SESQUITERPENE LACTONES OF *Ambrosia artemisiifolia* L. AND *Ambrosia trifida* L. SPECIES*

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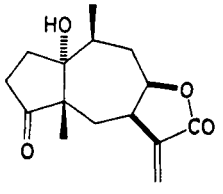
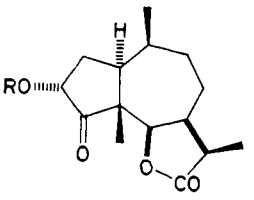
In addition to the already described peruvin (*I*), two further lactones, 3α-hydroxy-11α*H*,13-dihydrodamsin (*II*) and 3α-acetoxy-11α*H*,13-dihydrodamsin (*III*), were isolated from aerial parts of species *Ambrosia artemisiifolia* L. The full structure of these lactones was derived from their NMR and CD spectra and the X-ray structural analysis of compound *III*. In the aerial part of *Ambrosia trifida* L. species coronopilin (*V*) and ivoxanthin (*VI*) were also identified.

Within the framework of investigations on sesquiterpenic lactones in species of the *Asteraceae* (*Compositae*) family we studied inter alia species *Ambrosia artemisiifolia* L. (synon. *A. elatior* L.) and *A. trifida* L. (tribe *Heliantheae*, subtribe *Ambrosiinae*). Both species were cultivated in the botanical garden of the Department of Medicinal Plants in Poznań; the seeds of the former species were obtained from botanical garden in Budapest (Hungary), those of the latter from botanical garden in Bordeaux (France).

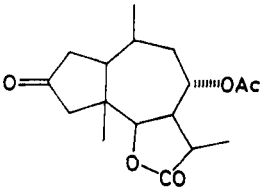
The species *A. artemisiifolia* was analyzed already earlier by several authors[1] who isolated a series of sesquiterpenic lactones of the germacranolide, pseudo-



I



II, R = H
III, R = $COCH_3$



IV

* Part CCCIV in the series On Terpenes; Part CCCIII: Collect. Czech. Chem. Commun. *55*, 1568 (1990).

guaianolide or secopseudoguaianolide type. From the aerial part of this species we isolated two sesquiterpenic lactones *II* and *III* in addition to peruvin (*I*) that had been already found[2] in this species.

We identified peruvin (*I*) by comparison of physical constants and ^{1}H NMR data. Since the published[3] ^{1}H NMR data obtained with a 60 MHz spectrometer are considerably incomplete, we publish our complete ^{1}H NMR 500 MHz data in Table I (with assignments proven by 2D-COSY spectrum); Table II contains the so far unpublished ^{13}C NMR data.

After elucidation of structure the hitherto undescribed lactone of composition $C_{15}H_{22}O_4$ was named 3α-hydroxy-11α*H*,13-dihydrodamsin (*II*). It melted at 146–148°C and its spectrum exhibited bands due to a γ-lactone ring (1 758 cm^{-1}), a five-membered ring ketone (1 735 cm^{-1}) and a hydroxyl (3 560, 3 470 cm^{-1}).

TABLE I

Proton NMR parameters of compounds *I*–*III* in $CDCl_3$

Proton	Chemical shifts in ppm (coupling constants in Hz)		
	I	*II*	*III*
H-1	—	2·30 ddd (12·2; 7·6; 3·1)	2·43 ddd (12·2; 7·6; 3·2)
H-2α	2·46 m ([a,b])	2·41 ddd (14·1; 12·2; 9·2)	2·52 ddd (12·2; 9·8; 4·4)
H-2β	1·67 ([b])	1·83 ddd (14·1; 7·6; 2·2)	1·81 ddd (14·4; 7·5; 2·6)
H-3α	2·46 m ([a,b])	—	—
H-3β	2·46 m ([a,b])	4·37 dd (9·2; 2·2)	5·20 dd (9·8; 2·6)
H-6α	2·55 dd (15·2; 5·3)	4·71 d (6·2)	4·72 d (5·9)
H-6β	1·46 dd (15·2; 13·0)	—	—
H-7	3·82 m (13·0; 8·1; 5·3; 2·8; 2·4)	2·53 m ([b])	2·54 m ([b])
H-8α	4·93 ddd (12·0; 8·1; 3·2)	1·90 ([b])	1·90 m ([b])
H-8β	—	1·56 m ([a,b])	1·56 m ([a,b])
H-9α	2·21 ddd (13·9; 4·9; 3·2)	1·56 m ([a,b])	1·56 m ([a,b])
H-9β	1·84 dt (13·9; 12·1; 12·0)	1·56 m ([a,b])	1·56 m ([a,b])
H-10	2·04 ddq (12·1; 4·9; 7·3)	2·18 m ([b])	2·16 m ([b])
H-11	—	2·87 dq (8·3; 7·5)	2·86 dq (8·2; 7·3)
H-13	6·24 d (2·8)	1·19 d (7·5)	1·19 d (7·3)
H-13′	5·64 d (2·4)	—	—
H-14	1·20 d (7·3)	1·11 d (7·7)	1·10 d (7·6)
H-15	1·08 s	1·22 s	1·23 s
OAc	—	—	2·11 s

