Phytochemistry, Vol. 26, No. 9, pp. 2597–2601, 1987.
Printed in Great Britain.

0031-9422/87 $3.00+0.00
Pergamon Journals Ltd.

SESQUITERPENE LACTONES FROM THE GENUS *BRACHYLAENA*

C. ZDERO and F. BOHLMANN

Institute for Organic Chemistry, Technical University of Berlin, D-1000 Berlin 12, F.R.G.

(*Received* 12 *January* 1987)

Key Word Index—*Brachylaena nereifolia, B. elliptica, B. discolor, B. rotundata*; sesquiterpene lactones; guaianolides, germacranolides; glucosides.

Abstract—The investigation of four *Brachylaena* species afforded in addition to known sesquiterpene lactones four new guaianolide glucopyranosides and three further derivatives of salonitenolide. The chemotaxonomic relevance of these findings is discussed briefly.

INTRODUCTION

The placement of the genus *Brachylaena* is still not solved [1]. While traditionally this South African genus is a member of the tribe Inuleae recent studies led to the exclusion of the Tarchonantheae from the Inuleae [1, 2]. However, so far no clear decision is possible whether these genera should be placed in the Anthemideae, in the Mutisieae or as a new tribe Tarchonantheae. In continuation of our investigations of South African endemics we therefore have studied the chemistry of four *Brachylaena* species. The results are discussed in this paper.

RESULTS AND DISCUSSION

The aerial parts of *Brachylaena elliptica* Less. afforded large amounts of onopordopicrin (**9**) [3] as well as the corresponding elemanolide [4]. From the aerial parts of *B. discolor* DC onopordopicrin was isolated while the aerial parts of *B. nereifolia* R. Br. gave a very complex mixture of highly polar compounds. The separation of this mixture caused some difficulties. Finally, a combination of different techniques led to the isolation of five guaianolide glucopyranosides (**1–5**) and of the germacranolides **6–8**. The known aglycones [5, 6] of **1** and **2** also were present in small amounts. While **1, 2, 4** and **5** could be isolated directly, the lactone **3** was obtained only as its pentaacetate **3a**.

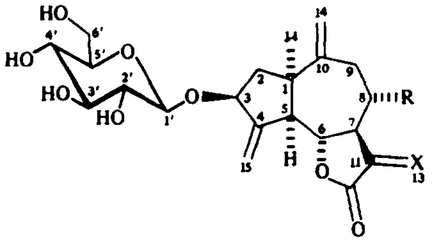
The ^{1}H NMR spectrum of **1** (Table 1) indicated the presence of a glycoside by the signals between δ3.3 and 4.5 which could be assigned only partially as most signals were overlapped multiplets. The additional signals were close to those of zaluzanin C [5]. Acetylation afforded a tetraacetate whose ^{1}H NMR spectrum (Table 1) was much simpler and the signals of the sugar moiety could be assigned by spin decoupling. The couplings observed indicated the presence of a β-glucopyranoside. Accordingly, compound **1** was glucozaluzanin C which was reported first from a *Vernonia* species [7] and also from an *Ainsliaea* species [8]. All data agreed with those presented in ref. [8]. Inspection of the ^{1}H NMR data (Table 1) of **2** and **2a**, which was obtained pure only after transformation of **1a** to the corresponding pyrazolin derivative **1b**, indicated that we were dealing with the corresponding 11,13-dihydro derivatives of **1** and **1a**, respectively. The configuration at C-11 followed from the large coupling $J_{7,11}$ and the chemical shift of H-13, which nicely agreed with the values of the corresponding aglycone [6]. The ^{1}H NMR spectrum of **1b** (Table 1) indicated that the addition of diazomethane was achieved from the β-face. Accordingly, the H-6 signal was shifted down field.

The ^{1}H NMR spectrum of **3a** (Table 1) was close to that of **2a**. However, an additional low field signal (δ4.85 *ddd*) and a further acetoxy methyl singlet indicated the presence of an acetoxy derivative of **2a**. Spin decoupling showed that this group must be placed at C-8 and that the couplings required an α-orientation.

