Phytochemistry, Vol. 21, No. 3, pp. 685–689, 1982.
Printed in Great Britain.

0031-9422/82/030685-05$03.00/0

α-HUMULENE DERIVATIVES INCLUDING A SESQUITERPENE ACID WITH A REARRANGED CARBON SKELETON FROM *LYCHOPHORA COLUMNARIS**

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(*Received* 3 *July* 1981)

Key Word Index—*Lychnophora columnaris*; Compositae; Vernonieae; sesquiterpenes; humulene derivatives; new carbon skeleton.

Abstract—An investigation of *Lychnophora columnaris* afforded in addition to known compounds six new α-humulene derivatives and a rearranged sesquiterpene with a new carbon skeleton. These compounds and several sesquiterpene lactones isolated from this species seem to be of chemotaxonomic importance. The structures were elucidated by spectroscopic methods and a few chemical transformations including partial synthesis.

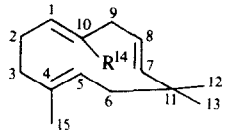
INTRODUCTION

So far eight species of the genus *Lychnophora* have been investigated chemically. As in other Brazilian genera, namely *Eremanthus*, *Piptolepis*, *Proteopsis* and *Vanillosmopsis*, all belonging to the subtribe *Lychnophorinae* [1], most species contain furanoheliangolides [2–11], while eremanthin has also been isolated from six *Lychnophora* sp. [6, 7, 11] which may be characteristic for the subtribe. Oxidized caryophyllene derivatives are also typical for *Lychnophora* [6, 11–13], while other constituents have been isolated from only one or two species. We have now investigated *Lychnophora columnaris*, which again afforded a furanoheliangolide, eremanthin and related lactones, while the caryophyllene derivatives were replaced by oxidized α-humulene derivatives, six of them not previously isolated. Furthermore, a sesquiterpenic acid with a new carbon skeleton was isolated.

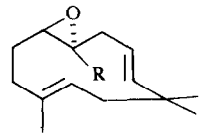
RESULTS AND DISCUSSION

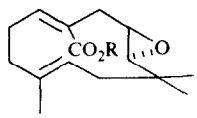
The aerial parts of *Lychnophora columnaris* Mattf. afforded lupeol and its acetate, stigmasterol, eremanthin (**21**) [14], lychnopholide (**24**) [6] and α-humulene (**1**) together with several compounds derived from the latter, the alcohol **2** [15], the corresponding acetate **4** and aldehyde **5** as well as the acid **3**. Furthermore, the epoxides **6–9** were present, only **8** having been previously isolated [16]. The structure of **3** followed from the ^{1}H NMR spectrum (Table 1), which showed signals of an olefinic methyl and of two tertiary methyls. The IR spectrum indicated the presence of an unsaturated acid, which was supported by a downfield olefinic broadened triplet at δ 6.09 in the ^{1}H NMR spectrum. A second broadened triplet at δ 4.98 was coupled with the olefinic methyl and with a broadened doublet at 1.93. Irradiation of a broadened double triplet at 2.69 collapsed the triplets at 6.09 and 2.22 to singlets, while irradiation of the olefinic signal at 5.60 allowed the assignment of the signals at 5.17 and 2.89. The resulting sequences led to the proposed structure **3**, which was confirmed by reduction, which afforded **2**, identical with the natural alcohol. The ^{13}C NMR spectrum also was in good agreement with the structure (see Experimental). The ^{1}H NMR spectral data of **4** (Table 1) were close to those of **2**, only the H-14 signals being shifted drastically downfield. Compound **5** was prepared previously by oxidation of **2** [15]. The spectral data of both aldehydes were identical. The ^{1}H NMR spectral data of **6** (Table 1) indicated an epoxide of **2**. All signals could be assigned by spin decoupling. However, due to the flexibility of the 11-membered ring system the stereochemistry of the epoxide could not be determined with certainty. We therefore have epoxidized **2**, which afforded two mono- and two diepoxides. The main product was identical with **6**. As inspection of models showed, the epoxidation of the 1, 10-double bond should be achieved from one side only leading to **6**. Obviously the preferred reaction of this double bond was influenced by neighbouring group participation of the hydroxyl. The ^{1}H NMR spectral data of the second monoepoxide (Table 1) led to the structure **18**. The stereochemistry at C-4 and C-5 was assigned indirectly by consideration of the data of the two diepoxides. The ^{1}H NMR spectral data of these compounds (**19** and **20**) (Table 1) clearly indicated that they differed in the stereochemistry at C-4 and C-5 only. The downfield shift of the H-9α signal in the spectrum of **20** could be explained by a deshielding effect of the 1, 10-epoxide. However, this required

*Part 393 in the series "Naturally Occurring Terpene Derivatives". For Part 392 see Bohlmann, F. and Wallmeyer, M. (1982) *Phytochemistry* **21** (in press).



