SESQUITERPENIC LACTONES OF THE *Inula caspica* BLUME SPECIES*

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From *Inula caspica* BLUME (*Compositae*) were isolated 3β-hydroxy-2α-senecioyloxyisoalanto-lactone (*I*), whose structure was confirmed by X-ray diffraction and completed by determination of its absolute configuration, and britannin (*II*) whose relative configuration was determined by X-ray diffraction and absolute configuration by CD spectroscopy.

Although the genus *Inula* (tribe *Inuleae*, family *Compositae*) involves about 100 species, only fifteen of them have been so far analyzed for sesquiterpenic lactones[1]. In Kazakhstan there are twelve *Inula* species[2], among them also *I. caspica* BLUME which we have chosen for the study of sesquiterpenic lactones.

Chloroform extract from the aerial parts of the studied species afforded 3β-hydroxy-2α-senecioyloxyisoalantolactone (*I*), m.p. 222–223°C. Its physical constants as well as the IR, MS and particularly ^{1}H NMR spectra were practically identical with those of the substance isolated[3] from *Inula britannica* L. species. The ^{1}H and ^{13}C NMR data of compound *I* are summarized in Table I. We have also established the absolute configuration of *I*: the γ-lactone group with conjugated exomethylene double bond gives rise to a negative Cotton effect in the CD spectrum (255 nm, Δε −1·9). For a *cis*-fused C(8)-lactone these values can be interpreted according to the rules of Geissman and coworkers[4] and lead to the *R*-configuration at C(7) in the lactone *I*. In combination with the known relative configuration[3], the absolute configuration of the isolated 3β-hydroxy-2α-senecioyloxyisoalantolactone can be represented by formula *I*.

The structure of the lactone *I* was also verified by X-ray diffraction. Table II shows the found coordinates of nonhydrogen atoms and Table III contains selected

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torsion angles, characterizing the spatial arrangement of *I* in crystal (Fig. 1). The bond lengths and angles are presented in Fig. 2. As shown by the X-ray results, both the six-membered rings in the compound *I* in crystal exist in chair conformation.
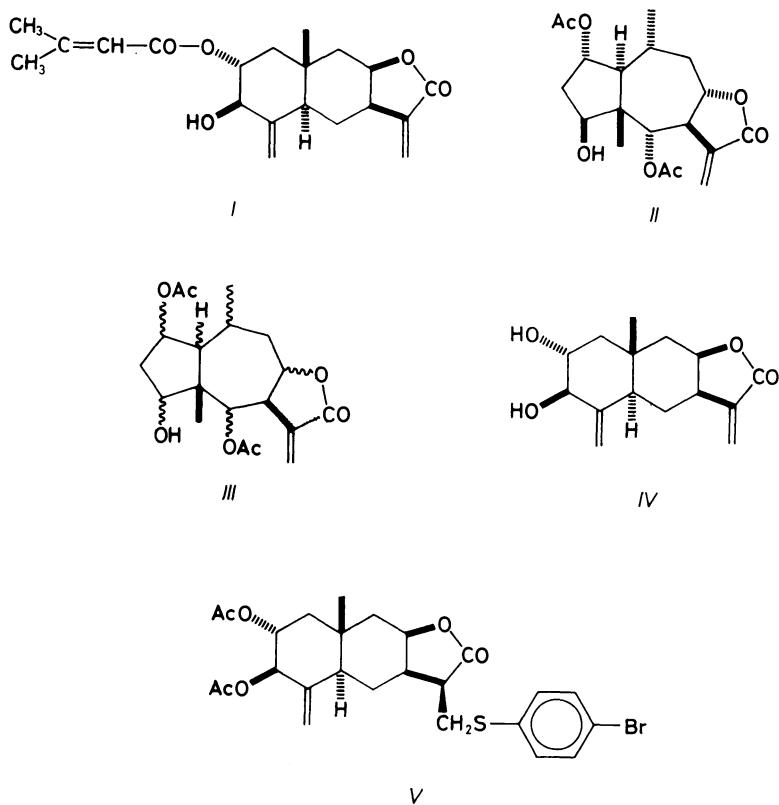
The ring B is markedly flattened at the site of fusion with the γ-lactone ring and exists as a deformed chair lying between the sofa $(\Delta C_s^5 = 2{\cdot}5°)$ and the half-chair $(\Delta C_2^{5,10} = 7{\cdot}1°)$ conformations. Conformation of the five-membered γ-lactone ring is between the half-chair and envelope forms, closer to the former one $(\Delta C_2^{12} = 4{\cdot}5°$ and $\Delta C_s^8 = 9{\cdot}3°)$. In this conformation, the methyl group on the carbon C(10) is axial whereas both the oxygen-containing substituents in positions 2 and 3 are equatorial.

