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THIRTEEN KOLAVANE DERIVATIVES FROM *SYMPHYOPAPPUS* SPECIES*

F. BOHLMANN†, C. ZDERO†, R. M. KING‡ and H. ROBINSON‡

† Institute for Organic Chemistry, Technical University Berlin, Strasse des 17. Juni 135, D-1000 Berlin 12, West Germany;
‡ Smithsonian Institution, Washington, DC 20560, U.S.A.

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Key Word Index—*Symphyopappus compressus; S. reticulatus;* Compositae; diterpenes; kolavane derivatives; diterpene lactones; tremetone derivative.

Abstract—The aerial parts of *Symphyopappus compressus* afforded three new kolavane derivatives and those of *S. reticulatus* ten diterpenes of this type, two of them esterified with long chain fatty acids. Furthermore, a dihydroxyphenylpropanol, also esterified with long chain fatty acids, was present in both species. The roots of *S. reticulatus* afforded a new tremetone derivative. The structures were elucidated by spectroscopic methods and some chemical transformations.

INTRODUCTION

The Brazilian genus *Symphyopappus* is placed in the tribe Eupatorieae in the *Disynaphia* group [1]. So far only one species has been investigated chemically and kolavane lactones were isolated [2]. In a continuation of our investigations on the chemotaxonomy of the tribe Eupatorieae, we have now studied the constituents of two further species. Again both species, *Symphyopappus compressus* and *S. reticulatus*, afforded kolavane derivatives mainly, none of them having been isolated before.

RESULTS AND DISCUSSION

The aerial parts of *S. compressus* (Gardn.) B. L. Robins afforded germacrene D, bicyclogermacrene, α-humulene, tridecapentaynene, fatty acids, betulonic acid, unidentified triterpenes, the kolavane derivatives **1**, **4** and **6** as well as the phenylpropanol derivatives **20a** and **20b**, esterified with stearic and arachidic acid, a mixture, which could not be separated. The relative position of the hydroxy groups followed from the chemical shifts of the signals of the aromatic protons in the ^{1}H NMR spectra of **20a/b** and those of the diacetate **20c/d** (see Experimental), which were not identical with those of 4-hexylresorcinol.

The structure of **1** followed from its ^{1}H NMR data, those of the corresponding acetate **2** and especially those of the ketone **3**, obtained by oxidation of **1** with pyridine dichromate (Table 1). The observed couplings $J_{1\alpha,10}$ and $J_{1\beta,10}$ in the spectrum of **3** clearly indicated a *trans*-fused decalin derivative, as a *cis*-decalin, which could explain the large coupling $J_{1\alpha,10}$ too, would require a conformation with the side chain at C-9 axially orientated. Therefore the configuration is different from those of the kolavanes from *S. itatiayensis* [2]. The α-orientation of the 3-hydroxy group followed from the observed couplings $J_{1\beta,2}$ and the very small coupling $J_{1\beta,10}$, while the stereochemistry at C-8 was assigned by comparing the chemical shifts of the methyl doublet only, which was supported by the same configuration of further diterpenes (see below). The presence of a butenolide could easily be deduced from the typical NMR signals. The absolute configuration of **1** and of all other diterpenes could not be assigned with certainty. Those shown are very probable since most diterpenes of this type isolated from the Eupatorieae are of this configuration. The structure of **4** could be deduced from the ^{1}H NMR data too (Table 1). The presence of an epoxide followed from the broadened singlet at δ 3.09 and the methyl singlet at 1.30, while the position of the hydroxyl could be assigned from the ^{1}H NMR spectrum of the corresponding acetate **5a** and the ketone **5b**, obtained by oxidation. The 1-H signals in the spectrum of **5b** showed that the stereochemistry at C-10 is the same as that of **1**; consequently **4** is the epoxide of **1**. The α-orientation of the epoxide followed from the downfield shift of 19-H when compared with that in the spectrum of **1**.

The ^{1}H NMR data of **6** and those of the oxidation product **7** (Table 1) clearly showed that the butenolide part of **4** was replaced by a saturated side chain, as could be seen by the signals of 15-H, while the same situation of the ring skeleton as in **4** could be deduced from the nearly identical ^{1}H NMR signals in the spectra of **1** and **6**. The stereochemistry at C-13, however, was not determined.

The aerial parts of *S. reticulatus* Baker afforded germacrene D, bicylcogermacrene, α-humulene, β-farnesene, artemetin (**21**) [3], the euparine derivative **22** [4], **21a/b** and again several kolavane derivatives, the diol **10**, a mixture of esters of **10** (**8a** and **8b**), the aldehydes **11** and **13**, the isomeric aldehydes **14** and **15**, the isomeric acids **16a** and **17a** as well as the diol **18** and the esters **19a** and **b**, again a mixture of an arachidate and a behenate. Saponification of **8a** and **8b**, which gave no molecular ion, afforded the diol **10** and a mixture of arachidic and behenic acid, as could be shown by the mass spectrum of the acids as well as by that of the natural ester mixture,

* Part 323 in the series "Naturally Occurring Terpene Derivatives". For Part 322 see Bohlmann, F. and Mailahn, W. (1981) *Chem. Ber.* (in press).

