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DITERPENES AND OTHER CONSTITUENTS OF *MORITHAMNUS CRASSUS**

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Key Word Index—*Morithamnus crassus*; Compositae; Eupatorieae; diterpenes; new *ent*-labdane derivative; new *ent*-kauranol derivative; new tremetone derivatives.

Abstract—The investigation of one representative of the genus *Morithamnus* afforded, in addition to several known compounds, a new *ent*-labdane derivative, a new hydroxy-*ent*-kauranol and three tremetone derivatives. The structures were elucidated by spectroscopic methods. The chemotaxonomic situation is discussed briefly.

The small new genus *Morithamnus* (Compositae, tribe Eupatorieae) [1], has not been previously investigated chemically. We have now isolated the main constituents from *M. crassus* K. et R. The roots contained the widespread trideca-3,5,7,9,11-pentayn-1-ene (**1**) [2], germacrene D (**2**), humulene (**3**), caryophyllene (**4**) and the unusual hydrocarbons silphinene (**5**) [3], modhephene (**6**) [4, 5], β-isocomene (**7**) [5] and isocomene (**8**) [6, 7]. Furthermore, in addition to 6-hydroxytremetone (**9**) [8], 3β,6-dihydroxytremetone (**10**) [9], 3β-hydroxytremetone (**11**) [10] and 3β-angeloyloxy-6-hydroxytremetone (**12**) [11], two acetoxy-angelicates of **10** and **11** were isolated (**14** and **15**, respectively). While **14** is relatively stable, **15** easily lost acetoxy-angelic acid (**26**), which was also partially transformed to the lactone **27** during the separation of the plant extract. The structures of **14** and **15** followed from the ^{1}H NMR data (Table 1). The substitution pattern of the aromatic ring can be assigned by the typical signals of the aromatic hydrogens, while the *trans* configuration at C-2 and C-3 followed from the observed small coupling $J_{2,3}$. The nature of the acid part was deduced from the characteristic ^{1}H NMR signals. As the olefinic proton was a triplet of quartets, the acetoxy group had to be placed in the 4′-position. During the TLC

Table 1. ^{1}H NMR spectral data of compounds **14**, **15**, **16**, **16a**, **26a** and **27** (270 MHz, $CDCl_3$)

	14	**15**	**16**	**16a**	**26a**	**27**
2-H	5.15 *d(br.)*	5.15 *d(br.)*	4.85 *s(br.)*	4.88 *d*		—
3-H	6.02 *d*	6.06 *d*	5.10 *s(br.)*	5.15 *s(br.)*		—
4-H	8.06 *d*	7.88 *s*	7.38 *d*	7.39 *d*	—	—
6-H	8.02 *dd*	—	7.24 *dd*	7.28 *dd*	—	—
7-H	6.98 *d*	6.46 *s*	6.84 *d*	6.86 *d*	—	
8-H	—		4.84 *q*	5.86 *q*	—	
9-H	2.56 *s*	2.57 *s*	1.47 *d*	1.53 *d*		—
11-H	5.10 *s(br.)*	5.08 *s(br.)*	5.08 *s(br.)*	5.10 *s(br.)*	—	—
11′-H	4.99 *s(br.)*	4.99 *s(br.)*	4.91 *s(br.)*	4.92 *s(br.)*	—	—
12-H	1.77 *s(br.)*	1.74 *s(br.)*	1.75 *s(br.)*	1.76 *s(br.)*	—	—
OCOR	6.08 *tq*	6.07 *tq*			6.02 *tq*	7.14 *tq*
	5.02 *dq*	5.02 *dq*	—	—	5.02 *dq*	4.77 *dq*
	1.92 *dt*	1.92 *dt*			1.94 *dt*	1.95 *dt*
OAc	2.08 *s*	2.07 *s*	—	2.05 *s*	2.08 *s*	—
OH	—	13.06 *s*	1.67 *s(br.)*	1.46 *s(br.)*	—	—

J (Hz): 2,3 = 2.3; 4,6 = 1.5; 6,7 = 8.5; 3′,4′ = 5.5; 3′,5′ = 4′,5′ = 1.7; **16**/**16a**: 8,9 = 6.

