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HELOGYNIC ACID, A HOMODITERPENE, AND OTHER CONSTITUENTS FROM *HELOGYNE APALOIDEA*

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Key Word Index—*Helogyne apaloidea*; Compositae; sesquiterpene lactones; germacradienolides; guaianolides; diterpenes; geranyl nerol derivatives; homoditerpene.

Abstract—The aerial parts of *Helogyne apaloidea* afforded in addition to 18 known sesquiterpene lactones four new germacradien-12,6-olides and 10 guaianolides as well as two geranyl nerol derivatives, one being a homoditerpene. The structures were elucidated by high field NMR techniques. The chemistry of this species is similar to that of *H. hutchisonii*.

INTRODUCTION

The South American genus *Helogyne* is placed in the subtribe Alomiinae [1]. The chemistry of one species showed that most likely this genus is a primitive element in the subtribe [2]. We now have studied a further species, from Peru, *H. apaloidea* Nutt.; the results are presented in this paper.

RESULTS AND DISCUSSION

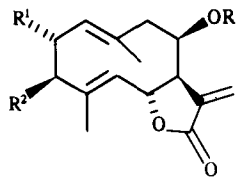
Careful separation of the extract of the aerial parts afforded lupeyl acetate, 6-methoxy- and 6-hydroxy-3α-angeloyloxytremetone [3], the germacranolides eupatolide [4], **1** [5], **2** [6], **7** [7], **8** [8], **9** [9] and **10** [10], the guaianolides **11** [11], **12** [12], **13** [13], **23** [12], **24** [14], **25** [15], **26** [16], **27** [17] and **28** [16], the heliangolide eucannabinolide [5] and its 20-desoxy derivative [18] as well as four new germacranolides (**3–6**), ten guaianolides (**14–22** and **29**), the geranyl nerol derivative **30** and the corresponding homoditerpene **31**, named helogynic acid.

The structures of **3–6** could easily be deduced from their ^{1}H NMR spectra (Table 1) which were close to those of **1** and **2**. The nature of the different ester residues followed from the typical NMR signals and from the mass spectra. Similarly the ^{1}H NMR spectra of **14–20** (Table 2) were close to that of **12** and the structure of the 8β-acyloxy groups could also be determined by the NMR data. Spin decoupling allowed the assignment of all signals. The somewhat different ^{1}H NMR spectrum of **29** was close to that of the corresponding 20-desacetyl derivative [14]. The main difference was the expected downfield shift of the H-5′ signals and the presence of an acetoxy methyl singlet.

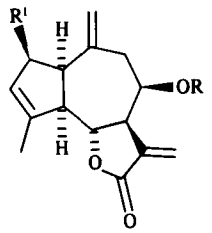
The acids **30** and **31** were purified as their methyl esters. The mass spectrum of the latter showed the highest ion at *m/z* 404 corresponding to $C_{24}H_{36}O_5$. The next ion, *m/z* 362 ($C_{22}H_{34}O_4$), obviously was formed by elimination of acetic acid. Accordingly, the natural product must be the acetate of a C_{21}-trihydroxy acid. This was established by the ^{13}C NMR spectrum of the methyl ester of **31** (see Experimental). Inspection of the ^{1}H NMR spectrum (see Experimental) further showed that a geranyl nerol derivative with an additional methyl group must be present where only one methyl was not oxygenated. Signals in deuteriobenzene at δ4.13 (*d*), 3.95 (*s*), 4.67 (*s*) (each 2 H) required three oxygen functions bearing methylene groups. Furthermore, a pair of olefinic methylene protons, an olefinic methyl signal and a methoxy singlet indicated that the necessary equivalents of methyl groups of a geranyl nerol derivative were present. However, an additional methyl doublet at δ1.14 showed that a homoditerpene was present. Spin decoupling allowed us to assign nearly all signals while the chemical shifts gave some indications about the relative position of the oxygen functions. Final proof was achieved by NOE difference spectroscopy. Thus, a clear effect between H-18 and H-9 indicated an *E*-configuration of the corresponding double bond. Similar the NOE between H-20 and H-2 established the neryl configuration, while the effect between H-19 and H-5 established the configuration of the remaining trisubstituted double bond. Furthermore the relative position of the olefinic methyl group could be established by the presence of an allylic coupling between H-10 and H-12. The signal of the latter was assigned by spin decoupling starting with H-14 which showed an allylic coupling with H-16′. This also showed that the secondary methyl group was at C-14.

