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FURANOHELIANGOLIDES AND FLAVONOIDS FROM *LOURTEIGIA BALLOTAEFOLIA*

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Key Word Index—*Lourteigia ballotaefolia*; Compositae; Eupatorieae; heliangolides; flavonoids.

Abstract—The aerial parts of *Lourteigia ballotaefolia* afforded, in addition to three known flavonoids, two furanoheliangolides. The structures and stereochemistries were determined by chemical and spectroscopic means and were established as the 8- and 9-acetylsarracinoyl esters of 1-keto-8β-9β-dihydroxygermacra-2,4,11(13)-trien-3,(10β)-oxo-6α,12-olide. The chemotaxonomic situation is discussed briefly.

INTRODUCTION

The genus *Lourteigia* contains seven species which are distributed in Colombia and Venezuela. This genus is placed in the *Gyptis* group (tribe Eupatorieae) [1], and to it belongs *Eupatorium ballotaefolium* H.B.K. which is now named *L. ballotaefolia* (H.B.K.) K. et R. [2]. No chemical investigations have been reported previously on these plants. We have investigated this species to determine if the chemistry might help in taxonomic revision within this diverse group. The aerial parts of this plant afforded several known flavonoids and two furanoheliangolides which are closely related to those isolated from other genera of this tribe.

RESULTS AND DISCUSSION

The aerial parts of *Lourteigia ballotaefolia* afforded the flavonoids hispidulin (**1**) [3], eupafolin (**2**) [4] and the 3-methyl ether of quercetin (**3**) [5], as well as two sesquiterpene lactones, **4** and **5**, which could only be separated with difficulty. The structure of **4** was identical to conoprasiolide 5′-*O*-acetate, isolated from *Conocliniopsis prasiifolia* [6], for which the stereochemistry was given, but the 8β-acyloxy group cannot be assigned with certainty. Acetylation of **4** using pyridine gave a mixture of several compounds. Acetylation using *p*-toluenesulfonic acid as a catalyst afforded the acetate **6**. Catalytic hydrogenation of **4** afforded **7**. The C-6 lactone closure was confirmed since the signal at δ5.15 in the ^{1}H NMR spectrum of **4** attributed to the C-6 allylic hydrogen of the lactone closure was shifted upfield to δ4.45 in **7** (Table 1). All the signals were clearly established by decoupling experiments. When **4** was hydrolysed with pyridine it afforded **8**. This reaction supports the stereochemistry at C-8 since the hydrolysis under these conditions occurs by an intramolecular catalysis, which is facilitated by the ester and the hydroxyl group in the *cis* position. The second sesquiterpene lactone was a furanoheliangolide isomer of **4**, in which the relative positions of the acetylsarracinate and the hydroxyl group were interchanged. The ^{1}H NMR spectral data (Table 1) and the obtainment of **8** by hydrolysis with pyridine showed that the structure was **5**. The free C-8 hydroxyl group caused a downfield shift of the H-6 signal, again supporting the stereochemistry at these centres. Compounds **4** and **5** were derivatives of atripliciolide, which is the 8-desacyl-9-desoxy derivative of **4** [7].

The sesquiterpene lactones isolated from *L. ballotaefolia* support the proposed relationship of this genus to the *Gyptis* group. Obviously more species of the genus *Lourteigia* need to be investigated but furanoheliangolides have been isolated in the tribe Eupatorieae only from the *Gyptis* group (*Conocliniopsis* [6], *Trichogonia* [8],