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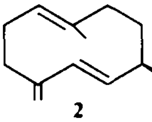
*Part 288 in the series "Naturally Occurring Terpene Derivatives". For part 287 see Bohlmann, F., Zdero, C., King, R. M. and Robinson, H. (1980) *Phytochemistry* **19**, 2663.

$Me[C{=}C]_5CH{=}CH_2$

1



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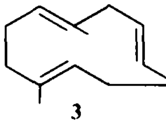

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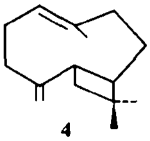

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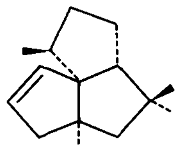

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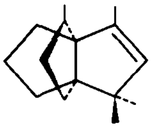

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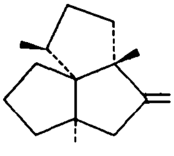

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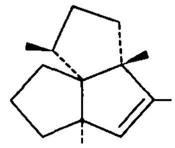

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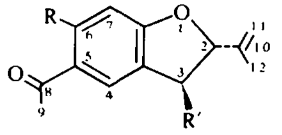
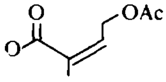
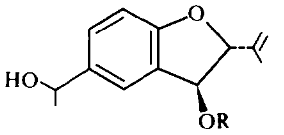
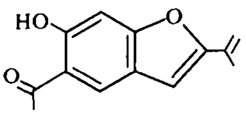


	9	**10**	**11**	**12**	**13**	**14**	**15**
R	OH	OH	H	OH	H	H	OH
R'	H	OH	OH	OAng	OAng		



16 R = H
16a R = Ac



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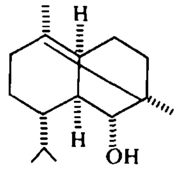

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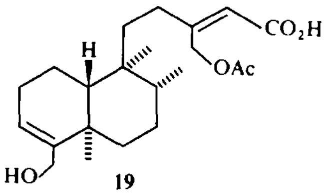

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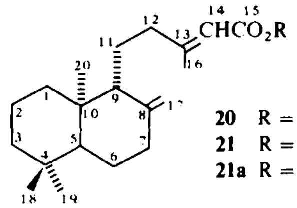
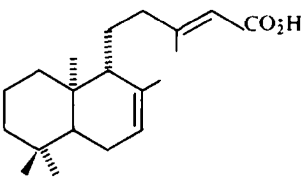


20 R = H(13,14*E*)
21 R = H(13,14*Z*)
21a R = Me(13,14*Z*)



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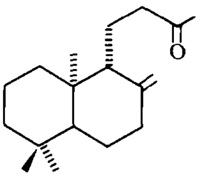

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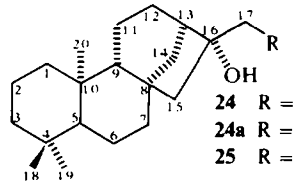
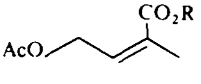
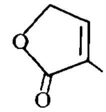


24 R = OH
24a R = OAc
25 R = H



26 R = H
26a R = Me



27

separation of **14** and **15**, the latter was always partially transformed to euparine (**17**) [12] and 4-acetoxy-angelic acid (**26**). Therefore it cannot be concluded that **17**, which has been directly isolated, is an artefact. The polar fractions contained the known *ent*-clerodane derivative **19** [13].

