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HOMOGERANYL NEROL DERIVATIVES AND A MELAMPOLIDE FROM *SMALLANTHUS GLABRATUS*

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Key Word Index—*Smallanthus glabratus*; Compositae; sesquiterpene lactones; melampolides; diterpenes; geranyl nerol derivatives; homoditerpenes.

Abstract—The investigation of the aerial parts of *Smallanthus glabratus* from two locations afforded the same known compounds but some additional new compounds which were not present in both collections. From the first location typical melampolides, one of them not isolated previously, and two homoditerpenes were isolated. The material from the second location gave four closely related homoditerpenes and two geranyl nerol derivatives from which the homoditerpenes were derived. The structures were elucidated by high field ^{1}H NMR spectroscopy. Chemotaxonomic aspects are discussed briefly.

INTRODUCTION

The re-established genus *Smallanthus* (Compositae, tribe Heliantheae, subtribe Melampodiinae) [1] is chemically characterized by the occurrence of *ent*-kaurene derivatives and melampolides which have been isolated so far from five species [2–7]. The only two species still representing the genus *Polymnia* [1], however, lack melampolides [2, 8] but do contain *ent*-kaurene derivatives [8]. From one species so far no melampolides are reported [9]. We now have studied a further species from Peru, which gave acyclic diterpenes including several homoditerpenes and one new melampolide. The results are discussed in this paper.

RESULTS AND DISCUSSION

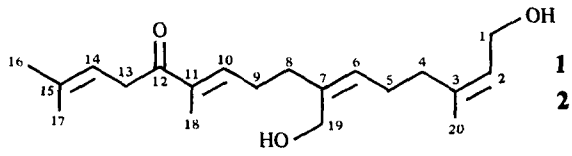
The aerial parts of two collections in Peru from *Smallanthus glabratus* (DC.) H. Robins. (= *Polymnia glabrata* DC.) afforded germacrene D, *ent*-kaurenal, *ent*-kaurenic acid, 18-angeloyloxy- and senecioyloxy-*ent*-kaurenic acid [6] and sakuranetin [10]. One of the collections contained also borneyl ferulate [11], the homo diterpenes **7** and **8**, the acanthospermolide **9** as well as the corresponding angelate [12]. From the second collection no lactones were obtained. However, in addition to two geranyl nerol derivatives (**1** and **2**) also four homo diterpenes (**3**–**6**) were present which were closely related to **7** and **8**. Furthermore 1α,2β-dihydroxy-α-phellandrene and phenylethyl cinnamate [9] was isolated.

The structure of **9**, which could not be separated by HPLC from the corresponding angelate but finally was obtained pure by repeated TLC, could be deduced from the ^{1}H NMR spectrum (Table 1) which was close to that of the corresponding angelate [12]. However, some protons showed small shift differences obviously due to the nature of the ester residue at C-8. The configuration of the 1(10)-double bond followed from the chemical shift of H-14 and the stereochemistry at C-6–C-8 could be deduced from the couplings. All signals were assigned by spin decoupling.

The diterpene **1** showed no molecular ion in the mass spectrum. However, by chemical ionization the ion $M+1-H_2O$ was the base peak. As from the ^{1}H NMR spectrum (Table 1) it clearly followed that two hydroxy groups were present; the molecular formula could be assigned indirectly. The structure and the stereochemistry was deduced from the ^{1}H NMR spectral data and by spin decoupling, which allowed the assignment of all signals. The position of the oxygen functions also followed from spin decoupling and from the chemical shifts. As the signal at δ 6.60 was that of a proton in β-position to the conjugated ketone and as the broadened doublet (2H) at δ 3.36 could only be assigned to the methylene group α to the keto group, the position of this group could be deduced from the fact that both methyl signals (H-16 and H-17) were coupled with the broadened triplet at δ 5.29 which itself was coupled with the doublet at δ 3.36. Accordingly, the two primary hydroxy groups could only be placed at C-1 and C-19. The configuration of the Δ^2 and Δ^6 double bond could be deduced by comparison of the chemical shifts with those of similar compounds; similarly that of the Δ^{10} bond followed from the chemical shift of H-10.