[a] The centre of overlapping multiplets of strongly coupled spin system; [b] the correct values of coupling constants could not be determined.

Mass spectrum displayed molecular peak of m/z 266 and characteristic fragments 248 (M − 18) and 238 (M − CO). CD spectrum showed Cotton effect at 315 nm ($\Delta\varepsilon$ +1·5) and at 217 nm ($\Delta\varepsilon$ −1·7). ^{1}H NMR spectrum (Table I) proved the presence of two secondary and one tertiary methyl groups (δ 1·11 d, 1·19 d, and 1·22 s) and two CH—O protons (δ 4·71 d, J = 6·2 Hz and 4·37 dd, J = 9·3 and 2·2 Hz), one of them belonging to a lactone ring and the other to a secondary hydroxyl (as shown by in situ TAI-acylation: N—H signal at δ 8·53 and acylation shift of the CH—O proton signal 0·90 ppm). ^{13}C NMR spectrum (Table II) proved a ketone and lactone carbonyl (δ 218·70 and 178·59) and two CH—O carbon atoms (δ 80·90 and 69·62). Proton 2D-COSY spectrum enabled us to assign all the proton signals and suggest a pseudoguaianolide skeleton with substituents in positions corresponding to the structure *II*. The value of $J(6, 7)$ = 6·2 Hz showed *cis*-annelation of the five-membered lactone ring and the values of $J(7, 11)$ and $J(1, 10)$ (8·3 and 3·1 Hz, respectively) were consistent with *cis*-orientation of protons in positions 7, 11 and 1, 10. The very small TAI-acylation effect on the H-15 methyl signals (0·03 ppm) indicated *trans*-orientation of the C(3)—OH and C(5)—CH_3 groups. Since the strongly coupled system of protons on C(8) and C(9) did not allow an extraction of the corresponding coupling constants even in the 500 MHz spectrum, complete

TABLE II

Carbon-13 chemical shifts (ppm) of compounds *I*—*III* in $CDCl_3$

Carbon	*I*	*II*	*III*
C-1	83·61	41·98	42·36
C-2	31·41	31·53	30·46
C-3	36·60	69·62	71·28
C-4	216·41	218·70	214·00
C-5	54·83	54·30	54·78
C-6	32·62	80·90	80·87
C-7	38·80	46·55	46·75
C-8	80·75	18·66	18·58
C-9	35·54	36·93	36·95
C-10	40·98	34·74	34·68
C-11	141·16	39·70	39·81
C-12	170·54	178·59	178·54
C-13	122·58	15·96	15·97
C-14	22·65	10·27	10·22
C-15	18·75	15·96	16·33
OAc: C=O	—	—	170·06
CH_3	—	—	20·70

conformational analysis of the seven-membered ring and unequivocal conclusions about configuration in positions 1, 3, 5, and 10 were not possible.

