Phytochemistry, Vol. 21, No. 1, pp. 161–165, 1982.
Printed in Great Britain.

0031-9422/82/010161-05 $03.00/0
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GUAIANOLIDES AND HOMODITERPENES FROM *LASIOLAENA MORII**

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(*Received* 14 *April* 1981)

Key Word Index—*Lasiolaena morii*; Compositae, Eupatorieae; sesquiterpene lactones; guaianolides; diterpenes; geranyl nerol derivatives; homoditerpenes; tremeton derivatives; lignane derivative.

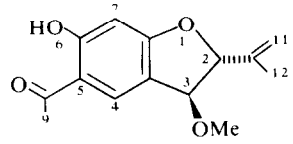
Abstract—The investigation of *Lasiolaena morii* afforded in addition to known compounds four new guaianolides, three diterpenes derived from geranyl nerol including two homoditerpenes, two tremetone derivatives and a dimer of coniferyl acetate. The structures were elucidated by spectroscopic methods and a few chemical transformations. The chemotaxonomic situation is discussed briefly.

INTRODUCTION

Recently we have isolated more than 20 sesquiterpene lactones from *Lasiolaena santosii* [1]. We now wish to report that *L. morii* K. et R. contains 15 sesquiterpene lactones, four of which have not been isolated before, three geranyl nerol derivatives, two of them being homoditerpenes, a coniferyl acetate dimer and two tremetone derivatives.

RESULTS AND DISCUSSION

The roots of *L. morii* afforded germacrene D, squalene, dammadienol and its acetate, dammadienone, friedelinol and the tremetone derivatives **1** and **2**, the structures of which followed from the ^{1}H NMR data (Experimental), especially when compared with those of closely related compounds. The aerial parts gave germacrene D, germacrene C, α- and γ-humulene, dammadienyl acetate, dammadienone, friedelinol, stigmasterol, **1**, **2**, **3** [2], **4**, **5** and **6** [1] as well as the guanianolides **7**–**9** [1], **11** [1], **13** [1], **16** [3], **17** [4] and the germacranolide **18** [1]. The ^{1}H NMR spectra of **16** and **17** were identical with those of two lactones isolated previously [3, 4], for which, however, a 9α-OH group was proposed. In the case of **18** the 9β-configuration was established, while **11** existed as two conformers, both with a small coupling $J_{8,9}$. Only with a *cis*-orientation of both oxygen functions at C-8 and C-9 is this possible, as otherwise a larger coupling would have been observed in one of the conformers. On biogenetic grounds, it is likely that all lactones from



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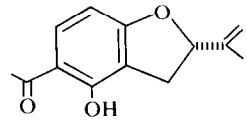

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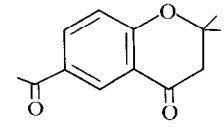

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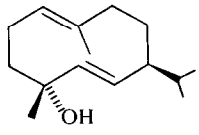

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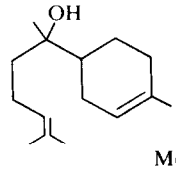

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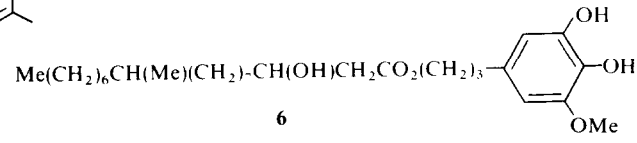

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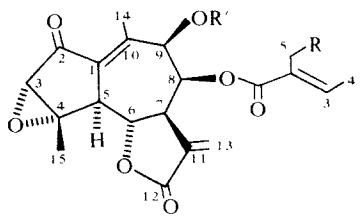
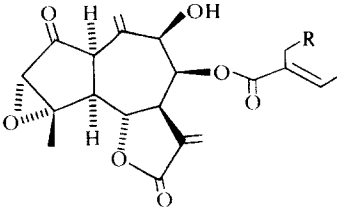
* Part 380 in the series "Naturally Occurring Terpene Derivatives". For part 379, see Bohlmann, F., Singh, P. and Jakupovic, J. (1982) *Phytochemistry* **21**, 157.



