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SESQUITERPENE LACTONES FROM *NEUROLAENA LOBATA**

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Key Word Index—*Neurolaena lobata*; Asteraceae; Heliantheae; Galinsoginae; sesquiterpene lactones; germacranolides; furanoheliangolides; neurolenins; lobatins.

Abstract—Eleven sesquiterpene lactones were isolated from above ground organs of *Neurolaena lobata*, obtained from Guatemala. Their structures were established by NMR spectroscopic methods, including 2D-NMR, as well as GC-MS analysis. Differences in the sesquiterpene lactone pattern and content in plants of different geographical origin is discussed.

INTRODUCTION

Neurolaena lobata (L.) R.Br. is a widespread Central American plant, which occurs throughout much of northwestern South America, through Central America into southern Mexico and throughout most of the Caribbean islands [1]. The placement of the tropical genus Neurolaena within the Asteraceae has been the subject of considerable discussion. In proposing the genus R. Brown (1817) considered its relationship to be with, or near *Calea* (tribe Heliantheae, subtribe Galinsoginae). Later Stuessy [2] and Robinson [3] in a first revision recognized *Neurolaena* and related genera as constituents of a new subtribe Neuroleninae, whereas Turner [1], after studying several members of the genus *Neurolaena* in greater detail, placed *Neurolaena* in the subtribe Galinsoginae (Heliantheae).

The caribs of Guatemala use *N. lobata* as a remedy against several diseases, including malaria, stomach pains, diabetes and skin diseases [4]. Furthermore, it is used by some ethnic groups in the Antilles for the treatment of cancer [5].

Up to now, the germacranolide sesquiterpene lactones neurolenin A (**1**) and neurolenin B (**2**) were isolated as the main constituents from *N. lobata* collected in Trinidad [6], whereas Borges del Castillo *et al.* [7] found beside **2** the new germacranolide lobatin A (**7**) as well as the furanoheliangolide lobatin B (**8**) in plants collected in Panama. Interestingly, the main compound **1** in plants from Trinidad was missing in this collection. Furthermore, 12 flavonoids were described by Kerr *et al.* [8] and Bohlmann *et al.* [9] reported thymol derivatives from roots of *N. lobata*.

The present paper deals with the isolation and structure elucidation of seven further sesquiterpene lactones, the germacranolides **3**–**6** and the furanoheliangolides **9**–**11** from above ground organs of *N. lobata*, grown in Guatemala. Owing to the incomplete NMR data of **2**, **7** and **8** [6, 7] we herein give the complete and in certain details revised data, confirmed by 2D-COSY, 2D-HMQC, 2D-HETCOR and ^{13}C-DEPT experiments.

RESULTS AND DISCUSSION

The dichloromethane extract of *N. lobata* was purified by CC on a Sephadex LH 20 column to give two fractions rich in sesquiterpene lactones. Further purification afforded neurolenin B (**2**) [6, 10] as the main constituent. Its complete NMR data are given in Tables 1 and 2, additionally confirmed by 2D-COSY, 2D-HETCOR and DEPT-135 experiments for the first time. Compared to the assignments made by Herz [10], the data only require an exchange of the assignments for the carbonyl-carbon shifts of the lactone moiety (C-12) and the carbonyl carbon (C-1″) of the acetate.

Neurolenin A (**1**), isolated from plants, collected in Trinidad [6], as the main constituent, could be detected only in traces. Its identity was established by TLC, GC and GC-MS analysis in direct comparison with an authentic sample of neurolenin A.

Further TLC studies, showed the same fraction to contain two relatively more hydrophilic compounds **3** and **4**, which both also gave brown coloured reaction products after treatment with anisaldehyde–H_2SO_4. It was not possible to separate them, therefore structure elucidation was made with the mixture. In comparison to

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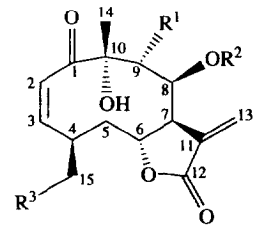
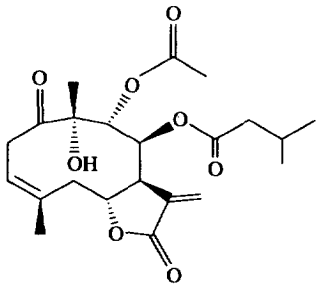


	R^1	R^2	R^3
1	H	ival	H
2	Oac	ival	H
3	Oival	H	H
4	OH	ival	H
5	Oac	ival	OH
6	Oac	5-OH-tig or 5-OH-ang	H



