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HELIANGOLIDES AND DITERPENES FROM *HARTWRIGHTIA FLORIDANA**

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Key Word Index—*Hartwrightia floridana*; Compositae; Eupatorieae; heliangolides; labdanes; kolavanes.

Abstract—*Hartwrightia floridana* Gray afforded, in addition to known compounds, two new heliangolides, two labdanes and a kolavane, the structures of which were elucidated by spectroscopic methods. The chemotaxonomic situation of the genus is discussed.

INTRODUCTION

The monotypic anomalous genus *Hartwrightia* (Compositae, tribe Eupatorieae), is placed in the *Liatris* group [1], as the geographical distribution and the alternate leaves with a basal rosette suggest this placement, though this species has no pappus, reduced another appendage and glands only in the achenes. We have, therefore, investigated this species to see whether its chemistry supports its placement in the *Liatris*.

RESULTS AND DISCUSSION

The roots of *H. floridana* afforded germacrene D, α-pinene, euparin (**2**) and the angelate **1**, while the aerial parts contained germacrene D, lupeyl acetate, the angelate **1**, several diterpenic acids and two sesquiterpene lactones. The structures of the lactones clearly followed from the ^{1}H NMR data (Table 1) which were very similar to those of punctatin. **4** was the 15-deoxy derivative of punctatin [2] and **3** the corresponding angelate.

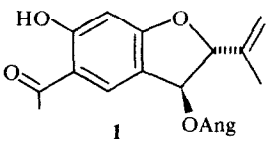
The diterpenic acids could be purified only as their methyl esters. The two less polar esters could be separated on silver nitrate coated plates. Careful inspection of the ^{1}H NMR data (Table 2) led to them being assigned the structures **5b** and **6b**. The structures of their side chains followed from the typical double doublets at $\delta = 2.33$ and 2.12 ppm and the methyl doublet at 0.94. **6b** obviously is identical with the acid isolated together with its 13,14-dehydro compound from a *Fleischmannia* species [3]. As the optical rotation of **6b** was negative it can be assumed to be a kolavane. The stereochemistry at C-13, however, was not determined. The ^{1}H NMR data of **5b** were in part very similar to those of a 15,16-lactone isolated from an *Acritopappus* species [4]. The chemical shifts for 6-, 7- and 17-H as well as those of the methyl groups were nearly identical indicating the same stereochemistry. The IR spectrum of **7b** showed the presence of a γ-lactone, while the structure of the side chain again followed from the ^{1}H NMR data (Table 2). The position of the lactone ring could be deduced by spin decoupling. Irradiation of the methyl signal at 1.81 ppm collapsed the broadened signal at 4.80 to a clear triple doublet and the broad olefinic

Table 1. ^{1}H NMR spectra data of compounds **3** and **4** (270 MHz, $CDCl_3$, TMS as internal standard)

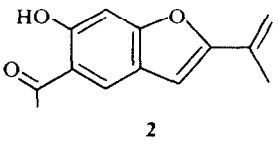
	3	**4**
1-H	3.29 *dd*	3.29 *dd*
2-H	5.55 *dd*	5.56 *dd*
3-H	6.14 *d*(*br.*)	6.14 *d*(*br.*)
5-H	5.31 *dq*	5.32 *dq*
6-H	5.10 *d*(*br.*)	5.12 *d*(*br.*)
7-H	2.17 *dd* (*br.*)	3.00 *dd* (*br.*)
8-H	5.25 *m*	5.26 *m*
8-H	2.82 *dd*	2.89 *dd*
9′-H	1.43 *dd*	1.45 *dd*
13-H	6.40 *d*	6.42 *d*
13′-H	5.80 *d*	5.84 *d*
14-H	1.39 *s*	1.41 *s*
15-H	1.88 *s* (*br.*)	1.90 *d*
OCOR	6.13 *qq*	6.40 *dt*
	1.98 *dq*	2.05 *dt*
	1.82 *dq*	4.26 *dd* (*br.*)
		4.14 *dd* (*br.*)

J (Hz): 1,2 = 7.5; 1,3 = 1; 2,3 = 11.5; 5,6 = 11; 5,15 = 1; 6,7 = 7,8 ~ 1; 7,13 = 2; 7,13′ = 1.7; 8,9 = 4; 8,9′ = 2.5; OAng: 3′,4′ = 7; 3′,5′ = 4′,5′ = 1.5; $OCOC(CH_2OH) = CHMe$; 3′,4′ = 7; 4′,5′ = 1; $5_1',5_2'$ = 13; 5′, OH ~ 5.

* Part 316 in the series "Naturally Occurring Terpene Derivatives". For Part 315 see: Bohlmann, F., Jakupovic, J., Gupta, R. K., Robinson, H. and King, R. M. (1981) *Phytochemistry* (in press).