Table 1. ^{1}H NMR spectral data of compounds **1**–**7** (270 MHz, $CDCl_3$, TMS as internal standard)

	1	**2**	**Δ***	**3**	**4**	**5a**	**5b**	**6**	**7**
1α-H	1.65 *m*	1.60 *m*	0.26	2.44 *dd*			2.65 *dd*		2.55 *dd*
1β-H	1.91 *br dd*	1.94 *br dd*	0.27	2.26 *dd*			1.93 *br d*		1.96 *br s*
2-H	4.22 *br t*	5.27 *br ddq*	0.60	—	3.89 *br dd*		—	3.89 *br dd*	—
3-H	5.23 *ddq*	5.18 *s*	0.28	5.74 *br s*	3.09 *br s*	3.06 *br s*	3.02 *br s*	3.06 *br s*	3.00 *br s*
8-H	1.45 *m*	1.5 *m*		1.57 *m*					
10-H	1.45 *m*	1.45 *m*	0.17 (*dd*)	1.86 *m*					
12-H	2.30 *m*	2.31 *m*	0.11	2.28 *dddd*	2.30 *m*	2.3 *m*	2.30 *m*		
12′-H	2.18 *m*	2.22 *m*	0.20	2.15 *dddd*	2.20 *m*		2.20 *m*	1.62 *m*	
14-H	5.85 *tt*	5.86 *tt*	0.60	5.84 *tt*	5.86 *br s*	5.84 *br s*	5.84 *br s*		2.40 *dd* 2.24 *ddd*
15-H	—	—	—	—	—	—	—	3.72 *dd*	9.76 *t*
15′-H	—	—	—	—	—	—	—	3.66 *dd*	
16-H	4.75 *d*	4.76 *d*	0.38	4.72 *d*	4.75 *d*	4.77 *d*	4.73 *br s*	0.91 *d*	0.97 *d*
17-H	0.83	0.83 *d*	0.01	0.86 *d*	0.78 *d*	0.82 *d*	0.84 *d*	0.78 *d*	0.80 *d*
18-H	1.63 *dd*	1.64 *dd*	0.03	1.90 *d*	1.23 *s*	1.22 *s*	1.30 *s*	1.20 *s*	1.28 *s*
19-H	1.07 *s*	1.09 *s*	0.07	1.15 *s*	1.08 *s*	1.08 *s*	1.23 *s*	1.05 *s*	1.20 *s*
20-H	0.80 *s*	0.79 *s*	0.05	0.88 *s*	0.74 *s*	0.71 *s*	0.78 *s*	0.65 *s*	0.70 *s*
OAc	—	2.05 *s*	0.40	—	—	2.09 *s*	—	—	—

* Δ-values after addition of $Eu(fod)_3$.

J(Hz): Compounds **1**/**2**: 1α,1β = 12; 1α,2 = 7; 1β,2 = 9; 1,3 = 1.5; 2,3 = 2; 2,18 = 3,18 = 1.5; 8,17 = 6.5; 12,14 = 14, 16 = 1.8; compound **3**: 1α,1β = 18; 1α,10 = 14; 1β,10 = 3; 2,18 = 3,18 = 1.5; 8,17 = 6.5; 11,12 = 10; 11,12′ = 6; 11′,12 = 6; 11′,12′ = 10; 12,12′ = 17; 12,14 = 1.5; 14,16 = 1.8; compounds **4**/**5a**: 1α,2β = 9; 1β,2β = 6; (compound **5a**: 1α,2β = 11; 1β,2β = 5); 8,17 = 6; 14,16 = 1.8; compound **5b**: 1α,1β = 1α,10 = 13; 8,17 = 6; compound **6**: 1α,2α = 6; 1β,2α = 9; 8,17 = 6; 14,15 = 7; 15,15′ = 11; compound **7**: 1α,2β = 13; 1α,10 = 13; 8,17 = 6; 13,14 = 7; 14,14′ = 15; 14,15 = 2.