Both the chloroform and aqueous extracts of the plant material afforded britannin (*II*), m.p. 188 – 190°C, $[\alpha]_D$ – 26° which was identified by comparison of the physical constants and IR, ^{1}H NMR and mass spectra with those of britannin obtained[5] from *Inula britannica* L. The ^{1}H and ^{13}C NMR data of britannin are given in Table IV.

The previously published[6] structure *III* has now been completed by the relative configuration obtained by our X-ray diffraction study. Coordinates of nonhydrogen atoms are given in Table V, selected torsion angles in Table VI, and the spatial arrangement of the molecule is depicted in Fig. 3. The bond lengths and bond angles are given in Fig. 4.

In crystal, the seven-membered ring in the molecule of *II* resembles a twist-chair conformation with a two-fold axis through C(6) (TC$_6$), whereas the conformation of the five-membered lactone ring $\left(\Delta C_2^{12} = 1 \cdot 1°\right)$ and the five-membered homocycle lies between a half-chair and an envelope form, closer to the former one $\left(\Delta C_2^2 = 6 \cdot 2°\right.$ and $\left.\Delta C_s^4 = 11 \cdot 1°\right)$.

The absolute configuration of britannin follows from its CD spectrum (Cotton effect at 265 nm, $\Delta \varepsilon + 0 \cdot 1$). Application of the Geissman's rule[4] leads to the *S*-configuration at C(7) and, in combination with the elucidated relative configuration, the given formula *II* for britannin represents its absolute configuration.
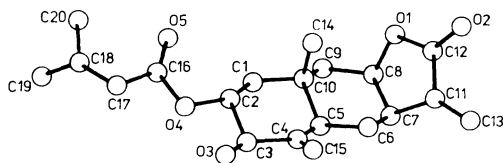

FIG. 1

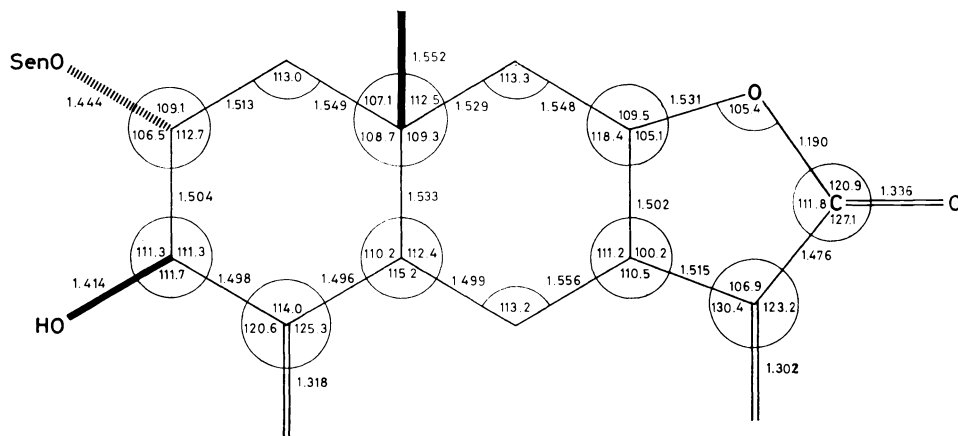Spatial arrangement of the molecule of 3β-hydroxy-2α-senecioyloxyisoalantolactone (*I*) in crystal

FIG. 2

Bond lengths and bond angles in 3β-hydroxy-2α-senecioyloxyisoalantolactone (*I*) in crystal

Since both lactones *I* and *II*, obtained from the *I. caspica* species, had also been isolated from *I. britannica*[3,5], we tried to isolate them also from *I. britannica* of the Polish origin. However, instead of these lactones, we obtained only pulchellin C (*IV*), in accord with the Soviet authors[7]. Its ¹H and ¹³C NMR data are listed in Table VII. The structure of pulchellin C (*IV*) − save its absolute configuration −
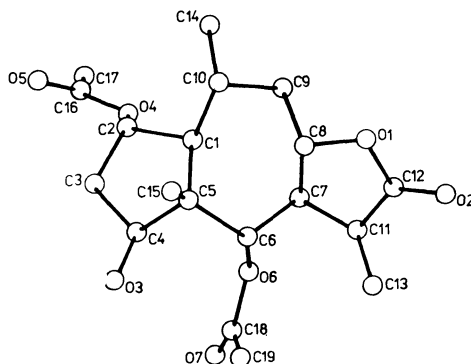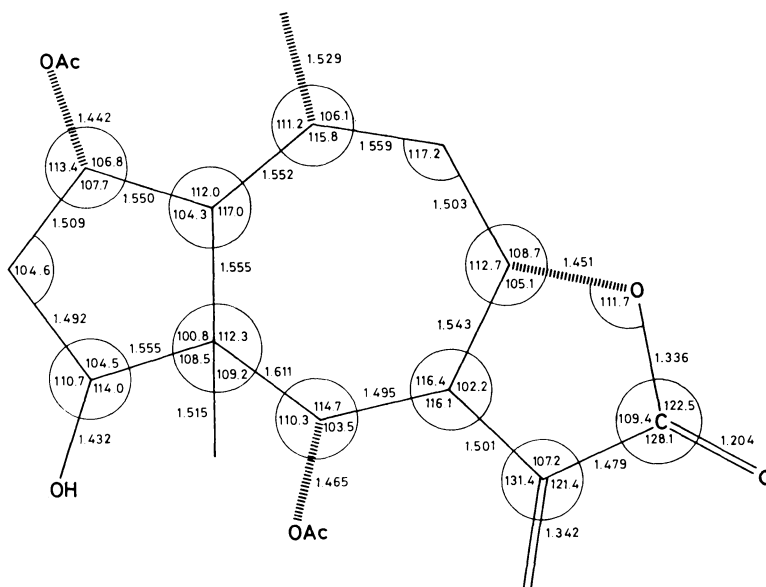

