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HELIANGOLIDES, AND NEROLIDOL AND *p*-HYDROXYACETOPHENONE DERIVATIVES FROM *CALEA* SPECIES*

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Key Word Index—*Calea teucrifolia*; *Calea* new sp.; Compositae; sesquiterpene lactone; *p*-hydroxyacetophenone derivatives; nerolidol derivatives.

Abstract—A new *Calea* species afforded a heliangolide, closely related to niveusin C, while from *Calea teucrifolia* two new nerolidol derivatives and eight *p*-hydroxyacetophenone derivatives were isolated. The structures were elucidated by spectroscopic methods and a few chemical transformations. The spectral data of 8β-angeloylatripliciolide, the main constituent of *C. teucrifolia*, are also included. The chemotaxonomic situation is discussed briefly.

As pointed out previously [1], the main part of the large genus *Calea* (Compositae, tribe Heliantheae) should not be placed in the subtribe Galinsoginae. This was supported by taxonomic features as well as by the chemistry of their constituents [2]. We now have investigated two further species from Brazil, *Calea teucrifolia* and a new species. Both again afforded furanoheliangolides and, therefore, should be placed away from the subtribe Galinsoginae. Furthermore, two new nerolidol derivatives and several new *p*-hydroxyacetophenone derivatives were isolated.

The aerial parts of the new *Calea* species afforded tridecapentaynene, germacrene D, bicyclogermacrene, α-humulene, spathulenol, the furanoheliangolides **1** [3], **2** [4], **3** [5] and **4** [5] and a further sesquiterpene lactone, the heliangolide **5**. The ^{1}H NMR spectral data of **5** could be fully interpreted only in a mixture of $CDCl_3$–C_6D_6 at 400 MHz. Spin decoupling allowed the assignment of all signals (Table 1). The presence of a heliangolide followed from the couplings of H-6, H-7 and H-13. Also the β-orientation of the angelate residue was deduced from the couplings of H-8. All data were very similar to those of 1β-acetoxyazacatechinolide, the corresponding 8β-methylacrylate [4], but were different from those of the corresponding lactones with a 1α-oxygen function [5], where the H-1 signal was a triplet. **5**, therefore, was 1-epi-niveusin-C-acetate. The roots also contain tridecapentaynene and bicyclogermacrene, but also γ-humulene, trideca-1,12-diene-3,5,7,9-tetrayne, the chromenes **7** [7], **8** [3] and **9** [8], as well as the thymol derivative **10** [9].

The aerial parts of *C. teucrifolia* (Gardn) Baker afforded germacrene D, bicyclogermacrene, α-humulene, the germacrene derivatives **12** and **13** [10], spathulenol, thymol (**11a**), the acid **14** [11], the Δ9,11- and 12,13-isomers of lupeyl acetate, caryophyllenepoxide and, as the main constituent, the furanoheliangolide **1**. In addition, the nerolidol derivatives **15** and **16** were isolated. The

Table 1. ^{1}H NMR spectral data of **5** (TMS as internal standard)

	400 MHz (C_6D_6–$CDCl_3$, 1:1)	270 MHz ($CDCl_3$)
H-1	4.72 d (*br*)	5.39 *d* (*br*)
H-2	2.09 *dd*	2.48 *dd*
H-2′	1.76 *d* (*br*)	2.14 *d* (*br*)
H-5	5.57 *dq*	5.75 *dq*
H-6	5.01 *m*	5.62 *m*
H-7	3.99 *dddd*	4.08 *dddd*
H-8	5.02 *m*	5.62 *m*
H-9	2.27 *dd*	2.48 *dd*
H-9	1.83 *dd*	2.07 *dd*
H-13	6.17 *d*	6.28 *d*
H-13′	4.83 *d*	5.64 *d*
H-14	1.36 *s*	1.54 *s*
H-15	1.69 *dd*	1.77 *dd*
OAng	5.79 *qq*	6.07 *qq*
	1.85 *dq*	1.93 *dq*
	1.70 *dq*	1.79 *dq*
OAc	1.78 *s*	2.12 *s*
OH	1.82 *s*	2.75 *s*

J (Hz): **5**: 1,2 = 6; 2,2′ = 14; 5,6 = 3.5; 5,15 = 6,15 ~ 1.5; 6,7 ~ 4; 7,8 ~ 5; 7,13 = 2.5; 7,13′ = 2; 8,9 = 10; 8,9′ = 5; 9,9′ = 14; 3′,4′ = 7; 3′,5′ = 4′,5′ = 1.5.