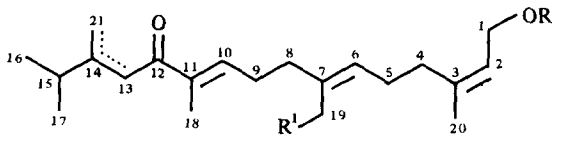
If the ^{1}H NMR spectrum of **2** (Table 1) was compared with that of **1** it was obvious that this diterpene was the 6,7-epoxide of **1**. Accordingly, the H-6 signal now was shifted upfield (δ2.89 *dd*) and the H-19 signal was replaced by a pair of doublets, their chemical shifts also indicating that this methylol group now was no longer allylic. As all the other signals except those for H-5 and H-8 were nearly identical with those of **1**, the stereochemistry also was the same as that of **1** The configuration of the epoxide centres could not be determined, but from biogenetic considerations the presence of a *trans*-epoxide was most likely.

The diol **3** also showed no molecular ion but a clear



1

2 6,7 – epoxide



3 Δ^{13E}, R = H, R^1 = OH

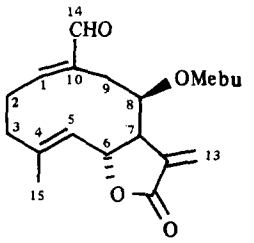
4 Δ^{13E}, R = H, R^1 = OH, 6,7 – epoxide

5 $\Delta^{14(21)}$, R = H, R^1 = OH

6 $\Delta^{14(21)}$, R = H, R^1 = OH, 6,7 – epoxide

7 Δ^{13E}, R = Ac, R^1 = H, 6,7 – epoxide, 10,11H

8 $\Delta^{14(21)}$, R = Ac, R^1 = H, 6,7 – epoxide, 10,11H



9

$[M-H_2O]$ ion (m/z 316 $C_{21}H_{32}O_2$) as well as a fragment m/z 305 $[M-CHO]$. Base peak was m/z 111 ($C_7H_{11}O$), most likely an acyl cation formed by splitting the 11,12-bond. The ^{1}H NMR spectrum (Table 1) was in part nearly identical with that of **1**. However, the signals of H-13, H-16, H-17 and an additional doublet at δ 1.98 (3H, J = 1.5 Hz) indicated a very different part of this diol in agreement with the mass spectrum. Spin decoupling allowed the assignment of all signals. As H-13 showed a small coupling with H-15 also the whole sequence could be established, thus indicating that we were dealing with a homo geranyl nerol derivative with an additional carbon at C-14 and a cross conjugated keto group which also followed from the IR band at 1660 cm^{-1}.

The similarity of the ^{1}H NMR spectra of **4** with that of **3** and in part with that of **2** (Table 1) indicated that **4** again was an epoxide. Accordingly, the molecular formula now was $C_{21}H_{34}O_4$ as shown by a weak molecular ion. High resolution of the larger $[M-H_2O]$ ion (m/z 332) corresponded with $C_{21}H_{32}O_3$. Spin decoupling allowed to establish this proposal as a sequence starting with the epoxide proton (H-6), the multiplet at δ 1.75 (H-5), the multiplets at δ 2.31 and 2.22 and the broadened triplet at δ 5.52 could be determined.

Inspection of the ^{1}H NMR spectrum of **5** (Table 1) showed that this compound again was similar to **3**. However, a changed position of one double bond was indicated by a pair of broadened singlets at δ 4.68 and 4.91. These signals obviously were due to a methylene group which replaced the Δ^{13} double bond of **3**. Accordingly, the methyl doublet at δ 1.98 and the broad singlet at δ 6.33 were missing. The broadened singlet at δ 3.38 (2H) was coupled with the methylene protons and a multiplet at δ 2.26 was due to H-15 as its irradiation collapsed the methyl doublet at δ 1.06 and sharpened the methylene singlets.

