SESQUITERPENE LACTONES FROM *Venidium hirsutum* BEROL. SPECIES*

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Nine sesquiterpene lactones were identified in the species *Venidium hirsutum* BEROL. Five of them (*I*–*III*, *VII* and *IX*) were hitherto undescribed and their structure was determined.

More than a decade ago two of us (H. G. and B. D.) described[1] the isolation of two sesquiterpene lactones, named venidiolide and hirsutolide, from the aerial part of the species *Venidium hirsutum* BEROL. (*Compositae* family, *Arctotae* tribe). Recently, working with new material of this species, we found no venidiolide. We isolated hirsutolide and a group of other sesquiterpene lactones.

Venidiolide was characterized by m.p. 51–54°C and composition $C_{20}H_{26}O_7$. Its IR spectrum indicated the presence of an exomethylene-γ-lactone group (1 763, 1 400 and 1 157 cm^{-1}), a saturated ester group (1 727 cm^{-1}), a double bond (1 655 cm^{-1}) and a hydroxyl group (3 505 cm^{-1}). The mass spectrum did not exhibit molecular peak but only characteristic fragments, *m/z* 276 (M − 102), 258 (M − 102 − 18), 240 (M − 102 − 18 − 18), 85 ($C_4H_9CO^+$) and 57 ($C_4H_9^+$). The CD spectrum displayed a negative Cotton effect (CE) at 250 nm ($\Delta\varepsilon$ −1·1) and a positive one at 216 nm ($\Delta\varepsilon$ +7·1). The mass spectrum and the active hydrogen determination indicated the presence of two hydroxyl groups whose vicinal position was shown by quantitative cleavage with periodic acid. ^{1}H NMR spectrum of venidiolide (Table I) proved the presence of an exomethylene-γ-lactone (H-13: 6·41 dd and H-13′: 6·49 dd) whose *trans*-anellation follows from the coupling constants $J(13, 7)$ = 3·4, $J(13', 7)$ = 3·0 and $J(7, 8)$ = 9·5 Hz (see ref.[2]). The lactone ring was closed in position 8α as evidenced by the multiplet of the corresponding -CH—O proton (H-8: 4·43 dt, $J(8, 7)$ = 9·5, $J(8, 9\alpha)$ = 7·7 and $J(8, 9\beta)$ = 9·6 Hz). The hydroxy groups

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TABLE I

Proton NMR parameters of sesquiterpene lactones *I*, *II*, *VII*, and *IX* in $CDCl_3$