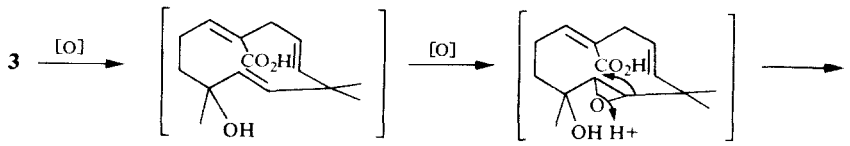
1*	2	3	4	5
R = Me	CH_2OH	CO_2H	CH_2OAc	CHO



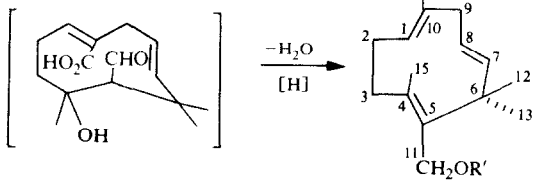


6 R = CH_2OH
7 R = CHO
8 R = Me

9 R = H
10 R = Me

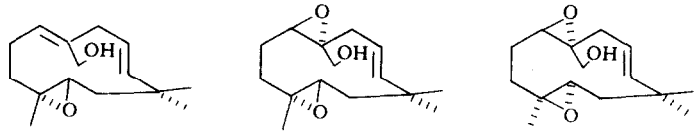


11 **12**

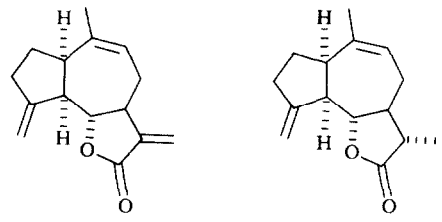


13

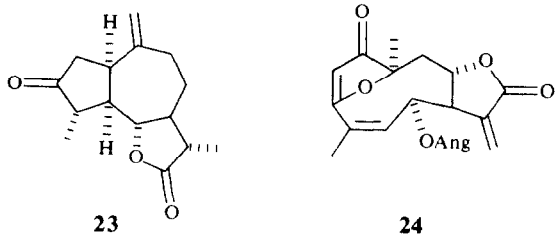
14*	15	16	17
R H	Me	Me	Me
R' Ac	Ac	H	Me



18 **19** **20**



21 **22**



23 **24**

Scheme 1.

*Numbering as in germacranes.

Table 1. ^{1}H NMR spectral data of compounds **3**, **4**, **6**, **7** and **18–20** (400 MHz, $CDCl_3$, TMS as internal standard)

	3	**4**	**6**	**7**	**18**	**19**	**20**
H-1	6.09*br t*	5.44*br t*	2.69*dd*	2.92*dd*	5.36*br dd*	2.79*dd*	2.87*dd*
H-2α	2.69*br dt*	2.17*br dt*	2.17*dddd*	2.07*m*	2.28*m*	2.02*ddd*	2.21*dddd*
H-2β			1.50*m*	1.55*m*	2.22*m*	1.67*dddd*	1.48*dddd*
H-3α	2.22*br t*	2.11*br t*	2.03*m*	2.27*m*	1.41*m*	1.25*ddd*	0.98*ddd*
H-3β			2.25*br ddd*		2.13*ddd*	2.23*ddd*	2.15*ddd*
H-5	4.98*br t*	5.12*br t*	4.99*br dd*	4.99*br dd*	2.57*br d*	2.67*d*	2.46*d*
H-6α	1.93*br d*	1.91*br d*	1.87*dd*	1.90*br d*	1.62*br d*	1.73*d*	1.61*d*
H-6β			1.98*dd*		1.41*br dd*	1.43*dd*	1.37*dd*
H-7	5.17*d*	5.37*d*	5.19*d*	5.23*d*	5.40*d*	5.54*m*	5.34*d*
H-8	5.60*dt*	5.78*dt*	5.31*ddd*	5.41*ddd*	5.78*ddd*		5.54*ddd*
H-9α	2.89*br d*	2.61*br d*	2.98*dd*	3.05*dd*	2.75*dd*	2.88*br d*	3.06*dd*
H-9β			1.50*m*	1.55*m*	2.69*dd*	1.79*dd*	1.53*dd*
H-12	1.06*s*	1.03*s*	1.10*s*	1.10*s*	1.18*s*	1.16*s*	1.19*s*
H-13			1.08*s*	1.07*s*	1.03*s*	1.08*s*	1.08*s*
H-14	4.76*s*		3.91*dd*	9.35*d*	4.22*d*	3.89*d*	3.87*d*
H-14			3.57*d*		4.12*d*	3.72*d*	3.58*dd*
H-15	1.45*d*	1.43*d*	1.54*br s*	1.46*br s*	1.19*s*	1.19*s*	1.30*s*
OH	—	—	1.72*br*	—	—	1.25*br s*	1.61*dd*