The ^{1}H NMR spectrum of the methyl ester of **30** (see Experimental) was in part close to that of the methyl ester of **31**. However, the changed situation at C-13–C-16 was obvious. The corresponding signals now indicated that the secondary methyl was missing and that the olefinic methylene group was replaced by a trisubstituted double bond as followed from a low field narrowly splitted triplet at δ5.82 and an additional olefinic methyl group (δ1.93 *d*). The configuration of the Δ^{14} bond followed from the chemical shift of H-14.

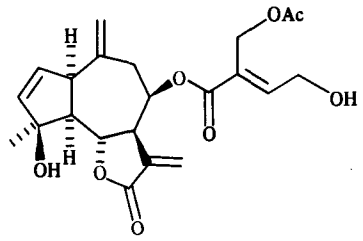
The chemistry of the second *Helogyne* species again shows that most likely this genus is less advanced than the other genera placed in the subtribe Alomiinae where 8β-substituted germacranolides and guaianolides, which are typical for other less advanced genera in the tribe, are



	1	2	3	4	5	6	7	8	9	10
R	Ac	Tigl	Ang	Prop	*i*Bu	I	K	B	Ang	C
R^1	H	H	H	H	H	H	H	H	OH	H
R^2	H	H	H	H	H	H	H	H	H	OH



	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28
R	H	A	B	C	Ang	D	E	F	G	I	C	D	K	H	Ang	Tigl	A	B
R^1	H	H	H	H	H	H	H	H	H	H	OH	OH	H	OH	OH	OH	OH	OH



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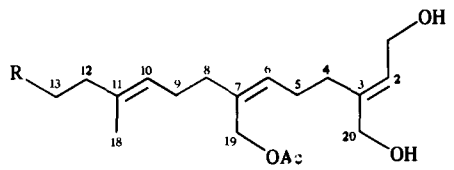
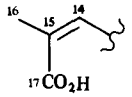
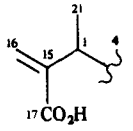


30 R = 

31 R = 

A = CO(Me)═CHCH$_2$OH(E), B = COC(CH$_2$OH)═CHCH$_2$OH(E), C = COC(CH$_2$OH)═CHCH$_2$OAc(E)
D = COC(CH$_2$OAc)═CHCH$_2$OH(E), E = COC(CH$_2$OAc)═CH(CH$_2$OAc)(E), F = COC(CH$_2$OAng)═CHCH$_2$OH
G = COC(CH$_2$OTigl)═CHCH$_2$OH(E), I = β-furoyl, K = α-hydroxy-2.5H-furoyl

Table 1. ^{1}H NMR spectral data of compounds **3**–**6** ($CDCl_3$, 400 MHz, δ-values)

H	3*	4†	5‡	6§	Multiplicity
1	4.87	4.88	4.89	4.91	*br dd*
5	4.78	4.77	4.78	4.83	*br d*
6	5.14	5.12	5.13	5.19	*dd*
7	2.92	2.90	2.91	2.98	*br dt*
8	5.79	5.74	5.73	5.94	*br d*
9	2.87	2.82	2.81	2.91	*br dd*
9′	2.35	2.34	2.34	2.38	*br d*
13	6.30	6.30	6.30	6.32	*d*
13′	5.61	5.59	5.58	5.68	*d*
14	1.48	1.50	1.51	1.50	*br s*
15	1.73	1.76	1.77	1.81	*d*

*OAng: 6.10 *qq*, 1.97 *dq*, 1.85 *dq* (*J* [Hz]: 3,4 = 7; 3,5 = 4,5 = 1.5);
†OProp: 2.33 *q*, 1.14 *t* (*J* = 7 Hz).
‡O*i*Bu: 2.54 *qq*, 1.16 *d*, 1.15 *d* (*J* = 7 Hz).
§furoyl: 7.96 *dd* (*J* = 1,1.5 Hz), 7.45 *t* (*J* = 1.5 Hz), 6.68 *br d* (*J* = 1.5 Hz).
J[Hz]: 1,2 = 11, 1,2′ = 4; 5,6 = 10; 5,15 = 1.5; 6,7 = 9; 7,13 = 3.5; 7,13′ = 3; 8,9 = 5; 9,9′ = 14.

missing. Most genera contain diterpenes. In this connection the isolation of **30** and **31** may be of interest as this could be an indication that the enzymes for the typical cyclization reaction of the alicyclic diterpenes are not present in the more primitive elements of the tribe Eupatorieae.