* Part 343 in the series "Naturally Occurring Terpene Derivatives". For Part 342 see Bohlmann, F., Abraham, W.-R., Robinson, H. and King, R. M. (1981) *Phytochemistry* **20**, 1639.

Table 2. ^{1}H NMR spectral data of compounds **15** and **16** (400 MHz, TMS as internal standard)

	15	**16**	
	($CDCl_3$)	($CDCl_3$)	(C_6D_6)
H-1*t*	5.38 *dd*	5.26 *dd*	5.39 *dd*
H-1*c*	5.17 *dd*	5.07 *dd*	5.03 *dd*
H-2	5.94 *dd*	5.90 *dd*	5.86 *dd*
H-4	1.84 *dd*	2.0 *m*	2.05 *dd*
H-4′	1.53 *dd*	1.75 *dd*	1.72 *dd*
H-5	4.64 *ddd*	5.61 *ddd*	5.95 *ddd*
H-6	5.21 *dq*	5.11 *d* (*br*)	5.27 *dq*
H-8	1.98 *t* (*br*)	2.0 *m*	2.01 *t* (*br*)
H-9	2.07 *dt* (*br*)	2.0 *m*	2.13 *dt* (*br*)
H-10	5.07 *qqt*	5.05 *m*	5.18 *qqt*
H-12	1.68 *s* (*br*)	1.68 *s* (*br*)	1.72 *s* (*br*)
H-13	1.60 *s* (*br*)	1.60 *s* (*br*)	1.56 *s* (*br*)
H-14	1.64 *d*	1.72 *s* (*br*)	1.80 *d*
H-15	1.38 *s*	1.28 *s*	1.25 *s*
OAc	—	2.01 *s*	1.68 *s*

J (Hz): 1*t*,2 = 17; 1*c*,2 = 10.5; 1*t*,1*c* = 1.4; 4,5 = 8; 4′,5 = 4.5; 4,4′ = 14; 5,6 = 9; 6,14 = 1; 8,9 = 9,10 = 7; 10,12 = 10,13 = 1; (**15**: 4,5 = 10.5,4′,5 = 2; 6 = 8.5).

structures of **15** and **16** followed from the ^{1}H NMR spectral data (Table 2). As **16** on reduction with lithium aluminium hydride afforded **15**, the stereochemistry was the same in both compounds. Careful spin decoupling allowed the assignment of all signals. The stereochemistry at C-3 and C-5, however, could not be established with certainty. If the configuration at C-3 was that of nerolidol the given one at C-5 was most likely. As in **15**, a hydrogen bridge was probably present; the differences in the chemical shifts of H-1 in the spectra of **15** and **16** could be explained better if the vinyl group was axially orientated, while in the 5-epimer both groups, the vinyl and the large chain, would be in an equatorial position.

The polar fraction also contained large amounts of **1** [3] and the benzofuran derivatives **17**–**20** as well as the hydroxyacetophenone derivatives **21**–**23**. The structures were elucidated by spectroscopic methods. The ^{1}H NMR spectral data of **17**–**20** (Table 2) indicated the presence of disubstituted acetophenone derivatives and established the natures of the ester residues. The relative positions of the isopropenyl and the methoxy group were assigned by biogenetic considerations as **17**–**20** were obviously derived from 6-desoxyeuparin. **21**–**22** were probably oxidation products of benzofuranones. Therefore, the isopropylidene group was placed at C-2. From the ^{1}H NMR spectral data (Table 4), however, a clear decision was not possible. The structure of **23** clearly followed from the spectroscopic data. In the mass spectrum the base peak was *m/z* 69 ($H_2C{=}C(Me)CO^+$). Furthermore, elimination of CH_2OAc followed by elimination of CO indicated the nature of the side chain, while the position of the carbomethoxy group could be assigned from the ^{1}H NMR spectral data (Table 4), as the downfield shift of H-4 could only be explained by two neighbouring carbonyl groups. We have named **17** as caleteucrin, the 9-desacyl derivative of **21** and **22** calefolione, and **23** caleteucrifolone.