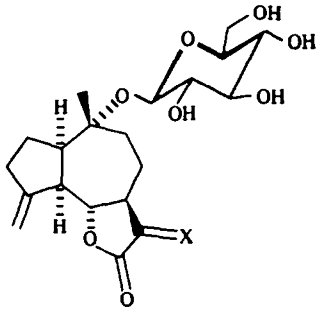
The ^{1}H NMR spectra of **4** and **4a** (Table 1) differed from those of the lactones discussed so far. While the typical signals of a β-glucopyranoside tetraacetate were present in the spectrum of **4a**, one pair of signals for exomethylene protons was replaced by a methyl singlet at δ1.24 and the low field signal of H-3 was absent. Spin decoupling again allowed the assignment of all signals and led to sequences which indicated the presence of a guaianolide with an oxygen function at C-10. This could only be the sugar moiety. The β-configuration of the C-10 methyl followed from the NOE's between H-14 and H-6 (5%), H-3β (6%), H-9β (6%) and the anomeric proton (17%). The ^{13}C NMR spectrum of **4a** also supported the structure (Experimental). We have named lactone **4** brachynereolide.

The ^{1}H NMR spectrum of **5a** (Table 1) was clearer when recorded in deuteriobenzene where all the signals could be assigned by spin decoupling though some were still multiplets. Comparison of the data of **4a** and **5a** showed that the latter was the 11,13-dihydro derivative of the former. The configuration at C-11 was deduced from the observed couplings of H-11 in the spectrum of **5**.

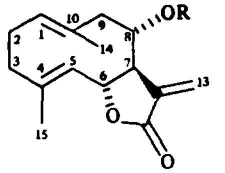
The ^{1}H NMR spectra of **6–8** were not clear at room temperature. However, at elevated temperature the spectra (Table 2) were close to that of onopordopicrin (**9**) and related derivatives of salonitenolide (**10**) [9]. The nature of the ester groups at C-8 clearly followed from the characteristic ^{1}H NMR signals. The rare ester group of **8** showed signals for RCH(OAc)Me (δ5.69 *q*, 1.43 *d*, 2.04 *s*) and for exomethylene protons (δ6.27 and 5.90). A very small allylic coupling of the latter with the proton, which led to the signal at δ5.69, finally established the structure



	1	2	3
R	H	H	OH
X	CH_2	αMe,H	αMe,H

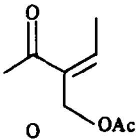


4 X = CH_2
5 X = αMe,H

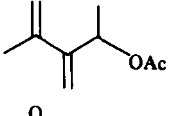


6 R = Ang

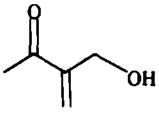
7 R =



8 R =



9 R =



10 R = H

1a – 5a are the corresponding peracetylated compounds
1b is the 11β, 13 - adduct of CH_2N_2 to **1a**

which was further supported by the fragments in the mass spectrum of **8**.

A reinvestigation of the aerial parts of *B. rotundata* S. Moore afforded large amounts of onopordopicrin (**9**), the corresponding elemanolide and also the corresponding alcohol salonitenolide (**10**) [9]. Three other derivatives of the latter were isolated previously from a Transvaal collection [6].

The overall picture of the chemistry of the genus *Brachylaena* again shows that this genus should be excluded from the Inuleae. The proposed relationship to Mutisieae [1] is supported by the co-occurrence of side chain oxygenated germacranolides and guaianolide glucopyranosides which are frequent in several genera of the subtribe Gochnatiinae (tribe Mutisieae). They are reported from the genera *Ainsliaea* [8, 10], *Pertya* [8] and *Macroclinidium* [11] while oxygenated germacranolides and guaianolides are present in *Dicoma* [12], *Cnicothamnus* [13] and *Gochnatia* [14]. So far from *Tarchonanthus* species, which are related to *Brachylaena*, the co-occurrence of special acetylenic compounds is reported [15]. Further investigations may show whether further common constituents are present in both genera.