EXPERIMENTAL

Air-dried aerial parts (720 g, collected in November 1986 in Peru, voucher M. O. Dillon 4792, deposited in the Herbarium of the Field Museum of Natural History, Chicago, U.S.A.) were extracted and worked-up as reported previously [19]. CC fractions were taken as follows: 1: petrol and Et_2O–petrol (1:9), 2: Et_2O–petrol (1:1), 3: Et_2O, 4: Et_2O–MeOH (9:1) and 5: Et_2O–MeOH (1:1) which were further sepd by TLC silica gel, solvents T1 = Et_2O, T2 = Et_2O–petrol (3:1), T3 = Et_2O–petrol–MeOH (18:6:1) and T4 = Et_2O–petrol–MeOH (36:12:1) and by HPLC RP 18, *ca* 100 bar, solvents: H1 = MeOH–H_2O (4:1), H2 = MeOH–H_2O (7:3) and H3 = MeOH–H_2O (3:2). TLC of fraction 1 (petrol) gave no definite compounds and fraction 2 afforded 100 mg lupeyl acetate. Fraction 3 was sepd by medium pressure chromatography (MPC) using silica gel θ 30–60 and Et_2O–petrol mixts as eluents affording two fractions (3/1 and 3/2). HPLC of 3/1 (H1) gave 4 mg **1**, 1 mg **6** (R_t 3.3 min), 1 mg **4** (R_t 3.4 min), 1 mg **5** (R_t 4.3 min), 1 mg **20** (R_t 4.5 min), 8 mg **2**, 80 mg **3** (R_t 5.6 min), 4 mg **15** (R_t 7.3 min), 3 mg 6-methoxy-3α-angeloyloxytremetone and 3 mg of the 6-hydroxy derivative. HPLC of 3/2 (H1) gave a mixt. (3/2/1) (R_t 1.8 min), 4 mg **17** (R_t 3.5 min), 20 mg **11** (R_t 6.0 min), 10 mg **12** (R_t 8.0 min), a mixt. (3/2/2) (R_t 12.3 min), a mixt. (3/2/3) (R_t 13.5 min) and 30 mg **18** (R_t 15.1 min). TLC of 3/2/1 (T2) gave 2 mg **25** and 3 mg **26**. TLC of 3/2/2 (T2, two developments) gave 2 mg **14** and 5 mg **16**. TLC of 3/2/3 (T2) gave 10 mg **18** and 10 mg **19** (R_t 0.35). CC fraction 4 was sepd by MPC (Et_2O, Et_2O–MeOH (3:2) into 8 fractions (4/1–4/8). HPLC of 4/1 (H2) afforded 2 mg **7**, 3 mg **9**, a mixt. (4/1/1), a mixt. (4/1/2), 20 mg **19** (R_t 9.0 min) and 60 mg **18** (R_t 9.8 min). TLC of 4/1/1 (T1) gave 2 mg **23**, 3 mg eupatolide, 10 mg **11** and 60 mg **16** (R_f 0.50). TLC of 4/1/2 (T2, two developments) afforded 20 mg **12**, 20 mg **14** (R_f 0.45) and 10 mg **16**. Fraction 4/2 contained 1 g **16** and fraction 4/3 500 mg coumaric acid. HPLC of fraction 4/4 (H2) gave 5 mg **27** (R_t 1.7 min), 2 mg 20-desoxyeucannabinolide (R_t 2.1 min) and 3 mg **9** (R_t 3.3 min). HPLC of 4/5 (H2) gave 30 mg **22** (R_t 1.3 min), a mixt. (4/5/1) (R_t 1.5 min), 10 mg **8** (R_t 2.2 min), 30 mg **13** (R_t 2.7 min), 15 mg **30** (R_t 4.9 min) and 20 mg **31** (R_t 9.8 min). Fraction 4/5/1 gave by TLC (T4) 5 mg **27** and 3 mg **21** (R_f 0.28). HPLC of fraction 4/6 (H3) gave 20 mg **10**, a mixt. (4/6/1) (R_t 2.6 min), 20 mg **22** (R_t 3.2 min), 100 mg **8** and 100 mg **13**. TLC of 4/6/1 (T3) gave 5 mg **24** and 8 mg **29** (R_f 0.30). HPLC of 4/7 (H3) gave 10 mg **10** and 60 mg eucannabinolide. Fraction 4/8 gave 1 g eucannabinolide. From fraction CC-5 5% was sepd by HPLC (H3) affording 50 mg eucannabinolide, 25 mg **28**, 25 mg **8** and 20 mg **13**. Known compounds were identfied by comparing the 400 MHz ^{1}H NMR spectra with those of authentic material. The data of the new lactones are given in Table 3.