Proton	*I* and *II*[a]	*VII*[b]	*IX*[c]
	Chemical shifts (TAI-acylation shifts), ppm		
H-1	1·86 dd (1·41)	2·63 bt (0·86)	1·95 bdd (1·12)
H-2α	2·59 ddd (0·08)	2·76 dt (0·20)	2·52 ddd (0·04)
H-2β	1·55 dt (0·09)	1·66 m (0·07)	1·49 ddd (0·02)
H-3	5·68 m (0·10)	5·71 m (0·07)	5·65 m (0·03)
H-6α	— —	2·12 bd (0·79)	2·29 dt (0·65)
H-6β	3·85 bt (1·60)	1·78 dd (0·02)	1·87 dd (0·05)
H-7	3·46 tt (0·59)	3·06 dtt (0·10)	3·40 m (−0·04)
H-8	4·43 dt (0·20)	4·15 dt (−0·20)	4·24 dt (−0·10)
H-9α	2·94 dd (0·02)	3·13 ddt (−0·02)	2·75 dd (−0·20)
H-9β	1·65 ddd (0·06)	2·58 dd (−0·09)	1·89 dd (0·17)
H-13	6·41 dd (−0·65)	6·23 d (0·01)	6·29 d (0·02)
H-13′	6·49 dd (0·02)	5·53 d (0·04)	5·62 d (0·04)
H-14	2·73 d (−0·03)	5·09 d (0·05)	2·65 d (0·04)
H-14′	2·66 dd (0·02)	5·09 d (0·07)	2·64 d (−0·04)
H-15	5·44 d (−0·13)	5·39 d (0·10)	5·38 d (0·08)
H-15′	5·41 d (0·13)	5·29 d (0·19)	5·24 d (0·19)
Ester	2·18 m, 2 H 2·37 m, 1 H	2·37 q, 2 H	2·56 h, 1 H
	2·08 m, 1 H 1·63 m, 1 H	1·18 t, 3 H	1·17 d, 6 H
	0·95 d, 6 H 1·43 m, 1 H		
	1·13 d, 3 H		
	0·90 t, 3 H		
	Coupling constants[d], Hz		
J(1,2α)	7·6	8·0	8·0
J(1,2β)	13·8	8·0	11·5
J(1,6)	≦1	≦1	≦1
J(2α,2β)	13·6	14·0	13·7
J(2α,3)	8·6	8·4	8·5
J(2β,3)	6·0	6·4	6·4
J(3, 15)	1·7	2·1	2·1
J(3,15′)	1·5	1·8	1·8
J(6α,6β)	—	15·0	14·9
J(6α,7)	—	1·6	1·4
J(6β,7)	10·1	10·6	10·8
J(7,8)	9·5	10·0	9·7
J(7, 13)	3·4	3·4	3·4
J(7, 13′)	3·0	3·1	3·2
J(8, 9α)	7·7	7·2	7·3
J(8,9β)	9·6	9·4	9·6
J(9α,9β)	15·2	14·1	14·7
J(14,14′)	4·1	≈0	4·3

in positions 5 and 6 were proven by the in situ acylation[3,4] of venidiolide with trichloroacetyl isocyanate (TAI): the spectrum of the obtained trichloroacetylcarbamoyl (TAC) derivative displayed signals of two NH protons (δ 8·65 and 8·58), characteristic downfield shifts of the H-6 (1·60 ppm), H-1 (1·41 ppm) and H-7 (0·59 ppm) signals and an upfield shift of the H-13 signal (−0·65 ppm). The spectrum of venidiolide also exhibited oxirane ring proton signals (H-14: 2·73 d and H-14′: 2·66 dd; $J(14, 14') = 4{\cdot}1$ Hz), localized in position 14 by the long-range coupling constant $J(14', 9\beta) = 0{\cdot}7$ Hz. A further exomethylene group was found in position 15 (H-15: 5·44 d and H-15′: 5·41 d) as shown by the homoallylic coupling constants $J(15, 3) = 1{\cdot}7$ and $J(15', 3) = 1{\cdot}5$ Hz. The signal of the H-3 proton (δ 5·68) indicated an ester group bonded to C-3. Detailed analysis of the ^{1}H NMR spectrum revealed that the sample represented an about 3 : 1 mixture of two esters, isovalerate and 2-methylbutanoate (for the ester identification see ref.[5]); the signals of all other protons differred by $\leq$0·01 ppm. The NMR data of venidiolide were strikingly similar to those for arctolide[6] (*X*), indicating the same configuration at carbon atoms C-1, C-3, C-5, C-7, C-8 and C-10. More marked differences were found only in the neighbourhood of C-6 which in venidiolide bears a hydroxyl group. The existence of an intramolecular hydrogen bond between this hydroxyl and the 5α-OH group (manifested by $J(6, OH) = 10{\cdot}2$ Hz), together with the value of $J(6, 7)$ (10·1 Hz), prove its α-configuraion. According to the presented evidence, the so-called venidiolide is a mixture of two compounds, consisting of venidiolide A (major part) of structural formula *I* and venidiolide B (minor part), represented by formula *II*.