which could not be separated. Oxidation yielded the aldehydes **9a** and **9b**, while the acetylation of the diol gave the diacetate **12**, **19a** and **19b** could not be obtained in a pure state. Saponification afforded **18**, which still contained **10**. Manganese dioxide oxidation of the diol, however, yielded **15**, which on reduction gave **18**. The ^{1}H NMR data of **10** and of the corresponding diacetate **12** (Table 2) were similar to those of kolavenol and its acetate respectively. However, the signals of 15-H were replaced by a multiplet, indicating a saturated side chain. Furthermore, two double doublets at δ 3.76 and 3.28 showed the presence of a secondary CH_2OH group, which could be placed at C-8 only. In the spectrum of **8a/b** the 15-H protons showed clear double triplets. From the ^{1}H NMR of **9a/b**, obtained by oxidation with pyridine dichromate, the stereochemistry at C-8 could be deduced from the observed couplings $J_{7,8}$. As the chemical shifts of the methyl groups were very similar to those of **1**, the same stereochemistry at C-1, C-4 and C-9 can be assumed. The latter was supported by the downfield shift at 20-H in the spectrum of **9a** and **9b**, which could only be explained if the aldehyde group was *cis* to the 9-methyl group. The ^{1}H NMR data of **11** clearly showed that a free 15-OH group was present. The other signals were similar to those of **9a/b** indicating the same stereochemistry. In **13** the 15-OH group was replaced by an aldehyde group as could be recognized by the corresponding triplet of the aldehyde proton in the spectrum of **13** (Table 2), which on irradiation of the multiplet at 2.44 collapsed to a singlet. The ^{1}H NMR spectra of **14** and **15** (Table 2) differed in the chemical shifts of 16-H and 12-H, clearly indicating the 13,14-double bond was *Z* in **14** and *E* in **15**. The spectral data of **16a** and **17a** (Table 2) indicated that a carboxyl group was present at C-8. Reaction with diazomethane consequently gave the methyl esters **16b** and **17b**. The stereochemistry at C-8 again followed from the coupling $J_{7,8}$. As **18** was obtained by reduction of **15**, the structure was clear as well as that for **19a/b** (see above). The stereochemistry of the kolavane derivatives at C-4 and C-10 were not established rigorously. Unfortunately, the absolute configurations could not be determined, since optical rotations are not very useful in this class of diterpenes.

The roots afforded traces of tridecapentayne, germacrene D, isocomene [5], β-isocomene [6], bisabolene, dammadienyl acetate, the euparin derivatives **22** and **24** [7] as well as a further one, which was not isolated before. Its structure directly followed from the ^{1}H NMR data (see Experimental).

The constituents isolated so far from *Symphyopappus* showed no close relationship to *Grazielia* [8]. Many similar diterpenes, however, are present in *Acritopappus* [9], a genus placed in a separate group [10]. Primary results on a *Disynaphia* species indicated a relationship to *Grazielia* but again not to *Symphyopappus*. The only *Campovassouria* species investigated [11] contains *ent*-kaurene derivatives, present in *Grazielia* too [8]. More representatives of the *Disynaphia* group have to be investigated to obtain a clearer picture.

EXPERIMENTAL

^{1}H NMR: 270 MHz, TMS as internal standard; optical rotation: $CHCl_3$. The air-dried plant material was extracted with Et_2O–petrol (1:2) and the resulting extracts were separated first by column chromatography (Si gel) and further by repeated TLC (Si gel). Known compounds were identified by comparing the IR and ^{1}H NMR spectra with those of authentic material.

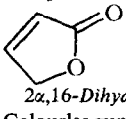
Symphyopappus compressus (*voucher RMK* 8266). The aerial parts (750 g) afforded 0.1 g tridecapentaynene, 20 mg germacrene D, 2 mg bicyclogermacrene, 9 mg α-humulene, 100 mg betulonic acid, 300 mg of a mixture of unidentified triterpenes, 4 g fatty acids, 20 mg **1** (Et_2O–petrol, 3:1), 50 mg **4** (Et_2O–petrol, 3:1), 80 mg **6** (Et_2O–petrol, 3:1) and 20 mg **20a** (Et_2O–petrol, 3:1).

Symphyopappus reticulatus (*voucher RMK* 8334). The aerial parts (300 g) afforded 100 mg germacrene D, 5 mg bicyclogermacrene, 5 mg α-humulene, 2 mg β-farnesene, 400 mg **8a/8b** (Et_2O–petrol, 1:1), 300 mg 10 (Et_2O–petrol, 3:1), 10 mg **11** (Et_2O–petrol, 3:1), 4 mg **13** (Et_2O–petrol, 1:1), 8 mg **14** (Et_2O–petrol, 1:1), 20 mg **15** (Et_2O–petrol, 1:1), 5 mg **16a** (Et_2O–petrol, 1:1), 5 mg **17a** (Et_2O–petrol, 1:1), 50 mg **18** (Et_2O–petrol, 1:1), 40 mg **19** (Et_2O–petrol, 1:1, still containing **8a/8b**), 40 mg **20a** (Et_2O–petrol, 3:1), 40 mg **21** and 20 mg **22**, while the roots (70 g) gave 0.1 mg tridecapentaynene, 2 mg isocomene, 2 mg β-isocomene, 5 mg germacrene D, 5 mg bisabolene, 10 mg dammadienyl acetate, 10 mg **22**, 10 mg **23** (Et_2O–petrol, 1:1) and 15 mg **24**.

