Phytochemistry, Vol. 21, No. 6, pp. 1343–1347, 1982.
Printed in Great Britain.

0031-9422/82/061343-05$03.00/0

EUDESMANOLIDES FROM *DIMEROSTEMMA BRASILIANUM**

FERDINAND BOHLMANN, PAHUP SINGH, JASMIN JAKUPOVIC, ROBERT M. KING† and HAROLD ROBINSON†

Institute for Organic Chemistry, Technical University of Berlin, D-1000 Berlin 12, West Germany; †Smithsonian Institution, Department of Botany, Washington DC, Stop No. 166, U.S.A.

(*Received* 13 *July* 1981)

Key Word Index—*Dimerostemma brasilianum*; Compositae; Heliantheae; sesquiterpene lactones; eudesmanolides; diterpene lactone.

Abstract—The investigation of *Dimerostemma brasilianum* afforded, in addition to known compounds, 18 new eudesmanolides and a new diterpene lactone derived from geranylgeraniol similar to that isolated from *D. asperatum*. The structures were elucidated by spectroscopic methods. The chemotaxonomic situation is discussed briefly.

INTRODUCTION

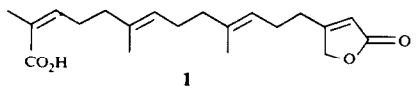
So far two species of the small Brazilian genus *Dimerostemma* (subtribe Verbesininae)[1] have been studied chemically[2, 3], both contained typical eudesmanolides. The substitution pattern was identical in all compounds and was not observed in any other genus. We have now investigated a third species, *D. brasilianum* Cass. In addition to known compounds, again many eudesmanolides of this type were isolated, but there are a few with a slightly changed substitution pattern. Furthermore, two unusual acetylenic compounds and two geranylgeraniol derivatives were present, one having being isolated previously from *D. asperatum*, as well as the acetylenes.

RESULTS AND DISCUSSION

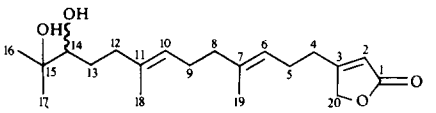
The roots of *D. brasilianum* Cass. afforded germacrene D, bicyclogermacrene, α-humulene, cyperene (**5**), the acetylenic esters **6** and **7**[3] as well as the new diterpene **2**. The ^{1}H NMR spectral data (see Experimental) were in part very similar to those of **1**[3]. However, the end group was obviously different. The IR spectrum showed that the carboxyl group was missing while hydroxyls were present. The position of these followed from the corresponding ^{1}H NMR signals. In addition to the signals of the olefinic methyls, two signals at δ 1.17 and 1.22 indicated a 2-propanol group. A broadened doublet at δ 3.35 had to be assigned to the proton at the hydroxyl bearing carbon which had to be placed at C-14 as all signals of the allylic protons showed the same splitting pattern as in the spectrum of **1**. The somewhat unusual doublet of H-14 was obviously due to a preferred conformation as a result of hydrogen bonding between the two hydroxyls which made the H-13–H-14 angle nearly 90°. The same situation existed in a similar geranylgeraniol derivative[4]. The structure was further supported by the mass spectrum of **2**; the molecular ion could not be detected, but elimination of water and of $Me_2CH(OH)$ was observed. A strong fragment *m/z* 98 was probably formed via McLafferty fragmentation. We have named **2** dimerobrasiolide.

The aerial parts afforded germacrene D, bicyclogermacrene, α-humulene, phytol, sitosterol, stigmasterol, linolenic acid, the diterpene lactone **1**[3], spathulenol (**3**), ledol (**4**), the eudesmanolides **8**[3], **9**[3], **16**[2], **17**[3] and **30**[4] as well as 18 further eudesmanolides, which were difficult to separate. In addition to the epoxides **8** and **9**, six similar lactones were isolated, all with the same substitution pattern and an α-4,15-epoxide grouping. **10** was identical with the acetate obtained by partial acetylation **9**[3]. The ^{1}H NMR spectral data of **11** (Table 1) showed that the

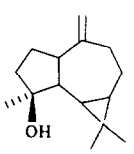
*Part 396 in the series "Naturally Occurring Terpene Derivatives". For Part 395 see Bohlmann F. and Gupta, R. K. (1982) *Phytochemistry* **21**, 1309.



