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NEW GERMACRANOLIDES AND OTHER CONSTITUENTS FROM *TRICHOGONIOPSIS MORII**

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Key Word Index—*Trichogoniopsis morii*; Compositae; sesquiterpene lactones; germacranolides; eudesmanolide; labdane derivative; kaurane triol; toxol derivative.

Abstract—*Trichogoniopsis morii* afforded, in addition to known compounds, a new toxol derivative, two diterpenes, a labdane and an *ent*-kaurane derivative, an eudesmanolide and five germacranolides, a furanoheliangolide and four 1-oxo-germacranolides. The structures were elucidated by spectroscopic methods and a few chemical transformations. The chemotaxonomy of the genus *Trichogoniopsis* is discussed briefly.

INTRODUCTION

Trichogoniopsis (tribe Eupatorieae) is a small Brazilian genus of four known species [1] placed in the subtribe Gyptidinae [2]. It is closely related to *Trichogonia*, but is distinguished from the latter by the lack of hairs on the coralla lobes, the cleft anther appendages and distinct ribs on the stems. Both genera are distinct from all others in this subtribe by the pappus setae which are plumose when present. The chemical investigation of the recently described *Trichogoniopsis morii* K. et R. [3] is discussed in this paper.

RESULTS AND DISCUSSION

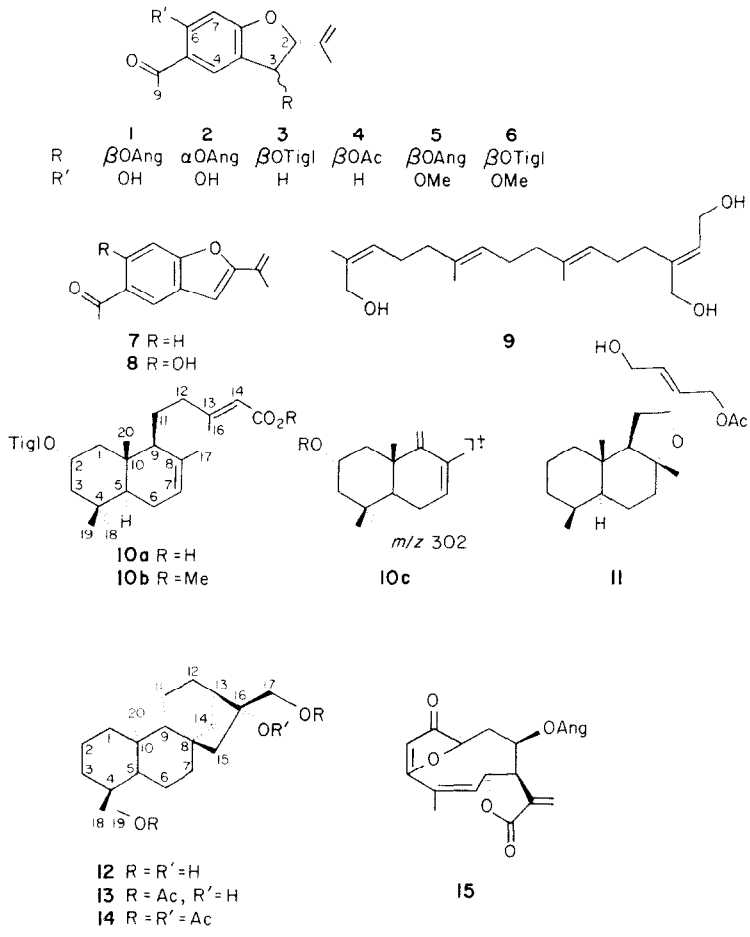
The roots of *T. morii* K. et R. afforded β-farnesene, dammadienyl acetate, **1**, **2** and **8**, while the aerial parts gave β-farnesene, germacrene D, stigmasterol, coumarin, **4–6**, **7** and a further toxol derivative, the tiglate **3**. The structure of **3** was deduced from its ^{1}H NMR spectrum (Table 1), which was close to that of the known angelate [4]. Furthermore, the geranylnerol derivative **9** [5] and the labdane acetate **11** [6] were present. Two further diterpenes, **10a** and **12**, were isolated as a methylester **10b** and a triacetate **14** respectively. The structure of **10b** followed from the molecular formula and the ^{1}H NMR data (Table 2). The presence of a labdane skeleton followed from the number and the chemical shifts of the methyl signals, while the position of the tiglate residue was deduced from the couplings of the corresponding lowfield signal, which obviously required an equatorial 2-tigloyloxy group. The *E*-configuration of the 13, 14-double bond followed from the chemical shift of H-16. All signals could be assigned by extensive spin decouplings as only two protons showed overlapping multiplets. The optical rotation favoured the presence of a labdane derivative, as that of eperua-7, 13-dien-15-oic acid with known absolute configuration showed opposite rotation [7]. The mass spectrum of **10b** contained no molecular ion. A prominent fragment was *m/z* 302 ($C_{20}H_{30}O_2$), obviously formed by a McLafferty reaction of H-9 with the side-chain double bond (see **10c**). The structure of **12** followed from the spectral data of the corresponding di- and triacetate. The ^{1}H NMR spectral data (Table 2) were close to those of 16, 17-dihydroxy- and 19-hydroxy-*ent*-kaurane respectively. As all simple *ent*-kauranes with known absolute configuration showed negative optical rotation, **12** most likely was 16α,17,19-trihydroxy-*ent*-kaurane. The 16α-orientation of the hydroxyl group followed from the downfield shift of H-13 in the spectrum of **14** if compared with the shift in the spectrum of **13**. In addition to **12**, the polar fractions contained a complex mixture of sesquiterpene lactones. Finally, seven compounds were obtained pure, the known furanoheliangolide **15** [8], the corresponding 4, 5-dihydro compound **16**, the eudesmanolide **17**, the ketones **18–20** and the heliangolide **21**. The struc-

