Phytochemistry, Vol 22, No 5, pp 1213–1218, 1983
Printed in Great Britain

0031-9422/83/051213-06$03 00/0
© 1983 Pergamon Press Ltd

FOUR HELIANGOLIDES AND OTHER SESQUITERPENES FROM *BRASILIA SICKII**

FERDINAND BOHLMANN, MICHAEL GRENZ, 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, Stop No 166, Washington, DC 20560, U.S.A.

(*Revised received* 5 *September* 1982)

Key Word Index—*Brasilia sickii*, Compositae, sesquiterpene lactones, heliangolides, sesquiterpenes; bisabolene derivatives; damsinic acid derivative; spathulenol derivative; thymol derivative; triterpene isovalerate.

Abstract—The investigation of *Brasilia sickii* afforded, in addition to known compounds, two new bisabolene derivatives, an acetate closely related to damsinic acid together with its methyl ester, a dihydroxyaromadendrane, a thymol derivative and four heliangolides, closely related to a similar lactone isolated from a *Calea* species. The structures were elucidated by high field ^{1}H NMR spectroscopy and a few chemical transformations, while the structure of the spathulenol derivative was established by partial synthesis. The chemotaxonomy is discussed briefly

INTRODUCTION

The monotypic genus *Brasilia* (Compositae, tribe Heliantheae) is placed by Stuessy in the subtribe Galinsoginae [1], while new taxonomic studies have shown that it should be transferred to the subtribe Neurolinae [2]. Since the chemistry of these two tribes is very different an investigation of *Brasilia sickii* should indicate where this genus should be placed. The results of such a study are discussed in this paper.

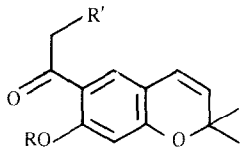
RESULTS AND DISCUSSION

The roots of *Brasilia sickii* Barrosa afforded the widespread tridecapentaynene, squalene, α-humulene, bornyl acetate, α- and β-bergamotene, bisabolene, the chromene derivatives **1**–**4** [3, 4], the thymol derivatives **5** and **6** [5, 6] and a further one, the isobutyrate **8**; the ^{1}H NMR spectral data for **8** (see Experimental) were close to those of similar compounds [5]. Furthermore a triterpene isovalerate was present, which most likely was butyrospermyl isovalerate. Saponification afforded the corresponding alcohol, its mp, however, was higher than that reported for this triterpene [7]. Since no material for direct comparison and no ^{1}H NMR spectral data were available, a final proof was not possible, though all data agreed with the proposed structure. An isomeric structure, perhaps at C-9, however, could not be excluded. The aerial parts afforded germacrene D, squalene, **6** and 7 [8], the bisabolene derivatives **13** and **15**, the pseudoguaiane derivatives **9** and **10**, the heliangolides **23** [9] and **24**–**27** as well as tiny amounts of **21**. The ^{1}H NMR spectral data of **21** (Table 1) were in part close to those of spathulenol (**17**). However, the olefinic methylene signals were replaced by an additional methyl singlet. The molecular formula ($C_{15}H_{26}O_2$) indicated the presence of a diol, which could be either **21** or **22**. Since only 0.5 mg of material was isolated, a decision was only possible by a partial synthesis. Epoxidation of **17** afforded the epoxides **18** and **19**; their ^{1}H NMR spectra (Table 1) showed typical differences. In particular, both signals of the epoxide protons of one of the isomers showed a *W*-coupling. Inspection of models clearly showed that only **18** could explain these couplings ($J_{1,14}$ and $J_{9\alpha,14'}$). Accordingly the stereochemistry of the epoxides was settled. Alanate reduction led to the isomeric diols **21** and **22**. The ^{1}H NMR spectrum of **21** was identical with that of the natural diol, its structure and stereochemistry being thus established as 4β,10α-dihydroxyaromadendrane. Compound **21** could be the direct precursor of spathulenol (**17**), which probably is formed via bicyclogermacrene epoxide, though its formation could proceed directly via the corresponding ion **20**.

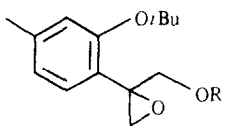
The structures of the bisabolenes **13** and **15**, which were transformed by addition of diazomethane to the corresponding esters **14** and **16**, respectively, followed from the molecular formulae and the ^{1}H NMR spectra (Table 2). That of **16** clearly showed that two conjugated carbonyl groups were present, since the signals of two olefinic protons were shifted downfield. Since the signals of the side chain were nearly identical in the spectra of **14** and **16**, the esters clearly differed only in the nature of C-15, **14** being the acetoxy derivative, while **16** was the corresponding aldehyde. Accordingly, a signal of an aldehyde proton was visible, its chemical shift clearly showing the *cisoid* arrangement of the olefinic proton and the aldehyde group. The stereochemistry of the 10,11-double bond followed from the chemical shift of H-10. Though the absolute stereochemistry could not be determined, the negative rotation indicated the normal configuration at C-1. The acid with an oxygen function at C-15 we have named brasilic acid.