EXPERIMENTAL

The plant material was grown in the Botanical Garden Kirstenbosch and the air-dried aerial parts were extracted at room temp. with a mixture of MeOH-Et_2O-petrol (1 : 1 : 1). The extracts obtained were treated with MeOH to remove longchain saturated compounds and the soluble part was first separated by CC (silica gel), further by TLC (silica gel, PF 254) and by HPLC (always RP 8, *ca* 100 bar).

The extract of 470 g of the aerial part of *B. elliptica* (voucher 86/169, always deposited in the Compton Herbarium, Kirstenbosch) afforded 2.5 g **9** and 50 mg of the corresponding elemanolide. The extract of 260 g aerial parts of *B. discolor*

Table 1. ^1H NMR spectral data of **1**, **2**, **4**, **5**, **1a**–**5a** and **1b** ($CDCl_3$, 400 MHz, δ-values)

H	**1a**	**1** (60°)	**2** (60°)	**2a**	**3a**	**4** (60°)	**4a**	**5** $CDCl_3$ CD_3OD	**5a**	**5a** (C_6D_6)	**1b**
1	2.98 *ddd*	2.96 *br ddd*	2.86 *ddd*	2.94 *ddd*	2.97 *ddd*	2.41 *m*	2.34 *m*	2.33 *ddd*	2.37 *m*′	2.17 *ddd*	3.00 *m*
2	2.26 *m* 2.05 *m*	2.32 *dddd* 2.05 *ddd*	2.25 *m* 1.94 *m*	2.23 *m* 2.00 *m*	2.23 *m* 2.00 *m*	1.82 *m* 1.68 *m*	1.78 *m* 1.64 *m*	1.89 *m* 1.70 *m*	1.76 *m*	1.70 *m* 1.53 *m*	2.25 *m* 2.13 *m*
3	4.55 *br t*	4.54 *br t*	4.46 *br t*	4.53 *br t*	4.52 *br t*	2.50 *br dd* 2.41 *m*	2.51 *br dd* 2.34 *m*	2.44 *br dd* 2.31 *m*	2.50 *br dd* 2.37 *m*	2.40 *m* 2.27 *m*	5.04 *br t*
5	2.79 *br dd*	2.78 *br dd*	2.82 *br dd*	2.74 *br dd*	2.77 *br dd*	2.95 *br dd*	2.94 *br dd*	2.78 *br dd*	2.83 *br dd*	2.76 *br dd*	2.76 *br dd*
6	4.02 *dd*	4.12 *dd*	4.02 *dd*	3.95 *dd*	4.00 *dd*	3.96 *dd*	3.94 *dd*	3.97 *dd*	3.98 *dd*	3.53 *dd*	4.82 *dd*
7	2.77 *m*	2.75 *m*	1.76 *dddd*	1.84 *dddd*	2.18 *m*	3.28 *m*	3.21 *m*	2.29 *m*	2.20 *m*	2.27 *dddd*	2.37 *ddd*
8α	2.26 *m*	2.23 *m*	2.02 *m*	2.10 *m*	4.85 *ddd*	2.30 *m*	2.19 *m*	2.10 *m*	1.93 *m*	1.70 *m*	2.25 *m*
8β	1.40 *m*	1.47 *m*	1.24 *m*	1.27 *m*		1.44 *m*	1.38 *m*	1.23 *m*	1.25 *m*	0.72 *m*	0.98 *m*
