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FIVE DITERPENES AND OTHER CONSTITUENTS FROM NINE *BACCHARIS* SPECIES*

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Key Word Index—*Baccharis* spp.; Compositae; diterpenes; new clerodanes; new labdanes; new flavanones; new aromatics.

Abstract—The investigation of nine *Baccharis* species afforded, in addition to known compounds, three new clerodane derivatives related to bacchotricuneatin B, two *ent*-labdane derivatives, two 3-acetoxyflavanones, a benzofuran derivative and a chromene. The overall picture of the chemistry of this large genus is still not very clear.

INTRODUCTION

The results on the chemistry of the large genus *Baccharis* (tribe Astereae, Compositae) so far available do not show a clear picture. In addition to simple acetylenes, typical for large parts of the tribe [1], clerodanes [2–7] and the triterpene baccharis oxide [6, 8, 9, 16] are widespread. Also the presence of flavones and flavanones have been reported several times [3, 5, 6, 10–14], while from one species unusual macrolide sesquiterpenes [15] and from a few, in addition to widespread ones, some unusual *p*-hydroxyacetophenone derivatives were isolated [6, 16]. We now have investigated nine further Brazilian species. Again a very complex picture was obtained.

RESULTS AND DISCUSSION

The aerial parts of *Baccharis cassinaefolia* DC. afforded germacrene D, bicyclogermacrene, squalene, lupenone, euphol acetate, spathulenol [17], lachnophyllum ester (**1**) [1], the chromene **2** [18] and the aldehyde **5** [16]. Furthermore, baccharisoxide (**25**) [8], as well as a mixture of diterpenes were present. Even by HPLC this mixture could be separated only in part. The ^{1}H NMR data indicated that the compounds were diesters differing in the ester residues only, which were angelate, senecioate and 2-methylbutyrate. The MS, however, showed no molecular ions; only the $M - RCO_2H$ peaks were detected. Partial saponification led to the formation of two monoesters, both with an additional methoxy group, obviously introduced by the solvent. Careful ^{1}H NMR studies led to the structures **14** and **15** (Table 1). In connection with the ^{1}H NMR data of the diesters the formation of **14** and **15** could be explained only if an elimination–addition reaction were assumed. Treatment of the diesters with potassium hydroxide first led to the elimination products **13a** and **b**, which by addition of methanol were transformed to the methoxy compounds **14** and **15**. As could be visualized from the 3-H couplings, the stereochemistry at C-3 had changed from an axial to an equatorial oxygen function. The ^{1}H NMR data of one of the diesters separated by HPLC showed the presence of an angelate and a 2-methylbutyrate residue. As the latter is missing in the methoxy compounds, obtained from the whole mixture, the 2-methylbutyrate must be placed at C-3; consequently the structure of this compound is **12** and those of the two other diesters **10** and **11**, as both methoxy compounds were obtained from the mixture of these two diester, which could not be separated. Compounds **10**–**12** are closely related to bacchotricuneatin B, where the stereochemistry was established by X-ray [5]. The ^{1}H NMR data are very similar to those of **10**–**12** and consequently the stereochemistry most probably is the same at C-5, C-8 to C-10 and C-12. We have therefore named the new compounds as diacyloxy-3,4βH-bacchotricuneatin B.

The roots again contain germacrene D, squalene, **1**, **2**, **5** and **25** as well as **8** [19], **9** [20] and the carbinol **3**, its structure following from the spectral data which were identical with those of the reduction product of **2** (see Experimental).

The aerial parts of *B. intermixta* Gardn. afforded germacrene D, β-farnesene, *ent*-kaurenic acid (**18**), grandifloric acid (**20**) [21], sakuranetin (**27**) and two diterpenes, the diacetate **16a** and the triacetate **17a**, which could be purified only after saponification to **16b** and **17b**. **17b** already has been isolated previously from *Achyrocline alata* and was transformed to the triacetate **17a** [22]. The structures clearly followed from the ^{1}H NMR data of the alcohols (Table 2). The roots afforded germacrene D, **5** and **6** [16] and **17a**.