The structure of the pseudoguaiane derivatives **9** and **10** followed from the spectral data (Table 3) as well as from chemical transformations. Addition of diazomethane to **9** afforded **10**, the pyrazoline **10a** and small amounts of the isomer **10b** formed by attack from the β-face, this followed from the ^{1}H NMR spectra. Saponification of **10**

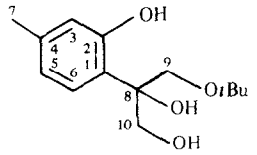
*Part 457 in the series "Naturally Occurring Terpene Derivatives". For Part 456 see Bohlmann, F. and Giencke, W. *Tetrahedron* (in press).



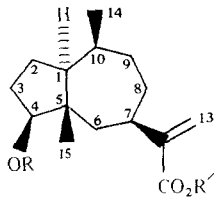
	1	2	3	4
R	H	Me	Me	Me
R′	H	H	OAc	OH



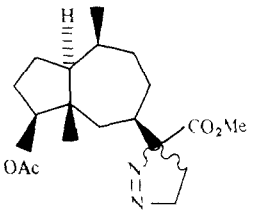
5 R = H
6 R = *t*Bu
7 R = Ac



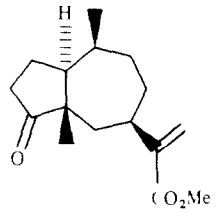
8



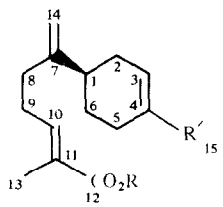
	9	10	11
R	Ac	Ac	H
R′	H	Me	Me



10a α-N
10b β-N



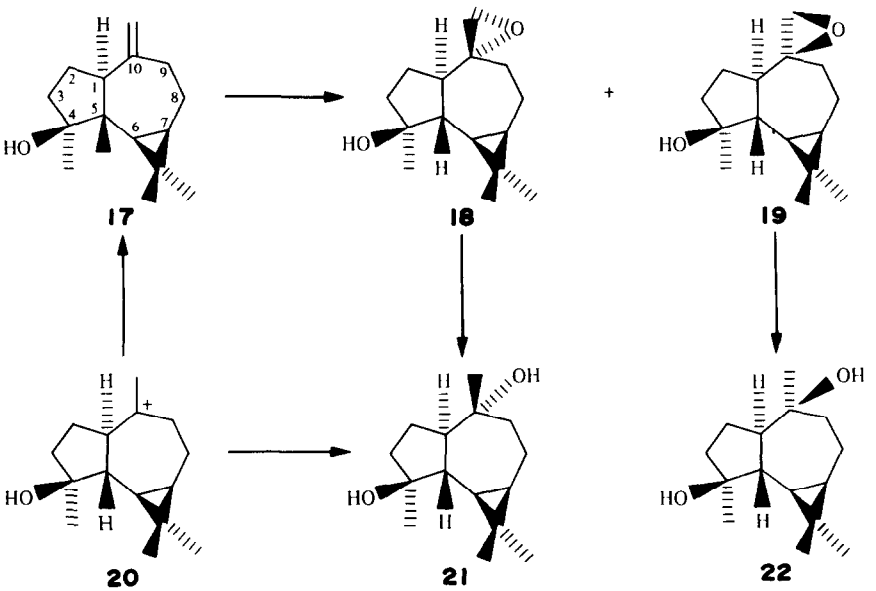
12

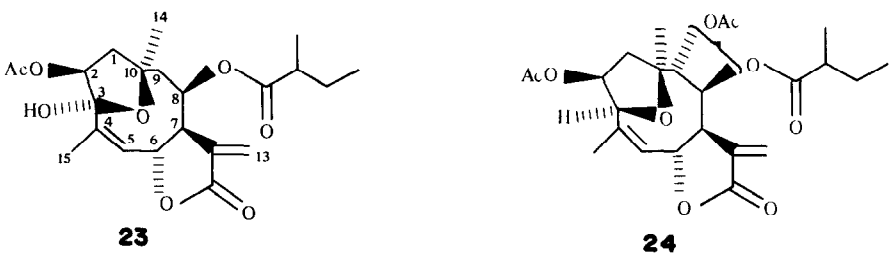


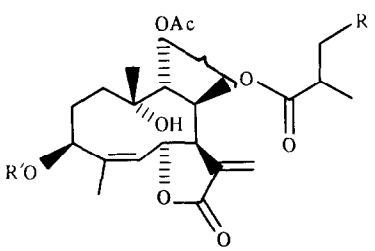
	13	14	15	16
R	H	Me	H	Me
R′	CH_2OAc	CH_2OAc	CHO	CHO