FIG. 3

Spatial arrangement of molecule of britannin (*II*) in crystal

FIG. 4

Bond lengths and bond angles in britannin (*II*) in crystal

has been elucidated already earlier[8,9] and confirmed[10] by X-ray diffraction analysis of 13β-p-bromophenylthio-11α,13-dihydropulchellin C diacetate (*V*). We derived now the absolute configuration of pulchellin C (*IV*) from the CD spectra of the native compound *IV* and its complex with tris(dipivaloylmethanato)praseodyme. The negative helicity found in the CD spectrum of this complex (318 nm, $\Delta\varepsilon$ −2·1) indicates the *R*-configuration at the C(2) and C(3) carbon atoms and the negative Cotton effect at 246 nm ($\Delta\varepsilon$ −1·4) observed for the native compound, together with the known relative configuration[9], shows the *R*-configuration at C(7). Thus, from the derived absolute configuration at C(2) and C(3) on the one hand and at C(7) on the other, the absolute configuration of pulchellin C can be represented by formula *IV*.

From the viewpoint of chemosystematics of the tribes of the *Asteraceae* (*Compositae*) family, both the studied compounds *I* and *II* belong to skeletal types of sesquiterpenic lactones (pseudoguaianolide, eudesmanolide) common in the *Inuleae* tribe. As far as the *Inula* genus is concerned, eudesmanolides (compound *I*) are common constituents of this genus whereas pseudoguaianolides (compound *II*) have been only rarely isolated from species of this taxon (see e.g. ref.[1]).

EXPERIMENTAL

Melting points were determined on a Kofler block and are uncorrected. Infrared spectra were recorded on a Perkin–Elmer PE 580 spectrophotometer. Mass spectra were measured on a ZAB-EQ V.G. Analytical (Manchester, U.K.); electron impact, 70 eV. Optical rotations were determined on a Perkin–Elmer 141 polarimeter, CD spectra (in methanol) on a Jobin–Yvonne Mark V autodichrographe. ^{1}H and ^{13}C NMR spectra were obtained with an FT-NMR Varian XL-200 spectrometer (at 200 and 50·3 MHz, respectively) in $CDCl_3$. Chemical shifts (internal standard tetramethylsilane) and proton coupling constants were obtained by the first order analysis from expanded spectra (2 Hz/cm) using exponential multiplication with Gaussian apodization function for resolution enhancement. ^{13}C NMR spectra were referenced to the solvent signal and the chemical shifts were related to tetramethylsilane using the relationship $\delta(CDCl_3) = 77·0$ ppm. The multiplicity of the signals, corresponding to the number of directly attached protons, was determined by the "attached proton test" pulse sequence[11]. The ^{13}C signals were assigned using multiplicity, chemical shifts and published data for structurally similar compounds.

Isolation of 3β-Hydroxy-2α-senecioyloxyisoalantolactone (*I*)

Aerial parts of *Inula caspica* BLUME (family *Asteraceae*, tribe *Inulae*) (2·4 kg) were collected at the stage of flowering in the Abrali mountains, Semipalatinsk region, Kazakh S.S.R., in 1981. The voucher is deposited in the Institute of Organic Synthesis and Coal Chemistry, Kazakh Academy of Sciences, U.S.S.R. The material was extracted with chloroform, the solvent evaporated and the residue (176 g) washed with an ethanol–water (2 : 1) mixture. After washing with chloroform, the aqueous–ethanolic portions were concentrated to give a residue (32·2 g) which was subjected to chromatography on a column of silica gel (480 g). Elution with ether and repeated crystallization from ethanol afforded 73 mg of 3β-hydroxy-2α-senecioyloxyisoalanto-

