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ISODAUCANE DERIVATIVES, NORSESQUITERPENES AND CLERODANES FROM *CHROMOLAENA LAEVIGATA*

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Abstract—The aerial parts of *Chromolaena laevigata* gave four new compounds derived from chromolaenin, four clerodane derivatives and a new type of norsesquiterpenes as well as two sesquiterpenes with a new carbon skeleton.

From the large genus *Chromolaena* (Compositae, tribe Eupatorieae) several cadinene derived furans have been isolated.[1] *Chromolaena laevigata* (Lam.) K. et R. which is used as 'Sanalotodo' in folk medicine also afforded these sesquiterpenes.[2] A reinvestigation of a sample from Paraguay afforded dehydrochromolaenin (**1**), already prepared by dehydrogenation of chromolaenin,[3] the lactones **2** and **3**, obviously oxidation products of the latter, the norsesquiterpene **4**, the sesquiterpene aldehydes **6** and **7**, the norsesquiterpene **9**, the clerodane derivatives **10–15** as well as some known compounds (Experimental).

The structure of **2** and **3** could easily be deduced from the ^{1}H-NMR spectra which were close to those of the corresponding tetrahydro derivatives.[1] The presence of an aromatic compound followed from the typical low field signals (Table 1). Of course the H-9 signal was shifted downfield if compared with the shift in the corresponding tetrahydro derivatives. The ^{1}H-NMR spectral data of **4** (Table 1) again showed the presence of an aromatic system with two vicinal protons and in contrast to **2** and **3** two broadened singlets which were also due to aromatic protons as followed from the chemical shifts. These shifts further indicated the relative position of the substituents. The keto group at C-6 caused a downfield shift of H-1 and H-4 while the phenolic hydroxy led to an upfield shift of H-8. The assignments were supported by the observed long range couplings which could be determined by spin decoupling. In agreement with the ^{1}H-NMR data the molecular formula showed the presence of a norsesquiterpene ($C_{14}H_{14}O_2$). The corresponding tetrahydro derivative chromoarnottione, was isolated from *Chromolaena arnottiana*.[4]

Table 1. ^{1}H-NMR spectral data of **1–4** (400 MHz, $CDCl_3$, TMS as internal standard)

	1	2	3[a]	4[b]
H-1	7.97 d	7.34 d	7.35 d	7.85 d
H-2	7.33 dd	7.23 d br	7.25 d br	7.25 dd
H-4	8.15 dq	7.37 s br	7.36 s br	7.85 s br
H-8 } H-8′ }	7.46 s br	2.66 dd 1.66 dd	2.69 dd 1.65 dd	6.93 s br
H-9	—	3.27 ddq br	3.26 ddq br	—
H-12	7.42 q	—	—	
H-13	2.62 d	2.13 s	2.15 s	2.84 s
H-14	2.73 s br	1.37 d	1.36 d	2.64 d
H-15	2.58 s br	2.38 s br	2.38 s br	2.53 s br

[a] OMe: 3.11 s.
[b] OH: 13.50 s. J (Hz): 1, 2 = 8; 2, 4 = 2, 15 = 3, 15 ~ 1.5; compound **1**: 12, 13 = 1.5; compounds **2** and **3**: 8, 8′ = 13; 8, 9 = 6; 8′, 9 = 12; 9, 14 = 7; compound **4**: 8, 14 = 1.

The molecular formula of **6** was $C_{15}H_{22}O_2$ and the IR spectrum indicated a keto aldehyde (2720, 1690 and 1710 cm^{-1}). The ^{1}H-NMR spectrum showed that a conjugated aldehyde was present (δ = 9.35 s and 6.63 d) and signals at δ = 2.76 and 2.47 supported a keto group with only two vicinal protons. In deuteriobenzene all signals could be assigned by spin decoupling. Inspection of a model together with NOE difference spectroscopy showed that a *cis* ring fusion was present. Accordingly, irradiation of H-14 caused a clear NOE with H-5 while H-5 showed no effect with H-6 indicating a *trans* diaxial orientation of these protons as also followed from the coupling $J_{5,6}$ = 9 Hz.