J(Hz): Compound **3**: 1,2 = 8; 2,3 = 6.5; 5,6 = 7; 5,15 = 1; 7,8 = 16; 8,9 = 7.5; compound **4**: 1,2 = 5,6 = 8,9 = 7.5; 2,3 = 7; 5,15 = 1; compound **6**: 1,2α = 4; 1,2β = 10; 2α,2β = 14; 2α,3α = 4; 3α3β = 12.5; 5,6α = 6; 5,6β = 8; 6α,6β = 14; 7,8 = 16; 8,9α = 5; 8,9β = 10; 9α,9β = 13; 14,14′ = 11.5; 14,OH = 6; compound **7**: 1,2α = 3.5; 1,2β = 10; 5,6 = 7; 7,8 = 16; 8,9α = 5; 8,9β = 10; 9α,9β = 13; 9α,14 = 1; compound **18**: 1,2 ~ 7; 2α,3β = 4.5; 2β,3β = 2.5; 3α,3β = 13; 5,6β = 10; 6α,6β = 14; 7,8 = 16; 8,9 = 7; 9α,9β = 14; 14,14′ = 12; compound **19**: 1,2α = 1; 1,2β = 10; 2α,2β = 15; 2α,3 = 4; 2β,3α = 12; 2β,3β = 4; 3α,3β = 14; 5,6β = 10; 6α,6β = 9α,9β = 14; 14,14′ = 12; compound **20**: 1,2α = 5; 1,2β = 10; 2α,2β = 14; 2α,3α = 13; 2α,3β = 5; 2β,3α = 5; 2β,3β = 2; 3α,3β = 13; 5,6β = 10; 6α,6β = 14; 7,8 = 15.5; 8,9α = 5; 8,9β = 10; 9α,9β = 13; 14,14′ = 12; 14,OH = 8; 14′,OH = 4.

the proposed configuration with a changed conformation. The presence of a hydrogen bridge was supported by the clear couplings of the hydroxyl signal. Furthermore, the presence of a rigid conformation of **20** was supported by the unusually high melting point and low solubility. As expected the 7, 8-double bond was not epoxidized, while the isolation of isomeric 4, 5-epoxides indicated flexible conformations of **2**, which allowed a reaction of the 4, 5-double bond from both sides. The shift differences of the H-9α signals in the spectra of **19** and **20** can be used for the assignment of the stereochemistry of **18**. As the signal of H-9α in the ^{1}H NMR spectrum of **18** was not shifted downfield, the proposed configuration was very likely. The acid **9** could be obtained pure only as its methyl ester. The ^{1}H NMR spectral data (Table 2) showed that the 7, 8-double bond of **3** was epoxidized, as the downfield signals of the olefinic protons were replaced by a narrowly splitted doublet at δ 2.33 and a threefold doublet at 3.01. Though the other signals, which could be assigned by spin decoupling, were slightly different, their couplings only agreed with the proposed structure. Though the stereochemistry at C-7 and C-8 could not be established with certainty, the proposed one was most likely, if models were inspected. We have named compound **9** lychnocolumnic acid.