The aerial parts of *B. calvescens* DC. afforded germacrene D, bicyclogermacrene, caryophyllene, squalene, friedelin, oleanolic acid, lupeol, spathulenol [17], **2**, **5**, the angelate **24** [23] and the clerodane derivative **23** [7], while the roots contain squalene, lachnophyllum ester (**1**), **2**, **4**, **5**, **8**, **25** and the acetate **7**, which has not been

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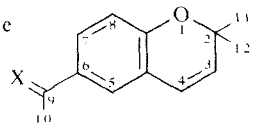
* Part 307 in the series "Naturally Occurring Terpene Derivatives". For Part 306 see Bohlmann, F. and Fiedler, L. (1980) *Chem. Ber.* (in press).

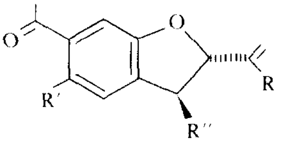
$MeCH_2CH_2[C{\equiv}C]_2CH{=}CHCO_2Me$

cis

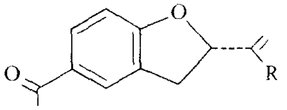
1



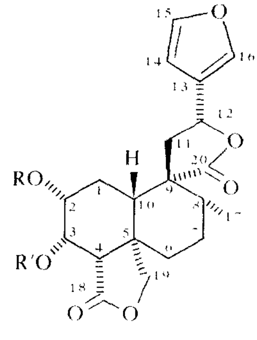
2 X = O
3 X = H, OH



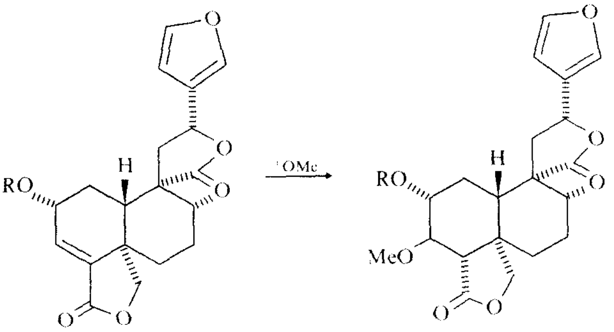
	4	**5**	**6**	**7**
R	Me	CHO	CH_2OAc	Me
R′	OH	OH	OH	OH
R″	H	H	H	OAc



8 R = Me
9 R = CHO



	10	**11**	**12**
R	Ang	Sen	Ang
R′	Sen	Ang	Mebu



13a R = Ang
13b R = Sen

14 R = Ang
15 R = Sen

reported previously. The structures clearly followed from the ^1H NMR spectrum (see Experimental).

The aerial parts of *B. varians* Gardn. afforded benzylbenzoate, naringenin (**26**), eriodictyol (**28**) and two further flavanones, the acetates **29** and **30**. **29** was transformed to the acetate **31**. The structures clearly followed from the ^1H NMR data (Table 3), which also indicated the *trans* stereochemistry at C-2 and C-3. The roots only gave baccharis oxide (**25**).

The aerial parts of *B. serrulata* (Lam.) Pers. afforded germacrene D, bicyclogermacrene, squalene, caryophyllene epoxide and sakuranetin (**27**), while the roots gave baccharis oxide (**25**).

The aerial parts of *B. reticularia* DC. afforded germacrene D, bicyclogermacrene, squalene, lupenone, lupeol, baccharis oxide (**25**) and eriodictyol (**28**) [24], while the roots gave **5** and **25**.

The aerial parts of *B. polyphylla* Gardn. afforded germacrene D, γ-humulene, bicyclogermacrene, *ent*-kaurenic acid (**18**), grandifloric acid (**20**), large quantities of its methyl ester (**21**) and the angelate **22a** [16] as well as the cinnamic acid derivatives **32** [25] and **33** [25]. The roots gave bicyclogermacrene and **25** only.