lactone (*I*), m.p. 222—223°C (ethanol). IR spectrum (cm^{-1}): 3 610, 3 510 (hydroxyl); 1 760 (γ-lactone); 1 712, 1 700 sh (conjugated ester); 1 668 (double bond); 1 647 (conjugated double bond). Mass spectrum, *m/z*: 346 (M), 328 (M — 18), 246 (M — 100), 228 (M — 100 — 18), 83 ($C_4H_7CO^+$), 55 ($C_4H_7^+$). CD spectrum (nm, Δε): 204, +23·4, 255, —1·9. For $C_{20}H_{26}O_5$ (346·4) calculated: 69·36% C, 7·51% H, 0·29% H act.; found: 69·41% C, 7·53% H, 0·37% H act.

Isolation of Britannin (*II*)

The aerial parts of *I. caspica* (1·2 kg) were extracted for 1 h with hot water (four times). The aqueous extract was shaken with chloroform. Evaporation of the chloroform gave 135 g of material which was dissolved in ethanol. Addition of diethyl ether precipitated crystals which after repeated crystallization afforded britannin (*II*), m.p. 188—190°C (ethanol–diethyl ether), [α]$_D$ —26° (*c* 0·1, methanol). IR spectrum (cm^{-1}): 3 625, 3 615, 3 530 (hydroxyl); 1 772, 1 110 (γ-lactone); 1 737, 1 725 (acetate). Mass spectrum, *m/z*: 367 (M + 1), 347 (M — 18 — 1), 306 (M — 60), 289 (M — 60 — 18 + 1), 246 (M — 60 — 60), 228 (M — 60 — 60 — 18), 43 (CH_3CO^+). CD spectrum (nm, Δε): 221, +1·22; 241, —0·12; 265, +0·14. For $C_{19}H_{26}O_7$ (366·4) calculated: 62·88% C, 7·15% H, 0·28% H act.; found: 62·44% C, 7·23% H, 0·36% H act.

TABLE I

^{1}H and ^{13}C NMR data of 3β-hydroxy-2α-senecioyloxyisoalantolactone (*I*) in CDCl$_3$

Proton	δ	(*J* in Hz)	Carbon	δ
H-1α	1·35 dd	(*J*(1α, 1β) = 12·7; *J*(1α, 2) = 11·6)	C-1	45·08
H-1β	1·97 dd	(*J*(1β, 1α) = 12·7; *J*(1β, 2) = 4·9)	C-2	76·22^a
H-2	4·77 ddd	(*J*(2, 1β) = 4·9; *J*(2, 1α) = 11·6; *J*(2, 3) = 9·6)	C-3	74·26
H-3	4·02 bd	(*J*(3, 2) = 9·6; *J*(3, 15) ≈ *J*(3, 15′) > 0)	C-4	146·80
H-5	1·88 bd	(*J*(5, 6α) = 2·7; *J*(5, 6β) = 12·4; *J*(5, 15) > 0)	C-5	44·28
H-6α	1·83 ddd	(*J*(6α, 5) = 2·7; *J*(6α, 6β) = 13·9; *J*(6α, 7) = 7·0)	C-6	27·22
H-6β	1·46 ddd	(*J*(6β, 5) = 12·4; *J*(6β, 6α) = 13·9; *J*(6β, 7) = 11·9)	C-7	40·13
H-7	2·99 m	(*J*(7, 6α) = 7·0; *J*(7, 6β) = 11·9; *J*(7, 8) = 5·2;	C-8	76·18^a
		J(7, 13) = 1·2; *J*(7, 13′) = 1·1)	C-9	40·52
H-8	4·50 dt	(*J*(8, 7) = 5·2; *J*(8, 9α) = 4·7; *J*(8, 9β) = 1·7)	C-10	33·81
H-9α	1·50 ddq	(*J*(9α, 8) = 4·7; *J*(9α, 9β) = 15·5; *J*(9α, 14) = 0·7)	C-11	141·62
H-9β	2·29 dd	(*J*(9β, 8) = 1·7; *J*(9α, 9β) = 15·5)	C-12	170·17
H-13	6·16 d	(*J*(13, 7) = 1·2)	C-13	120·65
H-13′	5·63 d	(*J*(13′, 7) = 1·1)	C-14	18·44
H-14	0·92 b	(*J*(14, 9α) = 0·7)	C-15	107·38
H-15	5·40 b		Sen^b	166·94
H-15′	4·79 b			158·39
Sen^b	5·71 h	(*J* = 1·3 (3×); *J* = 1·4 (3×))		115·39
	1·92 d	(*J* = 1·3)		27·51
	2·17 d	(*J* = 1·4)		20·33

^{a} The assignment of signals may be interchanged; ^{b} Sen: 3-methyl-2-butenoyl.