Table 1. ^{1}H NMR spectral data of compound **3** (400 MHz, $CDCl_3$, TMS as int. standard)

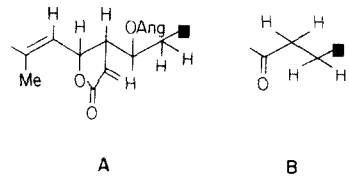
H-2	5.14 *d(br)*	H-11	5.09 *s(br)*
H-3	6.69 *d*	H-11′	4.98 *s(br)*
H-4	8.06 *d*	H-12	1.76 *s(br)*
H-6	7.99 *dd*	OTigl	6.60 *qq*
H-7	6.97 *d*		1.98 *dq*
H-9	2.55 *s*		1.87 *dq*

J (Hz): 2, 3 = 2.8; 4, 6 = 1.7; 6, 7 = 8.5; 3′, 4′ = 7; 3′, 5′ = 4′, 5′ = 1.5.

*Part 445 in the series "Naturally Occurring Terpene Derivatives". For Part 444, see Bohlmann, F., Zdero, C., King, R. M. and Robinson, H. (1982) *Phytochemistry* **21**, 2021.



ture of **16** followed from the molecular formula and the ^{1}H NMR data (Table 3), especially when compared with the data of the corresponding 8α-epimer [9]. The observed coupling $J_{2,4}$ required an α-orientated 4-methyl group, while the very small coupling $J_{7,8} < 1$ could only be explained with a β-orientated ester group at C-8. Spin decoupling established the assignment of all signals. The structure of **17**, molecular formula $C_{20}H_{24}O_5$, was deduced from the ^{1}H NMR data (Table 4), and by spin decoupling. Irradiation of the signal at δ 2.94 collapsed the doublets of the exomethylene protons to singlets and those at δ 5.09 and 5.89 to a broadened singlet and a double doublet respectively. As the latter was further coupled with two double doublets at δ 2.18 and 1.86 the signals of H-6–H-9 could be assigned. Irradiation of the olefinic methyl signal sharpened the H-6 doublet, which also was altered by irradiation of the multiplet at δ 2.43. These results could only be explained with a 4, 5-double bond. The downfield shifted threefold doublet at δ 2.74 was coupled with the multiplet at δ 2.43 thus supporting the presence of a keto group at C-1, which was in good agreement with the downfield shift of the H-14 signal. The ^{1}H NMR spectra of **18–20** (Table 3) showed that these three lactones were germacranolides, which only differed in the substitution at C-3. In the spectrum of **18** spin decoupling led to the sequences **A** and **B**:



The presence of a keto group in the **B**-part was deduced from the chemical shift of the corresponding methylene protons while the relative position of the two oxygen functions of part **A** was proposed from the chemical shifts, which were similar to those of related lactones. The chemical shift of an additional methyl singlet required a position at a hydrogen group bearing a carbon, its presence followed from the IR spectrum and the mass spectrum. These sequences could only be combined to give **18**. The stereochemistry followed from the couplings observed, while that at C-10 was assumed by analogy to a large number of lactones isolated from the tribe Eupatorieae. We have named **18** trichomoriolide. The ^{1}H NMR spectrum of **19** showed an additional lowfield double doublet at δ 4.91. The chemical shift indicated an allylic secondary hydroxyl group. Irradiation of the H-5 signal sharpened this slightly broadened signal thus establishing a 3-position of the hydroxy group. This was further supported by irradiation at δ