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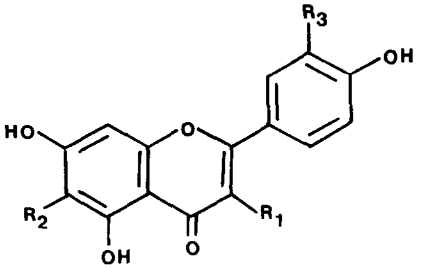
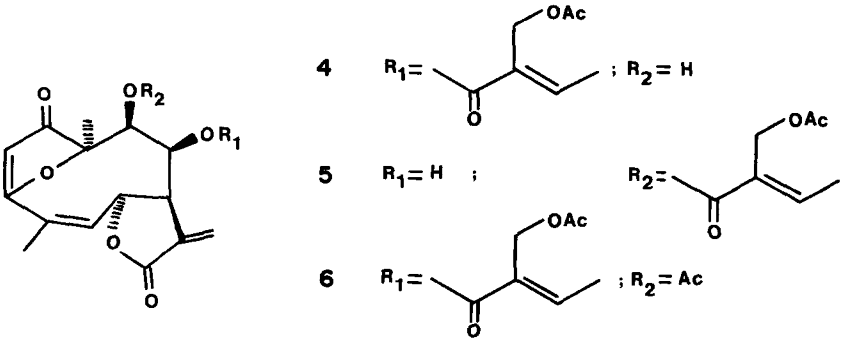


1 $R_1 = R_3 = H$; $R_2 = OMe$

2 $R_1 = H$; $R_2 = OMe$; $R_3 = OH$

3 $R_1 = OMe$; $R_2 = H$; $R_3 = OH$



8 $R_1 = R_2 = H$

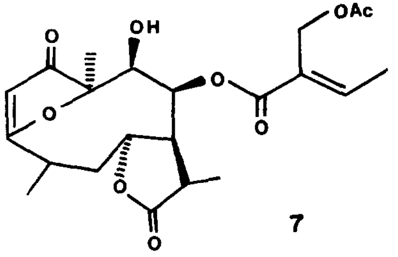


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Table 1. ^1H NMR spectral data of compounds 4–8 (60 MHz, $CDCl_3$)

	4	5	6	7	8
H-2	5 64 *s*	5 60 *s*	5.66 *s*	5.64 *s*	5.70 *s*
H-5	5 98 *m*	6.00 *m*	6.00 *m*	2.58 *m* 2 10 *m*	5.90 *m*
H-6	5.15 *m*	5.75 *m*	5.40 *m*	4.45 *m*	5.20 *m*
H-7	3 62 *m*	3.45 *m*	3.65 *m*	3 10 *m*	3.50 *m*
H-8	5.15 *m*	4.15 *m*	5.40 *m*	5.34 *m*	4.80 *m*
H-9	4.18 *m*	5.28 *d*	5.32 *d*	3.95 *m*	4.10 *m*
H-13	6.35 *d*	6.35 *d*	6.40 *d*	1.40 *d*	6.25 *d*
H-13′	5 73 *d*	5.68 *d*	5.85 *d*	—	5.60 *m*
H-14	1.67 *s*	1.46 *s*	1.50 *s*	1.67 *s*	1.67 *s*
H-15	2.07 *d*	2 03 *d*	2 07 *d*	1 38 *d*	2 05 *d*
H-3′	7.06 *q*	7.32 *q*	7 10 *q*	7.10 *q*	
H-4′	1 95 *d*	2.00 *d*	1.95 *d*	1 95 *d*	
$H-5'_1$	4.92 *d*	5.20 *d*	4.95 *d*	4.90 *d*	
$H-5'_2$	4.67 *d*	4.83 *d*	4.65 *d*	4.65 *d*	
OAc	2.03 *s*	2.03 *s*	2.04 *s* 2.10 *s*	2.04 *s*	
OH	3 62 *m*	3.45 *m*			

J(Hz). 5, 15 = 1 5, 7, 13 = 3; 7, 13′ = 3; 8, 9 = 3; 3′, 4′ = 7; $5'_1$, $5'_2$ = 12.

Bejaranoa [9] and *Trichogoniopsis* [10]) with the exceptions from *Disynaphia halimifolia* [11] and *Isocarpha atriplicifolia* [7].