9α	2.49 *ddd*	2.52 *ddd*	2.44 *ddd*	2.52 *ddd*	2.73 *dd*	1.94 *m*	1.90 *m*	2.10 *m*	2.00 *m*	1.22 *ddd*	2.53 *ddd*
9β	2.11 *m*	2.15 *ddd*	1.94 *m*	1.98 *m*	2.13 *dd*	1.82 *m*	1.64 *m*	1.90 *m*	1.56 *m*	1.53 *m*	1.91 *ddd*
11	—	—	2.15 *dq*	2.23 *dq*	2.47 *dq*	—	—	2.16 *dq*	2.20 *m*	1.70 *m*	—
13	6.21 *d*	6.17 *d*	1.13 *d*	1.23 *d*	1.29 *d*	6.12 *d*	6.14 *d*	1.16 *d*	1.25 *d*	1.18 *d*	2.23 *ded*
13′	5.47 *d*	5.45 *d*				5.37 *d*	5.41 *d*				0.98 *ddd*
14	5.03 *br s*	5.05 *br s*	4.92 *br s*	5.02 *br s*	5.16 *br s*	1.29 *s*	1.24 *s*	1.19 *s*	1.21 *s*	0.95*s*	5.08 *br s*
14′	4.91 *br s*	4.95 *br s*	4.84 *br s*	4.90 *br s*	5.02 *br s*						4.91 *br s*
15	5.46 *br s*	5.46 *br s*	5.29 *br s*	5.41 *br s*	5.41 *br s*	5.16 *br s*	5.17 *br s*	5.05 *br s*	5.13 *br s*	5.42 *br s*	5.51 *br s*
15′	5.23 *br s*	5.33 *br s*	5.25 *br s*	5.22 *br s*	5.24 *br s*	4.99 *br s*	4.98 *br s*	4.90 *br s*	4.95 *br s*	5.07 *br s*	5.28 *br s*
1′	4.70 *d*	4.52 *d*	4.41 *d*	4.70 *d*	4.68 *d*	4.58 *d*	4.75 *d*	4.47 *d*	4.72 *d*	4.38 *d*	4.76 *d*
2′	5.07 *dd*	3.38 *m*	3.20 *m*	5.05 *dd*	5.04 *dd*	3.35 *m*	5.00 *m*	3.25 *m*	4.98 *dd*	5.23 *dd*	5.10 *m*
3′	5.19 *dd*	3.56 *m*	3.37 *m*	5.20 *dd*	5.20 *dd*	3.53 *m*	5.21 *dd*	3.43 *m*	5.21 *dd*	5.45 dd	5.22 *dd*
4′	5.04 *dd*	3.46 *m*		5.08 *dd*	5.07 *dd*		5.00 *m*		5.03 *dd*	5.19 *dd*	5.10 *m*
5′	3.70 *ddd*	3.38 *m*	3.20 *m*	3.68 *ddd*	3.68 *ddd*	3.35 *m*	3.68 *ddd*	3.25 *m*	3.67 *ddd*	3.23 *ddd*	3.70 *ddd*
$6'_1$	4.25 *dd*	3.90 *dd*	3.78 *dd*	4.25 *dd*	4.24 *dd*	3.84 *dd*	4.13 *dd*	3.76 *dd*	4.14*d*	4.08 *dd*	4.25 *dd*
$6'_2$	4.16 *dd*	3.81 *dd*	3.68 *dd*	4.16 *dd*	4.15 *dd*	3.75 *dd*	4.08 *dd*	3.69 *dd*	4.10 *dd*	4.13 *dd*	4.16 *dd*
OAc	2.09 *s*	—	—	2.08 *s*	2.09 *s*	--	2.03 *s* (2×)	--	2.05 *s*	1.77 *s*	2.09 *s*
	2.03 *s*	—	—	2.03 *s*	2.08 *s*	—	2.01 *s*	—	2.04 *s*	1.74 *s*	2.04 *s*
	1.99 *s*	—	—	1.99 s (2×)	2.00 *s*	—	1.99 *s*	—	2.03 *s*	1.73 *x*	2.03 *s*
	1.96 *s*	—	—	—	1.99 *s*	—	—	—	2.01 *s*	1.70 *s*	1.99 *s*