afforded the alcohol **11**, which on oxidation gave a ketone, its data nicely agreeing with those reported for damsinic acid methyl ester (**12**) [10] Since boranate reduction of **12** only afforded **11**, the stereochemistry at C-4 was also settled A model showed that the attack of the hydride should be preferred from the α-face Compound **9**, therefore, is 4β-acetoxy-4-desoxodamsinic acid

The structure of **24** could be established by careful ^{1}H NMR investigations (Table 4) Spin decoupling allowed the assignment of all signals The presence of a heliangolide followed from the typical couplings of H-6 and H-7 while the position of an acetate group at C-2 could be deduced from the couplings of the proton under the acetoxy group The relative position of the two remaining ester groups could not be assigned with certainty







	25	26	27
R	Me	Me	H
R′	H	Ac	Ac

The stereochemistry at C-8 followed from the small coupling $J_{7,8}$, while the large value for $J_{8,9}$ required a 9α-acyloxy group. The stereochemistry at C-2 could not be assigned with certainty. Since, however, the couplings $J_{1,2}$ were similar to those of woodhousin [11] with established stereochemistry, a 2β-acetoxy group was likely. The structures of **25**–**27**, which only could be separated by HPLC (reversed phase), also followed from the molecular formulae and the ^{1}H NMR spectra (Table 4), which showed that these lactones were also heliangolides differing only in the oxygen functions. Compound **26** obviously was the acetate of **25**, while in **27** the ester group was changed to an isobutyrate residue. While spin decoupling allowed the assignment of all signals, the determination of the stereochemistry caused some problems. While that at C-6–C-9 obviously was the same as in **24**, that at C-3 could only be proposed, if a hydrogen bond between OH-3 and OH-10 was assumed. As the couplings $J_{2,3}$ were small and nearly equal, a β-orientation of the oxygen function at C-3 was likely if models were consid-

Table 1 ^{1}H NMR spectral data of compounds **18**, **19**, **21** and **22** (400 MHz, $CDCl_3$, TMS as int standard)

	18	**19**	**21**	**21** (C_6D_6)	**22**	**22** (C_6D_6)
H-5	*	*	1 19 *dd*	1 16 *dd*	1 72 *m*	1 87 *dd*
H-6	0 70 *dd*	0 67 *dd*	0 43 *dd*	0 26 *dd*	0 36 *dd*	0 25 *dd*
H-7	0 80 *ddd*	0 82 *ddd*	0 62 *ddd*	0 50 *dd*	0 57 *ddd*	0 52 *ddd*
H-8α	*	*	1 82 *ddd*	*	1 65 *m*	1 63 *m*
H-8β	*	*	0 89 *br ddd*	0 85 *ddd*	1 38 *br ddd*	1 55 *m*
H-9	*	*	1 52 *br dd*	*	1 52 *m*	1 35 *ddd*
H-9′	*	*	1.74 *br dd*	*	1 65 *m*	1 65 *m*
H-12	1 13 *s*	1 11 *s*	1 02 *s*	1 04 *s*	1 09 *s*	1 05 *s*
H-13	1 08 *s*	1 07 *s*		1 02 *s*	1 02 *s*	1 04 *s*
H-14	2 81 *dd*	2 82 *d*	1 24 *s*	1 11 *s*	1 24 *s*	1 21 *s*
H-14′	2 52 *dd*	2 57 *d*				
H-15	1 21 *s*	1 20 *s*	1 16 *s*	1 09 *s*	1 19 *s*	1 18 *s*

*Overlapping multiplets

J (Hz) 1, 5 = 9, 5, 6 = 11, 6, 7 = 9 5, 7, 8α = 6, 7, 8β = 11, 8α, 8β = 14, 8β, 9α = 11, 8α, 9β = 6, 9, 9′ = 13 compound **18** 1, 14 = 1, 9, 14′ = 1, 14, 14′ = 4, compound **19** 14, 14′ = 4 5

Table 2 ^{1}H NMR spectral data of compounds **14** and **16** (400 MHz, $CDCl_3$ TMS as int standard)