The roots afforded tridecapentaynene, germacrene D, bicyclogermacrene, α-humulene, β-sesquiphellandrene, thymol (**11a**), the isobutyrate (**11b**) of **11a**, **12**, **17**–**19**, the isothymol methyl ether **24** and a further benzofuran derivative, the angelate **25** [12]. The structure of **25** followed from the ^{1}H NMR spectral data (Table 3). If compared with those of **17**, the absence of the keto group

Table 3. ^{1}H NMR spectral data of compounds **17**–**20** and **25** (270 MHz, $CDCl_3$, TMS as internal standard)

	17	**18**	**19**	**20**	**25** (C_6D_6)
H-4	8.26 *d*	8.21 *d*	8.21 *d*	8.23 *d*	7.62 *d*
H-6	7.93 *dd*	7.86 *dd*	7.85 *dd*	7.85 *dd*	7.17 *dd*
H-7	7.43 *d*	7.44 *d*	7.44 *d*	7.47 *d*	7.23 *d*
H-9	2.68 *s*	5.40 *s*	5.40 *s*	4.94 *d*	1.50 *d*
H-11	5.73 *s* (*br*)	5.73 *s* (*br*)	5.73 *s* (*br*)	5.75 *s* (*br*)	5.97 *s* (*br*)
H-11′	5.18 *dq*	5.19 *dq*	5.19 *dq*	5.22 *dq*	5.13 *dq*
H-12	2.33 *dd*	2.22 *dd*	2.22 *dd*	2.23 *dd*	2.22 *dd*
OMe	4.05 *s*	4.03 *s*	4.03 *s*	4.05 *s*	3.57 *s*
OCOR	—	2.25 *s*	2.77 *qq*	—	5.75 *qq*
			1.29 *d*	—	2.00 *dq*
				—	1.92 *dq*
OH	—	—	—	3.59 *t*	—

J (Hz): 4,6 = 1.7; 6,7 = 8.5; 11,11′ = 1.5; 11,12 = 11′,12 = 1.5; **20**: 9,OH = 4; **25**: OAng: 3′,4′ = 7; 3′,5′ = 4′,5′ = 1.5; 8,9 = 6.5 (H-8 6.19 *q*).

Table 4. ^{1}H NMR spectral data of compounds **21**–**23** ($CDCl_3$, 270 MHz, TMS as internal standard)

	21	**22**	**23**
H-3	7.28 *s*	7.33 *s*	8.57 *d*
H-5	—	—	8.15 *dd*
H-6	6.63 *s*		7.30 *d*
H-8	5.24 *s*	5.32 *s*	5.35 *s*
H-12	2.30 *s*	2.36 *s*	—
H-13	2.05 *s*	2.11 *s*	—
OH	11.82 *s*	11.85 *s*	—
OCOR	2.75 *qq*	6.22 *qq*	6.41 *dq*
			5.84 *dq*
	1.28 *d*	2.05 *dq*	2.10 *dd*
		2.00 *dq*	
OAc	—	—	2.25 *s*
OMe	—	—	3.88

J (Hz): *i*-Bu: 2′,3′ = 7; OAng: 3′,4′ = 7; 3′,5′ = 4′,5′ = 1; OMeacr: 3′,4′ = 1; $3'_1$,$3'_2$ = 1; **23**: 3,5 = 2.3; 5,6 = 8.5.

at C-5 was obvious. A typical quartet at δ 6.10 (J = 6.5 Hz) and a doublet at 1.50 indicated the presence of an angelate or the dicond formed by reduction of it.

The investigation of these two *Calea* species showed that both belong to the group of species which should be placed away from the Galinsoginae. Obviously, the furanoheliangolides are characteristic for this group. However, the *p*-hydroxyacetophenone derivatives may also be of chemotaxonomic importance, especially the more unusual ones (**17**–**23** and **25**). Clearly further investigations are necessary for a clear decision to be made on the placement of this genus and related ones into subtribes of the Heliantheae.

EXPERIMENTAL

The air-dried plant material was extracted with Et_2O–petrol (1:2) and the resulting extracts were separated by column chromatography (Si gel) and by repeated TLC (Si gel). Known compounds were identified by comparing the IR and ^{1}H NMR spectra with those of authentic material.