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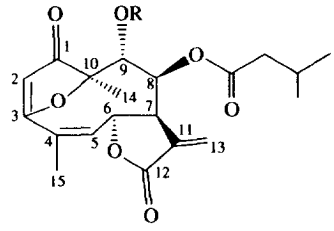
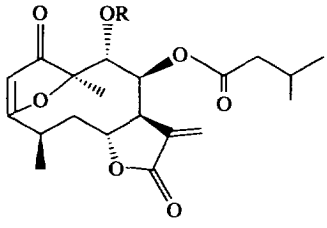


R	
8	H
9	ac



R	
10	H
11	ac

2 the mass spectrum of **3** and **4** showed a similar fragmentation pattern, but the molecular ion at *m/z* 380 indicated the absence of the acetyl group. In accordance with this the NMR spectra showed in comparison to **2** the absence of the signals for the acetyl ester group for both compounds and in agreement with this the ^{13}C NMR spectrum of the mixture, displayed the signals of a hydroxylated methine carbon at δ 74.1 (C-8 of **3**) and a further hydroxylated methine carbon at 74.7 (C-9 of **4**). In the ^1H NMR spectrum the signals for the corresponding protons were located at δ 3.99 (H-8 of **3**) and 3.82 (H-9 of **4**), which clearly showed the presence of a free OH-group at C-8 (**3**) or C-9 (**4**), respectively. Therefore, both compounds were isomeric isovalerianyl esters, differing only in the position of the ester group, for which we propose the names neurolenin C (**3**) and neurolenin D (**4**). The complete assignments of the ^1H and ^{13}C NMR signals of these new compounds were made by analysis of the DEPT-135, 2D-COSY and 2D-HMQC spectra in view of the different content of **3** and **4** in the mixture.

Besides **1**–**4** traces of **5** and **6** were detected and identified by GC-MS analysis (GC: R_t 13.3 and 13.05 min, respectively). Their fragmentation pattern was similar to that of **2**. Compound **5** ($[M]^+$ at *m/z* 438) showed characteristic fragment ions at *m/z* 396 $[M - CH_2CO]^+$, 378 $[M - MeCO_2H]^+$, 354 $[M - C_4H_8CO]^+$, 336 $[M - C_4H_9CO_2H]^+$ and 294 $[M - (C_4H_9COOH + CH_2CO)]^+$ owing to the presence of an acetyl- and a valerianoyl-moiety. The molecular ion at *m/z* 438 and the fragmentation pattern clearly indicated the presence of a CH_2OH-group at C-4. The mass spectrum of **6** ($[M]^+$ at *m/z* 436) was also similar to those of **2**–**5**. The main differences were the presence of three intensive fragment ions at *m/z* 99 $[Me - CH{=}C(CH_2OH)CO]^+$, 82 [99 – OH] and 71 [99 – CO]$^+$, which are characteristic for a hydroxytigloyl- or hydroxyangeloyl-ester group [11]. The molecular ion at *m/z* 436, and fragment ions, detected at *m/z* 394 $[M - CH_2CO]^+$, 338 $[M - C_4H_5(OH)CO]^+$ and 296 $[M - (CH_2CO + C_4H_5(OH)CO)]^+$ were in agreement with the presence of

Table 1. ^{13}C NMR data of isolated compounds (125 MHz, $CDCl_3$, TMS as int. standard)*