2α,16-Dihydroxykolavenic acid lactone (**1**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1782, 1750 (γ-lactone), 1640 (C=C); MS *m/z* (rel. int.): 318.220 [M]$^+$ (27) ($C_{20}H_{30}O_3$), 303 [M − ·Me]$^+$ (8), 300 [M − H_2O]$^+$ (4), 285 [300 − ·Me]$^+$ (12), 235.170 [M − C_5H_7O]$^+$ (90) ($C_{15}H_{23}O_2$), 84 [C_5H_8O]$^+$ (100), 69 [84 − ·Me]$^+$ (95).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{+4.1 \quad +4.7 \quad +5.8 \quad +13.9} (c = 0.99).$$

10 mg **1** in 1 ml Ac_2O was heated for 1 hr at 70°. TLC (Et_2O–petrol, 1:1) afforded 10 mg **2**, colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1780 (γ-lactone), 1750, 1240 (OAc), 1640 (C=C); MS *m/z* (rel. int.): 360 [M]$^+$ (1), 300 [M − HOAc]$^+$ (44), 285 [300 − Me]$^+$ (54), 119 (100). 10 mg **1** in 2 ml CH_2Cl_2 was stirred with 20 mg pyridine chlorochromate for 2 hr. TLC (Et_2O–petrol, 1:1) afforded 6 mg **3**, colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1785, 1750 (γ-lactone), 1670 (C=CCO); MS *m/z* (rel. int.): 316 [M]$^+$ (100), 301 [M − ·Me]$^+$ (8), 288 [M − CO]$^+$ (6), 219 [M − ·CH_2–



]$^+$ (18), 83 [C_5H_7O]$^+$ (100).

2α,16-Dihydroxy-3α,4α-epoxykolavenic-15-acid lactone (**4**). Colourles gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1790, 1750 (γ-lactone), 1640 (C=C); MS *m/z* (rel. int.): 334.214 [M]$^+$ (15) ($C_{20}H_{30}O_4$), 316 [M − H_2O]$^+$ (9), 301 [316 − ·Me]$^+$ (7), 69 [C_5H_9]$^+$ (100). To 6 mg **4** in 1 ml $CHCl_3$ were added 10 mg 4-pyrrolidinopyridine and 0.15 ml Ac_2O. After 2 hr standing at room temp. usual work-up and TLC (Et_2O–petrol, 1:1) afforded 4 mg **5**, colourless crystals, mp 227°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1790 (γ-lactone), 1750 (OAc); MS *m/z* (rel. int.): 376 [M]$^+$ (2), 361 [376 − ·Me]$^+$ (4), 316 [M − HOAc]$^+$ (18), 125 (100).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{-20.0 \quad -20.0 \quad -22.7 \quad -36.4} (c = 0.11).$$

2α-Hydroxy-3α,4α-epoxy-13,14-dihydrokolavenol (**6**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3410 (OH), 1785, 1750 (γ-lactone); MS *m/z* (rel. int.): 324.266 [M]$^+$ (4) ($C_{20}H_{36}O_3$), 306 [M − H_2O]$^+$ (6), 291 [306 − ·Me]$^+$ (4), 223 [M − ·$CH_2CH_2CH(Me)CH_2CH_2OH$]$^+$ (28), 205 [223 − H_2O]$^+$ (22), 69 [C_5H_9]$^+$ (100); CI (*i*-butane): 325 [M + 1]$^+$ (12), 307 (325 − H_2O]$^+$ (100), 289 [307 − H_2O]$^+$ (80). 10 mg **6** was acetylated as above. TLC (Et_2O–petrol, 3:1) afforded 8 mg **7**, colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740, 1245 (OAc); MS *m/z* (rel. int.): 408.288 [M]$^+$ (2) ($C_{24}H_{40}O_5$), 348 [M − HOAc]$^+$ (51), 305 (348 − Ac]$^+$ (47), 205 [348 − ·$CH_2CH_2CH(Me)CH_2CH_2OAc$]$^+$ (75), 125 (100).