Isolation of Pulchellin C (*IV*) from *Inula britannica*

Ground aerial parts of *Inula britannica* L. species (family *Asteraceae*, tribe *Inuleae*), collected in summer 1981 in the Poznań region (Poland (2 kg)) were extracted with methanol. After concentration, the residue was mixed with water and a solution of lead(II) acetate was added to this solution. The formed precipitate was filtered and the aqueous phase was extracted several times with chloroform. The combined chloroform extracts were worked up in the usual manner[12], affording the so-called lactone portion (3·2 g). This was chromatographed on a column of silica gel (300 g) in chloroform with increasing content of acetone. Elution with chloroform–acetone (9 : 1) furnished pulchellin C (*IV*), m.p. 137—139°C (ethanol). IR spectrum (cm^{-1}): 3 615, 3 580 (hydroxyl); 1 759 (γ-lactone); 1 667, 1 652 (double bond). Mass spectrum, m/z: 264 (M), 246 (M — 18), 228 (M — 18 — 18). CD spectrum (nm, $\Delta\varepsilon$): 246, —1·44; 206, +19·87. CD spectrum of complex of *III* with Pr(dpm)$_3$: 318 nm, $\Delta\varepsilon$ —2·1. These data (except the m.p.) correspond to the published[8,9] values for pulchellin C.

X-Ray Structure Determination of 3β-Hydroxy-2α-senecioyloxyisoalantolactone (*I*)

Crystal data: $C_{20}H_{26}O_5$, rhombic $P2_12_12_1$, $a = 6·622(5)$ Å, $b = 8·977(4)$ Å, $c = 31·465(9)$ Å, $V = 1\ 870$ Å^3, $D_c = 1·24$ g cm^{-3} for $Z = 4$.

Crystallographic measurement: A crystal of approximate dimensions 0·45 × 0·50 × 0·80 mm was used for data collection on a Syntex P2$_1$ diffractometer using graphite monochromated MoK$_\alpha$ radiation, 1 938 intensities were gathered in an $w - 2\Theta$ scan mode in the region 2Θ(Mo) < < 50°; there was very little diffracted intensity at values of 2Θ(Mo) > 50°. Of the independent data, only 1 018 reflections had $I > 2\sigma(I)$ and only these data were used in the subsequent structure refinement.

TABLE II

Coordinates of nonhydrogen atoms (.10^4) of 3β-hydroxy-2α-senecioyloxyisoantolactone (*I*)

Atom	x	y	z	Atom	x	y	z
C(1)	10688(17)	7070(14)	3547(4)	C(14)	7064(16)	7362(14)	3746(4)
C(2)	11021(15)	5614(12)	3779(3)	C(15)	9212(18)	6483(13)	4810(4)
C(3)	11564(17)	5834(12)	4239(3)	C(16)	12268(19)	3915(13)	3252(4)
C(4)	10119(14)	6873(12)	4454(4)	C(17)	14140(17)	3326(14)	3074(4)
C(5)	9884(15)	8342(11)	4235(4)	C(18)	14320(19)	2344(14)	2767(4)
C(6)	8626(18)	9464(12)	4468(4)	C(19)	16230(21)	1889(16)	2586(5)
C(7)	8606(19)	11022(13)	4251(5)	C(20)	12531(23)	1491(19)	2590(5)
C(8)	8245(18)	10890(14)	3781(6)	O(1)	5950(11)	10776(9)	3733(3)
C(9)	9264(18)	9593(13)	3538(4)	O(2)	3427(12)	11804(9)	4080(3)
C(10)	9172(17)	8110(13)	3776(4)	O(3)	11704(13)	4456(8)	4455(2)
C(11)	6741(18)	11888(12)	4381(4)	O(4)	12695(11)	4837(8)	3586(2)
C(12)	5187(16)	11545(13)	4059(4)	O(5)	10537(12)	3644(12)	3150(3)
C(13)	6489(20)	12873(14)	4680(5)				

Structure analysis: The structure was solved by direct method using SHELX-76 program[13]. E-map revealed the positions of 21 nonhydrogen atoms. The remaining nonhydrogen atoms were localized by differential synthesis. All hydrogen atoms were described geometrically. The co-ordinates of nonhydrogen atoms were refined in isotropic and then in anisotropic full-matrix approximation. Convergence obtained at $R = 0.083$ ($wR = 0.082$) for 1 018 reflections ($w^{-1} = \delta^2 F + 0.001 F^2$).

X-Ray Structure Determination of Britannin (*II*)

Crystal data: $C_{19}H_{26}O_7$, tetragonal $P4_12_12$, $a = b = 9.350(1)$ Å, $c = 42.205(7)$ Å, $V = 3\,690$ Å^3, $D_c = 1.32$ g cm^{-3} for $Z = 8$.