J[Hz]: 1′, 2′ = 7.5; 2′, 3′ = 3′, 4′; 4′, 5 = 9; 5′, $6'_1$ = 2.5; 5′, $6'_2$ = 5; $6'_1$, $6'_2$ = 12; **1**, **1a** and **1b**: 1, 2 = 1, 2′ = 1.5 ~ 9; 2, 3 = 2′, 3 ~ 5.5; 5, 6 = 6, 7 = 9.5; 7, 13 = 3.5; 7, 13′ = 3; 8, 9 = 8′, 9 = 6; 8′, 9′ = 9; 9, 9′ = 13; **1b**: 7, 8 = 4; 7, 8′ = 12); **2**, **2a** and **3a**: 1, 2 = 1, 2′ = 1, 5 ~ 9; 2, 3 = 2′, 3 = 5.5; 5, 6 = 6, 7 = 9.5; 7, 8 = 4; 7, 8′ = 7, 11 = 12; 8, 9 = 8′, 9 = 8, 9′ ~ 6; 8′, 9′ = 9; 9, 9′ = 13; 11, 13 = 7; (**3a**: 7, 8 = 10; 8, 9 = 5; 8, 9′ = 7.5); **4** and **4a**; 1, 5 = 7.5; 2, 3 = 10; 3, 3′ = 17; 5, 6 = 10.5; 6, 7 = 9.5; 7, 13 = 3.5; 7, 13′ = 3; **5** and **5a**: 1, 2 = 1, 2′ = 1, 5 = 8; 2, 3 = 10; 3, 3′ = 17; 5, 6 = 6, 7 = 10; 7, 11 = 12; 11, 13 = 7.

Table 2. ^{1}H NMR spectral data of **6–8** ($CDCl_3$, 400 MHz, δ-values)

H	**6** (60°)	**7** (60°)	**8** (60°)
1	5.01 *br d*	5.02 *br d*	5.01 *br d*
2	2.25 *m*	2.25 *m*	2.24 *m*
2′	2.00 *m*	2.00 *m*	2.00 *m*
3	2.61 *ddd*	2.60 *ddd*	2.60 *ddd*
3′	2.25 *m*	2.25 *m*	2.24 *m*
5	4.86 *br d*	4.86 *br d*	4.84 *br d*
6	5.09 *t*	5.11 *t*	5.08 *t*
7	3.04 *dddd*	3.05 *dddd*	3.06 *dddd*
8	5.17 *br t*	5.21 *br t*	5.19 *br t*
9	2.64 *br t*	2.63 *br t*	2.62 *br d*
9′	2.48 *br t*	2.49 *br t*	2.48 *br t*
13	6.29 *d*	6.29 *d*	6.29 *d*
13′	5.72 *d*	5.76 *d*	5.74 *d*
14	1.55 *br ds*	1.55 *br s*	1.53 *br s*
15	4.33 *br d*	4.32 *br d*	4.31 *br d*
15′	4.13 *br d*	4.14 *br d*	4.13 *br d*
OCOR	6.13 *qq*	6.50 *q*	5.69 *q*
	1.98 *dq*	2.10 *q*	1.43 *d*
	1.92 *dq*	4.85 *d*	6.27 *s*
		4.66 *d*	5.90 *s*
		2.05 *s*	2.04 *s*

J[Hz]: 1, 2 = 6; 1, 2′ = 9; 2, 3 = 2′, 3 = 4; 3, 3′ = 13; 5, 6 = 6, 7 = 7, 8 = 8, 9′ = 9; 8, 9 ~ 2; 7, 13 = 3.5; 7, 13′ = 3; 9, 9′ = 12; (CO_2R: **6** and **7**: 3, 4 = 7; **6**: 3, 5 = 4, 5 = 1.5; **8**: 3, 4 = 6.5).

(voucher 86/181) gave 80 mg **9**, 20 mg lupeyl acetate and 10 mg of the Δ^{12} isomer.