Hirsutolide (*III*), $C_{16}H_{20}O_5$, melted at 110−112°C and had $[\alpha]_D$ −149·6°. Its IR spectrum indicated the presence of an exomethylene-γ-lactone (1 765 and 1 150 cm^{-1}), an α,β-unsaturated ester (1 710 cm^{-1}) and a double bond (1 645 and 1 665 cm^{-1}). Its mass spectrum contained a molecular peak, *m/z* 292, CD spectrum exhibited a positive CE at 248 nm ($\Delta\varepsilon$ +0·8) and a negative one at 222 nm ($\Delta\varepsilon$ −4·2). The ^{1}H NMR spectrum of *III* at room temperature (22°C) displayed broad ill-resolved signals. Such behaviour is typical for 7,8-lactonized germacranolides with rather flexible ten-membered ring that in solution may exist in more conformations (for a discussion see refs[7,8]). A better resolution was achieved by measurement at 50°C (Table II); in this way we have proven the presence of an exomethylene-γ-lactone (H-13: 6·31 d and H-13′: 5·70 d), *trans*-fused[2] ($J(13, 7) = 3{\cdot}4$, $J(13', 7) = 3{\cdot}1$ and $J(7, 8) = 8{\cdot}2$ Hz) in position 8 (H-8: 4·25 ddd, $J(8, 7) = 8{\cdot}2$, $J(8, 9) = 2{\cdot}7$ and $J(8, 9') = 11{\cdot}7$ Hz). The spectrum further showed the presence of a tertiary methyl

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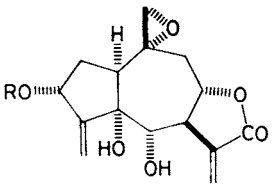
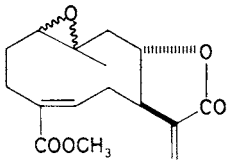
[a] Data for the mixture of *I* (73%) and *II* (27%); except of ester groups all the other signals differ less than 0·01 ppm; additional data; C(6)-OH: 3·21 d (J = 10·2); $J(13,13') = 1{\cdot}3$; $J(9\beta,14') = 0{\cdot}7$; for TAC-derivative — NH: 8·65 s and 8·58 s. [b] TAC-derivative of *VII* — NH: 8·40 s. [c] TAC-derivative of *IX* — NH: 8·27 s. [d] coupling constants are given in the absolute values.

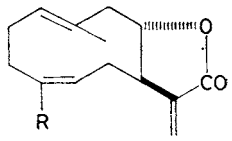
group (δ 1·38 s) bonded to the carbon atom, incorporated into the trisubstituted oxirane ring (CH—O: 2·83 dd, J = 10·4 and 4·0 Hz), and a methyl ester ($COOCH_3$: 3·78 s) attached to a trisubstituted double bond (C=CH: 6·97 m). Although the 200 MHz ^{1}H NMR spectrum was not completely analysable, the found structural fragments and comparison with the ^{1}H NMR data for liabinolide (*IV*) and scorpioidin (*V*) (see refs[9,10]) lead to the structure *III* for hirsutolide. Its ^{13}C NMR spectrum (Table III) is compatible with the structure *III*; the configuration at the C-1 and C-10 atoms remains undecided.



I, R = $COCH_2CH(CH_3)_2$
II, R = $COCH(CH_3)CH_2CH_3$



III



IV, R = CH=O
V, R = $COOCH_3$

Reduction of hirsutolide (*III*) with sodium borohydride afforded, inter alia, 11β*H*,13-dihydrohirsutolide (*VI*), $C_{16}H_{22}O_5$, m.p. 162–163°C. Its IR spectrum proved the presence of a γ-lactone ring (1 778 cm^{-1}), an α,β-unsaturated ester (1 713 cm^{-1})

TABLE II

Proton NMR parameters of sesquiterpene lactones *III* and *VI* in $CDCl_3$ at temperature 50°C