7 R = R′ = H
8 R = OAc, R′ = H
9 R = OAc, R′ = Ac



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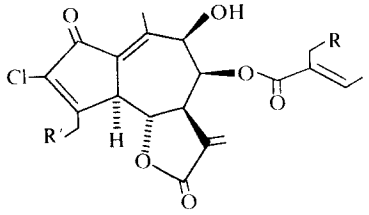
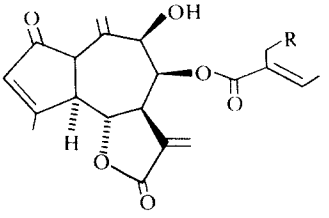


12 R = H, R′ = OH
13 R = OAc, R′ = H



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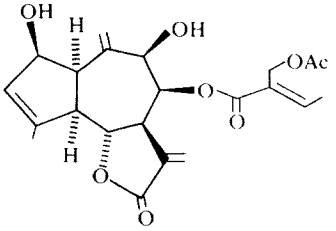
15 R = OAc



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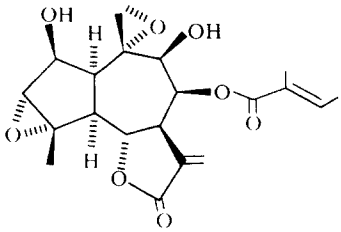

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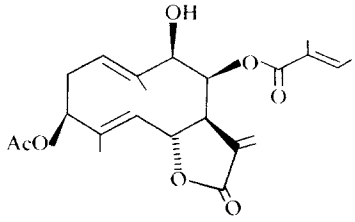

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Lasiolaena have a 9β-oxygen function. If this is true, the configuration at C-9 has to be changed in the corresponding lactones from *Agrianthus* [4] and *Stylotrichium* [3] and the differences in the couplings attributed to small changes in the conformations. We have reinvestigated the stereochemistry of **16**. Eu(fod)$_3$ induced shifts in the spectrum of **16** supported the 9β-hydroxyl group (Table 1). Both H-14 signals were shifted strongly, which required a β-orientation of both hydroxyls at C-2 and C-9.

The guaianolides **10**, **12**, **14** and **15** were present in the aerial parts of the plant. The ^{1}H NMR data of **10** (Table 1) were close to those of **11**, however, the ester group was replaced by a tiglyl residue. Again two conformers were present, all signals being doubled, as in the spectrum of **11** [1]. The ^{1}H NMR data of **12** (Table 1) were close to those of **13**. Again the ester residue was changed to tiglate, but an additional hydroxy group was present, obviously positioned at one of the olefinic methyl groups. The new broadened doublets at δ 4.98 and 4.77 replaced the methyl signal at higher fields, which most probably was that of H-15. This assumption was established by spin decoupling. Irradiation of the H-5 signal sharpened the methyl signal, while the doublets of H-15 were unaffected. The structures of **14** and **15**, which obviously only differed in the ester residue, also could be deduced from their ^{1}H NMR spectra (Table 1), which were in part similar to those of **10** and **11**, respectively. However, the H-3 signal was at much lower fields, indicating that the epoxide group was replaced by a 3,4-double bond. Consequently, the chemical shifts of the other protons in the spectra of **10** and **14** were somewhat different too, and only one conformer was present as clearly followed from the spectra of **14** and **15**. The polar fractions also contained a complex mixture of compounds with several oxygen functions, which could be separated with difficulty only. One of these compounds was the triol **24** [1], while a second had an additional acetoxy group. This compound, however, could only be isolated after oxidation to **23**. The ^{1}H NMR data (Table 2) showed that the aldehyde

Table 1. ^{1}H NMR spectral data of compounds **10**, **12** and **14–16** (400 MHz, $CDCl_3$, TMS as int. standard)

