. The presence of the conjugated diene system makes this ring somewhat more flattened than in (I) [the total puckering amplitude is $0.469(4)$ Å] and is responsible for the lengthening of the $C(4)-C(15)$ bond to a value of $1.338(4)$ Å as compared with the values of $1.319(5)$ and $1.316(5)$ Å observed, respectively, for the $C(4)-C(15)$ and $C(11)-C(13)$ exomethylene groups in (I). In the *B* ring the total puckering amplitude is $0.761(4)$ Å and the ring adopts a flexible-boat conformation. The approximate symmetry of this ring can best be described by two mutually perpendicular mirror planes and two mutually perpendicular two-fold axes, consistent with the presence of the conformation distorted half way from $5\beta, 8\beta$ boat towards $5\beta, 10\alpha$ twist boat. This conformational preference can be justified as follows. Owing to the saturation of the γ -lactone, an axial orientation of $C(7)-C(11)$ would lead to the $C(13)$ β -methyl having severe interactions with axial H atoms at $C(5)$ and $C(9)$ if the *B* ring and a chair form. These interactions

destabilize the chair form of ring *B* and favour a flexible boat form.

The change in the *B*-ring conformation is accompanied by the change of the pseudo-rotational type of the γ -lactone from *S* (see above) to *A* [H(7)—C(7) and C(6)—O(6) antiperiplanar, the corresponding torsion angle being 149°]. This is manifested by the endocyclic torsion angles whose signs are regularly opposite, excepting the angle C(6)—O(6)—C(12)—C(11) (Table 3). The saturated γ -lactone shows the same degree of ring puckering as the α -methylene- γ -lactone in (I), the puckering amplitude being 0.292 (3) Å, but the mode of puckering is different — the ring adopts an almost ideal 7 β envelope conformation. The overall conformation of (II) closely resembles the molecular conformation of isosilerolide, a related eudesmanolide (Rychlewska, 1983).

In both crystal structures the molecules are held together mostly by van der Waals forces.

Experimental

Compound (I)

Crystal data

C₂₀H₂₄O₅

M_r = 344.41

Monoclinic

*P*2₁

a = 7.842 (1) Å

b = 13.840 (2) Å

c = 8.536 (1) Å

β = 100.04 (1)°

Cell parameters from 15 reflections

θ = 11.1–16.2°

V = 912.2 (2) Å³

Z = 2

D_x = 1.253 Mg m⁻³

D_m = 1.25 Mg m⁻³

Cu *K*α

λ = 1.54178 Å

μ = 0.69 mm⁻¹

T = 292 K

Needle

0.6 × 0.25 × 0.2 mm

Colourless

Crystal source: Institute of

Botany, Baku, Azerbaijan

Data collection

Syntax *P*2₁ diffractometer

$\theta/2\theta$ scans

Absorption correction:

none

2600 measured reflections

2471 independent reflections

2377 observed reflections

[*I* ≥ 1.96σ(*I*)]

R_{int} = 0.023

θ_{\max} = 58°

h = 0 → 9

k = -16 → 16

l = -10 → 10

2 standard reflections

monitored every 98

reflections

intensity variation: ±2%

Refinement

Refinement on *F*

Final *R* = 0.039

wR = 0.053

S = 3.4

2377 reflections

236 parameters

Only H-atom *U*'s refined

w = 1/[σ²(*F*) + 0.0001*F*²]

(Δ/σ)_{max} = 0.10

Δρ_{max} = 0.24 e Å⁻³

Δρ_{min} = -0.27 e Å⁻³

Extinction correction: *F_c** =

F_c(1 - *xF_c*²/sin θ)

Extinction coefficient:

1.8(3) × 10⁻⁶

Atomic scattering factors

from *International Tables*

for *X-ray Crystallography*

(1974, Vol. IV)

Compound (II)