280 g of the aerial parts of *B. nereifolia* (voucher 86/191) gave an extract which was separated by CC affording two polar fractions 1; Et_2O–MeOH (9 : 1) and 2; Et_2O–MeOH (1 : 3). TLC of fraction 1 (Et_2O) gave two bands (1/1 and 1/2). HPLC of 1/1 (MeOH–H_2O, 7 : 3) gave 2 mg zaluzanin C (R_t 2.1 min.), 1 mg of the 11*β*,13-dihydro derivative (R_t 2.3 min.), 3 mg **7** (R_t 3.4 min.), 7 mg **8** (R_t 4.3 min.) and 4 mg **6** (R_t 7.0 min.). HPLC of 1/2 (MeOH–H_2O, 1 : 1) afforded 3 mg **5** (R_t 3.6 min.), 4 mg **4** (R_t 5.0 min.), 8 mg **1** (R_t 6.2 min.) and 6 mg **2** (R_t 7.2 min.). CC fraction 2 was first acetylated (Ac_2O, $CHCl_3$. 4-dimethylaminopyridine) and separated by medium pressure chromatography on silica gel, (ϕ 30–60 μ) starting with Et_2O–petrol (1 : 1), then Et_2O and finally Et_2O–MeOH (19 : 1), 20 ml fractions. Fractions 25–38 (Et_2O) gave 800 mg of a crystalline 1 : 1 mixture of **1a** and **2a**. Fractions 39–46 (Et_2O–MeOH, 19 : 1 gave by HPLC (MeOH–H_2O, 13 : 7) a crude fraction (A, R_t 7.8 min.), 50 mg **5a** (R_t 8.3 min.), 50 mg **4a** (R_t 9.7 min.) and 40 mg of a mixture (R_t 10.6 min.) which gave by crystallization 20 mg **1a**, mp. 163°. TLC of fraction A ($CHCl_3$–C_6H_6–Et_2O–MeOH, 30 : 30 : 30 : 1) gave 10 mg **3a** (R_f 0.45). To 50 mg of the mixture of **1a** and **2a** in Et_2O–CH_2N_2 was added. After 5 min. TLC ($CHCl_3$–C_6H_6–Et_2O–MeOH, 40:40:10:1) gave 20 mg **2a** and 20 mg of the pyrazolin derivative of **1a** (*β*-attack), mp 153° (decomp.), MS *m/z* (rel. int.): 618.243 $[M]^+$ (0.1) (calc. for $C_{30}H_{38}N_2O_{12}$: 618.243), 590 $[M-N_2]^+$ (0.2), 331 $[C_{14}H_{19}O_9]^+$ (33), 243 $[590 - \text{sugar}]^+$ (44), 169 $[331 - 2 \times \text{HOAc, ketene}]^+$ (100).

The extract of the aerial parts of *B. rotundata* (300 g, voucher 86/170) gave after CC and HPLC of 5% of the polar fractions (MeOH–H_2O, 1 : 1) 50 mg **9** (R_t 10.2 min.), 1 mg of the corresponding elemanolide (R_t 8.6 min.) and 12 mg **10** (R_t 3.8 min.). Known compounds were identified by comparing the 400 MHz ^{1}H NMR spectra with those of authentic material.

11*β*,13-*Dihydroglucozaluzanin C* (**2**). Colourless crystals, mp 96°; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1770 (γ-lactone); MS *m/z* (rel. int.): 410.194 $[M]^+$ (0.1) (calc. for $C_{21}H_{30}O_8$: 410.194), 303 (5.5), 277 (18), 248 (28), 231 (22), 159 (94), 158 (100), 91 (86), 79 (96), 73 (98). Tetraacetate **2a**: Colourless crystals, mp 173°; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1755 (γ-lactone); MS *m/z* (rel. int.): 578.236 $[M]^+$ (0.2) (calc. for $C_{29}H_{38}O_{12}$: 578.236), 518 $[M - HOAc]^+$ (0.2), 458 $[518 - HOAc]^+$ (0.4), 398 $[458 - HOAc]^+$ (0.3), 331 $[C_{14}H_{19}O_9]^+$ (38), 231 $[M - C_{14}H_{19}O_4]^+$ (48), 169 $[C_8H_9O_4]^+$ (100), 109 $[169 - HOAc]^+$ (58).