Finally, a further acid with an additional acetoxyl group was present in the plant extract. The molecular formula and the ^{1}H NMR spectral data (Table 2) indicated the presence of a monocyclic triene. However, the ^{1}H NMR signals clearly showed the presence of five methyl groups, one carboxyl, one olefinic, one acetoxy methylene and two tertiary methyl groups, a rearranged humulene derivative had to be assumed. Careful spin decoupling led to the structure **14**, which was supported by the ^{1}H NMR spectral data of the corresponding methyl ester **15** and those of **16** and **17** obtained by acid catalysed hydrolysis and methanolysis respectively. These reactions further established the allylic nature of the acetoxyl group. The stereochemistry of the 4, 5-

Table 2. ^{1}H NMR spectral data of compounds **10** and **14–17** (400 MHz, $CDCl_3$, TMS as internal standard)

	10	**14**	Δ*	**15**	**16**	**17**
H-1	5.86*dd*	6.04*br dd*	0.01	5.87*br dd*	5.89*br dd*	5.86*br dd*
H-2α	2.52*dddd*	2.49*br d*	0.21	2.42*br d*	2.40*br d*	2.43*br d*
H-2β	2.82*dddd*	2.92*m*	0.23	2.82*m*	2.75*m*	2.85*m*
H-3α	2.15*ddd*	2.32*br dd*	0.1	2.31*br dd*	2.33*br dd*	2.30*br dd*
H-3β	2.88*br d*	2.24*ddd*	0.1	2.20*ddd*	2.27*ddd*	2.23*ddd*
H-5	4.98*br d*	—	—	—	—	—
H-6α	2.28*br d*	—	—	—	—	—
H-6β	2.20*dd*	—	—	—	—	—
H-7	2.33*d*	5.17*d*	0.17	5.18*d*	5.15*d*	5.16*d*
H-8	3.01*ddd*	5.77*dt*	0.16	5.77*dt*	5.70*dt*	5.71*dt*
H-9α	3.08*dd*	2.85*br dd*	0.23	2.81*br dd*	2.69*br dd*	2.80*br dd*
H-9β	1.72*dd*	2.97*br dd*	0.13	2.96*br dd*	2.86*br dd*	2.93*br dd*
H-11		5.02*br d*	0.11	5.02*br d*	4.95*br d*	5.08*br d*
H-11′		5.16*d*	0.11	5.16*d*	3.45*d*	3.98*d*
H-12	1.08*s*	1.10*s*	0.07	1.10*s*	1.11*s*	1.13*s*
H-13	0.73*s*	1.02*s*	0.06	1.02*s*	1.01*s*	1.04*s*
H-15	1.53*br s*	1.67*br s*	0.14	1.63*br s*	1.53*br s*	1.54*br s*
OMe	3.76*s*	—	—	3.76*s*	3.75*s*	3.76*s*
					3.11*s*	—
OAc	—	2.03*s*	0.03	2.03*s*	—	—

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

J(Hz): Compound **10**: 1,2α = 8.5; 1,2β = 8.5; 2α,2β = 13; 2α,3α = 5; 2α,3β = 12; 2β,3α = 2.5; 2β,3β = 4; 3α,3β = 12.5; 5,6α = 2; 5,6β = 10.5; 6α,6β = 15; 7,8 = 2.5; 8,9α = 4; 8,9β = 9; 9α,9β = 13; compounds **14–17**: 1,2α = 5; 1,2β = 10; 2α,2β = 13; 2α,3α = 5; 2β,3α = 5; 2β,3β = 12; 3α,3β = 12.5; 7,8 = 16; 8,9 = 7; 9α,9β = 15; 11,11′ = 11.

double bond could not be determined with certainty. However, inspection of models showed that the proposed orientation was most likely. The chemical shifts of H-3, H-12 and H-13 and the mild reaction conditions of the methanolysis agreed with this assumption. Inspection of models led to the proposed assignment of the signals, which were in agreement with the couplings observed, if a conformation was assumed with the C-10 methyl in plane and the C-4 above the plane. This would explain the differences in the observed chemical shifts of H-9α and H-9β as well as of H-12 and H-13. The structure was further supported by the ^{13}C NMR signals. Biogenetically **14** may be formed starting with **3** by allylic oxidation leading to **11**, which after epoxidation could be rearranged to **13**. Elimination of H_2O, reduction and acetylation could then give **14** (Scheme 1). Compound **14** seems to be derived from a so far unknown carbon skeleton, for which we propose the name lychnene. Therefore compound **14** was named 11 - acetoxylychnen - 14 - oic acid.