19-*Acetoxy*-20-*hydroxygeranylnerol*-17-*acid* (**30**). Colourless oil which was purified as its Me ester, colourless oil, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1745 (OAc), 1720 (C=CCO$_2$R); MS *m/z* (rel. int.): 390.241 [M − H_2O]$^+$ (0.1) (calc. for $C_{23}H_{34}O_5$: 390.241), 348 [M − HOAc]$^+$ (1.2), 330 [348 − H_2O]$^+$ (5), 93 (100); ^{1}H NMR (C_6D_6): δ4.12 (*d*, H-1), 5.70 (*br t*, H-2), 2.20 (*m*, H-4, H-5, H-8, H-9), 5.31 (*br t*, H-6), 5.29 (*br t*, H-10), 2.14 (*br t*, H-12), 280 (*br q*, H-13), 5.82 (*tq*, H-14), 1.93 (*d*, H-16), 1.66 (*s*, H-18), 4.66 (*s*, H-19), 4.12 (*br d*, H-20), 1.74 (*s*, OAc) 3.44 (*s*, OMe) (*J* [Hz]: 1,2 = 5,6 = 9,10 = 12,13 = 13,14 = 7; 14,16 ≙ 1.5).

Helogynic acid (**31**). Colourless oil which was purified as its Me ester (CH_2N_2–Et_2O, 3 min, 20°), colourless oil; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1720 (CO_2R); MS *m/z* (rel. int.): 404 [M − H_2O]$^+$ (0.05), 362.246 [M − HOAc]$^+$ (3) (calc. for $C_{22}H_{34}O_4$: 362.246), 344 [362 − H_2O]$^+$ (5), 326 [344 − H_2O]$^+$ (4), 313 [344 − OMe]$^+$ (5), 261 (8), 213 (15), 135 (76), 93 (92), 81 (100); ^{1}H NMR (C_6D_6): δ4.13 (*br d*, H-1), 5.71 (*br t*, H-2), 2.10 (*t*, H-4), 2.19 *q* (H-5), 5.36 (*br t*, H-6), 2.22 (*br s*, H-8, H-9), 5.27 (*br t*, H-10), 2.08 and 2.04 (*m* H-12), 1.80 and 1.60 (*dddd*, H-13), 2.84 (*tq*, H-14), 5.36 (*t*, H-16), 6.24 (*d*, H-16′), 1.65 (*d*, H-18), 4.67 (*s*, H-19), 3.95 (*br s*, H-20), 1.14 (*d*, H-21), 1.74 (*s*, OAc), 344 (*s*, OMe) (*J* [Hz]: 1,2 = 3,4 = 5,6 = 9,10 = 12,13 = 12,13′ = 13,14 = 13′,14 = 13,21 = 7; 10,18 = 14,16′ = 16,16′ = 1; 13,13′ = 14); ^{13}C NMR (C_6D_6, C-1–C-21): δ58.5 *t*, 130.2 *d*, 134.5 *s*, 34.5 *t*, 28.2 *t*, 124.1 *d*, 146.2 *s*, 37.4 *t*,

Table 2. ^{1}H NMR spectral data of compounds **14–22** and **29** ($CDCl_3$, 400 MHz, δ-values)