C	2	3	4	7	8	10
1	204.7 *s*	204.2 *s*	204.4 *s*	210.6 *s*	203.9 *s*	204.3 *s*
2	125.4 *d*	124.4 *d*	124.2 *d*	36.0 *t*	104.2 *d*	103.7 *d*
3	148.2 *d*	147.0 *d*	147.2 *d*	121.4 *d*	185.7 *s*	193.1 *s*
4	28.3 *d*	27.3 *d*	27.0 *d*	136.8 *s*	131.4 *s*	31.4 *d*
5	40.3 *t*	39.3 *t*	39.3 *t*	42.9 *t*	134.3 *d*	40.9 *t*
6	76.4 *d*	75.5 *d*	75.5 *d*	72.5 *d*	73.4 *d*	72.9 *s*
7	41.3 *d*	41.4 *d*	40.7 *d*	42.1 *t*	44.1 *d*	45.8 *d*
8	74.0 *d*	74.1 *d*	76.4 *d*	76.6 *d*	77.2 *d*	77.4 *d*
9	73.9 *d*	75.3 *d*	74.7 *d*	76.6 *d*	75.2 *d*	74.6 *d*
10	79.4 *s*	78.4 *s*	80.0 *s*	80.5 *s*	89.8 *s*	91.0 *s*
11	134.9 *s*	136.6 *s*	134.7 *s*	134.3 *s*	139.1 *s*	139.9 *s*
12	168.7 *s*	168.8 *s*	168.1 *s*	168.3 *s*	168.6 *s*	168.8 *s*
13	126.5 *t*	122.8 *t*	124.5 *t*	124.4 *t*	124.6 *t*	123.9 *t*
14	23.7 *q*	24.6 *q*	24.4 *q*	25.5 *q*	19.6 *q*	18.8 *q*
15	19.7 *q*	18.7 *q*	18.7 *q*	22.5 *q*	17.7 *q*	16.2 *q*
1′	171.1 *s*	172.0 *s*	172.6 *s*	170.5 *s*	171.4 *s*	171.6 *s*
2′	42.6 *t*	42.0 *t*	42.0 *t*	42.1 *t*	42.8 *t*	42.8 *t*
3′	24.9 *d*	24.6 *d*	24.4 *d*	25.4 *d*	25.3 *d*	25.2 *d*
4′	22.3 *q*	21.3 *q*	21.2 *q*	22.3 *q*	22.2 *q*	22.3 *q*
5′	22.3 *q*	21.4 *q*	21.4 *q*	22.3 *q*	22.3 *q*	22.4 *q*
1″	170.3 *s*	—	—	170.8 *s*	—	—
2″	20.6 *q*	—	—	20.5 *q*	—	—

*Multiplicities were determined by ^{13}C-DEPT technique.

an acetyl and hydroxytigloyl- or hydroxyangeloyl ester group. Both characterized compounds are new natural products, to the best of our knowledge. Referring to the literature [6], we propose the names neurolenin E (**5**) and F (**6**).

Additionally, the already known compounds lobatin A (**7**) and lobatin B (**8**), first isolated by Borges del Castillo *et al.* [7] from *N. lobata* leaves, collected in Panama, were isolated. The complete NMR data, including ^{13}C NMR, confirmed by 2D-COSY and DEPT-135 experiments, are given in Tables 1–3. Traces of compound **9** were detected by GC-MS analysis (R_t 13.02 min; $[M]^+$ at *m/z* 418) and identified as an 8-*O*-acetyl derivative of **8** (= lobatin C).

The mass spectra of the isolated new compounds **10** and **11** showed molecular ions at *m/z* 378 and 420, two mass units higher than seen in **8** and **9**. The fragmentation indicated the presence of a saturated C_5-acid ester in both compounds, and for **11** additional fragments owing to the loss of an acetyl group. Thus, these compounds should be the dihydro-derivatives of **8** and **9**, respectively. As expected, the ^1H NMR spectra of both compounds displayed the signals for an isovalerianyl ester group and an additional *O*-acetyl group for **11**. In comparison to **8** the signals of H-5 and H-6 at δ5.98 and 5.33 were shifted to δ2.60 (H-5a), 2.06 (H-5b) and 4.49 (H-6), owing to the hydrogenation of the $\Delta^{4,5}$-double bond. This was also evident from the signals of H-4 and H-15, which were seen as a multiplet at δ3.04 and as a three proton doublet at δ1.40. The chemical shifts for H-8 and H-9 of **10** at δ4.12 and 5.08, respectively, corresponded to those of **8**. The esterification of the hydroxyl group at C-9 in **11** follows from the downfield shift of H-9 to δ5.32, compared to **8** and **10**. Furanoheliangolides with the carbon skeleton of **10** and **11** and various other ester derivatives were previously found in *Calea* species [10, 12–14]. The isovalerates **10** (8β-isovalerianyloxy-9α-hydroxy-calyculatolide) and **11** (8β-isovalerianyloxy-9α-acetoxy-calyculatolide) are new natural compounds to the best of our knowledge.