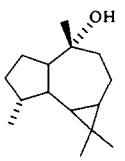
1



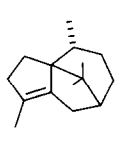
2



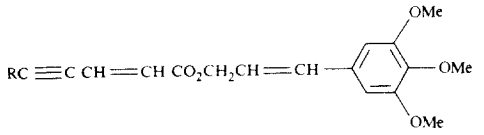
3



4



5



6 R = $MeCH_2CH_2CH=CH-$

7 R = $MeCH_2CH_2C\equiv C-$

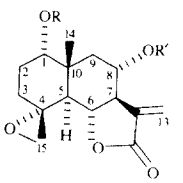
Table 1. ^1H NMR spectral data of compounds **11–15** (400 MHz, $CDCl_3$, TMS as int. standard)

	11	**12**	**13**	**14**	**15**
H-1	4.85 *dd*	4.85 *dd*	4.82 *dd*	4.78 *dd*	4.86 *dd*
H-5	2.38 *d*	2.38 *d*	2.42 *d*	2.36 *d*	2.41 *d*
H-6	3.85 *dd*	3.85 *dd*	3.86 *dd*	3.85 *dd*	3.86 *dd*
H-7	2.53 *dddd*	2.53 *dddd*	2.54 *dddd*	2.52 *dddd*	2.53 *dddd*
H-8	3.99 *ddd*	3.99 *ddd*	3.98 *ddd*	3.98 *ddd*	3.98 *ddd*
H-13	6.15 *d*	6.18 *d*	6.15 *dd*	6.16 *d*	6.16 *dd*
H-13	5.97 *d*	5.99 *d*	5.97 *br d*	5.97 *d*	5.97 *d*
H-14	1.10 *s*	1.10 *s*	1.10 *s*	1.10 *s*	1.10 *s*
H-15	3.22 *dd*	3.22 *dd*	3.22 *dd*	3.20 *dd*	3.22 *dd*
H-15	2.90 *d*	2.90 *d*	2.90 *d*	2.90 *d*	2.90 *d*
OCOR	6.12 *ddq*	6.80 *qq*	6.21 *br s*	3.16 *d*	6.37 *br s*
	5.05 *ddq*	1.97 *dq*	5.67 *dq*	2.85 *d*	5.97 *br s*
	5.10 *ddq*	1.95 *dq*	2.02 *dd*	1.64 *s*	4.40 *br s*
	2.04 *ddt*				
	2.13 *s*				

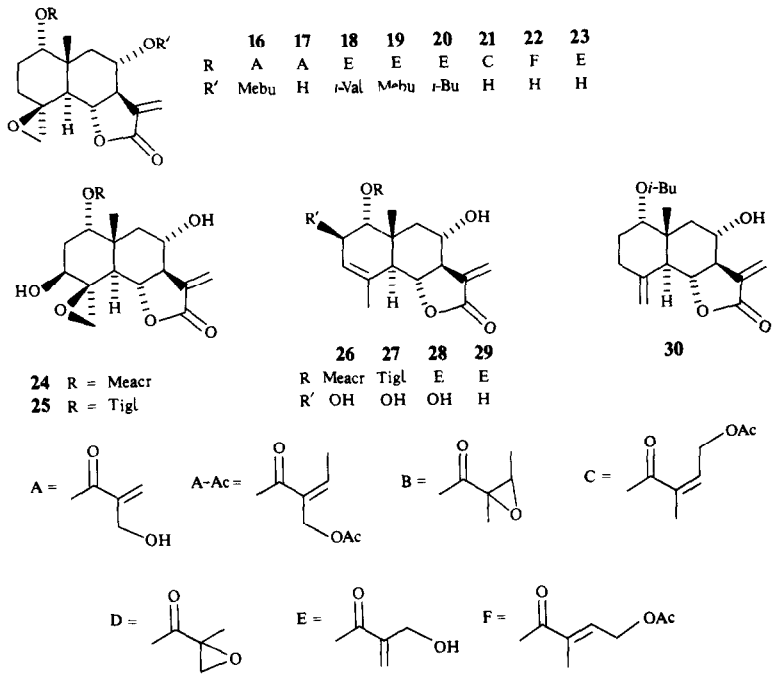
J (Hz): 1,2 = 1,2′ = 2.7; 3,15 = 1.5; 5,6 = 6,7 = 10; 7,8 = 11; 7,13 = 3.5; 7,13′ = 3; 8,9α = 11; 8,9β = 4.5; 15,15′ = 3.5 (compounds **13** and **14**: 13,13′ = 0.7); 5-acetoxy ang: 3′,4′ = 5; 3′, 5′ = 1.5; 4′,4′ = 17; 4′,5′ = 1.5; Tigl: 3′,4′ = 7; 3′, 5′ = 4′, 5′ = 1.3; Meacr: 3′,4′ = 1.3; 4′,4 = 1; epoxy butyrate: 3′,3′ = 6.