Lactone *III*, composition $C_{17}H_{24}O_5$, m.p. 159–161°C, $[\alpha]_D$ +67·9°, was named (after elucidation of its structure) 3α-acetoxy-11α*H*,13-dihydrodamsin. The compound is probably identical with the sesquiterpenic lactone isolated from *A. artemisiifolia* (composition $C_{17}H_{24}O_5$ melting at 158°C, $[\alpha]_D$ ±0°) for which, however, the authors[4] had already suggested structural formula *IV* and a name corresponding to it. According to IR spectrum, our compound contained a γ-lactone grouping (1 765 cm^{-1}), a ketone group in a five-membered ring and an acetate group (1 737 cm^{-1}). Its mass spectrum displayed a molecular peak, *m/z* 308, and characteristic fragments 266 (M − 42), 260 (M − 48), 248 (M − 60), and 43 (CH_3CO^+). CD spectrum of lactone *III* had a Cotton effect at 307 nm (Δε +2·4) and 217 nm (Δε −1·2). The ^1H and ^{13}C NMR spectra of lactone *III* were similar to those of lactone *II*, indicating a close structural similarity of both lactones. According to a detailed analysis of the NMR data we have proved that the lactone *III* is an acetate of *II* (^1H NMR: δ 2·11 s (OAc); 5·20 dd (CH—OAc, J = 9·8 and 2·6 Hz); changes in chemical shifts of other protons are negligible).

To determine unequivocally the structure of both compounds, particularly the configuration in positions 1, 3, 5, and 10, the lactone *III* was studied by X-ray diffraction analysis. Final positional parameters and selected torsion angles of non-H atoms are given in Table III; bond distances and bond angles are given in Fig. 1. The stereostructure of the molecule is shown in Fig. 2 and can be described as follows. The C(5)–methyl group is β-oriented and *trans* with respect to the α-hydrogen atom at C(1), indicating *trans*-junction of the cyclopentanone and cycloheptane rings. The C(7) α-hydrogen atom is *cis* to the C(6) α-hydrogen indicating a *cis*-fusion of the γ-lactone ring. Thus the three-ring system of the pseudoguaianolide skeleton is of the *trans–anti–cis* configuration. The methyl group at C(10) is β-oriented and *trans* to the C(1) α-hydrogen, a feature characteristic of the ambrosanolide subgroup of pseudoguaianolides. The C(11) methyl is β-oriented and the acetoxy group at C(3) is α. The cycloheptane ring adopts a twist-chair conformation with approximate twofold axis passing through C(6) and the midpoint of the C(10)—C(9) bond (TC_6 form). This approximate C_2 symmetry was also observed in one of two crystallographically independent molecules of hymenolin, a related ambrosanolide[5], but does not seem characteristic for ambrosanolides for which several other conformations of the seven-membered ring have been reported[5–7]. However, the TC_6 conformation is the most commonly adopted conformation in C(8) *trans*-lactonized pseudoguaianolides and is observed in amblydiol[8], nor-derivative of (±)-carpesiolin[9], diacethylspathulin[10], mexicanin *I* and linifolin A (ref.[11]), and in britannin[12]. In graveolide[13] and geigerinin[14] forms intermediate between TC_6 and C_9 have been observed.

Both five-membered rings are decidedly non-planar and display the same degree

of ring puckering, as evidenced by the average torsion angle moduli 26·0(12·7) and 26·0(14·1)° for cycloheptanone and α-methyl-γ-lactone, respectively. The average of the moduli in *cis*-fused lactones is usually much smaller, e.g. in the range of 14·9 to 18·3° in slovanolides[15–18]. Also the type of puckering of both five-membered rings is the same. They adopt an envelope form with a flap at C(1) in cyclopentanone, and at C(7) in α-methyl-γ-lactone. The molecules are held in the crystal by van der Waals forces.

The absolute configuration of lactones *II* and *III* was derived from their CD spectra, particularly on the basis of the sector rule for γ-lactones[19] according to which the negative elipticity about 217 nm indicates an *R*-configuration at C(11). The thus-determined absolute configuration agrees with the positive Cotton effect at about 310 nm (lactone *II*: 319 nm, Δε +1·4; lactone *III*: 307 nm, Δε +2·4), characteristic of the 7*R*-configuration of pseudoguaianolides with cyclopentanone moiety.