The roots afforded tridecapentaynene, trideca - 3,5,7,9 - tetrayn - 1,11 - diene, lupeol and its acetate, **21**, **22** [11], **23** [17] and **24**.

The chemistry of this species again showed that furanoheliangolides and erementhin may be characteristic for the subtribe *Lychnophorinae*. The α-humulene derivatives seem to replace the caryophyllene derivatives isolated from several other species. As caryophyllene and α-humulene are biogenetically closely related, this change is a very small one. Further investigations may show if enzymes for the oxidation of simple sesquiterpenes are widespread in this genus. So far derivatives of α-humulene are very rare in the Compositae.

EXPERIMENTAL

The air dried plant material (voucher RMK 8610, deposited in the United States National Herbarium, Washington) was extracted with Et_2O–petrol (1:2) and the resulting extracts were separated 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 material. The aerial parts (750 g) afforded 100 mg lupeol, 20 mg stigmasterol, 100 mg lupeyl acetate, 100 mg **1**, 500 mg **2**, 200 mg **3** (Et_2O–petrol, 1:3), 5 mg **4** (Et_2O–petrol, 1:0), 5 mg **5** (Et_2O–petrol, 1:10), 10 mg **6** (Et_2O–petrol, 1:1), 5 mg **7** (Et_2O–petrol, 1:10), 10 mg **8**, 10 mg **9** (Et_2O–petrol, 1:1), 20 mg **14** (Et_2O–petrol, 1:1), 20 mg **21** and 100 mg **24**. Compounds **9** and **14** were transformed to the corresponding methyl esters by addition of CH_2N_2. The roots (150 g) gave 1 mg tridecapentaynene, 0.1 mg trideca - 3,5,7,9 - tetrayn - 1,11 - diene, 100 mg lupeol, 500 mg lupeyl acetate, 4 mg **21**, 3 mg **22**, 3 mg **23** and 10 mg **24**.

α-Humulen-14-oic acid (**3**). Colourless crystals, mp 93° (petrol); IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3500–2500, 1690, 1640 (C=CCO$_2$H), 980 (*trans* CH=CH); MS *m/z* (rel. int.): 234.162 [M]$^+$ (18) ($C_{15}H_{22}O_2$), 219 (10), 201 (11), 189 (19), 165 (26), 151 (68), 59

(100); ^{13}C NMR ($CDCl_3$) (C-1 through C-15): 151.7 *d*, 25.3 *t*, 40.1 *t*, 132.9 *s*, 125.3 *d*, 41.9 *t*, 142.5 *d*, 127.5 *d*, 33.9 *t*, 133.4 *s*, 37.4 *s*, 27.0 *q*, 27.1 *q*, 174.0 *s*, 14.9 *q* (signals assigned by spin decoupling and gated decoupling). Compound **3** (10 mg) on reduction with $LiAlH_4$ in Et_2O afforded **2**, identical with the natural compound.

14-*Acetoxy*-α-*hymulene* (**4**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1745, 1240 (OAc), 980 (*trans* CH=CH); MS *m/z* (rel. int.): 218.167 $[M-ketene]^+$ (34) ($C_{15}H_{22}O$), 203 $[218-Me]^+$ (10), 187 $[M-CH_2OAc]^+$ (11), 119 (100).

α-*Humulen*-14-*al* (**5**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 2750, 1675 (C=CCHO), 980 (*trans* CH=CH); MS *m/z* (rel. int.): 218.167 $[M]^+$ (15) ($C_{15}H_{22}O$), identical with the aldehyde obtained by MnO_2 oxidation of **2** [15].

14 - *Hydroxy* - 1α, 10β - *epoxy* - 1, 10 - *dihydro* - α - *humulene* (**6**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1660, 865 (C=CH), 980 (*trans* CH=CH); MS *m/z* (rel. int.): 236.178 $[M]^+$ (4) ($C_{15}H_{24}O_2$), 221 (4), 205 (3), 154 (20), 107 (44), 93 (65), 91 (77), 79 (63), 67 (100), 55 (94).

$[\alpha]_{24°}^{\lambda}$ =	589	578	546	436 nm	($CHCl_3$; $c = 0.68$).
	+13.5	+14	+16	+29	

Partial synthesis of **6**. Compound **2** (100 mg) in 2 ml $CHCl_3$ was stirred for 30 min with 100 mg *m*-chloroperbenoic acid and 0.5 ml satd $NaHCO_3$ soln. TLC (Et_2O–petrol, 1:1) afforded 10 mg **2**, 10 mg **6** (^1H NMR spectrum identical with that of the natural compound), 5 mg **18**, 10 mg **19** and 5 mg **20**.