Proton	Chemical shifts, ppm (Coupling constants, Hz)	
	III	*VI*[a]
H-1	2·83 dd (10·4; 4·0)	2·79 dd (10·7; 3·9)
H-2	2·31 m (14·2; 9·2; 5·1; 4·0; 0·9)	2·29 m (14·0; 7·0; 7·0; 3·9; 0·7)
H-5	6·97 m ($\sum J$ = 17·4)	6·89 t (8·7; 8·6)
H-8	4·25 ddd (11·7; 8·2; 2·7)	4·21 ddd (11·4; 9·8; 2·5)
H-9	2·80 ddd (12·8; 2·7; 0·5)	2·77 bdd (13·1; 2·5; ≦0·5)
H-9′	1·28 m (13·0; 11·7; 0·7)	1·23 bt (13·1; 11·5; ≦0·5)
H-13	6·31 d (3·4)	1·35 d (7·0)
H-13′	5·70 d (3·1)	—
H-14	1·38 s	1·35 s
$COOCH_3$	3·78 s	3·79 s

[a] Additional parameters: H-7: 1·82 um ($W \approx$ 30 Hz); H-11: 2·53 dq, J(11,7) = 12·0; J(11,13) = = 7·0.

and a double bond (1 645 cm^{-1}). The mass spectrum had molecular peak of *m/z* 294, CD maxima were localized at 246 nm ($\Delta\varepsilon$ +0·8) and at 224 nm ($\Delta\varepsilon$ −4·1). In the ^1H NMR spectrum (Table II) a new doublet of secondary methyl on C-11 appeared at δ 1·35 (J(13, 11) = 7·0 Hz), instead of the signals of the exomethylene protons H-13 and H-13′. The signals of most other assignable protons in the reduced product are shifted slightly upfield ($\leq$0·05 ppm); a somewhat larger shift was observed for the H-5 proton (0·08 ppm) and the only marked shift was that of the H-7 proton (in compound *III* obscured, together with other signals, at δ ~2·50) which in the spectrum of *VI* appeared as an unresolved multiplet at δ 1·82. The α-configuration of the methyl on C-11 follows from the coupling constant of H-11 and H-7 (12·0 Hz) which indicates their *trans*-arrangement. Thus, the reduction of hirsutolide (*III*) afforded 11β*H*,13-dihydrohirsutolide (*VI*).

The chloroform extract of the mentioned plant material afforded, in addition to hirsutolide, sesquiterpene lactones *VII*–*XII*.

The least polar of them was the non-crystalline lactone *VII*, $C_{18}H_{22}O_5$, $[\alpha]_D$ +19·6°. Its IR spectrum showed the presence of a hydroxyl (3 450 cm^{-1}), a γ-lactone (1 780 cm^{-1}), a saturated ester (1 740 cm^{-1}) and a double bond (1 680 cm^{-1}). The spectrum had no molecular peak but contained characteristic fragments, *m/z* 244 (M − 74) and 226 (M − 74 − 18). The ^1H NMR spectrum (Table I) proved the presence of an exomethylene-γ-lactone (H-13: 6·23 d and H-13′: 5·53 d), *trans*-attached[2] in position 8 (J(13, 7) = 3·4, J(13′, 7) = 3·1; H-8: 4·15 ddd, J(8, 7) = = 10·0, J(8, 9α) = 7·2 and J(8, 9β) = 9·4 Hz), and two other exomethylene groups (H-14 and H-14′: 5·09 d (2 H), H-15: 5·39 d and H-15′: 5·29 d). The spectrum further revealed a propionate in position 3 (H-3: 5·71 m, J(3, 2α) = 8·4, J(3, 2β) = 6·4,

TABLE III

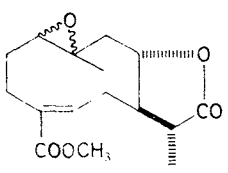
Carbon-13 chemical shifts of hirsutolide (*III*) in C_6D_6

Carbon	δ	Carbon	δ
C-1	60·23	C-9	45·47[a]
C-2	22·75[a]	C-10	55·67
C-3	27·46[a]	C-11	141·44
C-4	120·97	C-12	167·96[b]
C-5	139·61	C-13	118·99
C-6	45·47[a]	C-14	16·73
C-7	45·24	C-15	167·07[b]
C-8	78·75	C-16	51·53

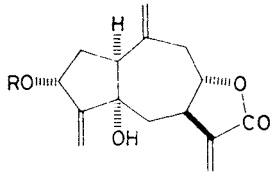
[a,b] The assignment of signals with the same symbol can be interchanged.