The ^{1}H-NMR of **7** was close to that of **6**. However, a double doublet at δ = 3.39 indicated the presence of the corresponding alcohol. The α-orientation could be deduced from the couplings of H-10.

The sesquiterpenes **6** and **7** belong to a new type of carbon skeleton which previously has only been observed in mintsulphide, a sulphur compound from peppermint oil.[5]

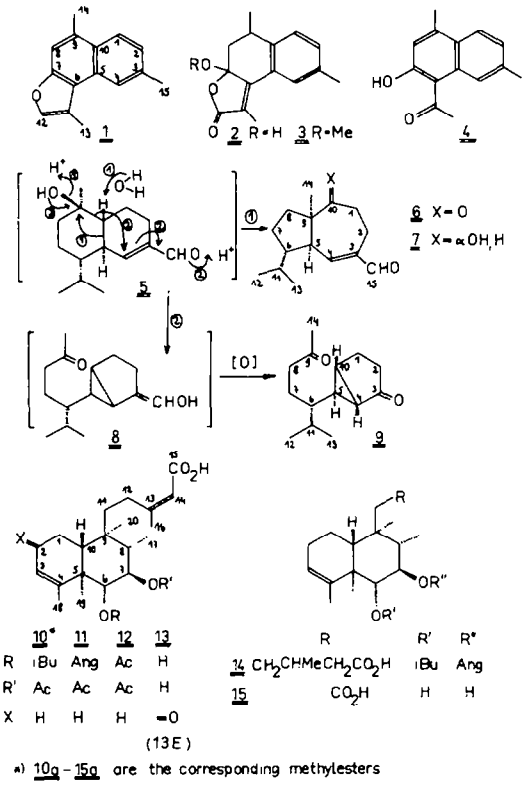
The structure elucidation of **9** was achieved again mainly by careful ^{1}H-NMR studies. In deuteriobenzene (Table 2) all signals could be assigned by spin decoupling though a few were overlapped multiplets. The presence of a cyclopropane derivative was deduced from the chemical shifts and the typical couplings of the signals of H-5 and H-10. As $J_{4,5}$ was 4 Hz the corresponding protons were *cis*-oriented,[6] while a 10 Hz coupling of H-5 with H-6 indicated a *trans*-relationship. Thus the stereochemistry was settled. The ^{13}C-NMR data (Experimental) also supported the proposed structure. The values observed for the cyclopropane carbons agreed well with those reported for a similar bicyclo[3.1.0]hexan-2-one.[7] In the CIMS the base peak was *m/z* 151, obviously formed by loss of methyl ethyl ketone which also supports the structure. It seems most likely that both **7** and **9** are biogenetically formed from a common precursor, the aldehyde **5** derived from α-cadinol. Proton attack at the OH would lead by pathway 1 to **7**, which by oxidation would give **6**, or by protonation of the aldehyde oxygen (pathway 2)

Table 2. ^{1}H-NMR spectral data of **6**, **7** and **9** (400 MHz, TMS as internal standard)

	6 (C_6D_6)	$CDCl_3$	**7** ($CDCl_3$)	**9** (C_6D_6)	$CDCl_3$
H-1	2.35 dt	2.52 m	2.28 m	1.54 m	*
H-1′	2.28 dt	2.47 m	2.15 m	1.47 m	*
H-2	2.62 dt	2.76 m	2.60 m	1.75 dddd	2.14 m
H-2′	2.15 dt br	2.21 m	2.47 m	1.67 ddd	2.03 m
H-4	6.01 d br	6.63 d br	6.52 d br	1.47 dd br	*
H-5	2.03 dd	2.52 m	*	0.62 ddd	1.03 ddd
H-6	1.42 dddd	*	*	0.28 dddd	*
H-7	1.62 dddd	*	*	1.54 m	*
H-7′	1.10 dddd	*	*	1.44 m	*
H-8	2.30 m	*	*	2.00 ddd	2.52 m
H-8′	1.24 ddd	*	*	1.94 ddd	
H-10	—	—	3.39 dd	1.28 ddd	1.86 ddd
H-11	1.28 dq	1.65 dq	1.60 m	1.54 m	*
H-12	0.73 d	0.94 d	0.90 d	0.81 d	0.90 d
H-13	0.71 d		0.89 d	0.79 d	
H-14	0.89 s	1.33 s	1.01 s	1.71 s	2.17 s
H-15	9.15 s	9.35 s	9.36 s	—	—