Table 2. ^{1}H NMR spectral data of compounds **10b**, **13** and **14** (400 MHz, $CDCl_3$, TMS as int. standard)

	10b	**13***	**14†**
H-1α	1.27 *dd*		
H-1β	1.80 *m*		
H-2	5.05 *dddd*		
H-3α	1.04 *dd*	1.83 *d(br)*	1.80 *d(br)*
H-3β	2.14 *d(br)*	0.78 *ddd*	0.76 *ddd*
H-5	1.22 *dd*		
H-6α	2.00 *d(br)*		
H-6β	1.88 *dd(br)*		
H-7	5.43 *s(br)*		
H-9	1.70 *m*		
H-11	1.37 *ddddd*		
H-11′	2.08 *dddd*		
H-12	2.35 *ddd*		
H-12′	1.59 *ddd*		
H-13	—	2.06 *s(br)*	2.48 *s(br)*
H-14	5.68 *q*		1.93 *d(br)*
H-16	2.17 *d*	—	—
H-17	1.70 *s(br)*	4.22 *s(br)*	4.93 *d* 4.41 *d*
H-18	0.98 *s*	1.04 *s*	1.01 *s*
H-19	0.92 *s*	4.20 *d* 3.88 *d(br)*	4.18 *d* 3.87 *d(br)*
H-20	0.85 *s*	0.95 *s*	0.92 *s*
OMe	3.68 *s*	—	—
OTigl	6.84 *qq*	—	—
	1.79 *dq*		
	1.83 *dq*		

*OAc 2.11 *s*, 2.05 *s*;† OAc 2.06 *s*, 2.05 *s*, 1.99 *s*.

J(Hz): compound **10b**: 1α, 1β = 12; 1α, 2 = 12; 1β, 2 = 3.5; 2, 3α = 12; 2, 3β = 3.5; 3α, 3β = 12; 5, 6α = 4.5; 5, 6β = 12; 6α, 6β = 17; 9, 11 = 10; 11, 11′ = 14; 11, 12 = 4; 11, 12′ = 12; 11′, 12 = 12; 11′, 12′ = 6; 12, 12′ = 15; 14, 16 = 1; 3′, 4′ = 7; 3′, 5′ = 4′, 5′ = 1.5.

Table 3. ^{1}H NMR spectral data of compounds **16** and **18–20** (400 MHz, $CDCl_3$, TMS as int. standard)

	16	**18**	**19**	**20**
H-1	—	—	—	—
H-2 H-2′	5.54 *s(br)*	2.90 *m** 2.86 *m**	3.06 *dd* 2.57 *dd*	3.05 *dd* 2.68 *dd*
H-3	—	2.34 *m** 2.21 *m**	4.91 *dd(br)*	5.70 *dd(br)*
H-4	3.05 *dq(br)*	—	—	—
H-5	2.61 *ddd* 2.07 *d(br)*	5.10 *dq*	5.17 *dq(br)*	5.28 *d(br)*
H-6	4.55 *dd*	5.01 *dd*	5.09 *dd*	5.07 *dd*
H-7	3.26 *dddd*	2.70 *dddd*	2.66 *dddd*	2.68 *d(br)*
H-8	5.21 *dd*	5.79 *ddd*	5.79 *ddd*	5.79 *ddd*
H-9	2.73 *dd*	2.18 *dd*	2.20 *dd*	2.22 *dd*
H-9′	2.24 *dd*	2.05 *dd*	2.04 *dd*	2.01 *dd*
H-13	6.36 *d*	6.24 *d*	6.25 *d*	6.26 *d*
H-13′	5.71 *d*	5.57 *d*	5.56 *d*	5.55 *d*
H-14	1.40 *s*	1.30 *s*	1.32 *s*	1.31 *s*
H-15	1.38 *d*	1.92 *d*	1.95 *s(br)*	1.88 *d*
OAng	6.11 *qq*	6.07 *qq*	6.09 *qq*	6.09 *qq*
	1.94 *dq*	1.94 *dq*	1.96 *dq*	1.94 *dq*
	1.80 *dq*	1.80 *dq*	1.82 *dq*	1.81 *dq*
OH	—	3.97 *s*	3.88 *s*	3.85 *s*
OAc	—	—	—	2.11 *s*

*Not first order.