ester group at C-1 was 4′-acetoxyangelate, while that of **12** was tiglate, that of **13** was methacrylate, that of **14** was epoxyisobutyrate and that of **15** was hydroxymethacrylate. Consequently, the ^1H NMR spectral data of **11–15** (Table 1) were nearly identical with those of **8** and **9**[3]. Again the ^1H NMR spectral data of **18–23** (Table 2) were close to those of **17**[3], the ^1H NMR spectrum of which differed from that of **9** in the chemical shifts of H-15 and the missing *W*-coupling $J_{3,15}$. The nature of the ester residues followed from the characteristic ^1H NMR signals. Though the relative positions of the ester groups in **18–20** could not be established with certainty, identical chemical shifts of H-1 strongly suggested that the unsaturated ester group was at C-1 in all cases. The ^1H NMR spectra of **24** and **25** (Table 3), which could not be separated, showed that these lactones differed only in the nature of the ester group, but contained an additional hydroxy group. Spin decoupling showed that this group had to be placed at C-3, while the stereochemistry followed from the couplings observed. The ^1H NMR spectrum of **29** (Table 3) was in part similar to that of **23**. However, the signals of the epoxy protons were replaced by the signal of an olefinic methyl. An additional olefinic proton displayed a broadened singlet at δ 5.34, which was coupled with the olefinic methyl group, thus establishing the position of the double bond. All other signals were in agreement with the proposed structures. We have named the 1-desacyl derivative of **29** dimerostemmabrasiolide.

While **26** and **27** could not be separated, **28** was obtained pure. Its ^1H NMR spectral data (Table 3) indicated that **28** differed from **29** only by an additional hydroxyl group, which had to be placed at C-2, as the corresponding proton showed a coupling



	8	**9**	**10**	**11**	**12**	**13**	**14**	**15**
R	B	A	A-Ac	C	Tigl	Meacr	D	F
R′	H	H	H	H	H	H	H	H



with that at C-1. The stereochemistry followed from the small coupling with that at C-1. The stereochemistry followed from the small coupling $J_{2,3}$. The spectrum of the mixture of **26** and **27** clearly showed that these compounds differed only in the nature of the ester group at C-1 (Table 3), therefore, the signals H-1–H-15 were nearly the same. Only a few signals differed slightly. Their assignments were possible, due to the different proportions **26** and **27** in the mixture.

The chemistry of *D. brasilianum* again showed that this genus can be characterized by typical eudesmanolides, which are not present in other genera of the subtribe Verbesininae. From *Zexmenia*

Table 2. ^{1}H NMR spectral data of compounds **18–23** (400 MHz, $CDCl_3$, TMS as int. standard)