* Overlapped multiplets. J (Hz): Compound **6**: 1,1′ = 14; 1,2 = 1,2′ = 1′,2 = 1′,2′ ~ 5.5; 2,2′ = 15; 4,5 = 6; 5,6 = 9; 6,7 = 7; 6,7′ = 11; 6,11 = 7; 7,7′ = 15; 7,8 = 7; 7,8′ = 2.5; 7′,8 = 11; 7′,8′ = 3.5; 8,8′ = 14; 11,12 = 11,13 = 7; compound **7**: 4,5 = 6; 9,10 = 11; 9′,10 = 5; 11,12 = 11,13 = 7; compound **9**: 1,2 = 7.5; 1,2′ = 1.5; 1′,2 = 9; 1′,2′ = 9; 2,2′ = 18; 2,4 = 1.5; 4,5 = 4; 5,10 = 3; 5,6 = 10; 6,7 = 5; 6,7′ = 9; 6,11 = 5; 7,8 = 6; 7,8′ = 9; 7′,8 = 9; 7′,8′ = 6; 8,8′ = 17; 11,12 = 11,13 = 7.

the intermediate **8** could be formed which by oxidation could give **9** with the proposed stereochemistry. Compounds with the carbon skeleton of **9** have not been reported previously. We have named the diketone chromolaevane dione. For the carbon skeleton of **6** and **7** we propose the name isodaucane as daucane is the isomer with a methyl at C-2.



*) 10a – 15a are the corresponding methylesters

The structures of the clerodane derivatives **10–12** followed from the ^{1}H-NMR spectra (Table 3), which were close to those of similar diterpenes. The couplings of H-6–H-8 clearly indicated the *trans*-diaxial positions of the corresponding protons. Furthermore the presence of a Δ^3 double bond was deduced from the typical signals of H-3 and H-18 while the configuration of the Δ^{13} double bond followed from the chemical shift of H-16. The nature of the ester groups could easily be deduced from the typical ^{1}H-NMR signal. The relative position of the ester groups, however, could not be assigned with certainty. The H-6 signal in the spectrum of **11** was shifted downfield if compared with the shift in the spectrum of **12**. As in similar cases this was probably due to the effect of the conjugated acid residue. Due to the minute amounts final proof was not possible. This was also true in the case of **10** and **14** (see below). The configurations at C-9 and C-10 were established by NOE difference spectroscopy. As an example clear effects were observed in the case of **10** between H-6, H-8 and H-10, between H-19, H-18, H-20 and the H-2 of the isobutyrate, which may be an indication that the isobutyrate was at C-6, and between H-7, H-17, H-19 and H-20. The ^{1}H-NMR data of **14** (Table 3) indicated the presence of a 13,14-dihydro kolavenic acid. Again the nature of the ester groups followed from the typical ^{1}H-NMR signal and the downfield shifted signal of H-7 favoured a 7-position of the angelate group. Identical couplings further showed that the configurations were the same as in **10–12**. The ^{1}H-NMR spectrum of **13a** (Table 3), which was obtained after saponification and esterification of an ester mixture, clearly indicated that this diterpene was a 2-keto derivative. Accordingly, the H-3 and H-18 signals were shifted downfield and the H-1 signal now clearly could be assigned. Therefore the presence of a *trans*-clerodane already followed from the coupling $J_{1\alpha,10}$. NOE difference spectroscopy es-

