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EUDESMANE DERIVATIVES FROM *PLUCHEA ODORATA**

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Key Word Index—*Pluchea odorata*; Compositae; eudesmane derivatives; sesquiterpenoids.

Abstract—From the leaves of *Pluchea odorata* three previously known compounds have been isolated. In addition, four new derivatives of 3α,4α,11-trihydroxy-6,7-dehydroeudesman-8-one have also been obtained from the same source. Their structures have been established by spectroscopic means.

INTRODUCTION

In our continuing search for biologically active natural products from Salvadorian Compositae, we have studied the leaves of *Pluchea odorata* (L) Cass., Compositae. The plant was obtained from Sonsonate, the west region of El Salvador, where it is known as 'sihuapate' which in nahualt idiom means 'woman illness' (from 'sihua' and 'pate'). We have isolated two previously known 3-methoxyflavones, artemetin (**1**) [1] and herbacetin-3,7-dimethylether (**2**) [2] and five derivatives of 3α,4α,11-trihydroxy-6,7-dehydroeudesman-8-one. Their structures have been established by spectroscopic methods.

RESULTS AND DISCUSSION

The eudesmane **3** had the molecular formula $C_{22}H_{32}O_7$. The IR spectrum had the following absorptions: 3410 (hydroxyl group), 1745 (acetate's carbonyl), 1730 (epoxyangelate's carbonyl) and 1670 cm^{-1} (α,β-unsaturated ketone). The ^1H NMR spectrum in deuterochloroform (Table 1) showed characteristic signals of the epoxiangelate at $\delta 3.08$ (1H, *q*, $J = 5$ Hz), 1.34 (3H, *d*, $J = 5$ Hz) and 1.60 (3H, *s*) and the acetate at $\delta 2.04$ (3H, *s*). The H-6 olefinic proton was observed at $\delta 6.97$ (*d*, $J = 2$ Hz). The mass spectrum of this compound showed a fragmentation pattern in accordance with the presence of these ester groups with ions at *m/z* 333 $[M - HOAc - Me]^+$ (base peak) and 233 $[M - RCOO - HOAc]^+$ (6%). The evidence so far described is fully in accordance with the structure for 4α-acetoxy-3α(2-methyl-2′,3′-epoxy-butyrloxy)-11-hydroxy-6,7-dehydroeudesman-8-one (**3**) [3].

Compound **4**, $C_{22}H_{32}O_6$, had an IR spectrum (3450, 1735, 1720 and 1650 cm^{-1}) similar to the IR spectrum of **3**. The ^1H NMR data (Table 1) showed a similar structure to **3**; the ester groups were now the angelate [$\delta 6.04$ (1H, *q*, $J = 7$ Hz), 1.92 (3H, *d*, $J = 7$ Hz) and 1.87 (3H, *s*)] and the acetate [$\delta 2.05$ (3H, *s*)]. The mass spectrum is in accordance with the presence of these ester groups with ions at *m/z* 83 $[Me\,CH{=}(Me)\,C \equiv O]^+$ (100) and 43 $[Ac]^+$ (68%).

The eudesmane **5**, $C_{22}H_{33}O_7Cl$, had an IR spectrum with bands at 3540–3420, 1750, 1720 and 1670 cm^{-1}. The

Table 1. ^1H NMR chemical shifts for compounds **3**–**7** (δ solvent $CDCl_3$)

	3	**4**	**5**	**6**	**7**
H-3β	5.93 *m*	5.88 *m*	5.97 *m*	4.91 *m*	4.97 *m*
H-5α	3.10 *d*	3.06 *d*	3.05 *d*	2.83 *d*	2.79 *d*
H-6	6.97 *d*	7.10 *d*	6.95 *d*	7.01 *d*	7.01 *d*
H-9	2.36 *brs*	2.32 *brs*	2.36 *brs*	2.32 *brs*	2.34 *br.s*
H-12 H-13	1.48 *s*	1.46 *s*	1.47 *s*	1.41–1.42 s	1.43–1.44 *s*
Me-14β	1.02 *s*	1.02 *s*	1.02 *s*	0.96 *s*	0.98 *s*
Me-15β	1.57 *s*	1.62 *s*	1.58 *s*	1.23 *s*	1.27 *s*
H-3′	3.08 *q*	6.04 *q*	4.31 *q*	3.09 *q*	4.34 *q*
Me-4′	1.34 *d*	1.92 *d*	1.57 *d*	1.34 *d*	1.57 *d*
Me-5′	1.60 *s*	1.87 *s*	1.41 *s*	1.59 *s*	1.47 *s*
OAc	2.04 *s*	2.05 *s*	2.01 *s*	—	—

J (Hz): **3** 5α,6 = 2; 3′,4′ = 5; **4** 5α,6 = 2; 3′,4′ = 7; **5** 5α,6 = 2; 3′,4′ = 7; **6** 5α,6 = 2; 3′,4′ = 5; **7** 5α,6 = 2; 3′,4′ = 7.