8*α*-*Acetoxy*-11*β*,13-*dihydrozaluzanin C tetraacetate* (**3a**). Colourless crystals, mp 130°; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1755 (OAc. γ-lactone); MS *m/z* (rel. int.): 636.242 $[M]^+$ (0.1) (calc. for $C_{31}H_{40}O_{14}$: 636.242), 331 $[C_{14}H_{19}O_9]^+$ (36), 289 $[M - C_{14}H_{19}O_9]^-$ (7), 229 $[289 - HOAc]^+$ (48), 169 $[C_8H_9O_4]^+$ (100), 109 $[169 - HOAc]^+$ (46).

Brachynereolide (**4**). Colourless gum; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1765 (γ-lactone); MS *m/z* (rel. int.): 248.141 $[M - C_6H_{10}O_5]^+$ (9) (calc. for $C_{15}H_{20}O_3$: 248.141), 231 $[C_{15}H_{19}O_2]^+$ (95), 230 $[248 - H_2O]^+$ (100), 159 (30), 93 (42), 73 (38); ^{13}C NMR ($CDCl_3$, C-1–C-15): δ52.3 *d*, 26.2 *t*, 29.0 *t*, 149.9 *s*, 51.6 *d*, 81.0 *d*, 43.3 *d*, 23.4 *t*, 30.4 *t*, 81.1 *s*, 141.8 *s*, 171.1 *s*, 118.9 *t*, 27.6 *q*, 109.8 *t*; C-1′–C-6′: 96.9 *d*, 73.5 *d*, 76.7 *d*, 70.2 *d*, 75.3 *d*, 61.8 *t*. Tetraacetate **4a**: Colourless crystals, mp 83°; IR $\nu_{max}^{CHCl_3}$ cm^{-1}, cm^{-1}: 1760 (OAc, γ-lactone); MS *m/z* (rel. int.): 518.215 $[M - H_2O]^+$ (0.2) (calc. for $C_{27}H_{34}O_{10}$: 518.215), 458 $[518 - HOAc]^+$ (0.1), 398 $[458 - HOAc]^+$ (0.1), 331 $[C_{14}H_{19}O_9]^+$ (30), 231 $[C_{15}H_{19}O_2]^+$ (48), 230 $(C_{15}H_{18}O_2]^+$ (59), 169 $[C_8H_9O_4]^+$ (100), 109 $[169 - HOAc]^+$ (60).

11*β*,13-*Dihydrobrachynereolide* (**5**). Colourless gum; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1770 (γ-lactone); MS *m/z* (rel. int.): 412.210 $[M]^+$ (0.05) (calc. for $C_{21}H_{32}O_8$: 412.210), 305 (0.6), 250 $[M - C_6H_{10}O_5]^+$ (8), 233 $[M - C_6H_{11}O_6]^+$ (100), 232 $[250 - H_2O]^+$ (90), 159 (88). Tetraacetate **5a**: Colourless crystals, mp 185 – 186°; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1760 (γ-lactone, OAc); MS *m/z* (rel. int.): 580.252 $[M]^+$ (0.3) (calc. for $C_{29}H_{40}O_{12}$: 580.252), 520 $[M - HOAc]^+$ (0.1), 460 $[520 - HOAc]^+$ (0.2), 400 $[460 - HOAc]^+$ (0.2), 331 $[C_{14}H_{19}O_9]^+$ (37), 233 $[M - \text{sugar}]^+$ (58), 232 $(C_{15}H_{20}O_2]^+$ (64), 169 $[C_8H_9O_4]^+$ (100), 109 $[169 - HOAc]^+$ (56).