The ^{1}H NMR spectral data of **6** (Table 1) were in part nearly identical with those of **5** and **3**, indicating that a 6,7-epoxide of **5** was present. Again no molecular ion could be detected, but the $[M-H_2O]$ ion (m/z 332) agreed with the molecular formula $C_{21}H_{32}O_3 + H_2O = C_{21}H_{34}O_4$.

The ^{1}H NMR spectra of **7** and **8** (Table 1) clearly showed that these ketones were 1-*O*-acetates. Accordingly, the signals of H-1 were shifted downfield while H-2 showed a small upfield shift.

Several signals were similar to those of **4** and **6** but the spectrum differed by the absence of the low field signals at δ 6.50 and 6.62 respectively. Furthermore the olefinic methyl signal (H-18) was replaced by a methyl doublet, thus indicating the presence of 10,11-dihydro derivatives of **4** and **6**. Again all signals could be assigned by spin decoupling. However, the configuration at C-11 could not be determined.

The carbon skeleton of **3–8** we have named smallanthane. So far only one further derivative has been reported from a *Lasiolaena* species [13].

The configuration of 1α,2β-dihydroxy-α-phellandrene was established by synthesis via epoxidation of (–)α-

Table 1. ^{1}H NMR spectral data of **1–8** (400 MHz, $CDCl_3$, TMS as internal standard)

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
H-1	4.08 *br d*	4.15 *br dd*	4.08 *br d*	4.15 *br dd*	4.08 *br d*	4.15 *br dd*	4.61 *br dd*	4.61 *br dd*
H-1′		4.09 *br dd*		4.09 *br dd*		4.09 *br dd*	4.55 *br dd*	4.55 *br dd*
H-2	5.48 *br t*	5.52 *br t*	5.47 *br t*	5.52 *br t*	5.48 *br t*	5.52 *br t*	5.39 *br t*	5.39 *br t*
H-4	2.14 *br t*	2.31 *m*	2.14 *m*	2.31 *m*	2.14 *m*	2.32 *m*	2.27 *m*	2.27 *m*
H-4′		2.22 *m*		2.22 *m*		2.23 *m*		
H-5	2.20 *br dt*	1.75 *m*	2.19 *m*	1.75 *m*	2.20 *m*	1.75 *m*	1.75 *m*	1.75 *m*
H-6	5.34 *br t*	2.89 *dd*	5.33 *br t*	2.89 *dd*	5.33 *br t*	2.89 *dd*	2.83 *t*	2.83 *t*
H-8	2.28 *br t*	1.90 *m*	2.28 *br t*	1.90 *m*	2.28 *br t*	1.88 *dt*	1.60 *m*	1.60 *m*
						1.80 *dt*		
H-9	2.37 *br dt*	2.36 *dt*	2.37 *br dt*	2.34 *dt*	2.38 *br dt*	2.35 *dt*	1.30 *m*	1.30 *m*
H-10	6.60 *tq*	6.59 *tq*	6.53 *tq*	6.50 *tq*	6.64 *tq*	6.62 *tq*		
H-11	—	—	—	—	—	—	2.51 *tq*	2.66 *tq*
H-13	3.36 *br d*	3.36 *br d*	6.33 *br s*	6.34 *br s*	3.38 *br s*	3.38 *br s*	6.08 *br s*	3.17 *br s*
H-14	5.29 *br t*	5.29 *br t*	—	—	—	—	—	—
H-15	—	—	2.37 *m*	2.37 *m*	2.26 *m*	2.26 *m*	2.35 *br qq*	2.23 *m*
H-16	1.73 *br s*	1.73 *br s*	1.08 *d*	1.08 *d*	1.06 *d*	1.02 *d*	1.07 *d*	1.02 *d*
H-17	1.63 *br s*	1.63 *br s*						
H-18	1.78 *br s*	1.78 *br s*	1.81 *br s*	1.82 *br s*	1.78 *br s*	1.79 *br s*	1.07 *d*	1.08 *d*
H-19	4.12 *br s*	3.75 *d*	4.12 *br s*	3.75 *d*	4.12 *br s*	3.74 *d*	3.69 *br s*	3.68 *br s*
H-19′		3.69 *d*		3.70 *d*		3.68 *d*		
H-20	1.77 *br s*	1.77 *br s*	1.75 *br s*	1.77 *br s*	1.75 *br s*	1.77 *br s*	1.77 *br s*	1.77 *br s*
H-21	—	—	1.98 *d*	1.98 *d*	4.91 *br s*	4.91 *br s*	2.09 *d*	4.97 *br s*
H-21′	—	—			4.68 *br s*	4.68 *br s*		4.78 *br s*
OAc	—	—	—	—	—	—	2.04 *s*	2.04 *s*