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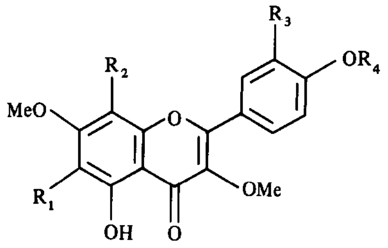
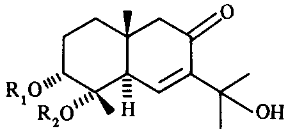
* Part 5 in the series "Salvadorian Compositae". For Part 4 see Borges, J., Bradley, A., Manresa, M. T., Luis, F. R. and Vázquez, P. (1983) *Phytochemistry* **22**, 782.



1 $R_1 = R_3 = OMe$, $R_4 = Me$, $R_2 = H$

2 $R_1 = R_3 = R_4 = H$, $R_2 = OH$



	R_1	R_2
3	EMB	Ac
4	Ang	Ac
5	HMCB	Ac
6	EMB	H
7	HMCB	H

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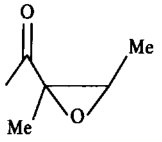

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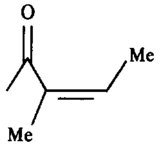
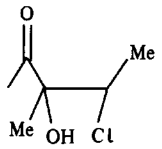


HMCB =



^1H NMR (Table 1) spectrum exhibited characteristic signals of the eudesmane structure, similar to **3** and **4**. One of the ester groups was acetate. The other ester group showed signals at $\delta 4.31$ (1H, *q*, $J = 7$ Hz), 1.57 (3H, *d*, $J = 7$ Hz) and 1.41 (3H, *s*) and is in accordance with the literature data for a 2′-methyl-2′-hydroxy-3′-chlorobutyryloxy residue [4]. The presence of this ester was confirmed by the mass spectrum which showed a ratio of 3:1 for the relative abundances of the peaks at *m/z* 369 (100%) and 371 (36%) $[M - HOAc - Me]^+$ and at 107 (15%) and 109 (7%) $[Me\ CHClC(OH)\ (Me)C{\equiv}O]^+$.

Compound **6**, $C_{20}H_{30}O_6$, had an IR spectrum which showed only one ester group and had the following absorptions: 3500, 3300, 1735 and 1670 cm^{-1}. The ^1H NMR data (Table 1) indicated the presence of an epoxyangelate residue, but the acetate group was absent.The chemical shift of the H-3β was $\delta 5.93$ in **3** but was at 4.91 in **6**. The small differences in the chemical shift values of the Me-15β (from $\delta 1.57$ in **3** to 1.23 in **6**) and the H-5α (from 3.10 in **3** to 2.83 in **6**) showed that the free hydroxyl must be on the C-4. The mass spectrum was in accordance with the absence of the acetate group.

Finally, the eudesmane, **7**, had a molecular formula $C_{20}H_{31}O_6Cl$. The IR spectrum was in accordance with a monoester derivative and had the following absorptions: 3500–3300, 1720 and 1670 cm^{-1}. The ^1H NMR spectrum (Table 1) showed the same chlorine containing residue as in **5** but the acetate group was absent. The chemical shift of the H-3β was at high field (from $\delta 5.97$ in **5** to 4.97 in **7**) and there were changes in the signals of H-5α and Me-15β.

Compounds **4**–**7** are described for the first time in nature.

EXPERIMENTAL

Mps were determined in a Kofler apparatus and are uncorr. ^1H NMR spectra were measured at 100 MHz in $CDCl_3$ soln with TMS as int. standard. Mass spectra were determined at 70 eV.

Extraction and isolation of the components. Dried and finely powdered *P. odorata* leaves (3.5 kg) were refluxed with petrol, C_6H_6 and $CHCl_3$ for 30 hr each. The C_6H_6 extract (22 g) was chromatographed on a Si gel column with toluene–EtOAc mixtures as eluents, yielding the following compounds in order of elution: artemetin **1** (100 mg), herbacetin-3,7-dimethyl-ether **2** (108 mg), **3** (250 mg), **4** (10 mg), **5** (100 mg), **6** (75 mg) and **7** (50 mg). The previously known products were identified by their physical (mp, $[\alpha]_D^{20}$) and spectroscopic (UV, IR, ^{1}H NMR, MS) data.

4α-Acetoxy-3α (2′-methyl-2′,3′-epoxy-butyryloxy)-11-hydroxy-6,7-dehydroeudesman-8-one (**3**). White needles (Et_2O–petrol), mp 105–106°. UV $\lambda_{\max}^{\mathrm{MeOH}}$ nm: 237.

$$[\alpha]_D^{20} = \frac{589 \qquad 578 \qquad 546 \qquad 436}{+105.6 \quad +110.2 \quad +124.8 \quad +205.8} (\mathrm{CHCl_3};\ c\ 2.4).$$

IR $\nu_{\max}^{\mathrm{nujol}}$ cm^{-1}: see Results and Discussion. ^{1}H NMR: see Results and Discussion. MS (direct inlet) m/z (rel. int.): 408 $[M]^+$ (–), 333 $[M - HOAc - Me]^+$ (100), 249 $[M - RCOOH - Me\,CO]^+$ (40), 233 $[M - RCOO - HOAc]^+$ (76), 217 $[M - RCOOH - HOAc - Me]^+$ (76), 43 $[Me\,C \equiv O]^+$ (80). (Found: C, 64.05; H, 8.34. Calcd for $C_{22}H_{32}O_7$: C, 64.69; H, 7.90%.)