	18	**19**	**20**	**21**	**22**	**23**
H-1	4.86 *br dd*		4.86 *br dd*	4.90 *br dd*	4.87 *br dd*	4.89 *br dd*
H-5	2.60 *d*		2.60 *d*	2.54 *d*	2.57 *d*	2.57 *d*
H-6	3.92 *dd*		3.92 *dd*	3.83 *dd*	3.85 *dd*	3.84 *dd*
H-7	2.76 *dddd*		2.76 *dddd*	2.52 *dddd*	2.53 *dddd*	2.53 *dddd*
H-8	5.22 *ddd*		5.20 *ddd*	4.11 *ddd*	4.15 *ddd*	4.10 *ddd*
H-13	6.12 *d*		6.12 *d*	6.15 *d*	6.16 *d*	6.15 *d*
H-13	5.54 *d*		5.52 *d*	5.99 *d*	5.97 *d*	5.97 *d*
H-14	1.28 *s*		1.28 *s*	1.22 *s*	1.22 *s*	1.22 *s*
H-15	3.42 *d*		3.42 *d*	3.42 *d*	3.43 *d*	3.42 *d*
H-15′	2.45 *d*		2.44 *d*	2.42 *d*	2.44 *d*	2.44 *d*
OCOR	6.32 *br s*		6.32 *br s*	6.03 *ddq*	6.80 *tq*	6.32 *br s*
	5.95 *br s*		5.94 *br s*	5.00 *ddq*	4.78 *dq*	5.92 *br s*
	4.40 *br s*		4.40 *br s*	5.10 *ddq*	1.95 *dt*	4.39 *br s*
	2.25 *br d*	2.37 *tq*	2.57 *qq*	2.01 *dt*	2.12 *s*	
	2.16 *m*	1.68 *ddq*	1.19 *d*	2.09 *s*		
	0.97 *d*	0.92 *t*	1.18 *d*			
		1.15 *d*				

J (Hz): 1,2 = 1,2′ ~ 2.5; 5,6 = 6,7 = 7,8 = 11; 7,13 = 3.3; 7,13′ = 3.0; 8,9α = 11; 8,9β = 4.5; 15,15′ = 4.3; *i*Val: 2′,3′ = 4′5′ = 7; MeBu: 2′,3′ = 2′,5′ = 3′,4′ = 7; 3′,3′ = 14; *i*Bu: 2′,3′ = 2′,4′ = 7; 4-acetoxy ang: 3′,3′ = 17; 3′,4′ = 5; 3′,5′ = 4′5′ = 1.5; 4′-acetoxy tigl: 3′,4′ = 6; 3′,5′ = 4′,5′ = 1.

Table 3. ^{1}H NMR spectral data of compounds **24–29** (400 MHz, $CDCl_3$, TMS as int. standard)

	24	**25**			**27**	**28**	**29**
H-1	4.94 *dd*		4.66 *br s*			4.71 *br s*	4.77 *br d*
H-2	2.33 *m* 1.97 *m*		4.01 *br s*			4.02 *br s*	2.47 *br d* 1.9 *m*
H-3	4.17 *dd*		5.53 *br s*			5.53 *br s*	5.34 *br s*
H-5	2.36 *d*		2.68 *br d*			2.67 *br d*	2.73 *br d*
H-6	3.93 *dd*		4.00 *dd*			4.00 *dd*	3.98 *dd*
H-7	2.54 *dddd*		2.58 *dddd*			2.58 *dddd*	2.57 *dddd*
H-8	4.00 *ddd*		4.23 *ddd*		4.22 *ddd*	4.21 *ddd*	4.17 *ddd*
H-13	6.16 *d*		6.19 *d*			6.19 *d*	6.18 *d*
H-13	5.97 *d*		5.99 *d*			5.99 *d*	5.98 *d*
H-14	1.11 *s*	1.12 *s*	1.11 *s*		1.10 *s*	1.10 *s*	0.97 *s*
H-15	3.39 *d*		} 1.96 *br s*			} 1.97 *br s*	} 1.90 *br s*
H-15'	3.15 *d*						
OCOR	6.18 *br s*	6.13 *qq*	6.12 *br s*		6.86 *qq*	6.27 *br s*	6.25 *br s*
	5.68 *dq*	1.89 *dq*	5.63 *dq*		1.85 *dq*	5.92 *br s*	5.88 *br s*
	2.00 *dd*	1.85 *dq*	1.96 *br s*		1.83 *dq*	4.36 *br s*	4.35 *br s*

J (Hz): Compounds **24** and **25**: 1,2 = 1,2' = 3; 2,3 = 12; 2'3 = 5; 5,6 = 6,7 = 7,8 = 10; 7,13 = 3; 15,15' = 4; compounds **26** and **27**: 1,2 ~ 3; 5,6 = 6,7 = 7,8 = 11; 8,9α = 11; 8,9β = 5; 7,13 = 3; compound **28**: 5,6 = 6,7 = 10; 7,8 = 8,9α = 11; 8,9β = 4.5; 7,13 = 3; compound **29**: 1,2 = 4.5; 2,2' = 17; 5,6 = 6,7 = 7,8 = 11; 7,13 = 3; 8,9α = 11; 8,9β = 4; Meacr: 3',4' = 4',4' ~ 1; Tigl: 3',4' = 7; 3',5' = 4',5' = 1.5.

species[4, 5] and from a *Podanthus* species[6], both belonging to the same subtribe, similar lactones without the epoxide grouping were isolated.