Calea new sp. (*voucher RMK* 8311). The roots (700 g) afforded 1 mg *tridecapentaynene*, *0.1 mg trideca-1,12-diene-3,5,7,9-tetrayne*, 30 mg *γ-humulene*, 5 mg *bicyclogermacrene*, 200 mg **7**, 10 mg **8**, 3 mg **9** and 3 mg **10**, while the aerial parts (2 kg) gave 1 mg tridecapentaynene, 30 mg germacrene D, 50 mg bicyclogermacrene, 10 mg spathulenol, 10 mg α-humulene, 10 mg **1**, 5 mg **2**, 20 mg **3**, 5 mg **4** and 20 mg **5**.

Calea teucrifolia (*voucher RMK* 8223). The extract of the aerial parts (698 g) were separated, after removal of saturated hydrocarbons by treatment with MeOH, first by column chromatography. The petrol fraction afforded 100 mg germacrene D, 80 mg bicyclogermacrene and 10 mg α-humulene. The next fractions (Et_2O–petrol, 1:10) gave, after repeated TLC, 10 mg spathulenol, 20 mg of the Δ9,11- and 12,13-isomers of lupeyl acetate (*ca* 1:1), 40 mg caryophyllenepoxide, 10 mg **11a**, 6 mg **12**, 10 mg **13**, 60 mg **14**, 20 mg **17** and 30 mg **19**. The fraction eluted with Et_2O–petrol (1:3) afforded 25 mg **1** and that with Et_2O–petrol (1:1) gave 300 mg **18** and 15 mg **21** together with 2 mg **22**, which could only be separated by HPLC (reversed phase, RP 18, MeOH–H_2O, 3:1). The Et_2O fractions gave 40 mg **15**, 30 mg **20**, 10 mg **23** and 0.8 g **1**. (**15** could only be separated from **1** by transforming **1** to its pyrazoline derivative by addition of CH_2N_2 to the mixture.) The roots gave 1 mg tridecapentaynene, 10 mg germacrene D, 10 mg bicyclogermacrene, 5 mg α-humulene, 100 mg β-sesquiphellandrene, 5 mg thymol (**11a**), 10 mg **11b**, 10 mg **12**, 300 mg **17**, 50 mg **18**, 20 mg **19**, 20 mg **24** and 26 mg **25** (Et_2O–petrol, 1:10).

8β-Angeloyloxyatripliciolide (**1**). (Previously isolated in an impure form [3].) Colourless crystals, mp 135° (Et_2O);

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\ \text{nm}}{-118.1 \quad -122.7 \quad -137.1 \quad -192.8}$$

(c = 0.95, $CHCl_3$).

Pyrazolidine derivative. Colourless crystals, mp 147° (Et_2O); ^{1}H NMR ($CDCl_3$): δ 5.64 (*s*, H-2), 6.25 (*dq*, H-5), 5.49 (*ddq*, H-6), 3.61 (*dd*, H-7), 5.20 (*ddd*, H-8), 2.34 (*dd*, H-9), 2.22 (*dd*, H-9′), 2.19 (*ddd*, H-13), 1.58 (*m*, H-13), 1.49 (*s*, H-14), 2.11 (*dd*, H-15), 4.90 (*ddd*, H-16), 4.69 (*ddd*, H-15′), 6.17 (*qq*, H-3′), 1.96 (*dq*, H-4′), 1.79 (*dq*, H-5′).

1-*Epi-niveusin C-acetate* (**5**). Colourless crystals, mp 167° (Et_2O–petrol); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1760 (γ-lactone), 1715 (C=CCO$_2$R); MS *m/z* (rel. int.): 420 (M$^+$, 4), 360 (M − HOAc, 1), 320 (M − AngOH, 1), 302 (320 − H_2O, 1), 278 (320 − ketene, 5), 260 (360 − AngOH, 9), 83 ($C_4H_7CO^+$, 100), 55 (83 − CO, 63);

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436 \quad 365\ \text{nm}}{-211 \quad -219 \quad -251 \quad -445 \quad -775}$$

(c = 0.57, $CHCl_3$).

5-*Hydroxynerolidol* (**15**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 3090, 930 (CH=CH$_2$), 1640, 850 (C=CH); MS *m/z* (rel. int.): 135 ($C_{10}H_{15}^+$, 1), 69 ($Me_2C{=}CHCH_2^+$, 100); CIMS (isobutane): 237 (M + 1, 2), 219 (237 − H_2O, 22), 151 ($C_{10}H_{14}O$ + 1, 100).