The aerial parts of *B. ramoisissima* Gardn. afforded germacrene D, bicyclogermacrene, lupeol, lupenone, **2**, **5**, **25** and a triterpene alcohol, its structure could not be established. All data agree with an isomer of euphol with an α-hydroxy group and a 9,11-double bond. The stereochemistry, however, could not be determined.

The aerial parts of *B. salzmannii* DC. afforded germacrene D, bicyclogermacrene, caryophyllene epoxide, spathulenol, *ent*-kaurenic acid (**18**), the tiglate **22b** [26], naringenin (**26**) and three triterpenes, a ketone, an acetate and an alcohol, closely related to that from *B.*

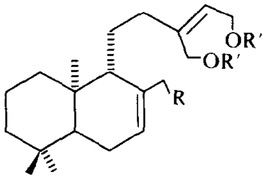
Table 1. ^{1}H NMR spectral data of compounds **10–12**, **14** and **15** (270 MHz, $CDCl_3$, TMS as int. standard)

	10		**11**	**12**	**14†**		**15‡**
1-H		2.21 *ddd*		2.20 *m*		2.33 *ddd*	
1′-H						1.42 *m*	
2-H		5.42 *m*		5.40 *m*		4.94 *ddd*	
3-H	6.52 *dd*		6.49 *dd*	6.45 *dd*		3.57 *dd*	
4-H		1.95 *br. s**				2.29 *d*	
11-H		2.60 *dd*		2.61 *dd*	2.48 *d*		2.47 *d*
11′-H		2.52 *dd*		2.53 *dd*			
12-H		5.48 *br. t*		5.45 *br. t*		5.42 *dd*	
14-H		6.38 *dd*		6.36 *dd*		6.39 *dd*	
15-H		7.43 *dd*		7.43 *br. s*		7.42 *dd*	
16-H		7.47 *br. s*				7.46 *dd*	
17-H		1.15 *d*		1.14 *d*		1.13 *d*	
19-H	4.68 *d*		4.67 *d*	4.68 *d*	4.53 *d*		4.50 *d*
19′-H	4.06 *dd*		4.05 *dd*	4.06 *dd*	4.38 *dd*		4.37 *dd*

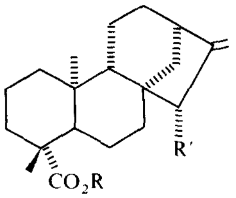
*In C_6D_6, †OMe 3.50 *s*, ‡OMe 3.48 *s*.

OAng: 6.13 *qq*, 1.96 *dq*, 1.87 *dq*, [*J* (Hz): 3′,4′ = 7; 3′,5′ = 4′,5′ = 1.3]; OSen: 5.65 *qq*, 2.15 *d*, 1.93 *d* [*J* (Hz): 3′,4′ = 3′,5′ = 1.3]; OMebu: 2.36 *tq*, 1.60 *ddq*, 1.42 *ddq*, 0.86 *t*, 1.13 *d* [*J* (Hz): 2′,3′ = 2′,5′ = 3′,4′ = 7; $3'_1,3'_2$ = 14].

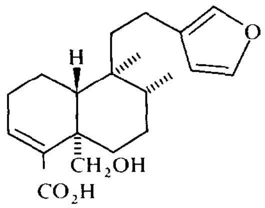
J (Hz): 1,1′ = 13; 1,2 = 7.5; 1′,2 = 7; 1,10 = 3.5; 2,3 = 3,4 ~ 1.5 (**14**/**15**: 2,3 = 7; 3,4 = 6.5); 6.19′ = 1.5; 8,17 = 7; 11,12 = 8; 12,12′ = 15; 14,15 = 15,16 ~ 1.5; 14,16 = 1; 19,19′ = 10.