	14	**16**
H-1	2 15 *m*	2 13 *m*
H-2	1 98 *m*	2 45 *br d*
H-2′	2 15 *m*	2 22 *m*
H-3	5 76 *br d*	6 83 *br d*
H-5	2 15 *m*	2 51 *br d*
H-5′	—	2 22 *m*
H-6	1 51 *dddd*	1 44 *dddd*
H-6′	1 89 *m*	1 92 *br d*
H-8	2 15 *m*	2 19 *br t*
H-9	2 33 *br dt*	2 34 *br dt*
H-10	6 76 *qt*	6 75 *qt*
H-13	1 85 *dt*	1 85 *dt*
H-14	4 82 *br s*	4 84 *br s*
H-14′	4 78 *dt*	4 83 *br s*
H-15	4 46 *br s*	9 44 *s*
OMe	3 74 *s*	3 74 *s*

J (Hz) 1, 6 = 11, 1 14 = 1, 2, 2′ = 17, 2, 3 = 4, 3, 5 ~ 1, 5, 5′ ~ 15, 5, 6 = 5, 5′, 6 = 11, 6, 6′ = 13, 8 9 = 9, 10 = 7 5, 10, 13 = 1 3, 8, 14′ = 1

ered This assumption also could explain the downfield shift of H-6 and H-9 Again the relative placement of the ester groups at C-8 and C-9 could not be established with certainty The 8,9-dihydroxy compound, which corresponds to **25**, we have named brasiloide and **24** with free 8- and 9-hydroxy groups, 3,10-anhydrobrasiloide

The chemistry of *Brasilia* shows a close relationship to that of *Neurolaena* and *Calea* where similar heliangolides are widespread Chromenes are frequent in *Calea* too [4, 12-14] Accordingly, the placement of *Brasilia* in the subtribe Neurolinae is supported by the chemistry, since the representatives of Galinsoginae contain very different compounds

EXPERIMENTAL

The air-dried plant material, collected in NE Brazil (voucher RMK 8879, deposited in the U S National Herbarium, Washington) was extracted with Et_2O-petrol (1 2) and the resulting extracts were separated first by CC (Si gel) and further by repeated TLC (Si gel) The roots (120 g) afforded traces of tridecapentaynene, 2 mg squalene, 5 mg bisabolene 10 mg α-humulene, 2 mg bornyl acetate, 5 mg α- and 5 mg β-bergamotene, 40 mg **1** 40 mg **2** 15 mg **3** 5 mg **4**, 3 mg **5**, 20 mg **6** and 1 mg **8** (Et_2O), colourless gum IR $\nu_{max}^{CCl_4}$ cm^{-1} 3600 (OH) 1740 (CO_2R), MS *m/z* (rel int) 268 131 $[M]^+$ (4) ($C_{14}H_{20}O_5$) 237 $[M-CH_2OH]^+$ (20), 167 $[237-O=C=CMe_2]$ (37) 149 $[167-H_2O]^+$ (64), 71 $[C_3H_7CO]^+$ (100), ^{1}H NMR ($CDCl_3$) δ 6 72 *br s* (H-3), 6 65 *br d* (H-5, *J* = 8 5 Hz) 6 91 *d* (H-6 *J* = 8 5 Hz), 2 28 *s* (H-7), 4 55 *d* and 4 43 *d* (H-9, *J* = 12 Hz), 3 87 *br d* and 3 79 *br d* (H-10 *J* = 12 Hz) 2 57 *qq* (H-2′, *J* = 7 7 Hz) 1 14 *d* and 1 13 *d* (H-3′, H-4′, *J* = 7 Hz)

Furthermore, 15 mg of a triterpene isovalerate (Et_2O-petrol 1 10) was obtained IR $\nu_{max}^{CCl_4}$ cm^{-1} 1730 (CO_2R), 1615, 1475, 1385, 1300, 1275, 1130, 1105, 1000; MS *m z* (rel int) 510 444 $[M]^+$ (26) ($C_{35}H_{58}O_2$), 459 $[M-Me]^+$ (42) 408 $[M-RCO_2H]^+$ (5), 393 $[495-RCO_2H]^+$ (42), 85 $[C_4H_9CO]^+$ (37), 69 $[C_5H_9]^+$ (100), 57 $[85-CO]^+$ (94) ^{1}H NMR ($CDCl_3$) δ 5 54 *ddd* (H-7, *J* = 6, 3, 3 Hz), 5 10 *br t* (H-21 *J* = 7 Hz) 4 47 *dd* (H-3, *J* = 9, 6 Hz), 1 68 *br s* (H-24), 1 60 *br s* (H-25), 1 02 *s* (H-3) 1 01 *s* (H-3), 0 95 *s* (H-3), 0 92 *s* (H-3), 0 91 *s* (H-3), (OiVal) 2 18 *d* (H-2, *J* = 7 Hz), 2 11 *dqq* (H-3′ *J* = 7 7, 7 Hz), 0 97 *d* (H-4′, H-5′, *J* = 7 Hz) Saponification (3 hr, MeOH H_2O 4 N KOH) afforded colourless crystals, mp 133 MS *m z* (rel int) 426 386 $[M]^+$ (11) ($C_{30}H_{50}O$), 411 $[M-Me]^+$ (25) 393 $[411-H_2O]^+$ (7), 69 $[C_5H_9]^+$ (100), ^{1}H NMR ($CDCl_3$) δ 5 56 *ddd* (H-7, *J* = 6 3, 3 Hz), 5 10 *br t* (H-12, *J* = 7 Hz), 3 21 *dd* (H-3, *J* = 10, 7 Hz), 1 68 *br s* (H-24), 1 60 *br s* (H-25), 1 02 *s* (H-6), 0 98 *s* (H-3) 0 90 (H-3), 0 87 (H-3)