Table 2. ^{1}H NMR spectral data of compounds **8–19** (270 MHz, $CDCl_3$, TMS as internal standard)

	8a/b	**8c***	**9**(C_6D_6)	**10**	**11**	**12**	**13**	**14**	**15**	**16a**	**17b**	**18**	**19a/b**
2-H	2.07 *m*	2.05 *m*	1.94 *m*	2.05 *m*	2.05 *m*		2.07 *m*	2.07 *m*	2.07 *m*	2.1 *m*	2.1 *m*	2.1 *m*	
3-H	5.30 *br s*	5.29 *br s*	5.30 *br s*	5.30 *br s*	5.33 *br s*	5.29 *br s*	5.31 *br s*	5.31 *br s*	5.31 *br s*	5.34 *br s*	5.34 *br s*	5.31 *br s*	
8-H	1.45 *m*		2.08 *ddd*							2.49 *dd*	2.46 *dd*		
12-H								2.62 *ddd*	2.45 *m*	2.75 *ddd*	2.40 *m*		
12′-H								2.44 *ddd*		2.52 *ddd*			
13-H	1.45 *m*	1.45 *m*		1.45 *m*		1.45 *m*		—	—	—	—		
14-H	1.60 *m*	1.60 *m*		1.60 *m*		1.60 *m*	2.44 *m*	5.88 *dtq*	5.93 *dtq*	5.87 *br d*	5.93 *br d*	5.45 *br t*	5.37 *br t*
15-H	4.28 *dt*	4.12 *m*	4.30 *dd*	3.73 *m*	3.72 *m*	4.12 *m*	9.78 *t*	9.93 *d*	9.98 *d*	9.98 *d*	9.98 *d*	4.16 *br d*	4.58 *br d*
15′-H	4.05 *dt*		4.22 *dd*										
16-H	0.93 *d*	0.93 *d*	0.92 *d*	0.93 *d*	0.95 *d*	0.93 *d*	1.00 *d*	2.01 *d*	2.20 *d*	2.02 *d*	2.21 *d*	1.71 *br s*	
17-H	3.75 *dd*	4.14 *dd*	9.69 *d*	3.76 *dd*	9.75 *d*	4.14 *dd*	3.73 *dd*	3.77 *dd*	3.74 *dd*	—	—	3.77 *dd*	3.74 *dd*
17′-H	3.26 *dd*	3.75 *dd*		3.28 *dd*		3.75 *dd*	3.29 *dd*	3.34 *dd*	3.33 *dd*	—	—	3.29 *dd*	3.25 *dd*
18-H	1.70 *br s*	1.67 *br s*	1.64 *br s*	1.69 *br s*	1.71 *br s*	1.70 *br s*	1.70 *br s*	1.70 *br s*	1.73 *br s*	1.73 *br s*	1.71 *br s*	1.70 *br s*	
19-H	1.10 *s*	1.04 *s*	1.02 *s*	1.04 *s*	1.04 *s*	1.04 *s*	1.04 *s*	1.07 *s*	1.07 *s*	1.08 *s*	1.08 *s*	1.07 *s*	1.05 *s*
20-H	0.82 *s*	0.85 *s*	1.00 *s*	0.82 *s*	1.06 *s*	0.85 *s*	0.83 *s*	0.86 *s*	0.87 *s*	1.09 *s*	1.07 *s*	0.84 *s*	0.82 *s*
OCOR	2.30 *t*	2.32 *t*	2.30 *t*	2.32 *t*	—	2.32 *t*	—	—	—	—	—	—	2.30 *t*
	1.27 *br s*	1.26 *br s*	1.35 *m*	1.27 *m*	—	1.27 *br s*	—	—	—	—	—	—	1.27 *br s*
	0.90 *t*	0.87 *t*	0.97 *t*	0.87 *t*	—	0.87 *t*	—	—	—	—	—	—	0.90 *t*
OAc	—	2.08 *s*	—	—	—	2.08 *s*	—	—	—	—	—	—	—

* 400 MHz.

J(Hz): 8,17 = 3; 8,17′ = 9; 14,15 = 14,16 = 6.5; 15,15′ = 17,17′ = 10; 2′,3′ = 7.5; 19′,20′ = 7; compounds **9** and **11**: 7,8 = 4.3; 7′,8 = 11.5; 8,17 = 2.8; compound **13**: 14,15 = 2; compounds **14**/**15**: 14,15 = 7.5; 14,16 = 1.5; compounds **14** and **16**: 11,12 = 11.5; 11′,12 = 5; 11,12′ = 5; 11′,12′ = 11.5; 12,12′ = 12; compounds **16a**/**17a**: 7,8 = 2.5; 7′,8 = 11.5.

Table 3. ^{1}H NMR spectral data of compounds **23** and **24** (270 MHz, $CDCl_3$, TMS as internal standard)

	23	**24**
2-H	5.31 *br dd*	5.33 *br dd*
3-H	3.33 *ddd*	3.34 *br dd*
3′-H	3.02 *ddd*	3.01 *br dd*
4-H	7.35 *t*	7.27 *t*
9-H	2.60 *s*	2.55 *s*
11-H	5.11 *br s*	5.11 *br s*
11′-H	4.96 *dq*	4.96 *dq*
12-H	1.79 *br s*	1.79 *br s*
OMe	3.98 *s*	3.98 *s*
	3.96 *s*	—
OH	—	13.06

J(Hz): 2,3 = 9; 2,3′ = 8.5; 2,11 = 1.5; 3,4 = 1; 11,12 = 1.