	16a	**16b**	**17a**	**17b**
R	H	H	OAc	OH
R′	Ac	H	Ac	H



	18	**19**	**20**	**21**	**22a**	**22b**
R	H	Me	H	Me	H	H
R′	H	H	OH	OH	OAng	OTigl



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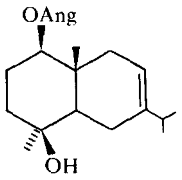

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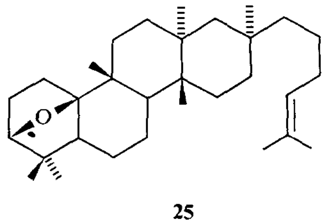

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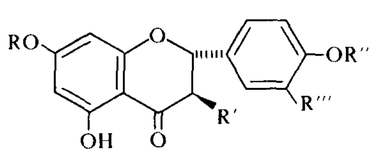
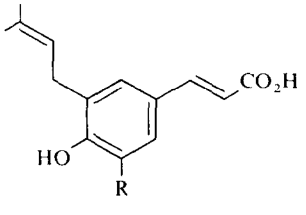


	26	**27**	**28**	**29**	**30**	**31**
R	H	Me	H	H	H	Ac
R′	H	H	H	OAc	OAc	OAc
R″	H	H	H	H	H	Ac
R‴	H	H	OH	OH	H	OAc



32 R = H
33 R = $CH_2CH{=}CMe_2$

Table 2. ^{1}H NMR spectral data of compounds **16a** and **17a**

	16a	**17a**
7-H	5.40 *br. s*	5.75 *br. d*
12-H	2.38 *br. ddd*	2.49 *br. ddd*
12'-H	2.07 *m*	2.08 *m*
14-H	5.65 *br. t*	5.62 *br. t*
15-H	4.24 *br. d*	4.18 *br. d*
16-H	4.24 *d*	4.18 *d*
16'-H	4.18 *d*	4.00 *d*
17-H	1.70 *br. s*	4.18 *br. s*
18-H	0.87 *s*	0.89 *s*
19-H	0.86 *s*	0.87 *s*
20-H	0.77 *s*	0.77 *s*

J (Hz: 6,7 = 5; 11,12 = 11; 11',12 = 5; 12,12' = 13; 14,15 = 7; 16,16' = 12.

ramoisissima. The structures could not be estimated. The roots yielded bicyclogermacrene, γ-humulene, squalene, **5**, **18** and baccharis oxide (**25**).

Comparing the chemistry of the *Baccharis* species investigated now, it is obvious that some species can be characterized by the presence of baccharis oxide, while others have typical clerodane derivatives. These are sometimes replaced by *ent*-kaurenes, while so far from one species only labdanes were isolated. Another group can be characterized by flavanones, which often co-occur with baccharis oxide. Probably the benzofurans **4**–**7** are also of chemotaxonomic importance as the unusual position of the acetyl group seems to be very rare. Surely further investigations are necessary to get a clearer picture.

EXPERIMENTAL

^{1}H NMR: 270 MHz, TMS as int. stand; MS: 70 eV, direct inlet. The air-dried plant material, collected in north-eastern Brazil, was extracted with Et_2O–petrol, 1:2 and the extracts obtained were separated first by column chromatography (SiO_2, act. grade II) and further by repeated TLC (SiO_2, GF 254). The mixture of **10**–**12** could be separated by HPLC (reversed phase, MeOH–H_2O, 7:3) in part. Known compounds were identified by comparing the IR and ^{1}H NMR data with those of authentic material.

Baccharis cassinaefolia (*roucher RMK* 8003). The roots (900 g) afforded 5 mg germacrene D, 80 mg squalene, 80 mg **1**, 20 mg **2**, 8 mg **3** (Et_2O–petrol, 1:3), 50 mg **5**, 8 mg **8**, 8 mg **9** and 100 mg **25**, while the aerial parts (800 g) yielded 10 mg germacrene D, 30 mg squalene, 2 mg bicyclogermacrene, 5 mg lupenone, 15 mg euphol acetate, 2 mg spathulenol, 2 mg **1**, 4 mg **2**, 3 mg **5**, 20 mg **10** and **11** (*ca* 1:1, Et_2O–petrol, 3:1), 7 mg **12** (Et_2O–petrol, 3:1) and 10 mg **25**.