J(Hz): compound **16**: 2, 4 ~ 1; 4, 5 = 4, 15 = 7; 5, 5′ = 15; 5, 6 = 9; 6, 7 = 5; 7, 8 < 1; 7, 13 = 3; 7, 13′ = 2.7; 8, 9 = 4.5; 8, 9′ = 2.5; 9, 9′ = 15; compound **18**: 2, 2′ ~ 14; 5, 6 = 11; 5, 15 = 1.5; 6, 7 = 9.5; 7, 8 = 1.5; 7, 13 = 3.5; 7, 13′ = 3; 8, 9 = 5; 8, 9′ = 11; 9, 9′ = 15; compounds **19** and **20**: 2, 2′ = 13; 2, 3 = 11.5; 2, 3′ = 4.5; 5, 6 = 11; 5, 15 ~ 1; 6, 7 = 9.5; 7, 8 = 1.5; 7, 13 = 3.5; 7, 13′ = 3; 8, 9 = 5; 8, 9′ = 11.5; 9, 9′ = 15; OAng: 3′, 4′ = 7; 3′, 5′ = 4′, 5′ = 1.5.

4.91, which collapsed the double doublets at δ 3.06 and 2.57 to doublets. Their chemical shifts obviously required a neighbouring keto group, while the couplings observed agreed with an α-orientated hydroxy group, if a model was inspected. The ^{1}H NMR spectral data of **20** were close to those of **19**, only the H-3 signal was shifted markedly downfield, indicating that **20** was the acetate of **19**. **18** most likely was the precursor of **17**. Protonation at the 10-hydroxy group would lead to a carbonium ion, which could be transformed to **25**, surely the direct precursor of **17**. The lactone **21** was isomeric with **19**. However, the ^{1}H NMR spectra (Table 5) differed completely, though obviously **19** and **21** had the same oxygen functions. Spin decoupling showed that the narrowly split signal at δ 2.61 was that of H-7. Consequently, the signals of H-6 and H-8 could be assigned. The marked downfield shift of the H-6 signal and the small coupling $J_{7,8}$ would be in agreement with a heliangolide with a 3β-hydrogen group [5, 10]. The corresponding signal at δ 4.65 showed a coupling with a hydroxy proton and with the lowfield double doublets at δ 3.33 and 2.87, obviously the signals of H-2. On heating with acetic anhydride, **21** afforded a small amount of the acetate **22** and, as the main compounds, the *cis*, *trans*-isomeric elimination products **23** and **24**.

Table 4. ^{1}H NMR spectral data of compound **17** (400 MHz, TMS as int. standard)

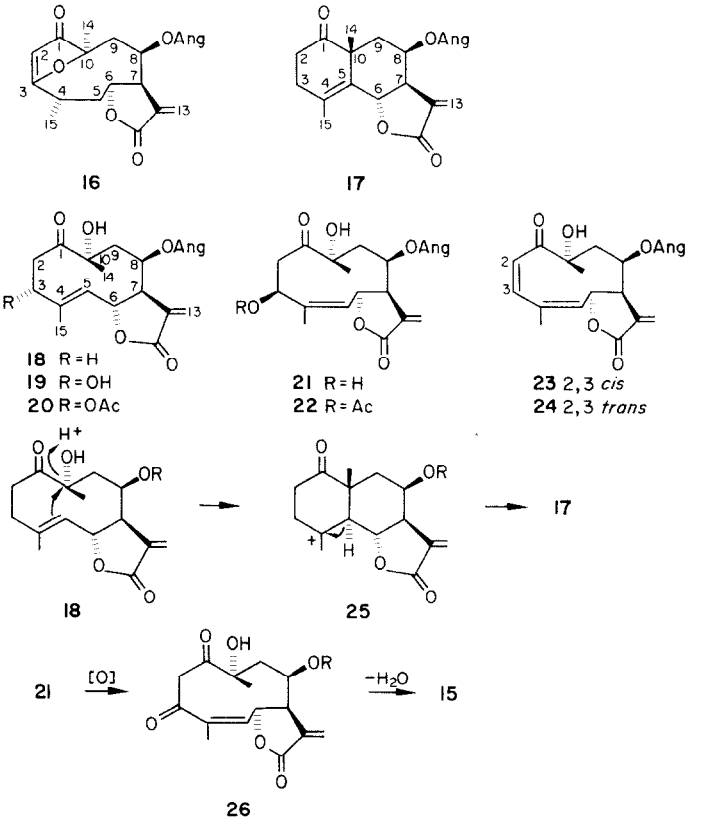
	$CDCl_3$	C_6D_6
H-2	2.74 *ddd*	2.32 *ddd*
H-2′	2.0 *m*	2.12 *m*
H-3 H-3′	2.43 *m*	1.87 *m*
H-6	5.09 *d(br)*	4.87 *d(br)*
H-7	2.94 *dddd*	2.08 *m*
H-8	5.89 *ddd*	5.57 *ddd*
H-9	2.18 *dd*	2.13 *dd*
H-9′	1.86 *dd*	1.48 *dd*
H-14	1.47 *s*	1.23 *s*
H-15	2.02 *s(br)*	1.91 *s(br)*
OAng	6.11 *qq*	5.69 *qq*
	1.98 *dq*	1.94 *dq*
	1.84 *dq*	1.64 *dq*