Table 3. ^{1}H-NMR spectral data of **10**–**14** and **10a** (400 MHz, $CDCl_3$, TMS as internal standard)

	10[a]	10a (C_6D_6)[b]	11[c]	12[d]	13a[e]	14[f]	15[g]
H-3	5.22 t br	5.25 s br	5.21 t br	5.22 t br	5.26 s br	5.18 s br	5.21 t br
H-6	4.90 d	5.24 d	4.99 d	4.87 d	3.38 d	4.94 d	3.26 d
H-7	5.08 dd	5.38 dd	5.12 dd	5.07 dd	3.48 dd	5.21 dd	3.40 dd
H-12	2.55 ddd	2.46 ddd	2.55 ddd	2.54 m	2.54 ddd	—	—
H-12′	2.26 ddd	2.17 ddd	2.26 ddd	2.27 m	2.29 ddd	—	—
H-14	5.68 s br	5.70 s br	5.68 s br	5.67 s br	5.73 s br	-	-
H-16	1.90 d	1.57 d	1.90 d	1.90 d	2.15 d	0.96 d	
H-17	0.81 d	0.94 d	0.83 d	0.82 d	1.03 d	0.75 d	1.06 d
H-18	1.63 dt	1.76 dt	1.55 s br	1.56 s br	1.86 d	1.55 s br	1.80 s br
H-19	1.20 s	1.29 s	1.24 s	1.19 s	1.15 s	1.21 s	1.04 s
H-20	0.82 s	0.75 s	0.84 s	0.81 s	0.83 s	0.83 s	0.80 s
OCOR	2.48 qq	2.49 qq	6.12 qq	2.03 s	–	2.41 qq	—
—	1.11 d	1.18 d	2.02 dq	—	—	1.06 d	—
		1.17 d	1.86 dq	—	—	1.02 d	

[a] OAc: 2.00 s.
[b] OAC: 1.88 s; OMe: 3.49 s.
[c] OAc: 1.96 s.
[d] OAc: 2.00 s.
[e] H-1α 2.45 dd, H-1β 2.51 dd, H-8 1.63 dq, H-10 2.05 dd, H-11 1.40 m, OMe 3.66 s.
[f] OAng: 6.13 qq; 2.00 q; 1.84 dq.
[g] 2.41 d and 2.35 d H-11, J = 14 Hz.

J (Hz): 2,3 = 2′,3 = 3.5; 6,7 = 10; 7,8 = 11.5; 11,12 = 11′,12′ = 5; 8,17 = 7; 11,12′ = 11′,12 = 12,12′ = 12; 14,16 ~ 1.5; compound **13**: 1α,1β = 17.5; 1α,10 = 13; 1β,10 = 3; 3,15 = 14,16 = 1; 6,7 = 9; 7,8 = 10.5; 7,17 = 7; 11,12 = 6.5; 12,12′ = 15; compound **14**: 13,16 = 7.

tablished this proposal. Clear effects were observed between H-20, H-19, H-17, H-11, H-1α and H-7, between H-8, H-10 and H-6 as well as between H-19, H-20, H-7 and H-1α. The chemical shift of H-16 indicated the presence of a 13*E*-configuration. The molecular formula of **15** indicated the presence of a norditerpene ($C_{16}H_{26}O_4$). The ^{1}H-NMR data (Table 3) were similar to those of the clerodanes. However, the chemical shifts of H-6 and H-7 indicated the absence of ester residues. The free hydroxyl at C-6 and C-7 caused the expected downfield shifts of H-18 and H-17 respectively. The position of the carboxyl group followed from pair of doublets for H-11 and identical stereochemistry at all chiral centres was indicated by the couplings which were identical with those of **10**–**12**.

The chemistry of *Chromolaena laevigata* again shows that cadinene derivatives like **1**–**4** are widespread in this genus. The isolation of the unusual sesquiterpenes **6**, **7** and **9** may be of chemotaxonomic relevance, especially as these compounds are also most likely derived from a cadinene precursor. The clerodanes so far have not been reported from *Chromolaena. Chr. corymbosa* also gave furocadinenes (Experimental).