H	**14***	**15**†	**16**‡	**17**§	**18**‖	**19**¶	**20****	**21**††	**22**‡‡	**29**§§	Multiplicity
1	3.17	3.16	3.14	3.17	3.15	3.15	3.19	3.17 *dd*	3.14 *dd*	3.37 *br d*	*ddd*
2	2.42	2.52	2.50	2.52	2.52	2.51	2.50	4.74 *br s*	4.70 *br s*	5.76 *dd*	*m*
2′	2.33	2.43	2.41	2.43	2.40	2.41	2.41				*br d*
3	5.57	5.56	5.56	5.58	5.56	5.57	5.57	5.77	5.72	5.95	*br s*
5	2.74	2.85	2.86	2.86	2.84	2.85	2.87	2.68	2.65	2.42	*br t*
6	4.49	4.51	4.52	4.51	4.50	4.51	4.51	4.66	4.65	4.97	*dd*
7	3.20	3.19	3.17	3.20	3.18	3.18	3.21	3.20	3.19	3.24	*dddd*
8	5.65	5.64	5.65	5.67	5.66	5.73	5.67	5.59	5.58	5.70	*ddd*
9	2.48 *d*	2.61	2.60	2.61	2.58	2.59	2.66	2.84 *m*	2.83	2.82	*dd*
9′		2.56	2.52	2.55	2.53	2.52	2.60		2.78	2.38	*dd*
13	6.29	6.30	6.26	6.29	6.24	6.24	6.29	6.30	6.26	6.32	*d*
13′	5.54	5.56	5.55	5.56	5.54	5.54	5.60	5.53	5.52	5.64	*d*
14	5.03	5.00	5.00	5.03	4.99	5.00	5.04	5.14	5.12	4.96	*br s*
14′	4.89	4.88	4.87	4.89	4.85	4.87	4.91	5.12	5.08	4.94	*br s*
15	1.79	1.88	1.87	1.89	1.87	1.87	1.90	2.02	1.98	1.57	*br s*

OCOR:* 6.67 *t* ($J=5.5$), 4.82 *d* ($J=5.5$), 4.33 *br s*, 2.01 *s*.
†OAng: 6.07 *qq*, 1.93 *dq*, 1.80 *dq*.
‡OCOR: 6.99 *t* ($J=5.5$), 4.45 *br t*, 4.88 and 4.75 *d* ($J=12$), 1.98 *s*.
§OCOR: 6.89 *t* ($J=5.5$), 4.88 *d* ($J=5.5$), 4.80 and 4.75 *d* ($J=12$), 2.00 and 2.11 *s*.
‖OCOR: 6.98 *t* ($J=5.5$), 4.45 *d* ($J=5.5$), 4.93 and 4.89 *d* ($J=12$), 6.08 *qq* ($J=7,1.5$), 1.93 *dq* ($J=7,1.5$), 1.82 *dq* ($J=1.5,1.5$).
¶OCOR: 7.01 *t* ($J=5.5$), 4.50 *d* ($J=5.5$), 4.94 and 4.89 *d* ($J=12$), 6.77 *qq* ($J=7,1$), 1.78 *dq* ($J=7,1$), 1.77 *br s*.
**7.92 *br s*, 7.42 *t* ($J=1.5$).
††OCOR: 6.68 *t* ($J=6$), 4.81 *dd* ($J=6,2$), 4.32 *br s*, 2.12 *s*.
‡‡6.97 *t* ($J=5.5$), 4.45 and 4.40 *dd* ($J=15,5$), 4.87 and 4.74 *d* ($J=12$), 1.99 *s*.
§§OCOR: 7.02 *t* ($J=5.5$), 4.48 and 4.43 *dd* ($J=16,5$), 4.90 and 4.76 *d* ($J=12$), 1.29 *s*.
J[Hz]: 1,2 = 1,5 ~ 10; 1,2′ = 5; 2,2′ = 16; 5,6 = 10; 6,7 = 8.5; 7,8 = 3; 7,13 = 3.5; 7,13′ = 3; 8,9 = 4.5; 8,9′ = 5; 9,9′ = 14; compounds **21**–**22**: 1,2 = 6; compound **29**: 1,2 = 2.5; 1,3 = 1.5; 2,3 = 5.5; 8,9 = 8,9′ = 3.

Table 3. Physical data of compounds **3–6**, **14–22** and **29**.