Crystallographic measurement: A crystal of approximate dimensions $0.3 \times 0.5 \times 1.0$ mm was used for data collection on a Syntex P2$_1$ diffractometer using graphite monochromated CuK$_\alpha$ radiation. 1 581 indepedent intensities were gathered in an $w - 2\Theta$ scan mode in the region $2\Theta(\text{Cu}) < 51°$; there was very little observable diffracted intensity at values of $2\Theta(\text{Cu}) > 51°$

TABLE III

Selected torsion angles (in deg) of nonhydrogen atoms in 3β-hydroxy-2α-senecioyloxyisoalantolactone (*I*)

C(10)–C(1)–C(2)–C(3)	−52·0	C(8)–C(9)–C(10)–C(5)	−49·4
C(10)–C(1)–C(2)–O(4)	−170·1	C(8)–C(9)–C(10)–C(14)	77·2
C(1)–C(2)–C(3)–C(4)	49·9	C(8)–C(9)–C(10)–C(1)	−166·2
O(4)–C(2)–C(3)–C(4)	169·5	C(9)–C(10)–C(1)–C(2)	171·7
C(1)–C(2)–C(3)–O(3)	175·2	C(5)–C(10)–C(1)–C(2)	54·4
O(4)–C(2)–C(3)–O(3)	−65·2	C(14)–C(10)–C(1)–C(2)	−68·1
C(2)–C(3)–C(4)–C(5)	−54·0	C(9)–C(10)–C(5)–C(6)	59·0
C(2)–C(3)–C(4)–C(15)	127·5	C(9)–C(10)–C(5)–C(4)	−171·1
O(3)–C(3)–C(4)–C(5)	−179·0	C(14)–C(10)–C(5)–C(6)	−67·2
O(3)–C(3)–C(4)–C(15)	2·5	C(14)–C(10)–C(5)–C(4)	62·7
C(3)–C(4)–C(5)–C(10)	58·0	C(1)–C(10)–C(5)–C(6)	174·0
C(3)–C(4)–C(5)–C(6)	−173·6	C(1)–C(10)–C(5)–C(4)	−56·1
C(15)–C(4)–C(5)–C(10)	−123·6	C(6)–C(7)–C(11)–C(12)	−31·5
C(15)–C(4)–C(5)–C(6)	4·8	C(6)–C(7)–C(11)–C(13)	95·5
C(4)–C(5)–C(6)–C(7)	174·1	C(8)–C(7)–C(11)–C(12)	25·9
C(10)–C(5)–C(6)–C(7)	−58·5	C(8)–C(7)–C(11)–C(13)	−147·2
C(5)–C(6)–C(7)–C(8)	46·6	C(7)–C(11)–C(12)–O(1)	−8·4
C(5)–C(6)–C(7)–C(11)	156·9	C(7)–C(11)–C(12)–O(2)	167·0
C(6)–C(7)–C(8)–C(9)	−39·2	C(13)–C(11)–C(12)–O(1)	165·3
C(6)–C(7)–C(8)–O(1)	83·5	C(13)–C(11)–C(12)–O(2)	−19·4
C(11)–C(7)–C(8)–C(9)	−156·0	C(11)–C(12)–O(1)–C(8)	−13·1
C(11)–C(7)–C(8)–O(1)	−33·3	O(2)–C(12)–O(1)–C(8)	171·2
C(7)–C(8)–C(9)–C(10)	42·5	C(12)–O(1)–C(8)–C(7)	30·1
O(1)–C(8)–C(9)–C(10)	−77·9	C(12)–O(1)–C(8)–C(9)	158·3