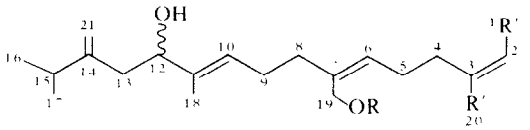
	10		**12**	**14**	**15** (50°)	**16**	Δ
	A	B					
H-1	3.57 *d*	2.96 *d*	—	3.30 *d* (*br*)	3.30 *d* (*br*)	3.62 *dd* (*br*)	0.11
H-3	3.34 *s*	3.41 *s*	—	6.18 *s* (*br*)	6.17 *s* (*br*)	5.63 *dq*	0.12
H-5	2.89 *dd*	2.54 *dd*	3.62 *d* (*br*)	3.16 *dd* (*br*)	3.16 *dd* (*br*)	2.83 *dd* (*br*)	0.07
H-6	5.01 *dd*	4.57 *dd*	4.00 *dd*	4.60 *dd* (*br*)	4.64 *dd* (*br*)	4.96 *dd*	0.13
H-7	3.29 *dddd*	3.65 *dddd*	3.35 *ddd* (*br*)	3.19 *ddd* (*br*)	3.22 *ddd* (*br*)	3.27 *dddd*	0.09
H-8	4.27 *dd*	5.37 *dd*	5.84 *s* (*br*)	5.79 *be*	5.80 *d* (*br*)	5.55 *dd*	0.19
H-9	4.89 *d* (*br*)	5.16 *d* (*br*)	4.91 *s* (*br*)	4.52 *br*	4.54 *d* (*br*)	4.70 *d*	0.19
H-13	6.31 *d*	6.24 *d*	6.29 *d*	6.35 *d*	6.34 *d*	6.27 *d*	0.04
H-13′	5.44 *d*	5.41 *d*	5.64 *d*	5.69 *d* (*br*)	5.68 *d* (*br*)	5.49 *d*	0.04
H-14	5.37 *s* (*br*)	5.38 *s* (*br*)	2.42 *s* (*br*)	5.51 *s* (*br*)	5.48 *s* (*br*)	5.35 *s* (*br*)	0.18
H-14′	5.17 *s* (*br*)	5.31 *s* (*br*)		5.13 *s* (*br*)	5.13 *s* (*br*)	5.27 *s* (*br*)	0.20
H-15	1.73 *s*	1.61 *s*	4.98 *d* (*br*)	2.35 *s* (*br*)	2.34 *s* (*br*)	1.92 *s* (*br*)	0.04
H-15′			4.77 *d* (*br*)				
OR	6.81 *m*	6.81 *m*	6.75 *q* (*br*)	6.78 *q* (*br*)	7.11 *q*	7.15 *q*	0.05
	1.76 *d* (*br*)	1.78 *d* (*br*)	1.78 *d* (*br*)	1.77 *d* (*br*)	4.79 *d*	1.95 *d*	0.0
	1.79 *s* (*br*)	1.77 *s* (*br*)	1.75 *s* (*br*)	1.76 *s* (*br*)	4.74 *d*	4.87 *d*	0.07
					1.94 *d*	4.76 *d*	0.07
					1.97 *s*	2.00 *s*	0.03
						H-2 4.76 *br*	0.26

J (Hz): conformer **10A**: 1,5 = 5,6 = 6,7 = 9; 7,8 = 5; 7,13 = 3.5; 7,13′ = 3; 8,9 = 6; conformer **10B**: 1,5 = 5,6 = 7; 6,7 = 11; 7,8 = 3.5; 13 = 3.5; 7,13′ = 3; 8,9 = 5; compound **12**: 5,6 = 6,7 = 10; 8,9 ~ 1; 7,13 = 7,13′ = 3; 15,15′ = 12; compound **14**: 1,5 = 8; 5,6 = 6,7 = 10; 7,13 = 3.5; 7,13′ = 3; compound **15**: 1,5 = 7.5; 5,6 = 6,7 = 10; 7,8 ~ 2; 7,13 = 3.5; 7,13′ = 3; 8,9 = 3; compound **16**: 1,2 = 7; 1,5 = 9; 2,3 = 2, 15 = 1.5; 5,6 = 6,7 = 10; 7,13 = 3.5; 7,13′ = 3; 7,8 = 3.5; 8,9 = 6; OTigl: 3′,4′ = 7; OTiglOAc: 3′,4′ = 7; 5′,5′ = 12.