TABLE III

Positional parameters (.10^4), equivalent isotropic thermal parameters (Å^2 . 10^3) with e.s.d.'s in parentheses and selected endocyclic torsion angles (°) for non-H atoms

Atom	*x/A*	*y/B*	*z/C*	U_{eq}	Endocyclic torsion angles	
C1	−757(4)	2095(2)	2786(1)	48(1)	5-membered ring	
C2	−573(5)	1888(2)	3561(1)	61(1)	C5—C1—C2—C3	−38·4(3)
C3	−1290(5)	2873(3)	3905(1)	63(1)	C2—C1—C5—C4	39·1(2)
C4	−2579(5)	3424(3)	3359(2)	61(1)	C1—C2—C3—C4	20·4(3)
C5	−2797(5)	2738(2)	2716(1)	51(1)	C2—C3—C4—C5	4·8(3)
C6	−2895(5)	3431(2)	2078(1)	51(1)	C3—C4—C5—C1	−27·3(3)
C7	−1631(5)	3170(2)	1439(1)	51(1)		
C8	−1643(5)	2024(2)	1231(2)	56(1)	7-membered ring	
C9	50(5)	1389(2)	1588(2)	62(1)	C10—C1—C5—C6	−75·7(3)
C10	−343(5)	1131(2)	2347(2)	56(1)	C5—C1—C10—C9	69·8(3)
C11	−2796(5)	3856(3)	922(2)	59(1)	C1—C5—C6—C7	25·1(3)
C12	−5006(5)	3735(3)	1152(2)	64(1)	C5—C6—C7—C8	42·8(3)
C13	−2439(7)	3701(3)	157(2)	78(1)	C6—C7—C8—C9	−86·7(3)
C14	−1922(6)	249(2)	2419(2)	72(1)	C7—C8—C9—C10	74·7(4)
C15	−4838(5)	2130(3)	2835(2)	69(1)	C8—C9—C10—C1	−54·8(4)
C16	1035(6)	3722(2)	4684(2)	62(1)		
C17	2957(6)	4354(3)	4723(2)	72(1)	γ-lactone ring	
O3	490(4)	3547(2)	4035(1)	70(1)	O6—C6—C7—C11	39·3(3)
O4	−3299(4)	4290(2)	3421(1)	82(1)	C7—C6—O6—C12	−25·7(3)
O6	−5044(3)	3493(2)	1824(1)	66(1)	C6—C7—C11—C12	−38·8(3)
O12	−6611(4)	3814(2)	830(2)	95(1)	C7—C11—C12—O6	25·9(4)
O16	81(5)	3382(3)	5165(1)	98(1)	C11—C12—O6—C6	−0·4(4)

For peruvin (*I*), application of the Geissman rule[20] (CD maximum at 255 nm, $\Delta\varepsilon$ −0·8) and the known relative configuration led to the *S*-configuration at C(7).

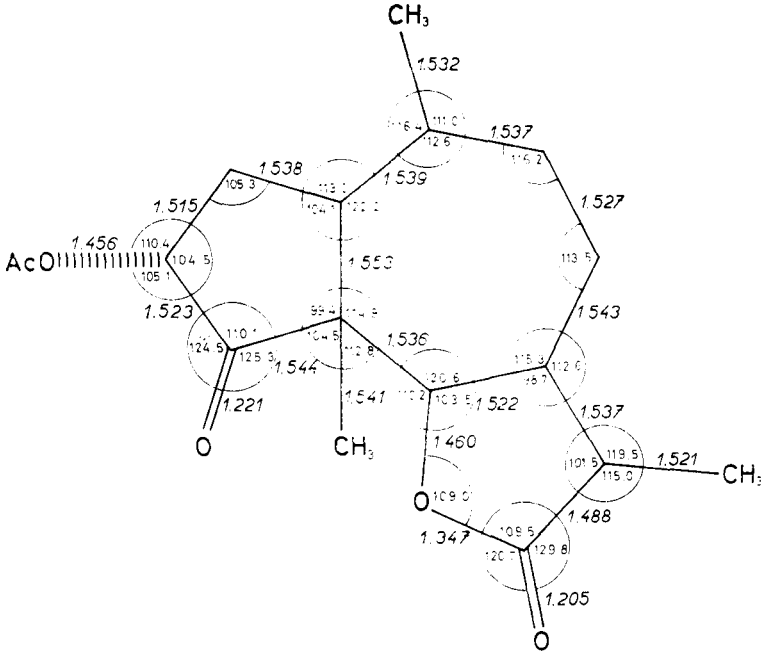


FIG. 1

Bond lengths and bond angles of non-H atoms found in 3α-acetoxy-11α*H*,13-dihydrodamsin (*III*) in crystal. The e.s.d.'s are in the range 0·002 to 0·005 Å and 0·2 to 0·3°

