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A KOLAVANE DERIVATIVE FROM *LIATRIS SCARIOSA**

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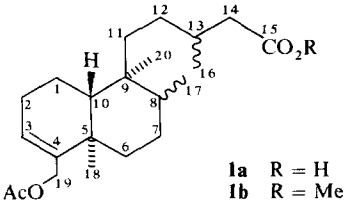
Key Word Index—*Liatris scariosa*; Compositae; diterpene; kolavane derivative; 18-acetoxy-kolav-3-en-15-oic acid; euparin derivative.

Abstract—A new kolavane derivative, 18-acetoxy-kolav-3-en-15-oic acid, has been isolated from *Liatris scariosa*.

The aerial parts of *Liatris scariosa* Willd afforded lupeol, $\Delta^{9(11)}$ and 12,13-dehydrolupeol and the kolavane derivative **1a**. The structure of **1a** followed from the ^{1}H NMR spectrum of its methyl ester **1b** (Table 1), if compared with that of the corresponding desacetoxy derivative [1]. The presence of a kolavane derivative was deduced from the H-3 signal and the chemical shifts of two methyl doublets. Compound **1a** was concluded to be 18-acetoxy-kolav-3-en-15-oic acid. However, the configurations at C-8, C-9 and C-13 were not established with certainty.

The roots afforded dammadienol, its acetate and the euparin derivatives **2** [2], **3** [2], **4** [3] and **5**. The latter compound, 11-hydroxy-10,11-dihydroeuparin (**5**) has not been isolated before. The ^{1}H NMR data (see Experimental) showed that **5** was a derivative of **4**, formed by addition of water to the isopropenyl group. While most *Liatris* species investigated previously also contained sesquiterpene lactones [4, 5] no lactones were detected in the extract of this species.



1a R = H
1b R = Me

Table 1. ^{1}H NMR spectra data of compound **1b** (270 MHz, TMS as internal standard, $CDCl_3$)

H-3	5.68 *br.t*	H-18	1.11 *s*
H-14	2.36 *dd*	H-19	4.59 *br.s*
H-14′	2.15 *dd*	H-20	0.77 *s*
H-16	0.96 *d*	OAc	2.08 *s*
H-17	0.75 *d*	OMe	3.68 *s*

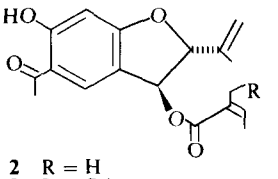
J(Hz): 2,3 = 3; 8,17 = 13,16 = 7; 13,14 = 5.5; 13,14′ = 7.5; 14,14′ = 14.

EXPERIMENTAL

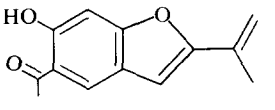
The air-dried plant material was extracted with Et_2O–petrol. CC (Si gel) and TLC (Si gel) of the extracts afforded from the roots (50 g) 10 mg dammadienol, 20 mg of its acetate, 10 mg **2**, 12 mg **3**, 25 mg **4** and 3 mg **5**, while from the aerial parts (100 g) 10 mg of a mixture of lupeyl acetate and its $\Delta^{9(11)}$ and Δ^{12} isomers as well as 4 mg **1a** were isolated.

18-Acetoxy-kolav-3-en-15-oic acid (**1a**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3330–2600, 1710 (CO_2H), 1740, 1230 (OAc), 1640 (C=C); MS *m/z* (rel. int.): 364 (M^+, 4), 304 (M − HOAc, 28), 289 (304 − ·Me, 22), 189 (304 − ·$CH_2CH_2CH(Me)CH_2COOH$, 100). Compound **1a** (4 mg) was transformed to its methyl ester by addition of CH_2N_2. TLC (Et_2O–petrol, 1:3) afforded 3 mg **1b**, colourless oil; MS *m/z* (rel. int.): 378.277 (M^+, 0.5) ($C_{23}H_{38}O_4$), 318 (M − HOAc, 25), 303 (318 − ·Me, 12), 271 (303 − MeOH, 10), 189 (318 − ·$CH_2CH_2CH(Me)CH_2CO_2Me$, 100).

11-Hydroxy-10,11-dihydro-euparin (**5**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 3300–2600, 1645, 1605 (chelated hydroxy acetophenone); MS *m/z* (rel. int.): 234.089 (M^+, 21) ($C_{13}H_{14}O_4$),



2 R = H
3 R = OAc



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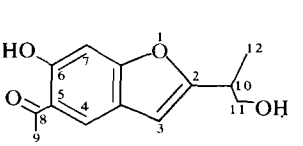

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* Part 340 in the series "Naturally Occurring Terpene Derivatives". For Part 339 see Rustaiyan, A., Dabiri, M., Gupta, R. K. and Bohlmann, F. (1981) *Phytochemistry* **20**, 1429.

219 (M − 'Me, 4), 203 (M − CH_2OH, 100). ^1H NMR ($CDCl_3$): 6.44 (*s*, H-3), 7.89 (*s*, H-4), 6.98 (*s*, H-7), 2.69 (*s*, H-9), 3.16 (*ddq*, H-10, J = 6.5,5,7 Hz), 3.88 (*dd*, H-11, J = 11,6.5 Hz), 3.83 (*dd*, H-11', J = 11,5 Hz), 1.39 (*d*, H-12).

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