J(Hz): 1, 1′ = 15; 1, 2 = 7; 1, 2′ = 9; 3, 6 ~ 1.5; 6, 7 = 11.5; 6, 15 ~ 1.5; 7, 8 = 2.5; 7, 13 = 3; 8, 9 = 2.5; 8, 9′ = 3.8; 9, 9′ = 15; OAng: 3′, 4′ = 7; 3′, 5′ = 4′, 5′ = 1.5.

Table 5. ^{1}H NMR spectral data of compounds **21–24** (400 MHz, $CDCl_3$, TMS as int. standard)

	21	22	23	24	
				C_6D_6–$CDCl_3$ (2:1)	$CDCl_3$
H-2	3.33 *dd*	3.42 *dd*	6.57 *d*	6.53 *ddq*	6.96 *d(br)*
H-2′	2.87 *dd*	3.07 *dd*			
H-3	4.65 *ddd*	5.58 *dd*	6.49 *d(br)*	5.93 *d*	6.64 *d*
H-5	5.30 *dq*	5.29 *dq*	5.27 *d(br)*	5.10 *ddq*	5.63 *s(br)*
H-6	6.18 *dd*	5.64 *d(br)*	5.15 *ddd*	5.35 *ddq*	5.68 *s(br)*
H-7	2.61 *dddd*	2.66 *dddd*	2.76 *dddd*	3.04 *dddd*	3.32 *dddd*
H-8	5.36 *ddd*	5.36 *ddd*	5.35 *ddd*	5.47 *ddd*	5.42 *ddd*
H-9	2.98 *dd*	2.56 *dd*	2.56 *dd*	2.07 *dd*	2.39 *dd(br)*
H-9′	2.37 *dd*	2.50 *dd*	2.40 *dd(br)*	1.75 *dd*	2.29 *dd*
H-13	6.29 *d*	6.31 *d*	6.28 *d*	6.02 *d*	6.21 *d*
H-13′	5.70 *d*	5.73 *d*	5.70 *d*	5.06 *d*	5.63 *d*
H-14	1.42 *s*	1.40 *s*	1.46 *s*	1.02 *s*	1.41 *s*
H-15	1.83 *d*	1.89 *s(br)*	1.91 *s(br)*	1.42 *dd*	1.92 *dd*
OH	3.93 *s*	3.67 *s*	3.94 *s*	3.58 *s(br)*	3.65 *s(br)*
	2.57 *d*				
OAc	—	2.16 *s*	—	—	—
OAng	6.03 *qq*	6.07 *qq*	6.05 *qq*	5.79 *qq*	6.07 *qq*
	1.92 *dq*	1.96 *dq*	1.94 *dq*	1.95 *dq*	1.96 *dq*
	1.75 *dq*	1.79 *dq*	1.77 *dq*	1.84 *dq*	1.77 *dq*

J(Hz). compounds **21** and **22**: 2, 2′ = 14.5; 2, 3 = 3.5; 2′, 3 = 7; 3, OH = 3.5; 5, 6 = 9.5; 5, 15 = 1.5; 6, 7 = 3; 7, 8 = 2.3; 7, 13 = 2.5; 7, 13′ = 2; 8, 9 = 11; 8, 9′ = 5; 9, 9′ = 15; (compound **22**: 2, 3 = 2′, 3 = 7; 5, 6 = 10; 6, 7 = 1.5; 7, 8 = 2.5); compound **23**: 2, 3 = 12; 3, 5 = 5, 15 ~ 1; 5, 6 = 9.5; 6, 7 = 7, 8 ~ 1.5; 7, 13 = 1.5; 8, 9 = 5.5; 8, 9′ = 11; 9, 9′ = 15; compound **24**: 2, 3 = 16; 3, 5 = 2; 3, 15 = 1; 5, 6 = 5, 15 ~ 1.5; 6, 7 = 7, 8 = 6, 15 ~ 1.5; 7, 8 = 2.5; 7, 13 = 1.5; 8, 9 = 3; 8, 9′ = 11; 9, 9′ = 15.5; OAng: 3′, 4′ = 7; 3′, 5′ = 4′, 5′ = 1.5.