EXPERIMENTAL

Air dried plant material, collected in north eastern Brazil, voucher RMK 8921, deposited in the U.S. National Herbarium was extracted with Et_2O–petrol (1 : 2). The resulting extracts were separated first by CC (Si gel) and further by repeated TLC (Si gel) and partly by HPLC (reversed phase, MeOH–H_2O, 3 : 2). Known compounds were identified by comparing the ^{1}H NMR spectra with those of authentic compounds. The roots (250 g) afforded 1 mg germacrene D, 3 mg bicyclogermacrene, 2 mg α-humulene, 25 mg **5**, 2 mg **6**, 3 mg **7** and 9 mg **2** (Et_2O–petrol, 2 : 1), while the aerial parts (110 g) gave 43 mg germacrene D, 45 mg bicyclogermacrene, 2 mg α-humulene, 2 mg phytol, 10 mg sitosterol, 12 mg stigmasterol, 5 mg linolenic acid, 2 mg **3**, 1 mg **4** and a complex mixture of sesquiterpene lactones, which were separated by repeated TLC using CH_2Cl_2–C_6H_6–Et_2O (3.5 : 3.5 : 3). A few pairs of lactones could not be separated completely even by HPLC (**12** and **13**, **18** and **19**, **24** and **25**, **26** and **27**). The separations led to some loss of material. The final yields were 2 mg **8**, 2.5 mg **9**, 1 mg **10**, 3.5 mg **11**, 1 mg **12**, 1.3 mg **13**, 1.2 mg **14**, 5 mg **15**, 5 mg **16**, 1 mg **17**, 1.5 mg **18**, 3.5 mg **19**, 4 mg **20**, 3 mg **21**, 2 mg **22**, 5 mg **23**, 0.5 mg **24**, 0.5 mg **25**, 0.4 mg **26**, 0.8 mg **27**, 1.3 mg **28**, 5 mg **29** and 1 mg **30**. Almost certainly some of these lactones will crystallize, however, due to the small amounts none of them could be induced to do so.

Dimerobrasiolide (**2**). Colourless gum, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1790 (γ-lactone); MS *m/z* (rel. int.): 336 $[M]^+$(0.1), 318.219 $[M-H_2O]^+$(2), 303 $[318-Me]^+$(2), 277 $[M-Me_2COH]^+$(15), 259 $[277-H_2O]^+$(7), 247 $[277-CH_2O]^+$(16), 98 $[C_5H_6O_2]^+$(100) (McLafferty), 81 (93), 71 (67), 69 (75), 59 $[Me_2C{=}OH]^+$(56); $[\alpha]_D \sim 0$ ($CHCl_3$; *c* 0.9) ^{1}H NMR ($CDCl_3$): δ 5.86 (*tt* H-2, *J* = 1, 1.5), 2.48 (*br t* H-4, *J* = 7), 2.32 (*br dt* H-5, *J* = 7, 7), 5.14 *br t* H-6, *J* = 7), 2.04 (*m*, H-8, H-9, H-12), 5.08 (*br t* H-10, *J* = 7), 3.35 (*br d* H-14, *J* = 10), 1.17 (*s*) 1.22 (*s*, H-16, 17), 1.62 (*br s*, αH-18, 19), 4.74 (*d*, H-20), *J* = 1.5).

4-*Isodimerostemmolide*-1-O-(5-*acetoxyangelate*) (**10**) Colourless gum, not free from **12**, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3470 (OH), 1775 (γ-lactone), 1740 (OAc), 1720, 1650 (C=CCO_2R); MS *m/z* (rel. int.): 420 $[M]^+$(1) ($C_{22}H_{28}O_8$), 262 $[M-RCO_2H]^+$(12), 99$[C_4H_6(OH)CO]^+$(100).