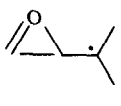
Compound **18**: Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3605 (OH), 980 (*trans* CH=CH); MS *m/z* (rel. int.): 236.178 $[M]^+$ (3) ($C_{15}H_{24}O_2$), 221 $[M-Me]^+$ (5), 203 $[221-H_2O]^+$ (5), 121 (68), 119 (63), 93 (90), 79 (89), 67 (89), 55 (100).

Compound **19**: Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1640, 980 (*trans* CH=CH); MS (CI, *iso*-butane) *m/z* (rel. int.): 253 $[M+1]^+$ (100), 235 $[253-H_2O]^+$ (82), 217 $[235-H_2O]^+$ (50).

Compound **20**: Colourless crystals, mp 154° (Et_2O), IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3580 (OH), 980 (*trans* CH=CH); MS (CI, *iso*-butane) *m/z* (rel. int.): 253 $[M+1]^+$ (100), 235 $[253-H_2O]^+$ (87), 217 $[235-H_2O]^+$ (51).

1α, 10β - *Epoxy* - 1, 10 - *dihydro* - α - *humulen* - 14 - *al* (**7**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 2730, 1720 (CHO), 980 (*trans* CH=CH); MS *m/z* (rel. int.): 234.162 $[M]^+$ (8) ($C_{15}H_{22}O_2$), 219 $[M-Me]^+$ (8), 205 $[M-CHO]^+$ (7), 187 $[205-H_2O]^+$ (6), 67 (100).

$[\alpha]_{24°}^{\lambda}$ =	589	578	546	436 nm	($CHCl_3$; $c = 0.24$).
	+13	+14	+16	+28	

Lychnocolumnic acid (**9**). Isolated as its methyl ester **10**, colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1715, 1640 (C=CCO_2Me); MS *m/z* (rel. int.): 264.172 $[M]^+$ (1) ($C_{16}H_{24}O_3$), 232 $[M-MeOH]^+$ (5), 204 $[232-CO]^+$ (8), 180 [M– ]$^+$ (27), 124 (100), 93 (91).

$[\alpha]_{24°}^{\lambda}$ =	589	578	546	436 nm	($CHCl_3$; $c = 0.51$).
	−32	−33	−40	−83	

*Not certain, very weak signals.

11 - *Acetoxylychnen* - 14 - *oic acid* (**14**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3500–2500, 1680, 1625 (C=CCO_2H), 1730, 1240 (OAc); MS *m/z* (rel. int.): 292.167 $[M]^+$ (4) ($C_{17}H_{24}O_4$), 232 $[M-HOAc]^+$ (90), 217 $[232-Me]^+$ (24), 203 (46), 189 (65), 176 (48), 166 (58), 163 (77), 162 (71), 151 (87), 145 (81), 133 (70), 121 (100), 107 (76), 105 (80), 91 (89), 84 (90), 79 (80), 69 (95).

Preparation of **16** *and* **17**. 15 mg of the methyl ester **15** (prepared by addition of CH_2N_2 in Et_2O, 5 min) in 2 ml MeOH and 0.5 ml 2 N H_2SO_4 was heated for 5 min at 70°. Usual work-up and TLC (Et_2O–petrol, 1:1) afforded 3 mg **16** (^1H NMR see Table 2) and 10 mg **17**, colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1710, 1640 (C=CCO_2Me), 980 (*trans* CH=CH); MS *m/z* (rel. int.): 278.188 $[M]^+$ (3) ($C_{17}H_{26}O_3$), 246 $[M-HOMe]^+$ (21), 231 $[246-Me]^+$ (6), 180 (41), 165 (68), 121 (100). ^{13}C NMR ($CDCl_3$) (C-1 through C-15): 148.4 *d*, 26.9 *t*, 40.8 *t*, 133.8 *s*, 137.9 *s*, 41.0 *s*, 141.4 *d*, 125.7 *d*, 33.6 *t*, 133.9 *s**, 83.8 *t*, 24.7 *q*, 24.7 *q*, 174.0 *s**, 17.7 *q*, 51.3 *q* and 56.3 *q* (OMe).

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

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