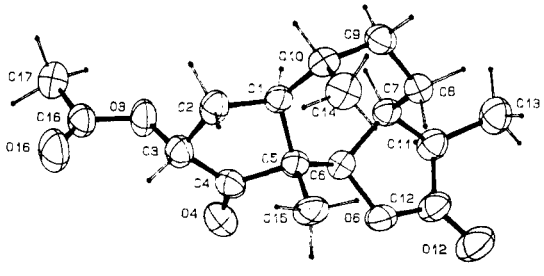
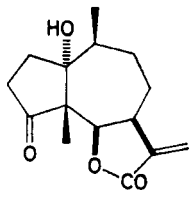


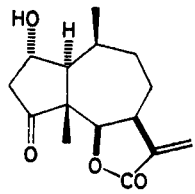
FIG. 2

Stereostructure of molecule of 3α-acetoxy-11α*H*,13-dihydrodamsin (*III*) (view of the β-face). Thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms are represented by spheres of arbitrary size

From *Ambrosia trifida* we isolated sesquiterpenic lactones coronopilin[21-25] (*V*) and ivoxanthin[24,25] (*VI*) whose structure (save absolute configuration) had been clarified already earlier. Whereas coronopilin (*V*) was found in some species of the *Ambrosia* genus as well as in some other genera of the *Ambrosiinae* subtribe[1], ivoxanthin (*VI*) has been found so far only in the species *Cyclachaena xanthifolia* FRESEN. (synon. *Iva xanthifolia* NUTT.) that also belongs to the *Ambrosiinae* subtribe[24].



V



VI

The absolute configuration of both lactones *V* and *VI* follows from their CD spectra and their known relative configuration. We derived the *R*-configuration at C(7) both from the Geissman rule[20] (positive elipticity at about 260 nm indicates the *R*-configuration at C(7); coronopilin: sh 273 nm, $\Delta\varepsilon$ +0·5, ivoxanthin: sh 263 nm, $\Delta\varepsilon$ +0·4) and from the positive Cotton effect at about 300 nm, again corresponding to the *R*-configuration at C(7), as mentioned for lactones *II* and *III*. Thus, the formulae *I*–*III*, *V*, and *VI* represent also the absolute configuration for peruvin, 3α-hydroxy-11α*H*,13-dihydrodamsin, 3α-acetoxy-11α*H*,13-dihydrodamsin, coronopilin, and ivoxanthin.

All the obtained sesquiterpenic lactones from the *Ambrosia trifida* and *A. artemisiifolia* belong to pseudoguaianolides which are typical constituents of the genus *Ambrosia* as well as subtribe *Ambrosiinae*. From the viewpoint of chemosystematics, the pseudoguaianolides isolated by us represent further contribution to the present knowledge about the discussed genus and subtribe.

EXPERIMENTAL

Melting points were determined on a Kofler block and are uncorrected. IR spectra were recorded on a Perkin–Elmer PE 580 spectrometer in chloroform solution (unless stated otherwise); wavenumbers are given in cm^{-1}. Mass spectra were measured on a ZAB-EQ V.G. Analytical spectrometer (Manchester, U.K.); electron impact, 70 eV. CD spectra (in methanol) were measured on an autodichrograph Jobin–Yvonne Mark V. Proton and carbon-13 NMR spectra were measured on FT NMR spectrometer Varian UNITY-500 (^1H at 500 MHz and ^{13}C at 125·7 MHz frequency) in deuteriochloroform solution with tetramethylsilane as internal reference. Proton 2D-COSY spectra were used for the structure assignment of proton signals in compounds *I*–*III*.