Baccharis intermixta (*roucher RMK* 8139). The roots (400 g) afforded 20 mg germacrene D, 4 mg **5**, 4 mg **6** and 65 mg **17a** (Et_2O–petrol, 1:1), while the aerial parts (800 g) yielded 260 mg germacrene D, 130 mg β-farnesene, 0.2 g **16a** (Et_2O–petrol, 1:1), 2 g **17a**, 500 mg **18**, 220 mg **20** and 300 mg **27**.

Baccharis calvescens (*voucher RMK* 7989). The roots (150 g) afforded 10 mg squalene, 2 mg **1**, 1 mg **2**, 10 mg **4**, 10 mg **5**, 1 mg **7** (Et_2O–petrol, 1:1), 2 mg **8** and 20 mg **25**, while the aerial parts (1 kg) yielded 50 mg squalene, 20 mg germacrene D, 5 mg bicyclogermacrene, 20 mg caryophyllene, 30 mg friedelin, 100 mg lupeol, 50 mg oleanolic acid, 3 mg spathulenol, 1 mg **2**, 10 mg **5**, 20 mg **23** and 3 mg **24**.

Baccharis varians (*voucher RNK* 8089). The roots (25 g) afforded 25 mg **25**, while the aerial parts (100 g) yielded 60 mg benzyl benzoate, 4 mg **26**, 16 mg **28**, 20 mg **29** (Et_2O) and 6 mg **30** (Et_2O).

Baccharis serraluta (*voucher RMK* 8058). The roots (40 g) afforded 18 mg **25** and the aerial parts (200 g) 18 mg germacrene D, 2 mg bicyclogermacrene, 40 mg squalene, 2 mg caryophyllene epoxide and 105 mg **27**.

Baccharis reticularia (*voucher RMK* 8106). The roots (100 g) afforded 3 mg **5**, 80 mg **25** and the aerial parts (1 kg) 50 mg germacrene D, 5 mg bicyclogermacrene, 30 mg squalene, 30 mg lupenone, 80 mg lupeol, 50 mg **25** and 30 mg **28**.

Baccharis polyphylla (*roucher RMK* 8108). The roots (100 g) afforded 10 mg bicyclogermacrene and 50 mg **25**, while the aerial

Table 3. ^{1}H NMR spectral data of compounds **29**–**31**

	29 ($(D_3C)_2CO$)	**30** ($(D_3C)_2CO$)	**31** ($CDCl_3$)
2-H	5.36 *d*	5.43 *d*	5.42 *d*
3-H	5.84 *d*	5.88 *d*	5.75 *d*
6-H	6.00 *d*	6.00 *d*	6.79 *d*
8-H	6.03 *d*	6.04 *d*	6.61 *d*
2'-H	7.08 *br. s*	7.42 *d*	7.31 *d*
3'-H	–	6.91 *d*	–
5'-H	6.90 *m*		7.28 *d*
6'-H		7.42 *d*	7.40 *dd*
OAc	1.98 *s*	1.98 *s*	2.08 *s* 2.30 *s* 2.32 *s* 2.32 *s*
OH	11.58 *s*	11.59 *s*	11.28 *s*

J (Hz): 2,3 = 12; 6,8 = 1.7; 2',3' = 8; 2',6' = 1.5.

parts (350 g) gave 150 mg germacrene D, 600 mg γ-humulene, 50 mg bicyclogermacrene, 400 mg **18**, 100 mg **20**, 1.5 g **21**, 50 mg **22a**, 40 mg **32** and 50 mg **33**.

Baccharis ramoisissima (*voucher RMK* 8176). The aerial parts (300 g) afforded 20 mg germacrene D, 10 mg bicyclogermacrene, 30 mg lupeol, 20 mg lupenone, 2 mg **2**, 3 mg **5**, 10 mg **25** and 30 mg of a triterpene alcohol, whose structure could not be fully established.