EXPERIMENTAL

^{1}H-*NMR spectra*

$CDCl_3$, TMS as internal standard, 400 MHz; IR spectra: CCl_4; MS: 70 eV, direct inlet; optical rotation: $CHCl_3$. Plant material collected in San Jose de los Arroyos, Paraguay. The air dried aerial parts (500 g) were extracted with EtOH–Et_2O, 1:1, and the extract obtained was separated first by CC (SiO_2) affording four fractions: 1 (Et_2O–petrol, 1:9 and 1:4), 2 (Et_2O–petrol, 1:1), 3 (Et_2O) and 4 (Et_2O–MeOH, 9:1). Fractions 2 and 4 gave nothing of interest. TLC of fraction 1 (SiO_2, PF 254, petrol) gave 10 mg curcumene, 20 mg squalene, 10 mg caryophyllen epoxide and a mixture which was separated by TLC (Et_2O–petrol, 1:4). The band with R_f 0.45 gave by HPLC (RP 8, MeOH–H_2O, 4:1, flow rate, 3 ml/min, *ca* 100 bar) 1 mg **6** and 8 mg spathulenol. TLC of half of fraction 3 (Et_2O–petrol, 3:2) gave four bands (3/1–3/4). HPLC of 3/1 (MeOH–H_2O, 4:1) gave 5.5 mg **10** (R_t = 7.8 min), 2 mg **11** (R_t = 9.5 min) and 3 mg **14** (R_t = 12.0 min). HPLC of 3/2 (MeOH–H_2O, 4:1) gave 1 mg **7** (after repeated HPLC (MeOH–H_2O, 7:3, R_t = 6.8 min) and 7 mg **12** (R_t = 5.0 min). HPLC (MeOH–H_2O, 3:2) of 3/3 gave 2 mg **9** (R_t = 4.5 min) and HPLC of 3/4 (MeOH–H_2O, 3:2) afforded a mixture (R_t = 8.0 min) which by TLC (Et_2O–petrol, 4:1, two developments) gave 4 mg **15** (R_f 0.30). The second part of fraction 3 was saponified by heating with KOH in MeOH–H_2O for 1 hr at 70°. TLC after addition of CH_2N_2 (Et_2O–petrol, 1:1) gave a polar band which after TLC (Et_2O, five developments) gave 5 mg **13a** (R_f 0.60) and unseparated mixtures. The extract of the roots (180 g) gave by CC (SiO_2) two fractions of interest. 1 (Et_2O–petrol, 1:9 and 1:4) and 2 (Et_2O–petrol, 1:1). TLC of fraction 1 (Et_2O–petrol, 3:17) gave 10 mg **1** (R_f 0.7), a mixture which gave by HPLC (MeOH–H_2O, 4:1) 1 mg **4** (R_t = 3.0 min), 9 mg **3** (R_f 0.35) and 15 mg lactiflorenol.[9] TLC of fraction 2 (Et_2O–petrol, 3:2) gave 21 mg **3** (R_f 0.25). The aerial parts (180 g) of *Chromolaena corymbosa* (voucher RMK 8548) gave 20 mg tetrahydrochromalaenin,[2] 15 mg dihydroisochromolaenin[8] and 10 mg chromoarnottione.[4] Known compounds were identified by comparing the 400 MHz ^{1}H-NMR spectra with those of authentic material. Lactiflorenol was identified by rigorous ^{1}H-NMR studies.

Dehydrochromolaenin (**1**)

MS: *m/z* (rel. int., %) = 220.104 (100) [M^+, calc for $C_{15}H_{14}O$: 220.104]; ^{1}H-NMR spectrum identical with that of the dehydrogenation product of chromolaenin.

7,7-Dihydroxycalamen-12-oic acid lactone (**2**)

Colourless oil; MS: *m/z* (rel. int., %) = 244.110 (37) [M^+, calc for $C_{15}H_{16}O_3$: 244.110], 226 (75) [$M-H_2O$], 211 (100) [226 – Me], 199 (48), 183 (23), 171 (42).