TABLE IV

^{1}H and ^{13}C NMR data of britannin *(II)* in $CDCl_3$

Proton	δ	(J in Hz)	Carbon	δ
H-1	$\approx 1 \cdot 92$		C-1	$51 \cdot 03$
H-2	$4 \cdot 90$ ddd	$(J(2, 1) = 5 \cdot 4; J(2, 3) = 9 \cdot 2; J(2, 3') = 1 \cdot 6)$	C-2	$76 \cdot 10^a$
H-3	$2 \cdot 07$ ddd	$(J(3, 2) = 9 \cdot 2; J(3, 3') = 14 \cdot 8; J(3, 4) = 11 \cdot 3)$	C-3	$44 \cdot 02$
H-3'	$1 \cdot 82$ ddd	$(J(3', 2) = 1 \cdot 6; J(3', 3) = 14 \cdot 8; J(3', 4) = 8 \cdot 4)$	C-4	$75 \cdot 25^a$
H-4	$4 \cdot 12$ ddd	$(J(4, 3) = 11 \cdot 3; J(4, 3') = 8 \cdot 4; J(4, OH) = 3 \cdot 2)$	C-5	$51 \cdot 09$
H-6	$5 \cdot 06$ d	$(J(6, 7) = 8 \cdot 3)$	C-6	$76 \cdot 61$
H-7	$3 \cdot 03$ m	$(J(7, 6) = 8 \cdot 3; J(7, 8) = 10 \cdot 3; J(7, 13) = 3 \cdot 5;$	C-7	$52 \cdot 41$
		$J(7, 13') = 3 \cdot 2)$	C-8	$72 \cdot 92$
H-8	$4 \cdot 52$ ddd	$(J(8, 7) = 10 \cdot 3; J(8, 9) = 2 \cdot 8; J(8, 9') = 11 \cdot 7)$	C-9	$36 \cdot 24$
H-9	$2 \cdot 44$ ddd	$(J(9, 8) = 2 \cdot 8; J(9, 9') = 13 \cdot 3; J(9, 10) = 4 \cdot 0)$	C-10	$\cdot 30 \cdot 19$
H-9'	$1 \cdot 44$ dt	$(J(9', 8) = J(9', 10) = 11 \cdot 7; J(9', 9) = 13 \cdot 3)$	C-11	$138 \cdot 56$
H-10	^{b}		C-12	$168 \cdot 80$
H-13	$6 \cdot 17$ d	$(J(13, 7) = 3 \cdot 5)$	C-13	$120 \cdot 01$
H-13'	$5 \cdot 37$ d	$(J(13', 7) = 3 \cdot 2)$	C-14	$15 \cdot 88$
H-14	$0 \cdot 99$ d	$(J(14, 10) = 6 \cdot 1)$	C-15	$20 \cdot 42$
H-15	$1 \cdot 02$ s		Ac	$172 \cdot 92$
Ac	$2 \cdot 04$ s			$170 \cdot 24$
	$2 \cdot 24$ s			$21 \cdot 25$
OH	$2 \cdot 27$ d	$(J(OH, 4) = 3 \cdot 2)$		$21 \cdot 25$

^{a} The signals may be interchanged; ^{b} overlapped.

TABLE V

Coordinates of nonhydrogen atoms $(.10^4)$ of britannin *(II)*

Atom	x	y	z	Atom	x	y	z
C(1)	2407(5)	−88(5)	1552(1)	C(14)	1562(6)	−600(7)	991(1)
C(2)	3883(5)	−739(5)	1467(1)	C(15)	1713(6)	−1767(6)	2010(1)
C(3)	4657(6)	−1050(6)	1773(1)	C(16)	5777(5)	−168(5)	1121(1)
C(4)	3872(5)	−204(6)	2017(1)	C(17)	6465(6)	976(6)	931(1)
C(5)	2276(5)	−308(5)	1916(1)	C(18)	2730(6)	2393(6)	2428(1)
C(6)	1314(5)	910(5)	2082(1)	C(19)	3505(6)	3808(6)	2441(1)
C(7)	102(5)	1447(5)	1884(1)	O(1)	−2239(3)	899(4)	1700(1)
C(8)	−807(5)	303(6)	1714(1)	O(2)	−3540(4)	2555(5)	1947(1)
C(9)	−303(5)	13(6)	1382(1)	O(3)	4155(4)	−747(5)	2328(1)
C(10)	1190(5)	−707(6)	1343(1)	O(4)	4607(3)	293(3)	1270(1)
C(11)	−1014(5)	2309(6)	2054(1)	O(5)	6210(4)	−1373(4)	1142(1)
C(12)	−2406(6)	1975(6)	1905(1)	O(6)	2172(3)	2194(3)	2140(1)
C(13)	−919(7)	3200(8)	2297(2)	O(7)	2644(5)	1563(5)	2641(1)

TABLE VI

Selected torsion angles (in deg) of nonhydrogen atoms in britannin (*II*)