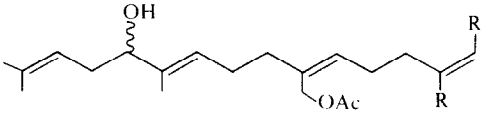
Table 2. ^{1}H NMR spectral data of compounds **19**, **20**, **21**, and **23** (400 MHz, $CDCl_3$, TMS as int. standard)

	19	**20**	**21**	**23**
H-1	4.15 *d*	4.18 *d*	10.30 *d*	10.30 *d*
H-2	5.69 *t*	5.68 *t*	6.54 *d*	6.54 *d*
H-4	2.25—	2.25—	2.77 *t*	2.77 *t*
H-5	2.1 *m*	2.1—	2.32 *dt*	2.33 *dt*
H-6	5.29 *t*	5.40 *t*	5.36 *t*	5.37 *t*
H-8	2.25—	2.25—	2.10 *m*	2.10 *m*
H-9	2.1 *m*	2.1 *m*		
H-10	5.41 *t* (*br*)	5.38 *t* (*br*)	5.39 *t* (*br*)	5.35 *t* (*br*)
H-12	4.09 *dd*	4.10 *dd*	4.08 *dd*	3.97 *dd*
H-13	2.31 *dd*	2.31 *dd*	2.29 *dd*	2.20 *m*
	2.25—	2.25	2.20 *dd*	
	2.1 *m*	2.1 *m*		
H-14	—	—	—	5.09 *t* (*br*)
H-15	2.25–2.1 *m*	2.25–2.1 *m*	2.26 *qq*	—
H-16	1.04 *d*	1.04 *d*	1.05 *d*	1.71 *s*
H-17	1.01 *d*	1.01 *d*	1.02 *d*	1.61 *s*
H-18	1.62 *s*	1.62 *s*	1.62 *s*	1.63 *s*
H-19	4.02 *s*	4.57 *s*	4.51 *s*	4.51 *s*
H-20	4.04 *s*	4.05 *s*	9.66 *s*	9.66 *s*
H-21	4.89 *s*	4.89 *s*	4.90 *s*	—
	4.80 *s*	4.80 *s*	4.82 *s*	
OAc	—	2.06 *s*	2.05 *s*	2.05 *s*

J(Hz): compounds **19**/**20**: 1,2 = 5,6 = 9,10 = 6.5; 12,13 = 9; 12,13′ = 4; 15,16 = 15,17 = 7; compound **21**: 1,2 = 4,5 = 5,6 = 9,10 = 15,16 = 15,17 = 7; 12,13 = 8.5; 12,13′ = 5; compound **23**: 1,2 = 4,5 = 5,6 = 9,10 = 12,13 = 13,14 = 7; 12,13′ = 5.



19 R = H, R' = CH_2OH
20 R = Ac, R' = CH_2OH
21 R = Ac, R' = CHO



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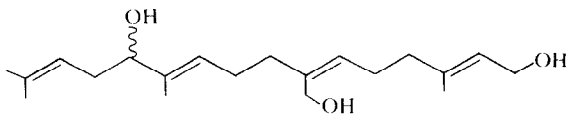
23 R = CHO



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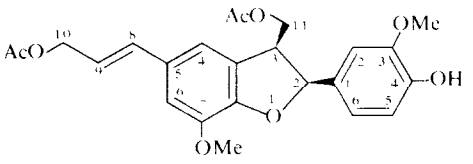