7-Hydroxy-7-methoxycalamen-12-oic acid lactone (**3**)

Colourless oil; MS: *m/z* (rel. int., %) = 258.126 (20) [M^+, calc for $C_{16}H_{18}O_3$: 258.126], 227 (39) [M – OMe], 226 (100) [M – MeOH], 211 (98) [226 – Me], 199 (44), 183 (22), 171 (40).

Tetradehydrochromoarnottione (**4**)
Colourless oil; IR: 3500–2700, 1630 (O-hydroxy ketone); MS: *m/z* (rel. int., %) = 214.099 (42) [M^+, calc for $C_{14}H_{14}O_2$: 214.099], 199 (100) [$M-H_2O$], 171 (6) [199 − CO].

10-*Oxo-isodauc-3-en-15-al* (**6**)
Colourless oil; IR: 2720, 1690 (C=CCHO), 1710 (C=O); MS: *m/z* (rel. int., %) = 234.162 (42) [M^+, calc for $C_{15}H_{22}O_2$: 234.162], 219 (10) [M − Me], 191 (100) [$M-C_3H_7$], 163 (45) [191 − CO], 151 (78) [$M-C_6H_{11}$], 123 (75) [151 − CO], 81 (69).

10α-*Hydroxyisodauc-3-en-15-al* (**7**)
Colourless oil; IR: 3600 (OH), 2720, 1700 (C=CCHO); MS: *m/z* (rel. int., %) = 236.178 (16) [M^+, calc for $C_{15}H_{24}O_2$: 236.178], 218 (15) [$M-H_2O$], 193 (70) [$M-C_3H_7$], 175 (52) [193 − H_2O], 147 (36) [175 − CO], 123 (94) [C_9H_{15}], 81 (100) [C_6H_9].

Chromolaevane dione (**9**)
Colourless oil; IR: 1730 (C=O); MS: *m/z* (rel. int., %) = 222.161 (7) [M^+, calc for $C_{14}H_{22}O_2$: 222.162), 179 (88) [$M-C_3H_7$], 164 (19) [179 − Me], 122 (61) [179 − CH_2COMe], 79 (100) [C_6H_7]; CIMS: 223 (51) [M + 1], 151 (100) [M + 1-MeCOEt]; ^{13}C-NMR ($CDCl_3$) (C-1–C-14): 24.9 t, 32.8 t, 208.6 s, 34.4 d, 29.9 d, 31.1 d, 22.9 t, 41.7 t, 205.6 s, 27.8 d, 31.1 d, 19.5 and 19.2 q, 30.0 q (assigned by comparing with signals of similar compounds).

6α-*Isobutyryloxy-7β-acetoxy-13-Z-kolavenic acid* (**10**)
Colourless oil; IR: 3600–2700, 1720, 1650 (C=CCO_2H), 1740, 1250 (OAc, CO_2R); MS: *m/z* (rel. int., %): 430 (4) [M − H_2O], 388.261 (6) [M − HOAc, calc for $C_{19}H_{30}O_4$: 388.261], 300 (62) [388 − Me_2CHCO_2H], 285 (4) [300 − Me], 187 (100) [300 − $CH_2CH_2C(Me)CHCO_2H$], 71 (52) [C_3H_7CO]. Addition of CH_2N_2 gave the methyl ester **10a**, colourless oil, ^{1}H-NMR, Table 3.

6α-*Angeloyloxy-7β-acetoxy-13Z-kolavenic acid* (**11**)
Colourless oil; IR: 3500–2700, 1720 (C=CCO_2H, C=CCO_2R), 1740 (OAc); MS: *m/z* (rel. int., %) = 460 (1) [M^+], 442 (5) [$M-H_2O$], 400.261 [M − HOAc, calc for $C_{25}H_{36}O_4$: 400.261], 300 (83) [400 − HOAng], 285 (20) [300 − Me], 201 (46) [300 − $CH_2C(Me)$=$CHCO_2H$], 187 (90) [300 − $CH_2CHC(Me)$=$CHCO_2H$], 83 (96) [C_4H_7CO], 55 (100) [83 − CO].