Carbon-13 chemical shifts were obtained from a broadband proton-decoupled spectra. Spin-echo J-modulated spectra ("attached proton test" pulse sequence) were used for the classification of carbon signals according to the number of directly bonded protons. Further arguments on the structural assignment of carbon signals were derived from the chemical shifts and from comparison with literature data on similar compounds.

Isolation of 3α-Acetoxy-11α*H*,13-dihydrodamsin (*III*), Peruvin (*I*), and 3α-Hydroxy-11α*H*,13-dihydrodamsin (*II*)

The aerial parts of species *Ambrosia artemisiifolia* L. (5·5 kg), cultivated in Poznań from seeds obtained from botanical garden, Budapest (Hungary), were collected in September 1979 (voucher No. 657/79 is deposited in Herbarium of the Department of Medicinal Plants, Academy of Medicine, Poznań, Poland). This plant material was dried and ground (770 g) and processed as described earlier[26]. The chloroform extract (6·5 g) was chromatographed on a column of silica gel (300 g). Elution with chloroform afforded 3α-acetoxy-11α*H*,13-dihydrodamsin (*III*; 130 mg), m.p. 159–161°C, $[\alpha]_D$ +67·9° (*c* 0·1). IR spectrum: 1 763 (γ-lactone); 1 741 (five-membered ring ketone and acetate); 1 241 (acetate). Mass spectrum, *m/z*: 308 (M), 291, 278, 266 (M − 42), 260 (M − 48), 121, 55, 43 (CH_3CO^+). CD spectrum (nm, Δε): 307, +2·4; 217, −1·2. For $C_{17}H_{24}O_5$ (308·4) calculated: 66·21% C, 7·84 %H; found: 66·42% C, 7·97% H. Elution with chloroform–acetone (4 : 1) afforded peruvin (*I*; 230 mg), m.p. 174–176°C, $[\alpha]_D$ +155° (*c* 0·15). Its identity was proved by comparison of IR, MS, and ^{1}H NMR spectra with analogous spectra of peruvin[3]. Elution with chloroform–acetone (7 : 3) afforded 3α-hydroxy-11α*H*,13-dihydrodamsin (*III*; 40 mg), m.p. 146–148°C. IR spectrum: 3 560, 3 470 (hydroxyl); 1 758 (γ-lactone); 1 735 (five-membered ring ketone). Mass spectrum, *m/z*: 266 (M), 248 (M − 18), 238, 208, 193, 179, 165, 121, 95. CD spectrum (nm, Δε): 315, +1·5; 217, −1·7. For $C_{15}H_{22}O_4$ (266·3) calculated: 67·64% C, 8·33% H, 0·38% H act.; found: 67·86% C, 8·17% H, 0·43% H act.

Isolation of Coronopilin (*V*) and Ivoxanthin (*VI*) from *Ambrosia trifida* L.

Aerial parts of *Ambrosia trifida* L. species (2 kg), cultivated in Poznań from seeds from botanica garden in Bodeaux (France), were collected in August 1979 (voucher No. 325/78 is deposited in Herbarium of Department of Medicinal Plants, Academy of Medicine, Poznań, Poland). This material was dried and ground (420 g) and processed as described earlier[26]. The chloroform extract (2·4 g) was chromatographed on a column of silica gel (200 g). Elution with benzene–acetone (9 : 1) gave coronopilin (*V*; 150 mg), m.p. 175–176°C (chloroform, diethyl ether), whose identity with a standard[6,7] was proved by comparison of its IR, MS, and ^{1}H NMR spectra and mixed melting point. CD spectrum (nm, Δε): 294, +1·5; sh 263, +0·5; 210, −6·2. Elution with benzene–acetone (4:1) afforded ivoxanthin (*VI*; 200 mg), m.p. 167–168°C (diethyl-ether), which was proved to be identical with an authentic sample[6,7] in the same manner as described for coronopilin. CD spectrum (nm, Δε): 304, +2·3; sh 263, +0·4; 210, −4·8.