The structures of **22–24** followed from the ^{1}H NMR spectra (Table 5). As the signals of H-6 and H-9 in the spectrum of **22** were shifted drastically upfield, the conformation surely had changed. Most likely the alcohol **21** had a conformation with the 3β-hydroxy group in a quasi-axial orientation leading to a deshielding effect, which caused a downfield shift of H-6 and H-9β. This fact supported the proposed stereochemistry at C-3. Also in the spectra of **23** and **24**, the signals of H-6 and H-9β were at higher fields. Again the conformations must be different as in the spectrum of **24** $J_{6,7}$ was very small, indicating an angle of about 90°. Accordingly, the signals of H-6 and H-7 were both only narrowly split. Spin decoupling allowed the assignment of all signals, establishing the unusual relative shifts H-2 and H-3 in the spectrum of **23**. Most likely the 10-hydroxy group in **21–24** was hydrogen bonded with the 1-keto group as in the IR spectra of all compounds a band around 3480 cm^{-1} was present, while in the ^{1}H NMR spectra a relatively sharp singlet around δ 3.8 was visible. Oxidation of **21** would lead to **26**, surely the precursor of **15**.

The constituents isolated from *T. morii* show relationships to those of *Trichogonia* [11] by the co-occurrence of prenylated *p*-hydroxyacetophenones and of sesquiterpene lactones like **15** and **16**. Similar lactones are also present in *Conocliniopsis* [12] and *Bejaronoa* [5] both also placed in the subtribe Gyptidinae, while the genera *Lasiolaena* [13], *Agrianthus* [14] and *Stylotrichium* [15], also placed in the Gyptidinae, afforded highly oxygenated guaianolides. Only the latter genus gave a germacranolide. The chemistry reflects the already recognized taxonomic diversity of the subtribe [2].

EXPERIMENTAL

The air-dried plant material, grown from seeds in the greenhouse of the Smithsonian Institution, voucher RMK 8178, deposited in the U.S. National Herbarium, was extracted with Et_2O–petrol (1:2) and the extracts obtained were separated first by CC (Si gel) and further by repeated TLC (Si gel). Known compounds were identified by comparing the ^{1}H NMR spectra with those of authentic compounds. The roots (70 g) afforded 10 mg β-farnesene, 100 mg dammadienyl acetate, 10 mg **1**, 5 mg **2**, and 5 mg **8**, while the aerial parts (300 g) gave 10 mg β-farnesene, 10 mg germacrene D, 3 mg coumarin, 2 mg stigmasterol, 15 mg **3** (Et_2O–petrol, 1:3), 2 mg **4**, 15 mg **5**, 5 mg **6**, 10 mg **7**, 50 mg **9**, 210 mg **10a** (purified as its methyl ester, Et_2O–petrol, 1:3), 50 mg **11**, 50 mg crude **12**, which was purified by acetylation affording **13** and **14** (Et_2O–petrol, 1:1), 50 mg **15** and a mixture of **16–21**, which was separated by TLC (using first Et_2O–petrol, 3:1, then C_6H_6–$CHCl_3$–Et_2O, 2:2:1, then Et_2O and C_6H_6–$CHCl_3$–Et_2O, 1:1:1, as these solvent mixtures changed the R_f values of some of the lactones). Finally 10 mg **16**, 3 mg **17**, 30 mg **18**, 8 mg **19**, 15 mg **20** and 15 mg **21** were obtained. The original concentration of **16–21** was higher as the total amount before sepn was about 200 mg.

Toxol tiglate (**3**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1720, 1640 (C=CCO$_2$R), 1685, 1615, 1595 (PhCO); MS *m/z* (rel. int.): 300.136 [M]$^+$ (3) ($C_{18}H_{20}O_4$), 285 [M − Me]$^+$ (0.5), 200 [M − RCO$_2$H]$^+$ (74), 185 [200 − Me]$^+$ (48), 157 [185 − CO]$^+$ (9), 83 [C_4H_7CO]$^+$ (100), 55 [83 − CO]$^+$ (61);

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546\ nm}{-100 \quad -105 \quad -122} \quad (c = 0.95, CHCl_3).$$