$J(3, 15) = 2{\cdot}1$ and $J(3, 15') = 1{\cdot}8$ Hz) and a tertiary hydroxyl group in position 5α (using the TAI-induced acylation shifts[4] of the H-1 (0·86 ppm) and H-6α (0·79) protons in the TAC-derivative of compound *VII*). Comparison with the ^{1}H NMR data for compound *VIII*, described by us earlier[11], has shown that the newly isolated compound differs from *VIII* only in the ester group and therefore can be assigned the structure *VII* (3-deacetyl-3-propionyl-11,14-deoxyarctolide). The determination of absolute configuration of the lactone *VII* is described below.

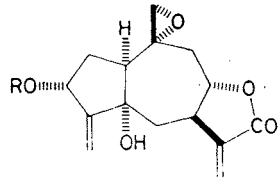
Another hitherto undescribed compound was the non-crystalline lactone *IX*, $C_{19}H_{24}O_6$, $[\alpha]_D$ +24·1°. According to the IR spectrum, the compound contained a hydroxyl group (3 500 cm^{-1}), a γ-lactone (1 768 cm^{-1}), a saturated ester (1 725 cm^{-1}) and a double bond (1 665 cm^{-1}). No molecular peak was observed in the mass spectrum which exhibited characteristic fragments *m/z* 260 (M − 88) and 242 (M − 88 − 18). The CD spectrum showed a CE at 205 nm (Δε +3·2). Proton NMR spectrum (Table I) indicated an exomethylene-γ-lactone (H-13: 6·29 d and H-13′: 5·62 d), again *trans*-attached in the position 8 ($J(13, 7) = 3{\cdot}4$, $J(13', 7) = 3{\cdot}2$ Hz; H-8: 4·24 dt, $J(8, 7) = 9{\cdot}7$, $J(8, 9\alpha) = 7{\cdot}3$, $J(8, 9\beta) = 9{\cdot}6$ Hz), and another exomethylene group (H-15: 5·38 d and H-15′: 5·24 d). Further we have proven an oxirane ring (H-14: 2·55 d and H-14′: 2·58 d, $J(14, 14') = 4{\cdot}3$ Hz) and an isobutyrate grouping (—CH<: 2·56 h, $J = 7{\cdot}0$ Hz; 2 × CH_3: 1·17 d, $J = 7{\cdot}0$ Hz) in position 3 (H-3: 5·65 m, $J(3, 2\alpha) = 8{\cdot}5$, $J(3, 2\beta) = 6{\cdot}4$, $J(3, 15 = 2{\cdot}1$ and $J(3, 15') = 1{\cdot}8$ Hz). A detailed comparison of the ^{1}H NMR data with those found previously by us for arctolide (*X*) or related compounds *XI* and *XII* has shown that the studied lactone differs from these compounds only in the character of the ester functionality and is thus 3-deacetyl-3-isobutyrylarctolide (*IX*).



VI



VII, R = $COCH_2CH_3$
VIII, R = $COCH_3$



IX, R = $COCH(CH_3)_2$
X, R = $COCH_3$
XI, R = $COCH(CH_3)CH_2CH_3$
XII, R = $COCH_2CH_3$

The absolute configuration of the hitherto undescribed lactones *VII* and *IX* was derived from comparison of their CD spectra and specific rotations with those of lactones *VIII* and *X*–*XII* of known[6,11] absolute configuration. Accordingly, the formulae *VII* and *IX* represent the actual configuration of the isolated lactones.