The sesquiterpene lactones of *N. lobata*, isolated so far, clearly show its relation to the well known large genus

Table 2. ^1H NMR spectral data of isolated compounds (500 MHz, $CDCl_3$, TMS as int. standard)

H	2	3	4	7	8	10	11
2	6.59 *d*	6.52 *d*	6.44 *d*	3.57 *dd* 3.07 *dd*	5.63 *s*	5.58 *s*	5.60
3	6.00 *t*	5.92 *t*	5.87 *t*	5.90 *t*	—	—	—
4	3.11 *m*	3.02 *m*	3.11 *m*	—	—	3.04 *m*	3.05 *m*
5a	1.83 *ddd*	1.77 *ddd*	1.73 *ddd*	2.83 *dd*	5.98 *m*	2.60 *m*	2.59 *m*
5b	1.42 *ddd*	1.37 *ddd*	1.34 *ddd*	2.74 *dd*	—	2.06 *dd*	2.06 *dd*
6	4.56 *dd*	4.42 *dd*	4.38 *dd*	4.92 *ddd*	5.33 *m*	4.49 *dd* (*br*)	4.39 *dd* (*br*)
7	2.58 *s*	2.43 *d*	2.56 *d*	2.62 *m*	3.83 *m*	3.63 *m*	3.53 *m*
8	5.55 *d**	3.99 *dd*	5.24 *dd*	5.86 *dd*	5.10 *dd*	5.08 *d*	5.02 *d*
9	5.55 *d**	5.40 *d*	3.82 *d*	5.66 *d*	4.04 *d*	4.12 *d*	5.32 *d*
13a	6.31 *s* (*br*)	6.25 *s* (*br*)	6.21 *s* (*br*)	6.31 *d*	6.36 *d*	6.34 *d*	6.33 *d*
13b	5.81 *s* (*br*)	5.64 *d*	5.69 *d*	5.69 *d*	5.75 *d*	5.74 *d*	5.47 *d*
14	1.33 *s*	1.26 *s*	1.45 *s*	1.33 *s*	1.56 *s*	1.49 *s*	1.36 *s*
15	1.14 *d*	1.06 *d*	1.06 *d*	1.85 *s*	2.07 *d*	1.40 *d*	1.40 *d*
2′a	2.09–	2.26 *m*	2.07 *m*	2.11 *m*	2.13 *m*	2.11 *m*	2.08 *m*
2′b	1.96 *m*	2.26 *m*	2.07 *m*	2.06 *m*	2.13 *m*	2.09 *m*	2.08 *m*
3′	1.95 *m*	2.05 *m*	1.98 *m*	1.96 *m*	2.00 *m*	1.98 *m*	1.99 *m*
4′	0.87 *d*	0.92 *d*	0.85 *d*	0.88 *d*	0.91 *d*	0.91 *d*	0.91 *d*
5′	0.87 *d*	0.91 *d*	0.85 *d*	0.86 *d*	0.89 *d*	0.90 *d*	0.89 *d*
2″	2.10 *s*	—	—	2.15 *s*	—	—	2.25 *s*

*Centre of an AB-system.

Table 3. Coupling constants J (Hz) of isolated compounds

H	2	3	4	7	8	10	11
2a, 2b				15.89			
2, 3	11.8	11.8	11.9				
2a, 3				9.58			
2b, 3				8.13			
3, 4	11.5	11.5	11.5				
4, 15	6.28	6.28	6.3			7.0	7.0
4, 5a	12.0	12.0	11.9				
4, 5b	5.4	5.4	5.4				
5a, 5b	13.7	13.5	13.3	15.13			
5a, 6	4.8	4.9	4.9	3.59			
5b, 6	12.1	11.8	11.8	4.19			
8, 9	10.0	9.4	9.5	10.5	5.0	5.0	5.0
7, 8			1.6	1.35	1.5		
7, 13a		0.98	1.0	3.27		3.0	3.0
7, 13b				2.88		2.5	3.0
3', (4', 5')	6.0	6.8	6.5	6.74	6.3	6.6	6.5

Calea (Galinsoginae). As in *Calea* [15], we have found sesquiterpene lactones with furanoheliangolide and germacranolide structures, which supports the placement of the genus Neurolaena in the subtribe Galinsoginae [1].

Interestingly, *N. lobata* plants of different geographical origin show some qualitative and quantitative variations in their sesquiterpene lactone content. Whereas neurolenin A (**1**) is the major compound in plants from Trinidad [6], we only found this compound in traces in our plants of Guatemalean origin and it is obviously lacking in plants from Panama. [7]. Therefore, *N. lobata* seems to be a species, which shows an infraspecific variability in its sesquiterpene lactone pattern, as described for many other widely distributed species of the Asteraceae [16–20].

EXPERIMENTAL

Plant material. Neurolaena lobata (L.) R. Br. was collected near San Pedro Carchá, Alta Verapaz (1090 m), Guatemala at flowering stage and air-dried, vouchers are on deposit at the herbarium of the Universidad del Valle de Guatemala and at the Institut für Pharmazeutische Biologie, Heinrich-Heine-Universität Düsseldorf (Reg. No. 143).