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{-18.3 \quad -19.3 \quad -20.3 \quad -38.9} (c = 0.72).$$

10 mg **6** in 1 ml CH_2Cl_2 was stirred with 10 mg pyridine dichromate for 2 hr. TLC (Et_2O–petrol, 1:1) afforded 6 mg **7**, colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 2710, 1730 (CHO), 1720 (C=O); MS *m/z* (rel. int.): 320 $[M]^+$ (15), 305 $[M - \cdot Me]^+$ (6), 221 $[M - C_6H_{11}O]^+$ (50), 43 $[C_2H_3O)^+$ (100).

17-*Hydroxy*-13,14-*dihydrokolavenol arachidate and behenate* (**8a/8b**). Colourless gum, which could not be separated; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3610 (OH), 1730 (CO_2R); MS *m/z* (rel. int.): 340.318 $[C_{21}H_{41}CO_2H]^+$ (10), 312.287 $[C_{19}H_{37}CO_2]^+$ (6), 1290 $[M - RCO_2H]^+$ (2), 207 $[C_{14}H_{23}O]^+$ (25), 189 $[C_{14}H_{21}]^+$ (45), 81 (100); CI (*i*-butane): 631 $[M + 1]^+$ (1), 605 $[M + 1]^+$ (1). 50 mg **8a** and **8b** was heated in 0.5 ml Ac_2O for 1 hr at 70°. TLC (Et_2O–petrol, 1:1) afforded the acetates **8c/8d**, colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740, 1240 (OAc, CO_2R). 20 mg **8a** and **8b** in 2 ml dioxane–MeOH (1:1) was heated with 0.5 ml 2 N KOH for 3 hr at 70°. TLC (Et_2O) afforded 6 mg **10**, identical with the natural compound and 10 mg of a mixture of arachidic and behenic acid, which was identified by GC/MS: *m/z* (rel. int.): 340 $[M]^+$ (18), 57 $[C_4H_9]^+$ (100) and 312 $[M]^+$ (21), 57 $[C_4H_9]^+$ (100). 20 mg **8a** and **8b** was stirred in 1 ml CH_2Cl_2 with 20 mg pyridine dichromate. TLC (Et_2O–petrol, 1:1) afforded 10 mg **9a/9b**, colourless gum. For ^{1}H NMR see Table 2.

17-*Hydroxy*-13,14-*dihydrokolavenol* (**10**). Colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620 (OH); MS *m/z* (rel. int.): 308.217 $[M]^+$ (22) ($C_{20}H_{36}O_2$), 293 $[M - \cdot Me]^+$ (20), 275 $[293 - H_2O]^+$ (12), 265 $[293 - CO]^+$ (13), 207 $[C_{14}H_{23}O]^+$ (71), 189 $[207 - H_2O]^+$ (27), 95 $[C_7H_{11}]^+$ (100).

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{+18.5 \quad +19.4 \quad +22.0 \quad +35.4} (c = 0.96).$$

10 mg **10** in 0.5 ml Ac_2O was heated for 1 hr at 70°. TLC (Et_2O–petrol, 1:1) afforded 11 mg **12**, colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740, 1245 (OAc); MS *m/z* (rel. int.): 392 $[M]^+$ (14), 332 $[M - HOAc]^+$ (26), 317 $[332 - \cdot Me]^+$ (15), 189 $[C_{14}H_{21}]^+$ (100).

15-*Hydroxy*-13,14-*dihydrokolaven*-17-*al* (**11**). Colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620 (OH), 2720, 1715 (CHO); MS *m/z* (rel. int.): 306.256 $[M]^+$ (6) ($C_{20}H_{34}O_2$), 288 $[M - H_2O]^+$ (9), 273 $[288 - \cdot Me]^+$ (5), 205 $[C_{14}H_{21}O]^+$ (31), 177 $[205 - CO]^+$ (88), 95 $[C_7H_{11}]^+$ (100).

17-*Hydroxy*-13,14-*dihydrokolaven*-15-*al* (**13**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3610 (OH), 2750, 1720 (CHO); MS *m/z* (rel. int.): 306.256 $[M]^+$ (5) ($C_{20}H_{34}O_2$), 207 $[C_{14}H_{23}O]^+$ (52), 95 (100).