The aerial parts afforded **2–5**, **8**, **10**, **11**, **14** and **15**, as well as the angelate **13** [14], euparine (**17**), copaborneol (**18**) [15], the known di-norditerpene **23** [16], the *ent*-labdanes **20** [17] and **22** [17] and also the *Z*-isomer **21**, which was isolated as its methyl ester **21a**. Its structure followed from the ^{1}H NMR spectral data (Table 2). The stereochemistry of the 13,14-double bond was deduced from the shift differences of 16-H in the two isomers (**20** and **21**). The other signals were very similar. Finally, from the most polar fractions **26** and **27** were isolated and a diol, which was identified as the 17-hydroxy derivative (**24**) of *ent*-kauranol (**25**) [18]. The ^{1}H NMR spectrum of **24** (Table 2) and that of the corresponding acetate **24a** were nearly identical with that of **25** except for the signals of 17-H, which clearly indicated that the hydroxyl had to be placed at C-17. The close similarity of the spectra of **24** and

Table 2. ^{1}H NMR spectral data of compounds **21a**, **24** and **24a** (270 MHz, $CDCl_3$)

	21a	**24**	**24a**
7-H	2.40 *ddd*		
12-H	2.56 *t*		
14-H	5.64 *s*(*br*.)		
16-H	1.89 *d*		
17-H	4.88 *s*(*br*.)	3.78 *d*	4.23 *s*
17'-H	4.67 *s*(*br*.)	3.65 *d*	
18-H	0.87 *s*	1.01 *s*	1.02 *s*
19-H	0.80 *s*	0.88 *s*	0.87 *s*
20-H	0.68 *s*	0.80 *s*	0.81 *s*
OMe	3.67 *s*		–
OAc			2.11 *s*

J (Hz): **21a**: 6,7 = 2; 6',7 = 3; 7,7' = 13; 11,12 = 8; 14,16 = 1.5; **24**: 17,17' = 12.

25 support the proposed 16α-position of the tertiary hydroxyl. The optical rotation indicated an *ent*-kaurane derivative, as the values were very close to that of *ent*-kauran-16-ol [18]. Compound **24** has been prepared from *ent*-kaurene previously [19].

The polar fractions further contain a tremetone derivative, which was shown to be **16**, as manganese dioxide oxidation led to **11**. Partial acetylation gave **16a**. The ^{1}H NMR data (Table 1) were also in good agreement with this structure.

The compounds isolated are all similar or closely related to constituents also found in other genera of the tribe Eupatorieae. Only the very high concentration of tremetone derivatives is unusual. The occurrence of three different types of diterpenes and the isolation of the di-norditerpene **23** may be of interest. However, more species have to be investigated to establish relationships to other genera.

EXPERIMENTAL

IR: CCl_4; ^{1}H NMR: 270 MHz; MS: 70 eV, direct inlet; optical rotation: $CHCl_3$. The air-dried plant material (voucher RMK 8166, collected in north-eastern Brazil) was chopped and extracted with Et_2O-petrol (1:2). The resulting extracts were first separated by CC (Si gel, act. grade II) and further by repeated TLC (Si gel GF 254). Known compounds were identified by comparison of the IR and ^{1}H NMR spectra. The roots (350 g) afforded 4 mg **1**, 2 mg **2**; 1 mg **3**, 2 mg **4**, 3 mg **5**, 6 mg **6**, 3 mg **7**, 6 mg **8**, 5 mg **9**, 180 mg **10**, 100 mg **11**, 70 mg **12**, 400 mg **14** (Et_2O–petrol, 1:1), *ca* 600 mg **15** (Et_2O–petrol, 1:1), 600 mg **17**, 10 mg **19**, 1 g **26** and 0.2 g **27** (the last two most probably artefacts). The aerial parts (450 g) gave 400 mg **2**, 100 mg **3**, 50 mg **4**, 10 mg **5**, 10 mg **8**, 100 mg **10**, 100 mg **11**, 100 mg **13**, 1.5 g **14**, 1.5 g **15**, 150 mg **16**, 300 mg **17**, 100 mg **18**, 3.3 g **20**, 250 mg **21** (Et_2O–petrol, 1:1, isolated as its methyl ester **21a** after addition of CH_2N_2), 250 mg **22**, 100 mg **23**, 60 mg **24** (Et_2O), 0.5 g **26** and 0.1 g **27**.