4α-Acetoxy-3α-angeloyloxy-11-hydroxy-6,7-dehydroeudesman-8-one (**4**). Oil UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm: 224. IR $\nu_{\max}^{\mathrm{nujol}}$ cm^{-1}: see Results and Discussion. ^{1}H NMR: see Results and Discussion. MS m/z (rel. int.): 392 $[M]^+$ (–), 317 $[M - HOAc - Me]^+$ (9), 217 $[M - HOAc - AngOH]^+$ (6), 83 $[Ang]^+$ (100), 55 $[Me\,CH{=}C(Me)]^+$ (49), 43 $[Ac]^+$ (68).

4α-Acetoxy-3α(2′-hydroxy-2′-methyl-3′-chloro-butyryloxy)-11-hydroxy-6,7-dehydroeudesman-8-one (**5**). White needles (Et_2O–petrol), mp 169°, UV $\lambda_{\max}^{\mathrm{MeOH}}$ nm: 238.

$$[\alpha]_D^{20} = \frac{589 \qquad 578 \qquad 546 \qquad 436}{+95.0 \quad +98.9 \quad +112.2 \quad +187.3} (\mathrm{CHCl_3};\ c\ 2.6).$$

IR $\nu_{\max}^{\mathrm{nujol}}$ cm^{-1}: see Results and Discussion. ^{1}H NMR: see Results and Discussion. MS m/z (rel. int.): 444 $[M]^+$ (–) 369,371 $[M - HOAc - Me]^+$ (100, 36), 235 $[M - Ac - RCOO - Me]^+$ (86), 217 $[M - HOAc - RCOOH - Me]^+$ (30), 135 $[Me\,CHClC(OH)\,Me\,C \equiv 0]^+$ (7), 107, 109 $[Me\,CHClC(OH)Me]^+$ (15, 7), 43 $[Ac]^+$ (82). (Found: C, 59.82; H, 7.88; Cl, 8.00. Calcd for $C_{22}H_{33}O_7Cl$: C, 59.79; H, 7.53; Cl, 8.02%.)

3α-(2′-Methyl-2′,3′-epoxy-butyryloxy)-4α,11-dihydroxy-6,7-dehydroeudesman-8-one (**6**). Oil. UV $\lambda_{\max}^{\mathrm{MeOH}}$ nm: 238.

$$[\alpha]_D^{20} = \frac{589 \qquad 578 \qquad 546}{+42.7 \quad +44.2 \quad +49.1} (\mathrm{CHCl_3};\ c\ 2.4).$$

IR $\nu_{\max}^{\mathrm{nujol}}$ cm^{-1}: see Results and Discussion. ^{1}H NMR: see Results and Discussion. MS m/z (rel. int.): 366 $[M]^+$ (–), 351 $[M - Me]^+$ (2), 333 $[M - Me - H_2O]^+$ (17), 233 $[M - RCOO - H_2O]^+$ (16), 217 $[M - RCOOH - H_2O]^+$ (10), 149 $[C_{10}H_{13}O]^+$ (33), 71 $[C_4H_7O]^+$ (100). (Found: C, 66.72; H, 7.61. Calcd for $C_{20}H_{30}O_6$; C, 65.55; H, 8.25%.)

3α-(2′-hydroxy-2′-methyl-3′-chloro-butyryloxy)-4α,11-dihydroxy-6,7-dehydroeudesman-8-one (**7**). Oil. UV $\lambda_{\max}^{\mathrm{MeOH}}$ nm: 240. IR $\nu_{\max}^{\mathrm{nujol}}$ cm^{-1}: see Results and Discussion.

$$[\alpha]_D^{20} = \frac{589 \qquad 578 \qquad 546 \qquad 436}{+43.6 \quad +45.3 \quad +51.0 \quad +77.3} (\mathrm{CHCl_3};\ c\ 1.0).$$

^{1}H NMR: See Results and Discussion. MS m/z (rel. int.): 402 $[M]^+$ (–), 371, 369 $[M - Me - H_2O]^+$ (1.5, 4), 235 $[M - RCOOH - Me]^+$ (11), 217 $[M - RCOOH - Me - H_2O]$ (7), 149 $[C_{10}H_{13}O]^+$ (58), 107, 109 $[RC \equiv O]^+$ (100, 64), 71 $[C_4H_7O]^+$ (92). (Found: C, 60.55; H, 8.46; Cl, 8.82 Calcd for $C_{20}H_{31}O_6Cl$: C, 59.62; H, 7.76; Cl, 8.80%.)

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