The aerial parts (300 g) gave 300 mg germacrene D, 70 mg squalene, 20 mg **6**, 60 mg **7**, 30 mg **9** (Et_2O-petrol, 1 1) 5 mg **10** (Et_2O-petrol, 1 3), 10 mg **13** and 25 mg **15** (Et_2O petrol, 1 1) 0 5 mg **21**, 50 mg **23**, 6 mg **24**, 2 mg **25** 1 mg **26** and 1 mg **27** Compounds **21** and **24** **27** were separated by HPLC (reversed phase, MeOH-H_2O, 6 5 3 5)

4β-Acetoxy-4-desoxodamsinic acid (**9**) Colourless gum

Table 3 ^{1}H NMR spectral data of compounds **10–12** (400 MHz, $CDCl_3$, TMS as int standard)

	10	Δ*	**11**	**12**	**10a**†	**10b**‡
H-1	1 97 *ddd*	0.05	1.93 *ddd*	2.28 *ddd*	1 99 *ddd*	1.92 *ddd*
H-2	1 77 *dddd*	0 03	1.72 *m*	1.93 *dddd*	1 77 *dddd*	1 76 *dddd*
H-2′	1 50 *m*	0 0	1 6 *m*	1 79 *m*	1 62 *m*	1 58 *m*
H-3	2 19 *dddd*	0 06	2.04 *dddd*	2.45 *br dd*	2 16 *dddd*	2 20 *dddd*
H-3′	1 37 *dddd*	0 10	1 35 *m*	2.17 *ddd*	1 43 *dddd*	1 41 *m*
H-4	4 59 *t*	0 26	3 69 *t*	—	4 71 *t*	4 61 *t*
H-6	1 58 *m*	0 2	1 48 *dd*	1 62 *dd*	1 10 *dd*	1 41 *m*
H-6′		0 87	1 6 *m*	2 20 *dd*	1 31 *dd*	
H-7	2 82 *dddd*	0.12	2.82 *dddd*	2 75 *dddd*	3 12 *dddd*	2 67 *dddd*
H-8	1.86*m*	0 03	1 86 *m*	1 87 *m*	1.62 *m*	1 76 *m*
H-8′	1 53 *m*	0 07	1 43 *m*	1 58 *m*	1 17 *m*	—
H-9	1 64 m	0.01	1.6 *m*	1 68 *m*	1 62 *m*	—
H-9′					1 50 *m*	—
H-10	1.89 *br ddq*	0.0	1 85 *m*	2.09 *dddq*	1.85 *ddq*	1 85 *ddq*
H-13	6 06 *d*	0.08	6 09 *br s*	6 09 *s*	2.09 *ddd*	1 99 *ddd*
H-13′	5 47	0.05	5.51 *br s*	5 52 *s*	1 43 *ddd*	1 50 *ddd*
H-14	0.97 *d*	0 02	0.96 *d*	1.04 *d*	0 94 *d*	0 95 *d*
H-15	0.99 *s*	0.07	0 90 *s*	1.03 *s*	0 96 *s*	0 97 *s*
OMe	3 73 *s*	0 14	3 75 *s*	3 74 *s*	3 74 *s*	3 74 *s*

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

†4 56 *ddd* and 4 45 *ddd* (H-16)

‡4.59 *ddd* and 4 46 *ddd* (H-16);

J (Hz): Compounds **10**/**11**: 1, 2 = 12; 1, 2′ = 7.5, 1, 10 = 7.5, 2, 2′ = 12, 2, 3 = 5 5, 2, 3′ = 12, 3, 3′ = 13; 3, 4 = 3′, 4 = 8 5; 6, 6′ = 14, 6, 7 = 12, 6′, 7 = 9 5; 7, 8 ~ 8, 9, 10 ~ 7, compound **12**. 1, 2 = 13; 1, 2′ = 5.5; 1, 10 = 5 5, 2, 3 = 9 5; 2, 3′ ~ 1; 2′, 3 = 9.5; 2′, 3′ = 9 5; 3, 3′ = 19, 6, 6′ = 14.5; 6, 7 = 12, 6′, 7 = 3 5; 7, 8 ~ 8; 9, 10 = 8.5; 9′, 10 ~ 7.