J (Hz): 1, 1′ = 12; 1, 2 = 1′, 2 = 4, 5 = 7; compounds **1–6**: 8, 9 = 9, 10 = 7; 10, 18 = 1.2; compounds **1** and **2**: 13, 14 = 7; compounds **1**, **3** and **5**: 5, 6 = 7; compounds **2**, **4** and **6**: 5, 6 = 6; 5′, 6 = 7; 19, 19′ = 12; compounds **3–8**: 15, 16 = 15, 17 = 7; compounds **3**, **4** and **7**: 13, 21 = 1.5; 13, 15 ~ 1; compounds **7** and **8**: 5, 6 = 5′, 6 = 6.5; 10, 11 = 11, 18 = 7.

phellandrene. The diol has been isolated and prepared previously [14].

The chemistry of *Smallanthus glabratus* again supports the separation of the genus from *Polymnia*. From the only two species of the latter genus no melampolides are reported [2, 8]. The occurrence of geranyl nerol derivatives and homoditerpenes like **3–8** may be also of chemotaxonomic relevance as these compounds may have been overlooked in previous investigations. So far only from *Smallanthus maculatus* (Cav.) H. Robins., in addition to the melampolides isolated previously [5], a similar compound, acanthoaustralide [15], was isolated (unpublished). The 18-acyloxy-*ent*-kaurenic acids also are present in other *Smallanthus* species [4, 6, 7].