25

carbonyls were *trans*-orientated at C-1 and C-20 (chemical shift of H-1 and H-20), while the free hydroxyl must be at C-12, as followed from spin decouplings in C_6D_6, where the signals of the olefinic protons were separated nicely. Irradiation of the signals of H-13 allowed the assignment of the signal of H-12 and H-14. As the latter proton showed couplings with two methyl groups the position of the hydroxyl was settled. Further decoupling showed that the acetoxy group was at C-19. Irradiation of the signal of H-4 (triplet at lowest field) led to the assignment of the signal of H-5. This signal was coupled with the olefinic one at the highest field. The latter showed an allylic coupling with the signal of the CH_2OAc group. The stereochemistry of the double bond was deduced by comparing the chemical shifts with those of similar compounds. The natural triol therefore was 12,20-dihydroxy-19-acetoxy geranyl nerol (**22**). Two further compounds were homoditerpenes, one being a tetrol, while the other was a monoacetate of the latter. The acetate on oxidation afforded a dialdehyde, its ^1H NMR spectrum (Table 2) led to the structure **21**. All signals could be assigned by spin decoupling. Starting with the signal of the proton under the hydoxy group, the signals of H-13 and H-10 could be assigned. As H-13 was coupled with H-21 and the latter with H-15, which was coupled with the methyl doublets (H-16 and H-17) the left part of the molecule was settled. The position of the aldehyde carbonyls clearly followed directly from the ^1H NMR spectrum, while that of the acetoxy group was assigned as above by spin decoupling starting with the H-4 signal. Consequently, the structure of the dialdehyde was **21** and that of the natural compounds **19** and **20**. All three compounds gave no molecular ion in the EIMS or CIMS. Short heating of **21** in benzene with *p*-toluene sulfonic acid, however, gave a mixture of conjugated trienes, which gave a clear molecular ion, establishing the presence of homoditerpenes. Obviously, the methylene group at C-14 was introduced into the corresponding geranyl nerol derivatives, most probably by using methionine as in the case of steroids with an extra carbon in the side-chain. **19** and **20** seem to be first examples of homogeranyl nerol derivatives. Finally, a small amount of **25** was isolated, its structure was deduced from the molecular formula and the ^1H NMR data (Experimental). The substitution pattern easily followed from the signals of the aromatic protons. The relative position of the methoxy group was assigned following biogenetic considerations, as **25** obviously was a dimer of coniferyl acetate. The stereochemistry at C-2 and C-3 was deduced from the coupling $J_{2,3}$, which in *trans*-disubstituted dihydrobenzofuranes is always about 3 Hz only, while the absolute configuration is not known.

The sesquiterpene lactones isolated from this *Lasiolaena* species again supported the close relationship of this genus to *Agrianthus* and *Stylotrichium* which are also placed in the subtribe Gyptidinae [5], and contain similar lactones [3, 4]. Further studies will show whether the homoditerpenes are of chemotaxonomic interest.

EXPERIMENTAL

The air-dried plant material (voucher RMK 8110, deposited in the U.S. National Herbarium) was extracted with Et_2O petrol (1:2) and the resulting extracts were sepd first by CC (Si gel) and further by repeated TLC (Si gel) (solvents given in parentheses). Known compounds were identified by comparing their IR and ^1H NMR spectra with those of authentic materials. The roots (110 g) afforded 20 mg germacrene D, 50 mg squalene, 20 mg dammadienyl and 100 mg of its acetate, 10 mg dammadienone, 15 mg friedelinol, 5 mg **1** (Et_2O petrol, 1:1) and 1 mg **2** (Et_2O–petrol, 1:1), while the aerial parts (550 g) gave 150 mg germacrene D, 100 mg germacrene C, 5 mg α- and 5 mg γ-humulene, 330 mg dammadienyl acetate, 30 mg dammadienone, 100 mg friedelinol, 10 mg stigmasterol, 10 mg **1**, 1 mg **2**, 2 mg **3**, 10 mg **4**, 8 mg **5**, 10 mg **6**, 27 mg **7**, 150 mg **8**, 20 mg **9**, 85 mg **10** (Et_2O, ×3), 10 mg **11**, 10 mg **12** (EtOAc–petrol, 1:1, ×3), 15 mg **13**, 8 mg **14** (Et_2O, ×3), 5 mg **15** (Et_2O, ×3), 5 mg **16**, 15 mg **17**, 5 mg **18**, 8 mg **19** (Et_2O, ×3), 30 mg **20** (Et_2O, ×3), 10 mg **22** (Et_2O, ×3), 20 mg **24** and 3 mg **25** ($CHCl_3$–MeOH, 20:1).