17-*Hydroxy*-13*Z*-*kolaven*-15*al* (**14**). Colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620 (OH), 2720, 1675, 1630 (C=CCHO); MS *m/z* (rel. int.): 304.240 $[M]^+$ (4) ($C_{20}H_{32}O_2$), 289 $[M - Me]^+$ (4), 271 $[289 - H_2O]^+$ (3), 207 $[C_{14}H_{23}O]^+$ (50), 95 $[C_7H_{11}]^+$ (100).

17-*Hydroxy*-13E-*kolaven*-15-*al* (**15**). Colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3630 (OH), 2740, 1680, 1635 (C=CCO_2R); MS *m/z* (rel. int.): 304.240 $[M]^+$ (7) ($C_{20}H_{32}O_2$), 289 $[M - Me]^+$ (5), 271 $[289 - H_2O]^+$ (5), 207 $[C_{14}H_{23}O]^+$ (22), 189 $[207 - H_2O]^+$ (22), 95 $[C_7H_{11}]^+$ (100).

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{+20.1 \quad +20.8 \quad +23.3 \quad +38.0} (c = 0.72).$$

To 10 mg **15** in 1 ml MeOH was added 15 mg $NaBH_4$. TLC (Et_2O) afforded 8 mg **18**, identical with the natural diol.

13*Z*-*Symphyoreticulic acid* (**16a**). Colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3500–2600, 1703 (CO_2H), 1685, 1630 (C=CCHO); MS *m/z* (rel. int.): 318.219 $[M]^+$ (6) ($C_{20}H_{30}O_3$), 300 $[M - H_2O]^+$ (42), 285 $[300 - Me]^+$ (8), 219 $[M - CH_2CH_2C(Me)=CHCHO]^+$ (34), 175 $[219 - CO_2]^+$ (32), 95 (100). To 5 mg **16a** in 1 ml Et_2O was added excess CH_2N_2. TLC (Et_2O–petrol, 1:1) afforded 5 mg **16b**, colourless gum. For ^{1}H NMR see Table 2.

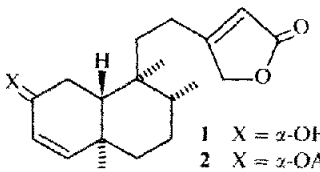
13E-*Symphyoreticulic acid* (**17a**). Colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3500–2600, 1700 (CO_2H), 1685, 1640 (C=CCO_2R); MS *m/z* (rel. int.): 318.219 $[M]^+$ (7) ($C_{20}H_{30}O_3$), 300 $[M - H_2O]^+$ (45), 285 $[300 - \cdot Me]^+$ (9), 219 $[C_{14}H_{19}O_2]^+$ (33), 175 $[219 - CO_2]^+$ (30), 95 $[C_7H_{11}]^+$ (100). As above with CH_2N_2 the ester **17b** was prepared, colourless gum. For ^{1}H NMR see Table 2.

17-*Hydroxy*-13E-*kolavenol* (**18**). Colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620 (OH), 1620, 855 (C=C); MS *m/z* (rel. int.): 306.256 $[M]^+$ (0.6), 288 $[M - H_2O]^+$ (10), 207 $[C_{14}H_{23}O]^+$ (70), 189 $[207 - H_2O]^+$ (45), 95 $[C_7H_{11}]^+$ (100).

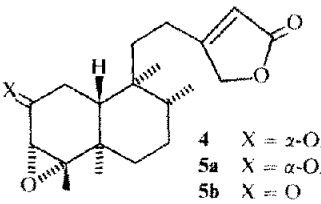
17-*Hydroxy*-13E-*kolavenol-arachidate and behenate* (**19a and 19b**). Colourless gum, containing **8a/b**; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620 (OH), 1730 (CO_2R); MS *m/z* (rel. int.): 340.318 $[C_{21}H_{41}CO_2H]^+$ (9), 312.287 $[C_{19}H_{39}CO_2H]^+$ (6), 81 (100). Saponification (see above) afforded **18**, still containing **10**. MnO_2 oxidation gave **15**, which could be separated from unchanged **10** by TLC (Et_2O–petrol, 1:1). $NaBH_4$ reduction yielded **18**, identical with the natural diol.