4 - *Isodimerostemmolide* - 1 - O - [4 - *acetoxyangelate*] (**11**). Colourless gum, not free from **11**, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3470 (OH), 177 (lactone), 1740 (OAc), 1720, 1650 (C=CCO_2R); MS *m/z* (rel. int.): 420 $[M]^+$(1)($C_{22}H_{28}O_8$), 360 $[M-AcOH]^+$(0.5), 262 $[M-RCO_2H]^+$(12), 99 $[C_4H_6(OH)CO]^+$(100).

4-*Isodimerostemmolide*-1-O-*tiglate* (**12**). Colourless gum, not free from **12**, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3470 (OH), 177 (lactone), 1740 (OH), 1775 (lactone), 1720, 1650 (C=CCO_2R); MS *m/z* (rel. int.): 362 $[M]^+$(0.1) ($C_{20}H_{26}O_6$), 262 $[M-RCO_2H]^+$(12), 83 $[C_4H_7CO]^+$(100).

4-*Isodimerostemmolide*-1-O-*methacrylate* (**13**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3460 (OH), 1775 (lactone), 1720 (C=CCO_2R); MS *m/z* (rel. int.): 348 $[M]^+$(0.5), 262.121 $[M-RCO_2H]^+$(15) ($C_{15}H_{18}O_4$), 244 $[262-H_2O]^+$(14), 229 $[244-Me]^+$(15), 69 $[C_3H_5CO]^+$(100).

4-*Isodimerostemmolide*-1-O-(2,3-*epoxyisobutyrate*) (**14**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3460 (OH), 1780 (lactone), 1740 (CO_2R); MS *m/z* (rel. int.): 364 $[M]^+$(0.1), 262.121 $[M-RCO_2H]^+$(7) ($C_{15}H_{18}O_4$), 244 (11), 229 (12), 85 $[RCO]^+$(33), 57 (100).

4-*Isodimerostemmolide*-1-O-(3-*hydroxymethacrylate*) (**15**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3440 (OH), 1780 (lactone), 1725 ($C=CCO_2R$); MS *m/z* (rel. int.): 364 $[M]^+$ (0.1), 262.121 $[M-RCO_2H]^+$(8), 244 (23), 229 (21), 85 $[RCO]^+$(52), 57 (100);

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-109 \quad -110 \quad -114 \quad -139} (CHCl_3;\ c\ 0.3).$$

8-O-*Isovaleryl- and* (2-*methylbutyryl-dimerostemmolide*-1-O-(3-*hydroxymethacrylate*) (**18** and **19**). Not separated, colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3500 (OH), 1780 (lactone), 1740 (CO_2R), 1720 ($C=CCO_2R$); MS *m/z* (rel. int.): 346.142 $[M-RCO_2H]^+$(7) ($C_{19}H_{22}O_6$), 244 $[346-RCO_2H]^+$(20), 229 $[244-Me]^+$(10), 85 $[C_4H_9CO$ and $C_3H_4(OH)CO]^+$(43), 57 *[85 − CO]⁺(100)*;

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{+158 \quad +165 \quad +188 \quad +326} (CHCl_3;\ c\ 0.5).$$

8 - O - *Isobutyryl-dimerostemmolide* - 1 - O - (3-*hydroxymethacrylate*) (**20**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3520 (OH), 1785 (lactone), 1740 (CO_2R), 1720 ($C=CCO_2R$); MS *m/z* (rel. int.): 346.142 $[M-RCO_2H]^+$(4), 244 $[346-RCO_2H]^+$(30), 85 $[C_3H_4(OH)CO]^+$(53), 71 $[C_3H_7CO]^+$(58), 57 $[85-CO]^+$(100);

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{+135 \quad +141 \quad +159 \quad +273} (CHCl_3;\ c\ 0.4).$$

Dimerostemmolide-1-O-(4-*acetoxyangelate*) (**21**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3520 (OH), 1775 (lactone), 1740 (OAc), 1720 ($C=CCO_2R$); MS *m/z* (rel. int.): 420.178 $[M]^+$(1) ($C_{22}H_{28}O_8$), 262 $[M-RCO_2H]^+$(12), 99 $[C_4H_6(OH)CO]^+$(54), 71 $[91-CO]^+$(46), 57 (100).