Crystal data

C₂₀H₂₆O₄

M_r = 330.43

Monoclinic

*P*2₁

a = 8.035 (1) Å

b = 7.208 (1) Å

c = 15.887 (3) Å

β = 90.92 (1)°

Cell parameters from 15

reflections

θ = 8.7–14.1°

V = 920.0 (2) Å³

Z = 2

D_x = 1.193 Mg m⁻³

D_m = 1.12 Mg m⁻³

Cu *K*α

λ = 1.54178 Å

μ = 0.62 mm⁻¹

T = 292 K

Needle

0.54 × 0.15 × 0.1 mm

Colourless

Crystal source: Institute of

Botany, Baku, Azerbaijan

Data collection

Syntax *P*2₁ diffractometer

$\theta/2\theta$ scans

Absorption correction:

none

2710 measured reflections

2491 independent reflections

2156 observed reflections

[*I* ≥ 1.96σ(*I*)]

R_{int} = 0.025

θ_{\max} = 58°

h = 0 → 10

k = -9 → 9

l = -18 → 18

2 standard reflections

monitored every 98

reflections

intensity variation: ±4%

Refinement

Refinement on *F*

Final *R* = 0.041

wR = 0.051

S = 3.1

2155 reflections

231 parameters

Only H-atom *U*'s refined

w = 1/[σ²(*F*) + 0.0001*F*²]

(Δ/σ)_{max} = 0.49

Δρ_{max} = 0.22 e Å⁻³

Δρ_{min} = -0.22 e Å⁻³

Extinction correction: *F_c** =

F_c(1 - *xF_c*²/sin θ)

Extinction coefficient:

0.6(4) × 10⁻⁶

Atomic scattering factors

from *International Tables*

for *X-ray Crystallography*

(1974, Vol. IV)

Density was measured by flotation in aqueous KI. The background and integrated intensity for each reflection were evaluated from a profile analysis according to Lehmann & Larsen (1974) using the program *PRARA* (Jaskólski, 1982). The positions of H atoms were calculated and allowed to ride on parent C atoms with the exception of H(21) and H(31) in (I) which were located on a Δρ map and their positions kept fixed; methyl groups were set up and refined as rigid groups. In (I), all atoms were given a common isotropic temperature factor which refined to a value *U* = 0.100(2) Å². In (II), methyl and methylene H atoms were given a common isotropic temperature factor which refined to a value *U* = 0.128(4) Å², while the common isotropic temperature factor for the remaining H atoms refined to a value *U* = 0.081(3) Å². In order to establish the absolute configuration the refinement of the structure was based, at first, on the averaged set of reflections with no *f''* corrections. The parameters obtained were used in two structure factor calculations, with and without inverted signs of *f''* corrections on a full data set, *i.e.* with Bijvoet pairs not averaged (Rogers, 1981). The *wR* values of 0.0671 and 0.0673 were obtained for the two models of (I) and those of 0.0530 and 0.0532 for the two models of (II). Although the results cannot be considered statistically significant, in both cases the enantiomorph with a slightly lower

wR value has the C(7) equatorial substituent in β position, as in all sesquiterpene lactones of authenticated stereochemistry (Fischer, Olivier & Fischer, 1979). Further refinement was carried out on a data set with Bijvoet pairs not averaged and with dispersion effects considered for O and C atoms.

Programs used for (I) and (II) were *PRARA* (Jaskólski, 1982), *SHELX76* (Sheldrick, 1976), *SHELXS86* (Sheldrick, 1986), *ORTEP* (Johnson, 1965), *PARST* (Nardelli, 1983) and *CRYSRULER* (Rizzoli, Sangermano, Calestani & Andreetti, 1986).