Salonitenolide 8-O-angelate (**6**). Colourless gum; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3620 (OH), 1765 (γ-lactone), 1715 ($C{=}CCO_2R$); MS *m/z* (rel. int.): 246.135 $[M - RCO_2H]^+$ (1.5) (calc. for $C_{15}H_{18}O_3$; 246.135), 228 $[246 - H_2O]^+$ (4), 83 $[C_4H_7CO]^+$ (100); $[\alpha]_D^{24°}$ + 104 ($CHCl_3$; *c* 0.41).

Salonitenolide 8-O-*acetyl sarracinate* (**7**). Colourless gum; IR $\nu_{max}^{CCl_4}$: 3610 (OH), 1775 (γ-lactone), 1750 (OAc), 1720 ($C{=}CCO_2R$); MS *m/z* (rel. int.): 246.135 $[M - RCO_2H]^+$ (4) (calc. for $C_{15}H_{18}O_3$: 246.135), 228 (11), 141 $[RCO]^+$ (70), 81 $[141 - HOAc]^+$ (100); $[\alpha]_D^{24°}$ + 67 ($CHCl_3$; *c* 0.27).

Salonitenolide 8-O-[1-*acetoxyethylacrylate*] (**8**). Colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1770 (γ-lactone), 1750 (OAc), 1720 ($C{=}CCO_2R$); MS *m/z* (rel. int.): 246.135 $[M - RCO_2H]^+$ (8) (calc. for $C_{15}H_{18}O_3$: 246.135), 228 (16), 141 $[RCO]^+$ (71), 81 $[141 - HOAc]^+$ (100); $[\alpha]_D^{24°}$ + 105 ($CHCl_3$; *c* 0.7).

Acknowledgement—We thank Prof. Dr. Eloff, Botanic Gardens, Kirstenbosch, for plant material.

REFERENCES

1. Skvarla, J. J., Turner, B. L., Patel, V. C. and Thomb, A. S. (1977) in *The Biology and Chemistry of the Compositae* (Heywood, V. H., Harborne, J. B. and Turner, B. L. eds) p. 577. Academic Press, London.

2. Leins, P. (1971) *Bot. J.* **691**, 91.
3. Drożdż, B., Samek, Z., Holub, M. and Herout, V. (1968) *Coll. Czech. Chem. Commun.* **33**, 1730.
4. Rustaiyan, A., Nazarians, L. and Bohlmann, F. (1979) *Phytochemistry* **18**, 879.
5. Romo de Vivar, A., Cabrera, A., Ortega, A. and Romo, J. (1967) *Tetrahedron* **23**, 3703.
6. Bohlmann, F. and Zdero, C. (1982) *Phytochemistry* **21**, 647.
7. Kisiel, W. (1975) *J. Pharmacol. Pharm.* **27**, 461.
8. Miyase, T. and Fukushima, S. (1984) *Chem. Pharm. Bull.* **32**, 3043.
9. Yoshioka, H., Renold, W. and Mabry, T. J. (1970) *Chem. Commun.* 148.
10. Nagumo, S., Izawa, K., Higahiyama, K. and Nagai, M. (1980) *Yakugaku Zasshi*, **100**, 427.
11. Miyase, T., Yamaki, K. and Fukushima, S. (1984) *Chem. Pharm. Bull.* **32**, 3912.
12. Bohlmann, F., Singh, P. and Jakupovic, J. (1982) *Phytochemistry* **21**, 2029.
13. Bohlmann, F. and Zdero, C. (1979) *Phytochemistry* **18**, 95.
14. Bohlmann, F., Zdero, C., Schmeda-Hirschmann, G., Jakupovic, J., Dominguez, X. A., King, R. M. and Robinson, H. (1986) *Phytochemistry* **25**, 1175.
15. Bohlmann, F. and Suwita, A. (1979) *Phytochemistry* **18**, 677.