Table 4 ^{1}H NMR spectral data of compounds **24–27** (400 MHz, $CDCl_3$, TMS as int standard)

	24	**25**	**26**	**27**
H-1	1 76 *dd*	2.06 *m*	2 07 *m*	2 07 *m*
H-1′	2 43 *br dd*	1.65 *m*	1 67 *m*	1 66 *m*
H-2	4 16 *br ddd*	2.06 *m*	2.07 *m*	2 07 *m*
		1.83 *m*	1.84 *m*	1 84 *m*
H-3	5 25 *d*	4 50 *ddd*	5.41 *dd*	5 40 *dd*
H-5	5 46 *br d*	5 50 *br d*	5.49 *dq*	5 49 *dq*
H-6	5 69 *br dd*	6.45 *dd*	6.01 *dd*	6 01 *dd*
H-7	3.49 *br s*	3.47 *br s*	3.51 *br s*	3 50 *br s*
H-8	5.63 *dd*	5.66 *dd*	5.65 *dd*	5.63 *dd*
H-9	5.46 *br d*	6 22 *d*	5.80 *d*	5 78 *d*
H-13	6 34 *d*	6.35 *d*	6 38 *d*	6 37 *d*
H-13′	5.75 *d*	5.77 *d*	5 80 *d*	5.79 *d*
H-14	1.33 *s*	1 26 *s*	1 22 *s*	1 22 *s*
H-15	1.87 *br s*	1.68 *br s*	1 75 *br s*	1 75 *br s*
OCOR	2 33 *tq*	2.21 *tq*	2.22 *tq*	2 41 *qq*
	1 56 *ddq*	1.56 *ddq*	1 56 *ddq*	1.03 *d*
	1 30 *m*	1.30 *m*	1 30 *m*	1 02 *m*
	0.83 *t*	0 83 *t*	0 83 *t*	
	1.01 *d*	1.00 *d*	1.00 *d*	
OAc	2 19 *s*	2.01 *s*	2.22 *s*	2.24 *s*
	2 01 *s*	—	2 03 *s*	2 02 *s*
OH	—	2.23 *br d*	—	—

J (Hz): Compound **24**: 1, 1′ = 15.5; 1, 2 = 5; 1′, 2 = 4; 2, 3 = 5; 5, 6 = 10, 6, 7 ~ 3, 7, 8 = 2; 7, 13 = 2; 7, 13′ = 1.5; 8, 9 = 9; compounds **25–27**: 2, 3 = 2′, 3 = 4 5, (**25**. 3, OH = 4); 5, 6 = 9, 6, 7 = 2.5, 7, 8 = 2, 7, 13 = 2.5; 7, 13′ = 2, 8, 9 = 8, OMeBu. 2′, 3′ = 2′. 5′ = 3′, 4′ = 7, 3′, 3′ = 14, OiBu 2′, 3′ = 2′, 4′ = 7

IR $\nu_{max}^{CCl_4}$ cm^{-1} 3500–2600, 1690, 1620 (C=CCO$_2$R), 1730, 1250 (OAc), MS *m/z* (rel int) 294 [M]$^+$ (3), 276 [M − H$_2$O]$^+$ (21), 248 [276 − CO]$^+$ (17), 234 [M − HOAc]$^+$ (52), 219 [234 − Me]$^+$ (19), 55 [C$_4$H$_7$]$^+$ (100)

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\ nm}{+23 \quad +24 \quad +27 \quad +44} (CHCl_3, c\ 1\ 2)$$

Addition of excess of CH_2N_2 in Et_2O afforded the methyl ester **10**, identical with the natural ester and two isomeric pyrazoline derivatives (**10a** and **10b**) The main product (**10a**) had mp 132 5°, MS *m/z* (rel int) 322 214 [M − N$_2$]$^+$ (11) (C$_{19}$H$_{30}$O$_4$), 290 [M − HCO$_2$Me]$^+$ (46), 262 [290 − N$_2$]$^+$ (36), 248 [290 − ketene]$^+$ (54), 230 [290 − HOAc]$^+$ (37), 215 [230 − Me]$^+$ (14), 55 [C$_4$H$_7$]$^+$ (100) 10 mg **10** in 1 ml MeOH was heated for 5 min with 100 mg KOH in 0 3 ml H_2O TLC (Et_2O–petrol, 1 1) afforded 6 mg **11** MS *m/z* (rel int) 266 188 [M]$^+$ (3) (C$_{16}$H$_{26}$O$_3$), 248 [M − H$_2$O]$^+$ (22), 234 [M − MeOH]$^+$ (33), 206 [234 − CO]$^+$ (59), 191 [206 − Me]$^+$ (31), 55 [C$_4$H$_7$]$^+$ (100)