3α-*Tigloyloxy-labda*-7, 13E-*dien*-15-*oic acid methyl ester* (**10b**). Colourless gum, IR $\nu_{max}^{CCl_4}$, cm^{-1}: 1720, 1650 (C=CCO$_2$R); MS *m/z* (rel. int.): 385 [M − OMe]$^+$ (0.5), 316 [M − RCO$_2$H]$^+$ (2), 302.224 [$C_{20}H_{30}O_2$]$^+$ (56) (McLafferty, H-9 with the side-chain), 202 [302 − RCO$_2$H]$^+$ (60), 187 [202 − Me]$^+$ (28), 107 [C_8H_{11}]$^+$ (100), 83 [C_4H_7CO]$^+$ (78), 82 [C_4H_6CO]$^+$ (58), 55 [83 − CO]$^+$ (91);

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\ nm}{+30 \quad +30 \quad +34 \quad +64} \quad (c = 0.53, CHCl_3).$$

16α, 17, 19-*Trihydroxy*-ent-*kaurane* (**12**). Colourless solid, which was acetylated by heating in 1 ml Ac_2O at 80° for 3 hr. TLC (Et_2O–petrol, 1:1) afforded 30 mg **13**, colourless gum, IR $\nu_{max}^{CCl_4}$, cm^{-1}: 3590 (OH), 1745 (OAc); MS *m/z* (rel. int.): 406, 256 [M]$^+$ (1) ($C_{24}H_{36}O_5$), 388 [M − H$_2$O]$^+$ (8), 333 [M − CH$_2$OAc]$^+$ (100), 273 [333 − HOAc]$^+$ (44), 255 [273 − H$_2$O]$^+$ (31) and 10 mg **14**, colourless crystals, mp 144–146°, IR $\nu_{max}^{CCl_4}$, cm^{-1}: 1745, 1240 (OAc); MS *m/z* (rel. int.): 448 [M]$^+$ (0.2), 388.261 [M − HOAc]$^+$ (75) ($C_{24}H_{36}O_4$), 373 [388 − Me]$^+$ (6), 346 [388 − ketene]$^+$ (16), 328 [388 − HOAc]$^+$ (100), 315 [388 − CH$_2$OAc]$^+$ (22), 313 [328 − Me]$^+$ (20), 268 [328 − HOAc]$^+$ (37), 255 [313 − HOAc]$^+$ (62), 123 (79), 81 (87), 69 (85), 55 (88);

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\ nm}{-82 \quad -85 \quad -98 \quad -163} \quad (c = 0.1, CHCl_3).$$

4β, 5-*Dihydroatripliciolide*-8O-*angelate* (**16**). Colourless gum, IR $\nu_{max}^{CCl_4}$, cm^{-1}: 1775 (γ-lactone), 1715 (C=CC=O, C=CCO$_2$R), 1600 (C=COR); MS *m/z* (rel. int.): 360.157 [M]$^+$ (9) ($C_{20}H_{24}O_6$), 261 [M − OCOR]$^+$ (5), 260 [M − RCO$_2$H]$^+$ (1), 83 [C_4H_7CO]$^+$ (100), 82 [C_4H_6CO]$^+$ (83), 55 [83 − CO]$^+$ (75);

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\ nm}{+8 \quad +10 \quad +13 \quad +49} \quad (c = 0.96, CHCl_3).$$

8β-*Angeloyloxy*-1-*oxo-arbusculin* (**17**). Colourless crystals, mp 165°, IR $\nu_{max}^{CCl_4}$, cm^{-1}: 1780 (γ-lactone), 1720 (CO, C=CCO$_2$R); MS *m/z* (rel. int.): 344 [M]$^+$ (0.3), 244.110 [M − RCO$_2$H]$^+$ (4) ($C_{15}H_{16}O_3$), 83 [C_4H_7CO]$^+$ (100), 55 [83 − CO]$^+$ (87); CI (isobutane): 345 [M + 1]$^+$ (100), 245 [345 − RCO$_2$H]$^+$ (81), 201 [245 − CO$_2$]$^+$ (33), 101 [RCO$_2$H + 1]$^+$ (40), 83 [101 − H$_2$O]$^+$ (42);

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\ nm}{-180 \quad -200 \quad -210 \quad -370} \quad (c = 0.1, CHCl_3).$$

Trichomoriolide (**18**). Colourless gum, IR $\nu_{max}^{CCl_4}$, cm^{-1}: 3480 (OH, hydrogen bonded), 1780 (γ-lactone), 1725, 1650 (C=CCO$_2$R), 1710 (C=O); MS *m/z* (rel. int.): 362.173 [M]$^+$ (0.5) ($C_{20}H_{26}O_6$), 262 [M − RCO$_2$H]$^+$ (8), 244 [262 − H$_2$O]$^+$ (3), 234 [262 − CO]$^+$ (11), 216 [234 − H$_2$O]$^+$ (8), 201 [216 − Me]$^+$ (7), 83 [C_4H_7CO]$^+$ (100), 55 [83 − CO]$^+$ (98);