Extraction and isolation. Ground material (1.35 kg) was extracted with CH_2Cl_2 in a Soxhlet apparatus. Evapn of the solvent *in vacuo* gave 75 g crude extract. A portion of this extract (30 g) was separated by CC on Sephadex LH 20 (Pharmacia) with MeOH to give 10 fractions (TLC controlled, toluene–EtOAc, 3:2). Fr. 3 (8.3 g) was chromatographed on a silica gel 60 column with toluene–EtOAc (6:4) to give 17 fractions. Further purification by prep. TLC or MPLC gave pure, crystalline **2** (260 mg), an inseparable mixture of **3** and **4** (68 mg), 3 mg **7**, 6 mg **8**, 5 mg **10** and 6 mg **11**.

NMR: Bruker AMX 500, 500 MHz (^{1}H NMR) and 125 MHz (^{13}C NMR) in $CDCl_3$, TMS as int. standard. MS: EI (70 eV) on Varian MAT CH7A using GC-MS combined with gas chromatograph Varian 2700 and MAT 1020 automated GC-MS. GC: column OV-01, 25 m × 0.25 mm. Temp. prog. 150° to 270° at 10° min^{-1} Inj./det. temp. 300°. Carrier N_2 at 1.3 ml min^{-1}. R_t (min): **1**: 12.84; **2**: 12.7; **3** and **4**: decomp.; **5**: 13.3; **6**: 13.05; **7**: 12.59; **8**: 12.08; **9**: 13.02; **10**: 11.58; **11**: 13.29. TLC: silica gel 60 F_{254}, toluene–EtOAc (3:2). Detection anisaldehyde–H_2SO_4. R_f: **1**: 0.58; **2**: 0.53; **3**: 0.42; **4**: 0.29; **5**: n.d.; **6**: 0.54; **7**: 0.39; **8**: 0.38; **9**: n.d.; **10**: 0.31; **11**: 0.49. MPLC: Knaur HPLC system (flow 5 ml min^{-1}), RP 18 silica gel column (Lichroprep 25–40 μm). Solvent system: MeOH–H_2O, 2:3 (10 min hold) to 1:1 in 20 min. HPLC: Hewlett Packard 1050 system, with UV detection at 225 nm, RP 18 (5 μm) silica gel column (12.5 cm × 5 mm), flow 1.8 ml min^{-1}. Solvent system: MeOH–H_2O (9:11). R_t (min): **1**: 15.31; **2**: 14.43; **3**: 7.49; **4**: 5.66; **5**: n.d.; **6**: n.d.; **7**: 19.26; **8**: 11.64; **9**: n.d.; **10**: 8.11; **11**: n.d.

Compound **1** (*neurolenin A*): $C_{20}H_{28}O_6$, MS *m/z* (rel. int.): 364 $[M]^+$ (1); 346 $[M - H_2O]^+$ (2); 280 $[M - C_4H_8CO]^+$ (3); 262 $[M - (C_4H_9COOH)]^+$ (3); 234 (5); 216 (10); 201 (18); 191 (12); 173 (20); 159 (14); 147 (29); 145 (30); 131 (21); 123 (37); 111 (50); 109 (53); 98 (82); 85 $[C_4H_9CO]^+$ (71); 66 (51); 57 $[85 - CO]^+$ (79); 43 (100).

Compound **2** (*neurolenin B*). $C_{22}H_{30}O_8$, white crystals, mp 157°; UV λ_{max}^{MeOH} nm: 212; MS *m/z* (rel. int.): 422 $[M]^+$ (1); 380 $[M - CH_2CO]^+$ (12); 362 $[M - HOAc]^+$ (5); 338 $[M - C_4H_8CO]^+$ (20); 320 (10); 278 (8); 250 (5); 235 (4); 217 (4); 207 (3); 189 (5); 165 (5); 149 (4); 125 (4); 111 (7); 97 (6); 85 $[C_4H_9CO]^+$ (45); 83 (35); 69 (13); 57 (55); 55 (18); 43 (100).

Compound **3** (*neurolenin C*) *and* **4** (*neurolenin D*). $C_{20}H_{28}O_7$, crystalline mixture, mp 78°; UV λ_{max}^{MeOH} nm: 212; MS 70 eV (direct inlet) *m/z* (rel. int.): 380 $[M]^+$ (1); 296 $[M - C_4H_8CO]^+$ (15); 235 (10); 193 (15); 111 (20); 85 $[C_4H_9CO]^+$ (50); 57 (55); 43 (100).