Baccharis salzmannii (*voucher RMK* 8056). The roots (360 g) afforded 5 mg γ-humulene, 5 mg bicyclogermacrene, 40 mg squalene, 5 mg **5**, 300 mg **18** and 520 mg **25**, while the aerial parts (820 g) yielded 100 mg germacrene D, 3 mg bicyclogermacrene, 20 mg caryophyllene epoxide, 3 mg spathulenol, 180 mg **18**, 5 mg **22b**, 500 mg **26**, 10 mg of a triterpene ketone, 10 mg of a triterpene acetate and 10 mg of a triterpene alcohol, their structures not being established.

[1-*Hydroxyethyl*]-2,2-*dimethylchromene* (**3**). Colourless oil, IR $\nu_{\max}^{CCl_4}$ cm^{-1}: 3620 (OH), 1495, 1270, 1160, 965; MS *m/e* (rel. int.): 204.115 (M^+, 11) ($C_{13}H_{16}O_2$, 189 (M − Me, 100), 171 (189 − H_2O, 12), 161 (189 − CO, 7); ^{1}H NMR ($CDCl_3$): 5.62 (*d*, 3-H), 6.31 (*d*, 4-H), 6.73 (*d*, 8-H), 7.08 (*dd*, 7-H), 6.99 (*d*, 5-H), 4.78 (*q*, 9-H), 1.45 (*d*, 10-H), 1.42 (*s*, 11,12-H) (*J* = (Hz): 3,4 = 9.5; 5,7 = 2; 7,8 = 8; 9,10 = 7). $LiAlH_4$ reduction of **2** afforded a compound, its spectral data being identical with those of **3**.

3β-*Acetoxy*-6-*acetyl*-2α-*isopropenyl*-5-*hydroxy*-2,3H-*benzofuran* (**7**). Colourless oil, 3500–2700, 1660 (chelated hydroxy ketone), 1755 (OAc); MS *m/e* (rel. int.): 276.100 (M^+, 80) ($C_{15}H_{16}O_5$), 216 (M − HOAc, 100), 201 (216 − Me, 95); ^{1}H NMR ($CDCl_3$): 4.98 *d*, 2-H), 6.12 (*d*, 3-H), 7.06 (*s*, 4-H), 7.23 (*s*, 7-H), 2.63 (*s*, 9-H), 5.09 and 4.98 (*br. s*, 11-H), 1.76 (*br. s*, 12-H).

2α-*Angeloyloxy*-3α-*senecioyloxy and* 2α-*senecioyloxy*-3α-*angeloyloxy*-3,4βH-*bacchotricuneatin* (**10** *and* **11**). Colourless, crystalline mixture, which could not be separated, IR $\nu_{\max}^{CCl_4}$ cm^{-1}: 1775, 1765 (lactone), 1725, 1710 (CO_2R), 1595, 880 (furan); MS *m/e* (rel. int.): 440.184 (M − $C_4H_7CO_2H$, 2) ($C_{25}H_{28}O_7$), 422 (440 − H_2O, 2), 382 (440 − CH_2CO_2, 1), 340 (440 − $C_4H_7CO_2H$, 3), 310 (340 − CH_2O, 3), 83 ($C_4H_7CO^+$, 100), 55 (83 − CO, 39).

$$[\alpha]_{24^\circ}^{\lambda} = \frac{\begin{array}{cccc}589 & 578 & 546 & 436\,\text{nm}\end{array}}{\begin{array}{cccc}-42.6 & -44.7 & -51.6 & -97.9\end{array}}$$

(c = 0.95, $CHCl_3$).

2α-*Angeloyloxy*-3α-[2-*methylbutyryloxy*]-3,4βH-*bacchotricuneatin* (**12**). Colourless oil, IR $\nu_{\max}^{CCl_4}$ cm^{-1}: 1775, 1765 (lactone), 1730, 1710 (CO_2R), 880 (furan); MS *m/e* (rel. int.): 442 (M − $C_4H_7CO_2H$, 3), 440 (M − $C_4H_9CO_2H$, 3), 340 (440 − $C_4H_7CO_2H$, 6), 310 (340 − CH_2O, 9), 85 ($C_4H_9CO^+$, 24), 83 ($C_4H_7CO^+$, 100), 57 (85 − CO, 48).