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\ nm}{+104 \quad +109 \quad +125 \quad +224} \quad (c = 1.81, CHCl_3).$$

3α-*Hydroxytrichomoriolide* (**19**). Colourless gum, IR $\nu_{max}^{CCl_4}$, cm^{-1}: 3600 (OH), 3450 (OH, hydrogen bonded), 1775 (γ-lactone), 1720, 1645 (C=CCO$_2$R), 1700 (C=O); MS *m/z* (rel. int.): 378.168 [M]$^+$ (0.3) ($C_{20}H_{26}O_7$), 360 [M − H$_2$O]$^+$ (1), 316

$[360-CO_2]^+$ (2), 278 $[M-RCO_2H]^+$ (1), 260 $[278-H_2O]^+$ (3), 83 $[C_4H_7CO]^+$ (100), 55 $[83-CO]^+$ (61).

3α-*Acetoxytrichomoriolide* (**20**). Colourless crystals, mp 151°, IR $\nu_{max}^{CCl_4}$, cm^{-1}: 3470 (OH, hydrogen bonded), 1775 (γ-lactone), 1750 (OAc), 1720 (C=CCO$_2$R), 1710 (C=O); MS *m/z* (rel. int.): 420.178 $[M]^+$ (0.3) ($C_{22}H_{28}O_8$), 402 $[M-H_2O]^+$ (0.1), 378 [M − ketene]$^+$ (1), 360 $[M-HOAc]^+$ (1.5), 320 $[M-RCO_2H]^+$ (0.5), 260 $[320-HOAc]^+$ (12), 242 $[260-H_2O]^+$ (3), 83 $[C_4H_7CO]^+$ (100), 55 $[83-CO]^+$ (91);

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\ nm}{+104 \quad +120 \quad +138 \quad +251} \quad (c = 0.55, CHCl_3).$$

3β-*Hydroxy*-4,5-cis-*trichomoriolide* (**21**). Colourless crystals, mp 180°; IR $\nu_{max}^{CCl_4}$, cm^{-1}: 3580 (OH), 3460 (OH, hydrogen bonded), 1770 (γ-lactone), 1720, 1650 (C=CCO$_2$R, C=O); MS *m/z* (rel. int.): 378.168 $[M]^+$ (0.5) ($C_{20}H_{26}O_7$), 360 $[M-H_2O]^+$ (1), 279 [M − OCOR]$^+$ (6), 261 [360 − OCOR]$^+$ (8), 260 $[360-RCO_2H]^+$ (2), 235 $[279-CO_2]^+$ (14), 217 $[235-H_2O]^+$ (12), 83 $[C_4H_7CO]^+$ (100), 55 $[83-CO]^+$ (98):

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\ nm}{-25 \quad -25 \quad -30 \quad -45} \quad (c = 0.04, CHCl_3).$$

15 mg **21** in 1 ml Ac_2O were heated at 80° for 2 hr. TLC (C_6H_6–$CHCl_3$–Et_2O, 2:2:1) afforded 2 mg **22**, colourless gum, MS *m/z* (rel. int.): 420.178 $[M]^+$ (0.5) ($C_{22}H_{28}O_8$), 360 $[M-HOAc]^+$ (0.5), 260 $[360-RCO_2H]^+$ (6), 83 $[C_4H_7CO]^+$ (100), 55 $[83-CO]^+$ (66), 4 mg **23**, colourless gum, IR $\nu_{max}^{CCl_4}$, cm^{-1}: 3490 (OH, hydrogen bonded), 1780 (γ-lactone), 1725 (C=CCO$_2$R), 1695 (C=CC=O); MS *m/z* (rel. int.): 360.157 $[M]^+$ (0.5) ($C_{20}H_{26}O_6$), 342 $[M-H_2O]^+$ (0.5), 260 $[M-RCO_2H]^+$ (6), 83 $[C_4H_7CO]^+$ (100), 55 $[83-CO]^+$ (73) and 8 mg **24**, colourless gum; IR $\nu_{max}^{CCl_4}$, cm^{-1}: 3490 (OH, hydrogen bonded), 1775 (γ-lactone), 1720 (C=CCO$_2$R), 1695 (C=CC=O); MS *m/z* (rel. int.): 360.157 $[M]^+$ (0.5) ($C_{20}H_{26}O_6$), 260 $[M-RCO_2H]^+$ (5), 83 $[C_4H_7CO]^+$ (100), 55 $[83-CO]^+$ (62).

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