Crystal Structure Determination of *III*

Orthorhombic, space group $P2_12_12_1$, $a = 6{\cdot}381(1)$, $b = 12{\cdot}992(2)$, $c = 19{\cdot}481(4)$ Å, $V = 1\,615{\cdot}0(3)$ Å^3, $D_m = 1{\cdot}26$ (by flotation in aquous solution of KI), $D_x = 1{\cdot}27$ g cm^{-3}, $Z = 4$, $\lambda(CuK_\alpha) = 1{\cdot}5418$ Å, $\mu = 0{\cdot}72$ mm^{-1}.

A crystal of approximate dimensions 0·5 × 0·2 × 0·2 mm was used for data collection on a Syntex $P2_1$ diffractometer using monochromated CuK_α radiation. Lattice constants and an

orientation matrix were obtained from a least-squares fit of 15 centered reflections. Intensities were measured using $\theta - 2\theta$ scan technique, with the scan rate depending directly on the net count obtained on rapid pre-scans for each reflection. Two standard reflections were monitored after collection of every 98 reflections as a check of electronic reliability and crystal stability, and the intensity fluctuations of these reflections were not greater than 2·6%. One forth of the reciprocal sphere was collected such that h and k were non-negative. An amount of 2 154 unique reflections (Bijvoet pairs not averaged) measured of which 1 934 were considered observed [$I < 2\sigma(I)$]. The background and integrated intensity for each reflection were evaluated from a profile analysis according to Lehmann and Larsen[27] using the PRAN (ref.[28]) program. Lorentz and polarization factors were applied in reducing the intensities to structure factor amplitudes, but no absorption correction was deemed necessary [$\mu(\mathrm{CuK}_\alpha) = 0{\cdot}72\ \mathrm{mm}^{-1}$]. All data having $I \geqq 2\sigma(I)$ were used in least squares refinement, with the exception of one (035) reflection found to be poorly determined. Anomalous dispersion corrections were applied to the scattering factors of the oxygen and carbon atoms.

The structure was solved by direct methods using SHELX86 (ref.[29]) and refined using F magnitudes by full-matrix least squares of SHELX76 (ref.[30]). Non-hydrogen atoms were refined anisotropically. The H-atoms were placed at calculated positions and were subjected to constrained refinement. All H-atoms were assigned a common isotropic thermal parameter $U = 0{\cdot}07\ \mathrm{Å}^2$. Methyl groups were set up and refined as a rigid group. In the final stages of the refinement an empirical isotropic extinction parameter x was introduced to correct the calculated structure factors by multiplying them by a factor $1 - xF_c^2/\sin\theta$ and it refined to a value $1{\cdot}6(2) \cdot 10^{-6}$. The solution and refinement of the structure was based, at first, on the set of reflections in which Bijvoet pairs were averaged, with no corrections for anomalous dispersion effects. The parameters obtained were used in two structure factor calculations, without and with inverted signs of "F" corrections[31]. The wR values obtained for the two models differed by only 0·0001 so the absolute configuration could not be determined by means of the anomalous dispersion method. Therefore, the usual assumption was made that the absolute configuration of the investigated compounds corresponds to that of other sesquiterpene lactones from higher plants[32]. After enantiomorph definition the refinement was carried out on the full data set (Bijvoet pairs not averaged) with oxygen and carbon atoms allowed for dispersion. The function minimized was $\sum(|F_o| - |F_c|)^2$ with $w = 1/[\sigma^2(F_o) + 0{\cdot}0003F_o^2]$, where $\sigma(F_o)$ is the standard deviation of the observed amplitudes, based on counting statistics. Convergence attained at $R = 0{\cdot}045$ ($wR = 0{\cdot}060$) for 1 933 observed reflections. The final difference map showed minima and maxima ranging from $-0{\cdot}24$ to $0{\cdot}25\ \mathrm{eÅ}^{-3}$. ORTEP (ref.[33]) was used for drawing and PARST (ref.[34]) for geometry calculations, as implemented in CRYSRULER package[35],

Elemental analyses were performed in the Analytical Department of this Institute (Dr V. Pechanec, Head) by Mrs E. Listíková and Mr V. Štěrba. Optical rotations were measured by Mrs Z. Ledvinová. Mass spectra were measured and interpreted by Dr J. Kohoutová. The IR and CD spectra were measured and interpreted by Dr S. Vašíčková. We express our thanks to all of them.

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