As further constituents from the studied *Venidium hirsutum* species, we isolated 3-deacetyl-3-(2'-methyl)butyrylarctolide (*XI*), 10,14-deoxoarctolide (*VIII*), 3-deacetyl-3-propionylarctolide (*XII*) and arctolide (*X*). Their identity was proven by comparison of the ^{1}H NMR, IR, mass and CD spectra with those of authentic samples described previously[11].

The presence of arctolide-type guaianolides in the *Venidium hirsutum* species is not unexpected because this species belongs to the *Arctotae* tribe (to which belongs also *Arctotis grandis*[11]). This tribe contains mostly sesquiterpene lactones with the guaiane and germacrane skeleton[12]. From this viewpoint, also the presence of hirsutolide (*III*) in the studied species appears to be plausible, even though a germacranolide of the heliangolide type (moreover with a C-15 carboxyl group) has not been described so far in this tribe[12].

EXPERIMENTAL

The melting points were determined on a Kofler block and they are not corrected. Silica gel for column chromatography was prepared according to Pitra and Štěrba (30–60 μm, deactivated by addition of 11% of water). Thin-layer chromatography was carried out on silica gel G (Merck) according to Stahl. HPLC was performed on a Waters HPLC apparatus with RI-detector. The IR spectra were taken in chloroform on a spectrometer UR 20 (C. Zeiss, Jena); wavenumbers are given in cm^{-1}. The mass spectra were measured on an AEI 902 spectrometer. Optical rotations were determined in chloroform on a Perkin–Elmer 141 polarimeter. The CD spectra were recorded on a Roussel Jouan CD 185 dichrographe in methanol. The ^{1}H NMR spectra (at 200 MHz) were obtained with a Varian XL-200 FT NMR instrument in deuterochloroform, using tetramethylsilane as internal reference. The TAI-acylation shifts were measured on TAC-derivatives prepared by in situ acylation – addition of small excess of TAI to a $CDCl_3$ solution of the corresponding hydroxy compound in an NMR sample tube[3,4]. ^{13}C NMR spectrum of hirsutolide (*III*) was measured on the same instrument (at 50·3 MHz) in C_6D_6 and referenced to TMS using the relation $\delta(C_6D_6) = 128{\cdot}0$.

11β*H*,13-Dihydrohirsutolide (*VI*)

A suspension of sodium borohydride (100 mg) in ethanol (5 ml) was added to a solution of hirsutolide (*III*; 150 mg) in ethanol (150 ml). The mixture was kept at pH 5 by addition of acetic acid. After 1 h, water was added, the mixture was extracted with chloroform and the combined chloroform extracts were worked up in the usual manner. After removal of the solvent, the residue (122 mg) was purified by chromatography on a column of silica gel (3 g). Elution with chloroform–acetone (9 : 1) afforded 11β*H*,13-dihydrohirsutolide (*VI*; 76 mg), m.p. 162–163°C, IR spectrum: 1 778 (γ-lactone), 1 713 (α,β-unsaturated ester), 1 645 (double bond). Mass spectrum, *m/z*: 294 (M), 279 (M – CH_3), 276 (M – H_2O), 266 (M – CO), 262 (M – CH_3OH), 250 (M – COO), 235 (M – $COOCH_3$). CD spectrum: 246 nm, $\Delta\varepsilon$ +0·8; 224 nm, $\Delta\varepsilon$ −4·1. For $C_{16}H_{22}O_5$ (294·4) calculated: 65·29% C, 7·54% H; found: 65·07% C, 7·73% H.

Isolation of Sesquiterpene Lactones *VII*–*XII* from *Venidium hirsutum* Berol.

The aerial parts of *Venidium hirsutum* Berol. (collected in 1979) were processed as described previously[1]. The chloroform extract was chromatographed on a column of silica gel. Elution

with chloroform–acetone (8 : 2) afforded the so-called lactone fraction (11 g). After separation of hirsutolide, the material was subjected to medium-pressure liquid chromatography in hexane–ethyl acetate (65 : 35), monitored by TLC on silica gel in the same elution mixture. The obtained 6 fractions were further separated by preparative HPLC on a series of five 9 mm columns packed with Lichrosorb (10 g) in hexane–ethyl acetate (6 : 4). This procedure afforded pure compounds *VII*—*XII* in the order of their increasing polarity.