Oxidation with pyridine chlorochromate in CH_2Cl_2 afforded 4 mg **12** MS *m/z* (rel int): 264 173 [M]$^+$ (80) (C$_{16}$H$_{24}$O$_3$), 246 [M − H$_2$O]$^+$ (20), 232 [M − MeOH]$^+$ (16), 204 [232 − CO]$^+$ (10), 137 (100) $[\alpha]_D + 64^\circ$ ($CHCl_3$, *c* 1 2)

15-*Acetoxybrasilic acid* (**13**) Colourless gum, which was separated as its methyl ester **14**, colourless gum IR $\nu_{max}^{CCl_4}$ cm^{-1} 1750, 1265 (OAc), 1725, 1650 (C=CCO$_2$R), MS *m/z* (rel int) 306 [M]$^+$ (0 5), 246 162 [M − HOAc]$^+$ (32) (C$_{16}$H$_{22}$O$_2$), 214 [246 − MeOH]$^+$ (17), 187 [246 − CO$_2$Me]$^+$ (44), 186 [214 − CO]$^+$ (44), 133 [214 − C$_7$H$_9$]$^+$ (100), 105 [133 − CO]$^+$ (68)

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\ nm}{-55 \quad -58 \quad -66 \quad -114} (CHCl_3, c\ 0\ 87)$$

15-*Oxobrasilic acid* (**15**) Colourless gum, isolated as its methyl ester **16**, colourless gum IR $\nu_{max}^{CCl_4}$ cm^{-1} 2730, 1695 (C=CCHO), 1725, 1655 (C=CCO$_2$R), MS *m/z* (rel int) 262.157 [M]$^+$ (16) (C$_{16}$H$_{22}$O$_3$), 230 [M − MeOH]$^+$ (41), 202 [230 − CO]$^+$ (36), 174 [202 − CO]$^+$ (21), 149 (100), 121 [149 − CO]$^+$ (97)

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\ nm}{-70 \quad -73 \quad -83 \quad -154} (CHCl_3, c\ 2\ 4)$$

4β,10α-*Dihydroxyaromadendrane* (**21**) Colourless crystals, mp 132° IR $\nu_{max}^{CHCl_3}$ cm^{-1} 3600 (OH), MS *m/z* (rel int) 238 193 [M]$^+$ (4) (C$_{15}$H$_{26}$O$_2$), 220 [M − H$_2$O]$^+$ (29), 205 [220 − Me]$^+$ (32), 202 [220 − H$_2$O]$^+$ (32), 187 [202 − Me]$^+$ (28), 177 [220 − CHMe$_2$]$^+$ (30), 162 [220 − Me$_2$CO]$^+$ (90), 147 [162 − Me]$^+$ (55), 93 [C$_8$H$_7$]$^+$ (100)

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\ nm}{-17 \quad -17 \quad -18 \quad -25} (CHCl_3, c\ 0\ 1)$$

Synthesis of **21** *and* **22** To 10 mg **17** in 2 ml $CHCl_3$ 10 mg *m*-chloroperbenzoic acid and 0 3 ml Na_2CO_3 soln were added Stirring for 2 hr afforded 6 mg **18** and 1 5 mg **19** Stirring of this mixture in Et_2O with excess of $LiAlH_4$ for 3 hr afforded after TLC (Et_2O) 1 mg **21**, identical with the natural diol, and 4 mg **22**, colourless crystals, mp 136° MS *m/z* (rel int) 238 193 [M]$^+$ (13) (C$_{15}$H$_{26}$O$_2$), 220 [M − H$_2$O]$^+$ (31), 205 [220 − Me]$^+$ (23), 202 [220 − H$_2$O]$^+$ (68), 187 [202 − Me]$^+$ (43), 177 [220 − CHMe$_2$]$^+$ (30), 162 [220 − Me$_2$CO]$^+$ (100), 147 [162 − Me]$^+$ (68), 93 (89)

2α-*Acetoxy*-3,10-*anhydrobrasiloide*-8,9-O-*acetate and* -(2-*methylbutyrate*) (**24**) Colourless crystals, mp 148° IR $\nu_{max}^{CHCl_3}$ cm^{-1} 1770 (γ-lactone), 1750 (OAc, CO$_2$R), MS *m/z* (rel int) 464 [M]$^+$ (0 1), 422 194 [M − ketene]$^+$ (2) (C$_{22}$H$_{30}$O$_8$), 320 [422 − RCO$_2$H]$^+$ (3), 260 [320 − HOAc]$^+$ (11), 85 [C$_4$H$_9$CO]$^+$ (41), 57 [85 − CO]$^+$ (100)