EXPERIMENTAL

The air dried aerial parts (540 g, voucher RMK 9138 and 220 g, RMK 9269, collected in Peru, 41 km NE of Cajamarca, 10400 ft and 17 km SE of Chachapoyas, 8700 ft, respectively) was extracted separately with MeOH–Et_2O–petrol, 1:1:1, and worked-up in the usual fashion [16]. The quantities obtained from the second collection are given in parentheses. The CC fractions were as follows: 1 (petrol), 2 (Et_2O–petrol, 1:19), 3 (Et_2O–petrol, 1:9), 4 (Et_2O–petrol, 1:3 and 1:1), 5 (Et_2O) and 6 (Et_2O–MeOH, 9:1 and 4:1). TLC of fraction 1 (petrol) gave 30 mg (200 mg) germacrene D. TLC of fraction 2 (Et_2O–petrol, 1:9) afforded 30 mg (120 mg) *ent*-kaurenal (and 20 mg 2-phenyl ethyl cinnamate from the second collection) and TLC of fraction 3 (Et_2O–petrol, 1:9) gave 4.6 g (2.6 g) *ent*-kaurenic acid (only 5% of the fraction was taken and total amount was calculated). TLC of 5% of fraction 4 (Et_2O–petrol, 1:1) afforded (total amount) 1.8 g (0.96 g) 18-angeloyloxy- and 0.4 g (0.12 g) 18-senecioyloxy-*ent*-kaurenic acid. TLC of fraction 5 (Et_2O) gave 200 mg (−)borneyl ferulate and 200 mg (80 mg) sakuranetin while fraction 6 gave 3.2 g (6a) and (0.19 g) (6b) as mixtures. TLC of 6a (Et_2O–petrol, 4:1) gave 20 mg sakuranetin, 250 mg of a mixture of **9** and the angelate [12] (6a/2) (*ca* 2:1) and 40 mg of a mixture, which was separated again by TLC (C_6H_6–CH_2Cl_2–Et_2O, 9:9:2, four developments) affording 20 mg **9** and the corresponding angelate, 5 mg **8** (R_f 0.16) and 4 mg **7** (R_f 0.10). Repeated TLC of 6a/2 (Et_2O–petrol, 4:1, several developments, gave incomplete separation. However, the first part of the band contained the angelate [12] and the lowest part pure **9** (R_f values by repeated TLC 0.79 and 0.67 respectively). TLC of 6b (Et_2O) gave two mixtures (6b/1 and 6b/2). HPLC (RP 8, MeOH–H_2O, 7:3, always 100 bar and flow rate 3 ml/min.) of 6b/1 afforded 30 mg 1α,2β-dihydroxy-α-phellandrene (R_t 6 min), 1 mg **1** (R_t 9.4 min), 16 mg **5** (R_t 11 min) and 3 mg **3** (R_t 13.2 min). TLC of 6b/2 (Et_2O) gave three bands. The least polar gave 8 mg 1α,2β-dihydroxy-α-phellandrene, the next (12 mg, 6b/2/3) and the third (5 mg, 6b/2/3) were mixtures. HPLC (MeOH–H_2O, 3:2) of 6b/2/2 gave 7 mg **6** (R_t 7.1 min) and 3 mg **4** (8.2 min). HPLC (MeOH–H_2O, 3:2) of 6b/2/3 afforded 1 mg **2** (R_t 7.0 min), 2 mg **6** (R_t 7.2 min) and 2 mg **4** (R_t 8.3 min). Known compounds were identified by comparison of the 400 MHz ^{1}H NMR spectra with those of authentic material and by co-TLC. 1α,2β-dihydroxy-α-phellandrene was prepared by epoxidation of (−)-α-phellandrene followed by acid catalysis hydrolysis. The product obtained was identical with the natural compound and the data agreed with those reported in the literature [15]. The purity of the new compounds was tested by ^{1}H NMR spectroscopy, by TLC and by HPLC in different solvent mixtures.

19-Hydroxy-12-oxo-geranyl nerol (**1**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3400 (OH), 1680 (C=CC=O); CIMS (isobutane) *m/z* (rel. int.): 321 $[M+1]^+$ (4), 303 $[M+1-H_2O]^+$ (100), 285 $[303-H_2O]^+$ (29).

6,7-Epoxy-19-hydroxy-12-oxo-6,7-dihydrogeranylnerol (**2**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3400 (OH), 1680 (C=CC=O); CIMS (isobutane) *m/z* (rel. int.): 337 $[M+1]^+$ (12), 319 $[M+1-H_2O]^+$ (100), 301 $[319-H_2O]^+$ (88).

1,19-Dihydroxy-12-oxo-smallantha-2Z,6Z,10E,13E-tetraene (**3**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3400 (OH), 1660 (C=CCOC=C); MS *m/z* (rel. int.): 334 $[M]^+$ (0.5), 316.240 $[M-H_2O]^+$ (4) (calc. for $C_{21}H_{32}O_2$: 316.240), 111 $[C_6H_{11}CO]^+$ (100).

1,19-Dihydroxy-6,7-epoxy-12-oxo-smallantha-2Z,10E,13E-triene (**4**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3400 (OH), 1650 (C=CCOC=C); MS *m/z* (rel. int.): 350 $[M]^+$ (0.5), 332.246 $[M-H_2O]^+$ (2) (calc. for $C_{21}H_{32}O_3$: 332.246), 314 $[332-H_2O]^+$ (2), 203 $[314-C_6H_{11}CO]^+$ (6), 123 (55), 111 $[C_6H_{11}CO]^+$ (100), 55 (82).