EXPERIMENTAL

Mps are uncorr. UV were recorded in EtOH. ^{1}H NMR spectra were recorded at 60 MHz using TMS as internal standard. The aerial parts of the air-dried plant material (3.5 kg) (voucher J. Triana 2 Herbario Fac. de Farmacia, collected in Mérida, Venezuela) was extracted with EtOH at room temp. The resulting extracts were concd and treated with lead acetate soln; the suspension was filtered and extracted with EtOAc. The extract (55 g) was first separated by CC (silica gel) and further by repeated TLC (silica gel). The flavonoids were separated by recrystallization and identified by mps, UV, ^{1}H NMR spectra and comparison of their acetyl derivatives with published data. 65 mg **1**, 114 mg **2**, 28 mg **3**, 460 mg **4** (EtOAc–petrol, 1:2) and 48 mg **5** (EtOAc–petrol, 1:2) were obtained.

9β-Hydroxyatripliciolide-8-O-(*5′-acetoxysarracinate*) (**4**). Colourless gum, $[\alpha]_D^{25} - 82.1°$ ($CHCl_3$; c 2.1). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3500 (OH), 1765 (γ-lactone), 1725, 1650 ($C{=}CCO_2R$), 1690, 1590 (O=C–C=C–OR); UV λ_{max}^{EtOH} nm: 210, 265; MS *m/z* (rel. int): 372 $[M - HOAc]^+$ (2), 274 $[M - RCO_2H]^+$ (5), 141 $[MeCH{=}C(CH_2OAc)CO]^+$ (61), 99 $[141 - \text{ketene}]^+$ (20). To 80 mg **4** in 1 ml Ac_2O, 40 mg *p*-toluenesulfonic acid was added. After 12 hr, CC (EtOAc–petrol, 2.1) afforded 60 mg **6**, colourless gum; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1760 (broad), 1715 (C=O), 1650, 1595 (C=C); UV λ_{max}^{EtOH} nm: 265. Compound **4** (142 mg) was hydrogenated in the presence of palladium on C (5%) (8 hr). CC (C_6H_6–EtOAc, 3:2) afforded 40 mg **7**, colourless crystals, mp 147–148° (EtOAc–petrol). $[\alpha]_D^{25} + 23.5°$ ($CHCl_3$; *c* 0.79). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3470 (OH), 1770 (γ-lactone), 1725, 1690 (C=O), 1590 (C=C); UV λ_{max}^{EtOH} nm: 262; MS *m/z* (rel. int.): 436.171 $[M]^+$ (17) ($C_{22}H_{28}O_9$), 394 $[M - \text{ketene}]^+$ (5), 376 $[M - HOAc]^+$ (9), 141 $[MeCH{=}C(CH_2OAc)CO]^+$ (50). A soln of **4** (120 mg) in C_5H_5N (3 ml) was left to stand for 12 hr at room temp. Work-up in the usual manner and CC (C_6H_6–EtOAc, 3:1) afforded 32 mg **8**, colourless crystals, mp 198–200° (EtOAc). $[\alpha]_D^{25} - 152°$ ($CHCl_3$; *c* 0.321). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3400 (OH), 1770 (γ-lactone), 1695 (C=O), 1650, 1590 (C=C). MS *m/z* (rel. int.) 292 $[M]^+$ (0.2), 274 $[M - H_2O]^+$ (1.2).

9β-(5′-Acetoxysarracinoyloxy)-atripliciolide (**5**). Colourless gum $[\alpha]_D^{25} - 63.6°$ ($CHCl_3$; *c* 0.245). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3490 (OH), 1760 (γ-lactone), 1715, 1650 ($C{=}CCO_2R$), 1700, 1598 (O=C–C=C–OR); UV λ_{max}^{EtOH} nm: 212, 264; MS *m/z* (rel. int.): 432.142 $[M]^+$ (4) ($C_{22}H_{24}O_9$), 372 $[M - HOAc]^+$ (2), 274 $[M - RCO_2H]^+$ (4), 245 $[274 - CHO]^+$ (2), 232 $[274 - C_2H_2O]^+$ (7), 141 $[MeCH{=}C(CH_2OAc)CO]^+$ (31), 99 $[141 - \text{ketene}]^+$ (22). 23 mg **5** treated with C_5H_5N as above afforded **8** (TLC and IR spectrum).

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