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\ nm}{-34 \quad -34 \quad -39 \quad -75} (CHCl_3, c\ 0\ 57)$$

Brasiloide-8,9-O-(2-*methylbutyrate*) (**25**) Colourless crystals, mp 208°, IR $\nu_{max}^{CHCl_3}$ cm^{-1} 3610 (OH), 1765 (γ-lactone), 1745 (OAc, CO$_2$R), MS *m/z* (rel int) 424 210 [M]$^+$ (0 1) (C$_{22}$H$_{32}$O$_8$), 322 [M − RCO$_2$H]$^+$ (1), 304 [322 − H$_2$O]$^+$ (1), 244 [304 − HOAc]$^+$ (8), 226 [244 − H$_2$O]$^+$ (27), 85 [C$_4$H$_9$CO]$^+$ (44), 57 [85 − CO]$^+$ (100)

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\ nm}{-37 \quad -37 \quad -44 \quad -80} (CHCl_3, c\ 0\ 2)$$

3-O-*Acetyl-brasiloide*-8,9-O-(2-*methylbutyrate*) (**26**) Colourless crystals, mp 158°, IR $\nu_{max}^{CHCl_3}$ cm^{-1} 3610 (OH), 1765 (γ-lactone), 1730 (OAc, CO$_2$R), MS *m/z* (rel int) 466 220 [M]$^+$ (1) (C$_{24}$H$_{34}$O$_9$), 424 [M − ketene]$^+$ (2), 406 [M − HOAc]$^+$ (1), 364 [M − RCO$_2$H]$^+$ (2), 304 [M − HOAc]$^+$ (3), 244 [304 − HOAc]$^+$ (8), 226 [244 − H$_2$O]$^+$ (6), 85 [C$_4$H$_9$CO]$^+$ (37), 57 [85 − CO]$^+$ (100)

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\ nm}{-87 \quad -87 \quad -105 \quad -185} (CHCl_3, c\ 0\ 1)$$

3-O-*Acetyl-brasiloide*-8-O-*isobutyrate* (**27**) Colourless crystals, mp 192°, IR $\nu_{max}^{CHCl_3}$ cm^{-1} 3620 (OH), 1765 (γ-lactone), 1750 (OAc, CO$_2$R), MS *m/z* (rel int) 452 205 [M]$^+$ (0 5) (C$_{23}$H$_{32}$O$_9$), 410 [M − ketene]$^+$ (3), 392 [M − HOAc]$^+$ (1), 364 [M − RCO$_2$H]$^+$ (1.5), 322 [410 − RCO$_2$H]$^+$ (2 5), 304 [322 − H$_2$O]$^+$ (4), 244 [304 − HOAc]$^+$ (12), 226 [244 − H$_2$O]$^+$ (10), 71 [C$_3$H$_7$CO]$^+$ (100)

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\ nm}{-58 \quad -58 \quad -69 \quad -123} (CHCl_3, c\ 0\ 08)$$

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 645 Academic Press, London
2 Robinson, H (1981) *Smithson Contrib Botany* 51
3 Bohlmann, F and Grenz, M (1970) *Chem Ber* **103**, 90
4 Bohlmann, F, Fritz, U, King, R M and Robinson, H (1981) *Phytochemistry* **20**, 743
5 Bohlmann, F, Niedballa, U and Schulz, J (1969) *Chem Ber* **102**, 864
6 Bohlmann, F and Zdero, C (1977) *Phytochemistry* **16**, 1243
7 Irvine, D S, Lawrie, W, McNab, A S and Spring, F S (1956) *J Chem Soc* 2029
8 Bohlmann, F and Suwita, A (1978) *Phytochemistry* **17**, 1929.
9 Chowdhury, P K, Sharma, R P, Thyagarajan, G, Herz, W and Govindan, S V (1980) *J Org Chem* **45**, 4993
10 Herz, W, Cage, D and Kumar, N (1981) *Phytochemistry* **20**, 1601
11 Herz, W and Bhat, S V (1972) *J Org Chem* **37**, 906
12 Herz, W and Kumar, N (1980) *Phytochemistry* **19**, 593
13 Bohlmann, F, Mathur, R, Jakupovic, J, Gupta, R K, King, R M and Robinson, H (1982) *Phytochemistry* **21**, 2045
14 Manchand, P S and Blount, J F (1978) *J Org Chem* **43**, 4352