3-*Deacetyl*-3-*proptonyl*-11,14-*deoxoarctolide* (VII), non-crystalline, $[\alpha]_D$ +19·6° (*c* 0·1). IR spectrum: 3 450 (OH), 1 780 (γ-lactone), 1 740 (saturated ester), 1 680 (double bond). Mass spectrum, *m/z*: 244 (M − 74), 226 (M − 74 − 18). For $C_{18}H_{22}O_5$ (318·4) calculated: 67·97% C, 6·97% H, 0·32% H act.; found: 67·58% C, 7·01% H, 0·51% H act.

3-*Deacetyl*-3-*isobutyrylarctolide* (IX), non-crystalline, $[\alpha]_D$ +24·1° (*c* 0·1). IR spectrum: 3 500 (OH), 1 768 (γ-lactone), 1 725 (saturated ester), 1 665 (double bond). Mass spectrum, *m/z*: 260 (M − 88), 242 (M − 88 − 18). CD spectrum, 205 nm, Δε +3·2. For $C_{19}H_{24}O_6$ (384·4) calculated: 65·50% C, 6·94% H, 0·29% H act.; found: 65·33% C, 6·94% H, 0·37% H act.

3-*Deacetyl*-3-(2′-*methyl*)*butyrylarctolide* (XI), non-crystalline, IR spectrum: 3 430 (OH), 1 765 (γ-lactone), 1 730 (ester), 1 630 and 1 670 (double bond). Mass spectrum, *m/z*: 260 (M − 102), 242 (M − 102 − 18), 85 ($C_4H_9CO^+$), 57 ($C_4H_9^+$). CD spectrum: 205 nm, Δε +1·7. ^{1}H NMR, IR, MS and CD spectra have proven the identity of this compound with an authentic sample[11] of 3-deacetyl-3-(2′-methyl)butyrylarctolide (*XI*).

10,14-*Deoxoarctolide* (VIII), non-crystalline, $[\alpha]_D$ +15·1° (*c* 0·1). IR spectrum: 3 580 (OH), 1 770 (γ-lactone), 1 735, 1 250 (acetate), 1 670, 1 630 (double bond). Mass spectrum, *m/z*: 304 (M), 244 (M − 60), 226 (M − 60 − 18). CD spectrum: 235 nm, Δε +0·6; 211 nm, Δε +2·5. ^{1}H NMR, IR, MS and CD spectra have proven the identity of this compound with an authentic sample[11] of 10,14-deoxoarctolide (*VIII*).

3-*Deacetyl*-3-*propionylarctolide* (XII), non-crystalline, $[\alpha]_D$ +30·3° (*c* 0·1). IR spectrum: 3 250 (OH), 1 770 (γ-lactone), 1 745 (saturated ester), 1 670, 1 630 (double bond). Mass spectrum, *m/z*: 260 (M − 74), 242 (M − 74 − 18). CD spectrum: 209 nm, Δε +3·5. ^{1}H NMR, IR, MS and CD spectra have proven the identity of this compound with an authentic sample[11] of 3-deacetyl-3-propionylarctolide (*XII*).

Arctolide (X), m.p. 139—141°C, $[\alpha]_D$ +10·9° (*c* 0·1). IR spectrum: 3 540 (OH), 1 770 (γ-lactone), 1 740, 1 245 (acetate), 1 675 (double bond). Mass spectrum, *m/z*: 320 (M), 260 (M − 60), 242 (M − 60 − 18). CD spectrum: 206 nm, Δε +5·5. ^{1}H NMR, IR, MS and CD spectra have proven the identity of this compound with an authentic sample[13] of arctolide (*X*).

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