5-*Acetoxynerolidol* (**16**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620 (OH), 1740, 1245 (OAc), 3090, 930 (CH=CH$_2$), 1645, 840 (C=CH); MS *m/z* (rel. int.): 280.204 (M$^+$, 0.3) ($C_{17}H_{28}O_3$), 220 (M − HOAc, 2), 151 (220 − $Me_2C{=}CHCH_2$, 10), 71 (HO=C(Me)CH=CH$_2$, 68), 69 ($Me_2C{=}CHCH_2^+$, 100);

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546\ \text{nm}}{+3.5 \quad +3.9 \quad +4.1} \quad (c = 1.0,\ CHCl_3).$$

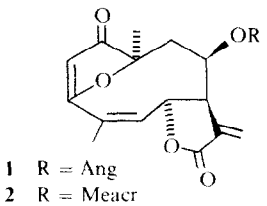
To 10 mg **16** in 1 ml Et_2O, 20 mg $LiAlH_4$ was added. TLC (Et_2O–petrol, 1:1) afforded 7 mg **15**, identical with the natural *diol*.

Calateucrin (**17**). *Colourless gum, IR* $\nu_{max}^{CCl_4}$ *cm*$^{-1}$: *1695 (PhCO), 1595 (aromatic); MS m/z (rel. int.): 230.094 (M*$^+$, *100)* ($C_{14}H_{14}O_3$), 215 (M − Me, 68), 187 (215 − CO, 22).

9-*Acetoxycalateucrin* (**18**). Colourless crystals, mp 81° (Et_2O–petrol), IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1755 (OAc), 1705, 1590 (PhCO); MS *m/z* (rel. int.): 288.100 (M$^+$, 56) ($C_{16}H_{16}O_5$), 273 (M − Me, 4), 259 (M − CHO, 0.5), 215 (M − CH_2OAc, 100), 187 (215 − CO, 11).

9-*Isobutyryloxycalateucrin* (**19**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1750 (CO$_2$R), 1710, 1600 (PhCO); MS *m/z* (rel. int.): 316.131 (M$^+$, 19) ($C_{18}H_{20}O_5$), 215 (M − $CH_2OCOC_3H_7$, 100).

9-*Hydroxycalateucrin* (**20**). Colourless crystals, mp 115° (Et_2O–petrol), IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3560 (OH), 1680 (PhCO), 1610, 1590 (aromatic); MS *m/z* (rel. int.): 246.089 (M$^+$, 53)



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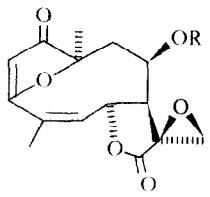

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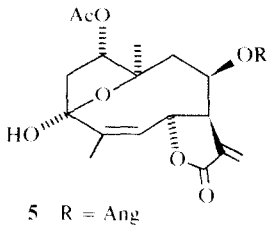

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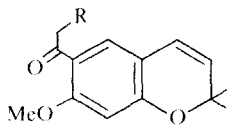

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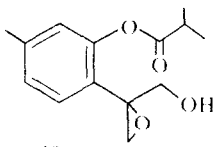
9 R = OH



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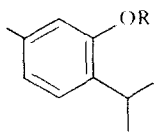
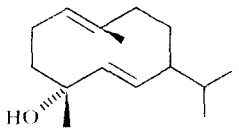


11a R = H
11b R = *i*-Bu



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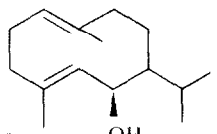

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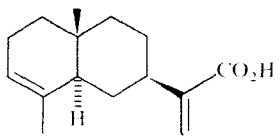

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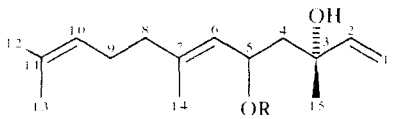

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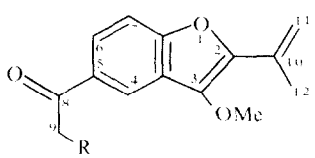

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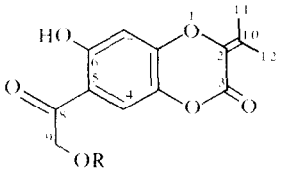

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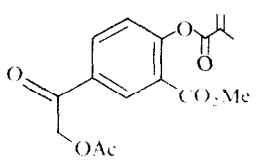

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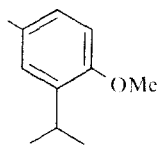

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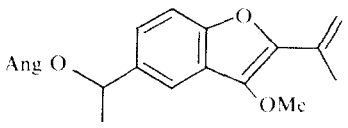

25

($C_{14}H_{14}O_4$), 215 (M − CH_2OH, 100), 187 (215 − CO, 15), 172 (187 − Me, 21), 147 (187 − CH_2O, 11).