1,19-Dihydroxy-12-oxo-smallantha-2Z,6Z,10E,14(21)-tetraene (**5**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1680 (C=CCO); CIMS (isobutane) *m/z* (rel. int.): 335 $[M+1]^+$ (8), 317 $[M+1-H_2O]^+$ (100), 299 $[317-H_2O]^+$ (26), 233 (26), 205 (26).

1,19-Dihydroxy-6,7-epoxy-12-oxo-smallantha-2Z,10E,14(21)-triene (**6**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3400 (OH), 1670 (C=CCO); MS *m/z* (rel. int.): 332.235 $[M-H_2O]^+$ (1.5) (calc. for $C_{21}H_{32}O_3$: 332.235), 81 (90), 69 (75), 55 (100);

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\ \text{nm}}{+29 \quad +32 \quad +37 \quad +57} (c\ 0.14, CHCl_3).$$

1-Acetoxy-6,7-epoxy-19-hydroxy-12-oxo-smallantha-2Z,13E-diene (**7**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3400 (OH), 1740, 1240 (OAc), 1680, 1610 (C=C–C=O); CIMS (isobutane *m/z* (rel. int.): 335 $[M+1-HOAc]^+$ (38), 317 $[335-H_2O]^+$ (95), 225 $[335-C_6H_{10}CO]^+$ (80), 111 $[C_6H_{11}CO]^+$ (100).

1-Acetoxy-6,7-epoxy-19-hydroxy-12-oxo-smallantha-2Z,14(21)-diene (**8**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3450 (OH), 1740, 1230 (OAc), 1710 (C=O); MS *m/z* (rel. int.): 334.251 $[M-HOAc]^+$ (1) (calc. for $C_{21}H_{34}O_3$: 334.251), 316 $[334-H_2O]^+$ (1), 233 $[316-C_6H_{11}]^+$ (10), 205 $[233-CO]^+$ (8), 111 $[C_6H_{11}CO]^+$ (100).

8β-[2-Methylbutyryloxy]-14-oxo-acanthospermolide (**9**). Colourless oil IR $\nu_{max}^{CCl_4}$ cm^{-1}: 2730, 1690, 1630 (C=CCHO), 1780 (γ-lactone), 1740 (CO_2R); MS *m/z* (rel. int.): 346.178 $[M]^+$ (0.6) (calc. for $C_{20}H_{26}O_5$: 346.178), 262 $[M-O=C=C(Me)Et]^+$ (10), 244 $[M-RCO_2H]^+$ (25), 85 $[C_4H_9CO]^+$ (60), 57 $[85-CO]^+$ (100); ^{1}H NMR ($CDCl_3$): 6.54 *ddd* (H-1), 2.45 m (H-2), 2.23 m (H-2'), 2.33 *ddd* (H-3), 2.05 *ddd* (H-3'), 5.00 *m* (H-5, H-6), 2.38 *m* (H-7), 6.29 *ddd* (H-8), 2.71 *br dd* (H-9), 1.83 *br dd* (H-9'), 6.15 *d* (H-13), 5.50 *d* (H-13'), 9.37 *d* (H-14), 1.85 *br s* (H-15); OCOR: 2.30 *tq*, 1.55 *ddq*, 1.37 *ddq*, 0.79 *t*, 1.01 *d* (*J* [Hz]: 1, 2 = 10; 1,2' = 7; 1,14 = 1.5; 2,3 = 6; 2',3 = 2,3' = 2; 2',3' = 11; 3,3' = 13; 7,8 = 2; 7,13 = 3.5; 7,13' = 3; 8,9 = 6.5; 8,9' = 10; 9,9' = 14; OCOR: 2,3 = 2,5 = 3,4 = 7; 3,3' = 14).

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