3β-[4'-Acetoxyangeloyloxy]-tremetone (**14**). Colourless oil. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1742 (OAc), 1715, 1650 ($C{=}CCO_2R$), 1680, 1610 (PhCO); MS *m/e* (rel. int.): 358.142 (M^+, 17) ($C_{20}H_{22}O_6$), 200 (100) ($M - RCO_2H$), 185 (40) (200 − Me), 99 (40) ($HOCH_2CH{\equiv}C(Me)CO^-$), 43 (90) ($MeCO^+$).

$$[\alpha]_{24}^{\prime} = \frac{589}{-81.0}\;\frac{578}{-85.0}\;\frac{546}{-98.6}\;\frac{436\text{ nm}}{-187.2}\;(c = 1.0)$$

3β-[4'-Acetoxyangeloyloxy]-6-hydroxytremetone (**15**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3500–2700, 1650 (*O*-hydroxyacetophenone), 1750 (OAc), 1723 ($C{=}CCO_2R$) MS *m/e* (rel. int.): 374.137 (M^+, 5) ($C_{20}H_{22}O_7$), 216 (90) ($M - RCO_2H$), 201 (50) (216 − $^{\cdot}$Me), 99 (35) ($HOCH_2CH{=}C(Me)CO^+$), 43 (100) ($MeCO^+$). During TLC, formation of **17** and **26** was observed.

3β-Hydroxy-5-[1-hydroxyethyl]-2α-propen-2-yl-dihydrobenzofuran (**16**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3320 (OH), 1655, 910 ($C{=}CH_2$), 1615 (aromate); MS *m/e* (rel. int.): 220.110 (M^+, 95) ($C_{13}H_{16}O_3$), 205 (100) ($M - {}^{\cdot}Me$), 164 (39) (205 − C_3H_5), 149 (68) (164 − Me). 10 mg **16** were stirred for 3 hr in Et_2O with 100 mg MnO_2. TLC afforded 7 mg **11**, identical with authentic material. 10 mg **16** were partially acetylated (1 hr, 60°) yielding 8 mg **16a**, colourless oil; ^{1}H NMR see Table 1.

$$[\alpha]_{24}^{\lambda} = \frac{589}{-66.0}\;\frac{578}{-68.8}\;\frac{546}{-80.5}\;\frac{436\text{ nm}}{-165.0}\;(c = 0.7)$$

Z-Copalic acid methyl ester (**21a**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1720, 1640 ($C{=}CCO_2R$), 890 ($C{=}CH_2$); MS *m/e* (rel. int.): 318.256 (M^+, 52) ($C_{21}H_{34}O_2$), 303 (66) (M − Me), 287 (7) (M − $^{\cdot}CH_2C(Me){=}CHCO_2Me$), 81 (100) ($C_6H_9^+$).

$$[\alpha]_{24}^{\prime} = \frac{589}{-1.2}\;\frac{578}{-0.8}\;\frac{546}{-0.3}\;\frac{436\text{ nm}}{+4.5}\;(c = 0.7).$$

17-Hydroxy-ent-*kauranol* (**24**). Colourless crystals, mp 191° (Et_2O), IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600, 3420 (OH); MS *m/e* (rel. int.): 306 (M^+, 3), 288.245 (10) ($C_{20}H_{32}O$), 275 (100) ($M - {}^{\cdot}CH_2OH$), 257 (24) (275 − H_2O). 20 mg **24** in 0.1 ml Ac_2O were heated for 1 hr to 70°. TLC afforded 20 mg **24a**, colourless crystals, mp 153° (petrol); IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3590 (OH), 1740, 1235 (OAc); MS *m/e* (rel. int.): 348.266 (M^+, 5) ($C_{22}H_{36}O_3$), 330 (14) ($M - H_2O$), 315 (6) (330 − Me), 288 (5) (M − HOAc), 275 (100) (330 − CH_2OAc), 257 (18) (275 − H_2O), 232 (23) (257 − Me).

$$[\alpha]_{24}^{\prime} = \frac{589}{-47.3}\;\frac{578}{-48.0}\;\frac{546}{-52.7}\;\frac{436\text{ nm}}{-83.0}\;(c = 1.0).$$

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