7-Hydroxy-2β-methoxytremetone (**1**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3500–2600, 1650 (hydrogen bonded PhCO), 1590 (aromatic); MS *m/z* (rel. int.): 248.105 $[M]^+$(15)($C_{14}H_{16}O_4$), 233 $[M - Me]^+$ (20), 57 (100); ^1H NMR ($CDCl_3$): δ 4.96 [*d* (*br*), H-2], 4.74 (*d*, H-3), 7.25 (*d*, H-4), 6.92 (H-7), 2.61 (*s*, H-9), 5.07

[*s* (*br*), H-11], 4.92 [*s* (*br*), H-11′], 1.73 [*s* (*br*), H-12], 12.01 (*s*, OH), 3.45 (*s*, OMe, $J_{2,3} = 3.5$ Hz).

5-Hydroxytremetone (**2**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3500 2600, 1650 (hydrogen bonded PhCO), 1590 (aromatic); MS *m/z* (rel. int.): 218.094 $[M^+]$ (80)($C_{13}H_{14}O_3$), 203 $[M - Me]^+$ (60), 178 $[203 - CO]^+$ (41), 161 $[203 - C_3H_6]^+$ (100); ^1H NMR ($CDCl_3$): δ 5.19 (*dd*, H-2), 3.63 (*dd*, H-3), 3.29 (*dd*, H-3′), 6.99 (*d*, H-6), 6.81 (*d*, H-7), 2.59 (*s*, H-9), 5.11 [*s* (*br*), H-11], 4.95 [*s* (*br*), H-11′], 1.80 [*s* (*br*), H-12], 12.16 (OH) [*J*(Hz): 2,3 = 2,3′ = 8.5; 3,3′ = 16.5; 6,7 = 8.5].

3α,4α-Epoxy-9β-hydroxy-8β-tiglinoyloxy-2-oxo-3,4-dihydrolasiolaenin (**10**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3580 (OH), 1780 (γ-lactone), 1740 (C=O), 1720, 1650 (C=CCO$_2$R); MS *m/z* (rel. int.): 374.117 $[M]^+$(1)($C_{20}H_{22}O_7$), 274 $[M - RCO_2H]^+$ (65), 83 $[C_4H_7CO]^+$ (100), 55 $[83 - CO]^+$ (90).

3-Chloro-9β,15-dihydroxy-8β-tiglinoyloxy-dehydroleucodin (**12**). Colourless gum, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1780 (γ-lactone), 1730 (C=O, C=CCO$_2$R), 1650, 1625 (C=C); MS *m/z* (rel. int.): 408 $[M]^+$ (0.1), 308.040 $[M - RCO_2H]^+$ (1) ($C_{15}H_{13}O_5Cl$), 290 $[308 - H_2O]^+$ (5), 83 $[C_4H_7CO]^+$ (100), 55 $[83 - CO]^+$ (61);

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546\,nm}{-23 \quad -27 \quad -32} (c = 0.5, CHCl_3).$$

9β-Hydroxy-8β-tiglinoyloxy-2-oxo-lasiolaenin (**14**). Colourless gum, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1780 (γ-lactone), 1710 (C=O, C=CCO$_2$R), 1660, 1630 (C=C); MS *m/z* (rel. int.): 358.142 $[M]^+$ (8) ($C_{20}H_{22}O_6$), 258 $[M - RCO_2H]^+$ (5), 83 $[C_4H_7CO]^+$ (100), 55 $[83 - CO]^+$ (52);

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{+21 \quad +23 \quad +29 \quad +44} (c = 0.3, CHCl_3).$$