C(10)–C(1)–C(2)–O(4)	100·2	C(5)–C(6)–C(7)–C(11)	165·9
C(10)–C(1)–C(2)–C(3)	−137·6	O(6)–C(6)–C(7)–C(8)	165·7
C(5)–C(1)–C(2)–O(4)	−132·2	O(6)–C(6)–C(7)–C(11)	−73·9
C(5)–C(1)–C(2)–C(3)	−10·1	C(6)–C(7)–C(8)–C(9)	−93·6
C(1)–C(2)–C(3)–C(4)	−16·6	C(6)–C(7)–C(8)–O(1)	148·2
O(4)–C(2)–C(3)–C(4)	101·3	C(11)–C(7)–C(8)–C(9)	138·8
C(2)–C(3)–C(4)–C(5)	37·2	C(11)–C(7)–C(8)–O(1)	20·6
C(2)–C(3)–C(4)–O(3)	160·3	C(7)–C(8)–C(9)–C(10)	67·0
C(3)–C(4)–C(5)–C(1)	−42·8	O(1)–C(8)–C(9)–C(10)	−176·9
C(3)–C(4)–C(5)–C(6)	−162·4	C(8)–C(9)–C(10)–C(1)	−45·0
C(3)–C(4)–C(5)–C(15)	77·1	C(8)–C(9)–C(10)–C(14)	−168·9
O(3)–C(4)–C(5)–C(1)	−163·8	C(9)–C(10)–C(1)–C(2)	−172·9
O(3)–C(4)–C(5)–C(6)	76·6	C(9)–C(10)–C(1)–C(5)	66·8
O(3)–C(4)–C(5)–C(15)	−43·9	C(14)–C(10)–C(1)–C(2)	−51·6
C(4)–C(5)–C(1)–C(2)	31·4	C(14)–C(10)–C(1)–C(5)	−172·0
C(4)–C(5)–C(1)–C(10)	155·8	C(6)–C(7)–C(11)–C(12)	−145·2
C(6)–C(5)–C(1)–C(2)	150·6	C(6)–C(7)–C(11)–C(13)	33·2
C(6)–C(5)–C(1)–C(10)	−85·0	C(8)–C(7)–C(11)–C(12)	−17·4
C(15)–C(5)–C(1)–C(2)	−84·6	C(8)–C(7)–C(11)–C(13)	161·0
C(15)–C(5)–C(1)–C(10)	39·8	C(7)–C(11)–C(12)–O(1)	7·9
C(4)–C(5)–C(6)–O(6)	30·3	C(7)–C(11)–C(12)–O(2)	−170·9
C(4)–C(5)–C(6)–C(7)	146·6	C(13)–C(11)–C(12)–O(1)	−170·7
C(1)–C(5)–C(6)–O(6)	−82·2	C(13)–C(11)–C(12)–O(2)	10·6
C(1)–C(5)–C(6)–C(7)	34·1	C(11)–C(12)–O(1)–C(8)	6·3
C(15)–C(5)–C(6)–O(6)	150·5	O(2)–C(12)–O(1)–C(8)	−174·8
C(15)–C(5)–C(6)–C(7)	−93·2	C(12)–O(1)–C(8)–C(7)	−17·5
C(5)–C(6)–C(7)–C(8)	45·5	C(12)–O(1)–C(8)–C(9)	−138·4

^{1}H and ^{13}C NMR data of pulchellin C (*IV*) in $CDCl_3$

Proton	δ	(*J* in Hz)	Carbon	δ
H-1α	1·30 dd	(*J*(1α, 1β) = 12·8; *J*(1α, 2) = 11·5)	C-1	47·41
H-1β	1·92 dd	(*J*(1β, 1α) = 12·8; *J*(1β, 2) = 4·8)	C-2	72·39
H-2	3·55 ddd	(*J*(2, 1α) = 11·5; *J*(2, 1β) = 4·8; *J*(2, 3) = 9·0)	C-3	78·70
H-3	3·85 d	(*J*(3, 2) = 9·0)	C-4	147·37
H-5	a		C-5	44·44
H-6	1·81 ddd	(*J*(6, 5) = 2·8; *J*(6, 6') = 14·0; *J*(6, 7) = 7·0)	C-6	27·23
H-6'	a		C-7	47·15
H-7	2·99 ddd	(*J*(7, 6) = 7·0; *J*(7, 6') = 11·7; *J*(7, 8) = 4·8)	C-8	76·36
H-8	4·52 dt	(*J*(8, 7) = 4·8; *J*(8, 9) = 1·5; *J*(8, 9') = 4·8)	C-9	40·67
H-9	2·31 dd	(*J*(9, 8) = 1·5; *J*(9, 9') = 15·6)	C-10	33·91
H-9'	1·52 dd	(*J*(9', 8) = 4·8; *J*(9', 9) = 15·6)	C-11	141·63
H-13	6·17 s		C-12	a
H-13'	5·63 s		C-13	120·69
H-14	0·86 s		C-14	18·77
H-15	5·26 t	(*J*(15, 5) = 1·5; *J*(15, 15') = 1·4)	C-15	106·00
H-15'	4·74 t	(*J*(15', 5) = 1·8; *J*(15', 15) = 1·4)		

a The value of parameter could not be determined.

Of the independent data, only 1 524 reflections had $I > 2\sigma(I)$ and only these data were used in the subsequent structure refinement.

Structure analysis: The structure was solved by direct method using the MULTAN program[14]. E-map showed the positions of all 26 nonhydrogen atoms. Hydrogen atoms were described geometrically. The coordinates of nonhydrogen atoms were refined in isotropic and then in anisotropic full-matrix approximation. Convergence obtained at $R = 0·063$ ($wR = 0·068$) for 1 524 observed reflections ($w^{-1} = \delta^2 F - 0·00017F^2$).

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Translated by M. Tichý.