6α,7β-*Diacetoxy-13Z-kolavenic acid* (**12**)
Colourless oil; IR: 3500–2700, 1705, 1640 (C=CCO_2H), 1745, 1250 (OAc); MS: *m/z* (rel. int., %) = 420 (0.3) [M^+], 402 (4) [$M-H_2O$], 360.230 (4) [M − HOAc, calc for $C_{22}H_{32}O_4$: 360.230], 300 (44) [360 − HOAc], 285 (9) [300 − Me], 201 (40) [300 − $CH_2C(Me)$=$CHCO_2H$], 187 (100) [300 − $CH_2CHC(Me)$=$CHCO_2H$].

Methyl-6α,7β-dihydroxy-2-oxo-13E-kolavenoate (**13a**)
Colourless oil; MS: *m/z* (rel. int., %) = 364.225 (37) [M^+, calc for $C_{21}H_{32}O_5$: 364.225], 332 (18) [M − MeOH], 317 (10) [332 − Me], 299 (11) [317 − H_2O], 238 (23) [$M-C_7H_{10}O_2$], 95 (100) [C_6H_7O].

6α-*Isobutyryloxy-7β-angeloyloxy-13,14-dihydrokolavenic acid* (**14**)
Colourless oil; IR: 3500–2700, 1720 (CO_2H), 1740 (CO_2R), 1720, 1650 (C=CCO_2R); MS: *m/z* (rel. int., %) = 490.329 (1) [M^+, calc for $C_{29}H_{46}O_6$: 490.329], 402 (5) [$M-Me_2CHCO_2H$], 390 (6) [M − HOAng], 302 (78) [402 − HOAng], 287 (19) [302 − Me], 187 (94) [302 − $CH_2CH_2CHMeCH_2CO_2H$], 83 (100) [C_4H_7CO], 55 (74) [83 − CO].

6α,7β-*Dihydroxy-norkolavenic acid* (**15**)
Colourless oil; IR: 3500–2700, 1720 (CO_2H); MS: *m/z* (rel. int., %) = 282.183 (8) [M^+, calc for $C_{16}H_{26}O_4$: 282.183], 264 (3) [$M-H_2O$], 246 (21) [264 − H_2O], 187 (27) [246 − CH_2CO_2H], 95 (72), 81 (78), 55 (100).

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REFERENCES

[1] F. Bohlmann, P. Singh, J. Jakupovic, R. M. King and H. Robinson, *Phytochemistry* **21**, 371 (1982), and refs cited.
[2] F. Bohlmann and C. Zdero, *Chem. Ber.* **110**, 487 (1977).
[3] A. Braga de Oliveira, G. G. de Oliveira, R. Carazza, R. Braz Filho, C. T. Moreira Bacha, L. Bauer, G. A. de A. B. Silva and N. C. S. Siqueira, *Tetrahedron Letters* 2653 (1978).
[4] F. Bohlmann, C. Zdero, R. M. King and H. Robinson, *Phytochemistry* **18**, 1177 (1979).
[5] T. Yoshida, S. Muraki, K. Takahashi, T. Kato, C. Kabuto, T. Suzuki, T. Uyehara and T. Ohnuma, *J. Chem. Soc. Chem. Commun.* 512 (1979).
[6] J. C. Rees and D. Whittaker, *Org. Magn. Res.* **15**, 363 (1981).
[7] T. Hudlicky, F. J. Koszyk, T. M. Kutchan and J. P. Sheth, *J. Org. Chem.* **45**, 5020 (1980).
[8] F. Bohlmann and M. Lonitz, *Phytochemistry* **17**, 453 (1978).
[9] C. Xu, X. Zeng, Q. Zhang and Y. Zhau, *Zhongcaoyao* **13**, 529 (1982).