Partial saponification of **10**–**12**. To 15 mg **10**–**12** in 2 ml MeOH 200 mg KOH in 0.5 ml H_2O were added. After 1 min dil. H_2SO_4 was added. TLC (Et_2O) afforded 6 mg **14**, colourless crystals (Et_2O–petrol), mp 195°, IR $\nu_{\max}^{CCl_4}$ cm^{-1}: 1785, 1768 (lactone), 1720 ($C{=}CCO_2R$), 880 (furan); MS *m/e* (rel. int.): 472.210 (M^+, 48) ($C_{26}H_{32}O_8$), 442 (M − CH_2O, 5), 440 (M − MeOH, 2), 372 (M − $C_4H_7CO_2H$, 22), 343 (372 − CHO, 8), 312 (343 − OMe, 45), 83 ($C_4H_7CO^+$, 90), 55 (83 − CO, 100). The second fraction still was a mixture of **14** and **15** as shown by the ^{1}H NMR spectrum (Table 1).

15,16-*Diacetoxy*-ent-*labda*-6,14-*diene* (**16a**). Colourless gum, purified as its diol **16b** ($LiAlH_4$ in Et_2O, room temp.), colourless gum, IR $\nu_{\max}^{CCl_4}$ cm^{-1}: 3620 (OH), 860 ($CH{=}C\langle$); MS *m/e* (rel. int.): 306.256 (M^+, 4) ($C_{20}H_{34}O_2$), 288 (M − H_2O, 5), 273 (288 − Me, 5), 204 (M − $C_5H_{10}O_2$, 100).

$$[\alpha]_{24^\circ}^{\lambda} = \frac{\begin{array}{cccc}589 & 578 & 546 & 436\,\text{nm}\end{array}}{\begin{array}{cccc}+1.8 & +1.9 & +2.4 & +2.9\end{array}}$$

(c = 0.34, $CHCl_3$).

15,16,17-*Triacetoxy*-ent-*labda*-6,14-*diene* (**17a**). IR and ^{1}H NMR data identical with those of the triacetate prepared previously [16]. $LiAlH_4$ reduction afforded the triol **17b**, colourless gum, IR $\nu_{\max}^{CCl_4}$ cm^{-1}: 3620 (OH), 860 ($CH{=}C\langle$); MS *m/e* (rel. int.): 304 (M − H_2O, 0.3), 286.230 (304 − H_2O, 15) ($C_{20}H_{30}O$), 273 (288 − Me, 5), 220 ($C_{15}H_{24}O$, 25), 109 ($C_8H_{13}^+$, 100).

3β-*Acetoxyeriodictyol* (**29**). Colourless gum, MS *m/e* (rel. int.): 346 (M^+, 1), 286 (M − HOAc, 5), 65 (100). 10 mg **29** in 0.2 ml Ac_2O were heated for 2 hr at 70°. Evaporation and TLC (Et_2O–petrol, 3:1) afforded 10 mg **31**, Colourless gum, IR $\nu_{\max}^{CCl_4}$ cm^{-1}: 1790 (PhOAc), 1665, 1635, 1580; MS *m/e* (rel. int.): 472.101 (M^+, 16) ($C_{23}H_{20}O_{11}$), 430 (M − ketene, 22), 412 (M − HOAc, 15), 370 (430 − HOAc, 24), 57 (100).

3β-*Acetoxynaringenin* (**30**). Colourless gum, IR $\nu_{\max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1715 (C=); MS *m/e* (rel. int.): 330.074 (M^+, 20) ($C_{17}H_{14}O_7$), 270 (M − HOAc, 55), 153 (100), 136 (72).

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