9β-Hydroxy-8β-[5-acetoxytiglinoyloxy]-2-oxo-lasiolaenin (**15**). Colourless gum, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1780 γ-lactone), 1740 (OAc, CO, C=CCO$_2$R), 1655, 1625 (C=C); MS *m/z* (rel. int.): 416 $[M]^+$ (4), 258.089 $[M - RCO_2H]^+$ (18) ($C_{15}H_{14}O_4$), 83 $[C_4H_7CO]^+$ (100), 55 $[83 - CO]^+$ (88);

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{+18 \quad +19 \quad +24 \quad +32} (c = 0.25, CHCl_3).$$

12,19,20-Trihydroxy-14-methylene geranyl nerol (**19**). Colourless gum, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH); CIMS (isobutane) *m/z* (rel. int.): 335 $[M + 1 - H_2O]^+$ (37), 317 $[335 - H_2O]^+$ (100), 299 $[317 - H_2O]^+$ (77).

12,20-Dihydroxy-19-acetoxy-14-methylene geranyl nerol (**20**). Colourless gum, which was stirred for 2 hr in Et_2O with 400 mg MnO_2. TLC (Et_2O) afforded **21**, colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1745, 1240 (OAc), 1700, 1690 (C=CCHO); MS *m/z* (rel. int.): 307.155 $[M - C_6H_{11}]^+$ (10) ($C_{17}H_{23}O_5$), 247 $[307 - AcOH]^+$ (21), 229 $[247 - H_2O]^+$ (17), 219 $[247 - CO]^+$ (9), 201 $[229 - CO]^+$ (11), 55 $[C_4H_7]^+$ (100).

5 mg **21** in 5 ml C_6H_6 were heated for 5 min with 5 mg *p*-toluene sulfonic acid. TLC (Et_2O–petrol, 1:1) afforded 1.5 mg of the anhydro compounds, UV $\lambda_{max}^{Et_2O}$ nm: (295), 285, (273); MS *m/z* (rel. int.): 372.230 $[M]^+$ (4) ($C_{23}H_{32}O_4$), 312 $[M - AcOH]^+$ (4), 269 $[312 - C_3H_7]^+$ (5), 55 $[C_4H_7]^+$ (100).

12,20-Dihydro-19-acetoxy geranyl nerol (**22**). Colourless gum, sepd from **20** after oxidation with MnO_2, which afforded **23**, colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740 (OAc), 1700, 1690 (C=CCHO); MS *m/z* (rel. int.): 307.155 $[M - C_5H_9]^+$ (7) ($C_{17}H_{23}O_5$), 247 $[307 - HOAc]^+$ (12), 229 $[247 - HOAc]^+$ (12), 229 $[247 - H_2O]^+$ (11), 201 $[229 - CO]^+$ (10), 69 $[C_5H_9]^+$ (100).

Dimeric coniferyl acetate (**25**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3549 (OH), 1745, 1245 (OAc), 1610, 970 (CH=CH *trans*); MS *m/z* (rel. int.): 442.163 $[M]^+$ (100) ($C_{24}H_{26}O_8$), 382 $[M - AcOH]^+$ (54), 322 $[382 - AcOH]^+$ (21), 291 $[322 - OMe]^+$ (25); ^1H NMR ($CDCl_3$): δ 5.49 (*d*, H-2), 3.79 (*ddd*, H-3), 6.90 (*s*, H-4, H-6, H-2′, H-5′, H-6′), 6.62 [*d* (*br*), H-8], 6.17 (*dt*, H-9), 4.73 (*d*, H-10), 4.45 (*dd*, H-11), 4.32 (*dd*, H-11′), 5.63 (*s*, OH), 3.93 (*s*, OMe), 3.89 (*s*, OMe), 2.12 (*s*, OAc), 2.04 (*s*, OAc) [*J*(Hz): 2,3 = 7.5; 3,11 = 6; 3,11′ = 8; 8,9 = 16; 9,10 = 7; 11,11′ = 11].

Acknowledgements—We thank Drs. Scott A. Mori and P. Alvim, Herbario Centro de Pesquisos do Cacau at Itabanu, Bahia, Brazil, for their help during plant collection and the Deutsche Forschungsgemeinschaft for financial support.

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