Lists of structure factors, anisotropic thermal parameters and H-atom coordinates, have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55085 (31 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: NA1003]

References

- Appending, G., Calleri, M., Chiari, G. & Viterbo, D. (1984). *J. Chem. Soc. Perkin Trans. 2*, pp. 903–907.
- Brecknell, D. J. & Carman, R. M. (1979). *Aust. J. Chem.* **32**, 2455–2471.
- Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
- Fischer, N. H., Olivier, E. J. & Fischer, H. D. (1979). In *Progress in the Chemistry of Organic Natural Products*, Vol. 38, edited by W. Hertz, H. Griesebach & G. W. Kirby. Vienna, New York: Springer-Verlag.
- Holub, M. & Buděšínský, M. (1986). *Phytochemistry*, **25**, 2015–2016.
- Jaskólski, M. (1982). *Collected Abstracts, Symposium on Organic Crystal Chemistry*, edited by Z. Kałuski, p. 70. A. Mickiewicz Univ., Poznań, Poland.
- Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
- Kirialov, N. P. & Serkerov, S. V. (1966). *Khim. Prir. Soedin.* pp. 93–99.
- Lehmann, M. S. & Larsen, F. K. (1974). *Acta Cryst.* **A30**, 580–584.
- Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.
- Rizzoli, C., Sangermano, V., Calestani, G. & Andreetti, G. D. (1986). *CRYSRULER*. Version 1.0. Univ. of Parma, Italy.
- Rogers, D. (1981). *Acta Cryst.* **A37**, 734–741.
- Rychlewska, U. (1983). *J. Chem. Soc. Perkin Trans. 2*, pp. 1675–1678.
- Rychlewska, U. (1986). *Structural Studies of Sesquiterpene Lactones of the Species of Compositae and Umbelliferae Families*. In *Proceedings of the Sixth Symposium on Organic Crystal Chemistry*, edited by Z. Kałuski, pp. 191–203. A. Mickiewicz Univ., Poznań, Poland.
- Samek, Z. (1978). *Collect. Czech. Chem. Commun.* **43**, 3210–3226.
- Serkerov, S. V. (1969). *Khim. Prir. Soedin.* pp. 378–381.
- Serkerov, S. V. (1971). *Khim. Prir. Soedin.* pp. 590–594.
- Serkerov, S. V. (1972). *Khim. Prir. Soedin.* pp. 63–66.
- Serkerov, S. V. (1980). *Khim. Prir. Soedin.* pp. 510–512.
- Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
- Sheldrick, G. M. (1986). *SHELXS86*. Program for the solution of crystal structures. Univ. of Göttingen, Germany.

Acta Cryst. (1992). **C48**, 1547–1549

Structure of 2-(4-Methylphenyl)-1H-indene-1,3(2H)-dione

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Abstract

The structure determination of the title compound was undertaken in order to obtain more structural information about the derivatives of 1,3-indenedione and the effects of different substituents in different positions on the conformation of these compounds. The least-squares plane through the atoms of the six-membered ring fused to the five-membered ring and the least-squares plane through the atoms of the tolyl ring form a dihedral angle of $81.31(7)^\circ$. The atoms bound to the linking atom C(1') in the five-membered ring nearly form a tetrahedron (maximum deviation from the ideal angle 8.3°). The bond distances and angles are in the normal range. The length of the C—C bond between the ring systems is $1.514(3)$ Å and the tolyl C—C_{methyl} bond length is $1.513(3)$ Å.

Comment

By the removal of one proton from the methine group, the title compound may be easily transformed into the corresponding carbanion which is of great interest as an intermediate species in some chemical reactions. This compound also shows hypolipidemic activity in mice. 2-(4-Methylphenyl)-1H-indene-1,3(2H)-dione reduced both serum cholesterol and triglycerides after some days of administration (Murthy, Wyrick & Hall, 1985).

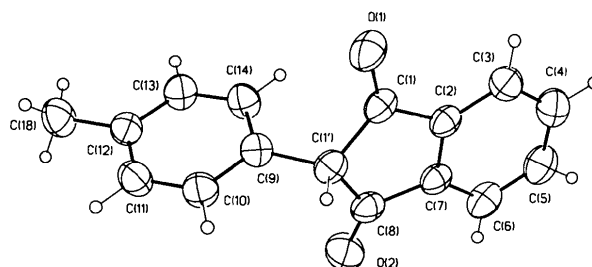


Fig. 1. General view (*SHELXTL-Plus* graphic) of the molecule, showing the atom-numbering scheme. Anisotropic ellipsoids represent 50% probability boundaries. H atoms are represented as spheres of arbitrary radii.