3-[3′,4′-*Dihydroxyphenyl*]-*propan*-1-*ol stearate and arachidate* (**20a and 20b**). Colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3550 (OH), 1735 (CO_2R); MS *m/z* (rel. int.): 462.371 $[M]^+$ (10) and 434.339 $[M]^+$ (6) ($C_{29}H_{50}O_4$ and $C_{27}H_{46}O_4$), 150 $[M - RCO_2H]$ (100); ^{1}H NMR ($CDCl_3$): δ 6.71 (*d*, 2-H, *J* = 2 Hz), 6.78 (*d*, 5-H, *J* = 8 Hz), 6.59 (*dd*, 6-H), 2.57 (*t*, 7-H, *J* = 7.5 Hz), 1.90 (*tt*, 8-H), 4.08 (*t*, 9-H, *J* = 6.5 Hz), 2.30 (*t*, 2′-H, *J* = 7 Hz), 1.25 (*br s*, $(CH_2)_n$), 0.89 (*t*, Me). 10 mg **20a/b** in 1 ml Ac_2O was heated for 1 hr at 70°. TLC (Et_2O–petrol, 1:1) afforded 10 mg **20c/d**, colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1775 (PhOAc), 1740 (CO_2R); MS *m/z* (rel. int.): 546.392 $[M]^+$ (0.5) ($C_{33}H_{54}O_6$), 518 $[M]^+$ (0.5), 504 $[M - ketene]^+$ (3), 462 $[504 - ketene]^+$ (24), 434 $[M - 2 \times ketene]^+$ (10), 150 $[462 - RCO_2H]^+$ (100), CI (*i*-butane): 547 $[M + 1]^+$ (100) and 519 $[M + 1]^+$ (15); ^{1}H NMR ($CDCl_3$): δ 7.01 (*d*, 2-H), 7.10 (*d*, 5-H), 7.05 (*dd*, 6-H), 2.68 (*t*, 7-H), 1.95 (*tt*, 8-H), 4.10 (*t*, 9-H), 2.28 *s* and 2.27 *s* (OAc).

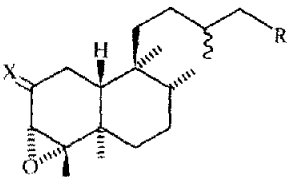
6,7-*Dimethoxytremetone* (**23**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1670, 1615, 1590 (PhCO); MS *m/z* (rel. int.): 262.121 $[M]^+$ (96)



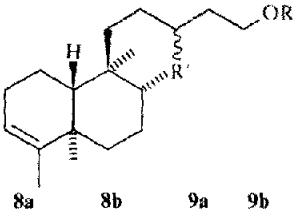
1 X = α-OH, H
2 X = α-OAc, H
3 X = O



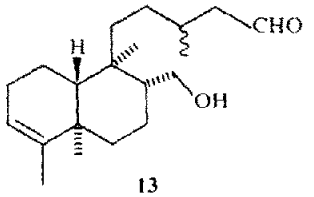
4 X = α-OH, H
5a X = α-OAc, H
5b X = O



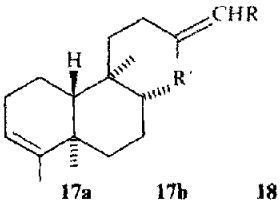
6 R = CH_2OH, X = α-OH, H
7 R = CHO, X = O



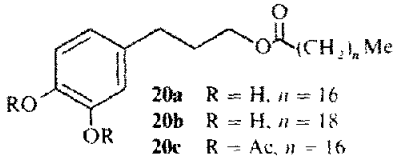
	8a	8b	8a	8b	9a	9b	10	11	12
R	Arach*	Behen*	Arach	Behen	Arach	Behen	H	H	Ac
R′	CH_2OH	CH_2OH	CH_2OAc	CH_2OAc	CHO	CHO	CH_2OH	CHO	CH_2OAc



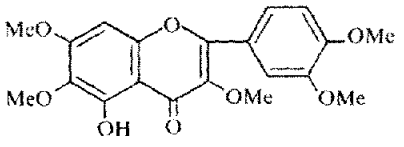
13



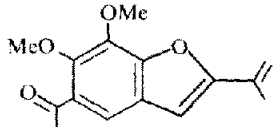
	14	15	16a	16b	17a	17b	18	19a	19b
R	CHO	CHO	CHO	CHO	CHO	CHO	CH_2OH	CH_2OAra	CH_2O Behen
R′	CH_2OH	CH_2OH	CO_2H	CO_2Me	CO_2H	CO_2Me	CH_2OH	CH_2OH	CH_2OH
13, 14	*Z*	*E*	*Z*	*E*	*E*	*E*	*E*	*E*	*E*



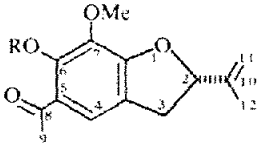
20a R = H, *n* = 16
20b R = H, *n* = 18
20c R = Ac, *n* = 16
20d R = Ac, *n* = 18



21



22



23 R = Me
24 R = H

* Arach = $CO(CH_2)_{18}Me$, Behen = $CO(CH_2)_{20}Me$.

($C_{15}H_{18}O_4$), 247 $[M - {}^{\cdot}Me]^+$ (100), 231 $[M - OMe]^+$ (21), 219 $[247 - CO]^+$ (10), 187 $[219 - C_3H_6]^+$ (61), 159 $[187 - CO]^+$ (16).

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