	IR ν				MS *m/z* (*rel. int.*)				
	OH	γ-lactone	CO_2R	solvent	$[M]^+$	Calc. for	main fragments	$[\alpha]_D^{24°}$	($CHCl_3$; *c*)
3*	—	1770	1715	CCl_4	330.183 (1)	$C_{20}H_{26}O_4$	230 (26), 215 (8), 83 (100), 55 (92)	+68	0.91
4	—	1780	1745	CCl_4	304.167 (1)	$C_{18}H_{24}O_4$	230 (28), 215 (12), 57 (100)		
5	—	1775	1740	CCl_4	318.183 (1)	$C_{19}H_{26}O_4$	230 (51), 215 (19), 71 (100)		
6	—	1775	1725	CCl_4	342.147 (0.5)	$C_{20}H_{22}O_5$	230 (26), 215 (18), 95 (100)		
14	3480	1770	1745, 1715	CCl_4	402.168 (4.5)	$C_{22}H_{26}O_7$	228 (100), 213 (13), 115 (69), 97 (57)	+38	1.86
15	—	1780	1720	CCl_4	328.167 (5)	$C_{20}H_{24}O_4$	228 (27), 213 (6), 83 (100), 55 (55)		
16	3600	1770	1740, 1720	CCl_4	402.168 (2.5)	$C_{22}H_{26}O_7$	228 (100), 213 (26), 157 (43), 115 (37), 97 (59)	+43	4.11
17	—	1770	1725, 1715	CCl_4	444.178 (2)	$C_{24}H_{28}O_8$	384 (2.5), 228 (53), 157 (29), 115 (52), 55 (100)	+36	0.36
18	3610	1775	1720	CCl_4	442.199 (2)	$C_{25}H_{30}O_7$	228 (36), 83 (100), 55 (45)	+40	2.39
19	3620	1775	1720	CCl_4	442.199 (1.5)	$C_{25}H_{30}O_7$	228 (27), 83 (100), (55) (49)		
20	—	1775	1725	CCl_4	340.131 (6)	$C_{20}H_{20}O_5$	228 (22), 95 (100)		
21	3620	1760	1740, 1720	$CHCl_3$	418.163 (0.5)	$C_{22}H_{26}O_8$	358 (2), 244 (27), 226 (37), 115 (100), 97 (89)		
22	3610	1760	1720	$CHCl_3$	418.163 (1)	$C_{22}H_{26}O_8$	358 (2), 244 (32), 226 (35), 115 (80), 97 (100)	−26	4.38
29				$CHCl_3$	403.139 (3.5) $[M-Me]^+$	$C_{21}H_{23}O_8$	343 (5), 244 (12), 226 (26), 115 (81), 97 (100)	−42	0.79

*Mp 89°, all other colourless oils.

27.1 *t*, 125.5 *d*, 141.1 *s*, 35.4 *t*, 26.7 *t*, 34.5 *d*, 135.2 *s*, 122.5 *t*, 167.2 *s*, 15.8 *q*, 66.2 *t*, 61.4 *t*, 19.6 *q*; OMe: 51.1 *q*; OAc: 20.3 *q*, 170.3 *s* (a few triplets may be interchangeable).

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SPHAEROPYRANE, A DITERPENE FROM THE MARINE RED ALGA *SPHAEROCOCCUS CORONOPIFOLIUS*

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Key Word Index—*Sphaerococcus coronopifolius*; Rhodophyta; diterpenes; sphaeropyrane.

Abstract—A new diterpene, sphaeropyrane has been isolated from the marine red alga *Sphaerococcus coronopifolius*. Its structure has been assigned mainly on the basis of ^{1}H and ^{13}C NMR experiments.

INTRODUCTION

The cosmopolitan bright-red alga *Sphaerococcus coronopifolius*, generally growing on rocks in shallow places, has been the subject of numerous studies for secondary metabolites [1–13]. Until now 18 new diterpenes based on six new rearranged polycyclic skeletons have been isolated and their biogenesis has been hypothesized [9, 10, 11]. This paper reports on the isolation of sphaeropyrane (**1**), a compound which belongs to a new class of diterpenes with a non-rearranged carbon skeleton.

Stereostructure **1** (relative stereochemistry) has been based on spectral data including extensive spin decoupling experiments and 2D ^{13}C–^{1}H shift correlated NMR spectroscopy via ^1J, ^2J and ^3J.

RESULTS AND DISCUSSION

A chloroform extract of the freeze-dried *S. coronopifolius*, after repeated chromatographies over silica gel, provided crude **1** which was purified by reversed-phase HPLC to yield **1** (0.003% dry weight), $C_{20}H_{32}O$ (HRMS), mp 136–138°.

Sphaeropyrane was recognized to possess a $-\overset{|}{\underset{|}{C}}-O-\overset{|}{\underset{|}{C}}-$ group by IR (ν_{max} 1025, 1070 and 1120 cm^{-1}) and by