9-*Isobutyryloxycalefolione* (**21**). Colourless crystals, mp 144° (Et_2O–petrol), IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3400–2600, 1640 (*O*-hydroxyketone), 1755 (CO_2R), 1660 (C=O); MS *m/z* (rel. int.): 334.105 (M^+, 10) ($C_{17}H_{18}O_5$), 264 (M − $Me_2C{=}C{=}O$, 20), 246 (M − RCO_2H, 24), 233 (M − $CH_2OCOC_3H_7$, 100), 71 ($C_3H_7CO^+$, 28).

9-*Angeloyloxycalefolione* (**22**). Colourless gum, not free from **21**, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3400–2600, 1640 (*O*-hydroxyketone), 1730

($C{=}CCO_2R$), 1660 (C=O); MS *m/z* (rel. int.): 346.105 (M^+, 10) ($C_{18}H_{18}O_7$), 246 ($M - RCO_2H$, 26), 233 ($M - CH_2OCOR$, 100), 83 ($C_4H_7CO^+$, 60), 55 (83 − CO, 42).

Caleteucrifolone (**23**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1755 (OAc), 1740 (PhOCOC=C), 1715 (PhCO); MS *m/z* (rel. int.): 320.090 (M^+, 4) ($C_{16}H_{16}O_7$), 305 (M − Me, 0.5), 289 (M − OMe, 4), 247 ($M - CH_2OAc$, 60), 69 ($C_3H_5CO^+$, 100).

8-*O*-*Dihydrocaleteucrin angelate* (**25**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1720 ($C{=}CCO_2R$); MS *m/z* (rel. int.): 314.152 (M^+, 62) ($C_{19}H_{22}O_4$), 299 (M − Me, 6), (M − OAng, 100), 214 (M − AngOH, 47), 199 (214 − Me, 32), 83 ($C_4H_7CO^+$, 30), 55 (83 − CO, 48);

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-53.2 \quad -56.1 \quad -64.6 \quad -124.2}$$

($c = 2.56$, $CHCl_3$).

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REFERENCES

1. Bohlmann, F., Gupta, R. K., Jakupovic, J., King, R. M. and Robinson, H. (1981) *Phytochemistry* **20**, (in press).
2. Robinson, H., Bohlmann, F. and King, R. M. (1978) *Phytologia* **41**, 50.
3. Bohlmann, F., Fritz, U., King, R. M. and Robinson, H. (1980) *Phytochemistry* **20**, 743.
4. Baruah, N. C., Sharma, R. P., Madhusudanan, K. P., Thyagarajan, G., Herz, W. and Murari, R. (1979) *J. Org. Chem.* **44**, 1831.
5. Bohlmann, F. and Zdero, C. (1977) *Phytochemistry* **16**, 1065.
6. Ohno, N. and Mabry, T. J. (1980) *Phytochemistry* **19**, 609.
7. Anthonsen, T. (1969) *Acta Chem. Scand.* **23**, 3605.
8. Bohlmann, F. and Jakupovic, J. (1978) *Phytochemistry* **17**, 1677.
9. Bohlmann, F. and Zdero, C. (1977) *Phytochemistry* **16**, 1243.
10. Bohlmann, F., Knoll, K.-H., Zdero, C., Mahanta, P. K., Grenz, M., Suwita, A., Ehlers, D., LeVan, N., Abraham, W.-R. and Natu, A. A. (1977) *Phytochemistry* **16**, 965.
11. Shtacher, G. (1970) *J. Med. Chem.* **13**, 1221.
12. Bohlmann, F., Mahanta, P. K., Suwita, A., Suwita, Ant., Natu, A. A., Zdero, C., Dorner, W., Ehlers, D. and Grenz, M. (1977) *Phytochemistry* **16**, 1973.