Dimerostemmolide-1-O-(4-*acetoxytiglate*) (**22**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3580 (OH), 1780 (lactone), 1740 (OAc), 1715 ($C=CCO_2R$); MS *m/z* (rel. int.): 420.178 $[M]^+$(1) ($C_{22}H_{28}O_8$), 262 $[M-RCO_2H]^+$(4), 99 $[C_4H_6(OH)CO]^+$(34), 71 $[99-CO]^+$(56), 57 (100).

Dimerostemmolide-1-O-(3-*hydroxymethacrylate*) (**23**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1770 (lactone), 1720 ($C=CCO_2R$); MS *m/z* (rel. int.): 364 $[M]^+$(0.1), 262.121 $[M-RCO_2H]^+$(28)($C_{15}H_{18}O_4$), 247 $[262-Me]^+$(30), 229 $[247-H_2O]^+$(20), 85 $[C_3H_4(OH)CO]^+$(100), 57 $[85-CO]^+$(88).

*In this paper, due to an error, the assignments of the 4,15-epoxides were changed: **6–11** should be 4α, 15-epoxides and **12a–13b** 4β, 15-epoxides (see ref. [2]).

3β-*Hydroxy-dimerostemmolide*-1-O-(*methacrylate and tiglate*) (**24** and **25**). Not separated, colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3500 (OH), 1780 (lactone), 1720 ($C=CCO_2R$); MS *m/z* (rel. int.): 378 and 364 $[M]^+$(0.1), 278.115 $[M-RCO_2H]^+$(3)($C_{15}H_{18}O_5$), 260 $[278-H_2O]^+$(4), 242 $[260-H_2O]^+$(5), 83 $[C_4H_7CO]^+$(92), 69 $[C_3H_5CO]^+$(67), 55 $[83-CO]^+$(100);

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-10 \quad -10 \quad -14 \quad -28} (CHCl_3;\ c\ 0.08).$$

2β-*Hydroxy-dimerostemma brasiolide*-1-O-(*methacrylate and tiglate*) **26** *and* **27**. Not separated, colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1780 (lactone), 1715 ($C=CCO_2R$); MS *m/z* (rel. int): 362 and 348 $[M]^+$(0.2), 262.121 $[M-RCO_2H]^+$(10)($C_{15}H_{18}O_4$), 247 $[262-Me]^+$(13), 229 $[247-H_2O]^+$(14), 83 $[C_4H_7CO]^+$(83), 69 $[C_3H_5CO]^+$(70), 55 $[83-CO]^+$(100).

2β-*Hydroxy-dimerostemma brasiolide*-1-O-(3-*hydroxymethacrylate*) (**28**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3560 (OH), 1770 (lactone), 1720 ($C=CCO_2R$); MS *m/z* (rel. int.): 364 $[M]^+$(0.1), 262.121 $[M-RCO_2H]^+$(10)($C_{15}H_{18}O_4$), 247 $[M-Me]^+$(11), 229 $[247-H_2O]^+$(12), 85 $[C_3H_4(OH)CO]^+$(32), 57 $[85-CO]^+$(100);

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-188 \quad -190 \quad +211 \quad +327} (CHCl_3\ c\ 0.13).$$

Dimerostemma brasiolide-1-O-(3-*hydroxymethacrylate*) (**29**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1770 ($C=CCO_2R$); MS *m/z* (rel. int.): 246.126 $[M-RCO_2H]^+$(100) ($C_{15}H_{18}O_3$), 228 $[M-H_2O]^+$(23), 213 $[228-Me]^+$(23), 85 $[C_3H_4(OH)CO]^+$(33), 57 $[85-CO]^+$(48).

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.

REFERENCES

1. Stuessy, T. F. (1977) *The Biology and Chemistry of the Compositae* (Heywood, V. H., Harborne, J. B. and Turner, B. L., eds) p. 641. Academic Press, London.
2. Bohlmann, F., Dhar, A. K., Jakupovic, J., King, R. M. and Robinson, H. (1981) *Phytochemistry* **20**, 838.
3. Bohlmann, F., Ziesche, J., King, R. M. and Robinson, H. (1981) *Phytochemistry* **20**, 1335.*
4. Bohlmann, F. and Lonitz, M. (1980) *Chem. Ber.* **113**, 2410.
5. Bohlmann, F. and Lonitz, M. (1978) *Chem. Ber.* **111**, 843.
6. Hoeneisen, M., Silva, M. and Bohlmann, F. (1980) *Phytochemistry* **19**, 2765.