Compound **5** (*neurolenin E*). $C_{22}H_{30}O_9$, MS *m/z* (rel. int.): 438 $[M]^+$ (1); 420 $[M - H_2O]^+$ (1);

396 $[M - CH_2CO]^+$ (11); 378 $[M - MeCO_2H]^+$ (1); 354 $[M - C_4H_8CO]^+$ (1); 336 $[M - C_4H_9CO_2H]^+$ (5); 312 $[M - (C_4H_8CO + CH_2CO)]^+$ (7); 294 $[M - (C_4H_9COOH + CH_2CO)]^+$ (4); 278 (2); 265 (3); 248 (2); 236 (7); 223 (5); 206 (12); 190 (3); 180 (15); 163 (5); 153 (5); 138 (10); 125 (12); 111 (5); 100 (12); 95 (10); 85 $[C_4H_9CO]^+$ (71); 71 (18); 57 (69); 55 (12); 43 $[MeCO]^+$ (100).

Compound **6** (*neurolenin F*). $C_{22}H_{28}O_9$, MS *m/z* (rel. int.): 436 $[M]^+$ (1); 394 $[M - CH_2CO]^+$ (1); 338 $[M - C_4H_5(OH)CO]^+$ (2); 320 (1); 296 $[M - CH_2CO + C_4H_5(OH)CO]^+$ (2); 278 (8); 260 (4); 250 (6); 235 (4); 217 (7); 207 (3); 193 (5); 189 (5); 179 (5); 175 (4); 165 (4); 149 (5); 125 (4); 111 (10); 99 $[Me - CH = C(CH_2OH)CO]^+$ (48); 82 $[99 - OH]^+$ (32); 71 $[99 - CO]^+$ (41); 55(15); 43 $[MeCO]^+$ (100).

Compound **7** (*lobatin A*). $C_{22}H_{30}O_8$, gum, UV λ_{max}^{MeOH} nm: 209.

Compound **8** (*lobatin B*). $C_{20}H_{24}O_7$, gum, UV λ_{max}^{MeOH} nm: 210, 263.

Compound **9** (*lobatin C*). $C_{22}H_{26}O_8$, MS *m/z* (rel. int.): 418 $[M]^+$ (4); 376 $[M - CH_2CO]^+$ (3); 355 (2); 336 (4); 334 $[M - C_4H_8CO]^+$ (3); 318 (2); 294 (3); 275 (10); 246 (2); 233 (13); 221 (2); 203 (3); 180 (2); 151 (3); 138 (35); 125 (26); 111 (4); 92 (3); 85 $[C_4H_9CO]^+$ (62); 69 (23); 57 (77); 43 $[CH_3CO]^+$ (100).

Compound **10** (*8β-isovalerianyloxy-9α-hydroxy-calyculatolide*). $C_{20}H_{26}O_7$, gum, UV λ_{max}^{MeOH} nm: 210, 256; MS *m/z* (rel. int.): 378 $[M]^+$ (1); 350 (3); 294 $[M - C_4H_8CO]^+$ (1); 277 (1); 276 (1); 259 (2); 248 (15); 233 (3); 219 (5); 206 (21); 194 (31); 175 (35); 161 (38); 147 (23); 133 (21); 119 (13); 108 (17); 105 (15); 91 (17); 85 $[C_4H_9CO]^+$ (71); 79 (10); 77 (11); 69 (12); 57 $[C_4H_9]^+$ (88); 43 (100).

Compound **11** (*8β-isovalerianyloxy-9α-acetoxy-calyculatolide*). $C_{22}H_{28}O_8$, MS *m/z* (rel. int.): 420 $[M]^+$ (1); 378 $[M - CH_2CO]^+$ (12); 360 $[M - MeCO_2H]^+$ (5); 336 $[M - C_4H_8CO]^+$ (6); 328 $[M - C_4H_9CO_2H]^+$ (4); 294 $[M - (C_4H_8CO + CH_2CO)]^+$ (13); 277 (26); 255 (4); 249 (5); 236 (9); 230 (5); 216 (6); 203 (2); 180 (4); 167 (8); 151 (11); 138 (14); 125 (100); 111 (7); 91 (4); 85 $[C_4H_9CO]^+$ (38); 69 (13); 57 $[C_4H_9]^+$ (58); 43 $[MeCO]^+$ (82).

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