1



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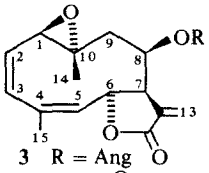
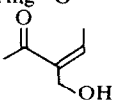
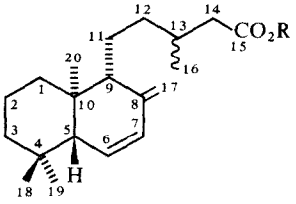


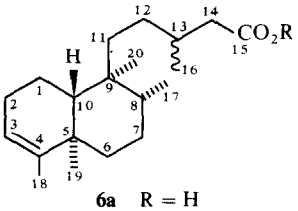
3 R = Ang

4 R =

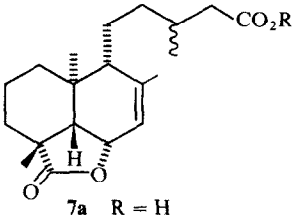




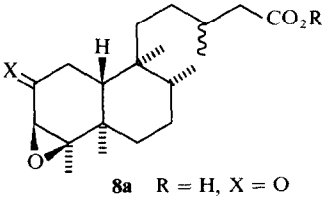
5a R = H
5b R = Me



6a R = H
6b R = Me



7a R = H
7b R = Me



8a R = H, X = O
8b R = Me, X = O
8c R = Me, X = αOH, H

signal at 5.75 to a double doublet. As the remaining signals indicated the presence of a labdane derivative the signals at 5.75 could be assigned to 7-H and that at 4.80 to 6-H (obviously the proton under the lactone oxygen). Further decouplings allowed the assignment of the signals for 5-H, 9-H and 13-H. Inspection of models showed that the coupling constants agreed with the stereochemistry at C-5 through C-9 presented in **7b**. The configuration at C-13, however, could not be determined. The natural compound, therefore, is most probably **7a**, which we have named hartwrightia acid.

The last ester was most probably the keto epoxide **8b**. The presence of an epoxide group was indicated by a sharp singlet at 3.08 ppm (Table 2). The presence of the same side chain as in the other diterpenes was easily deduced from the ^{1}H NMR data, while the presence of a kolavane type diterpene was indicated by the chemical shifts of the methyl signals. Signals around 2.3 ppm showed that the keto group must have two neighbouring hydrogens. The sharp signal of the epoxide proton could be explained if the keto group was vicinal to the latter. This, however, seemed to be possible only if these oxygen functions were placed at C-2 and C-3, and C-4 respectively. To establish the configuration of the epoxide we reduced the keto group with sodium borohydride. Only one alcohol (**8c**) was obtained, indicating that one side of the decalin system was sterically hindered. This, however, required a β-epoxide, as the alcohol obtained was an equatorial one and the very small coupling $J_{2,3}$ required an angle of nearly 90°. The configuration at C-8 was assigned by analogy and therefore is not certain. Though the absolute configuration of the ketone was not determined the given one is most likely as it is the one found in other kolavanes in the tribe. The sign of the optical rotation unfortunately is not very conclusive in this series.

The isolation of **3** and **4** supports the placement of *Hartwrightia* in the *Liatris* group, though diterpenes, very common in other genera of the tribe, seem to be rare in this group, only one unusual diterpene so far having been reported [5]. Unfortunately, nearly nothing is known of the chemistry of the other small genera, which are placed in

Table 2. ^{1}H NMR spectral data of compounds **5b**, **7b**, **8b** and **8c** (270 MHz, $CDCl_3$, TMS as internal standard)

	5b	7b	8b	8c
1-H			2.28 *m*	1.67 *m*
1′-H		1.2 1.7 *m*	2.15 *m*	1.27 *m*
2-H				3.98 *dd*
3-H			3.08 *s*	2.84 *d*
5-H	1.95 *s* (*br.*)	1.69 *d*	—	—
6-H	5.72 *d* (*br.*)	4.80 *dddq*	—	—
7-H	6.16 *dd*	5.75 *ddq*		—
9-H	2.01 *m*	1.68 *m*	—	—
13-H	—	1.95 *ttq*	1.87 *m*	1.87 *m*
14-H	2.35 *dd*	2.31 *dd*	2.31 *dd*	2.33 *dd*
14′-H	2.15	2.14 *dd*	2.13 *dd*	2.12 *dd*
16-H	0.98 *d*	0.96 *d*	0.93 *d*	0.93 *d*
17-H	4.89 *s*(*br.*)	1.81 *ddd*	0.80 *d*	0.78 *d*
17′-H	4.81 *s*(*br.*)			
18-H	0.95 *s*	1.27 *s*	1.34 *s*	1.22 *s*
19-H	0.84 *s*	—	0.96 *s*	1.11 *s*
20-H	0.68 *s*	0.80 *s*	0.72 *s*	0.70 *s*
OMe	3.68 *s*	3.65 *s*	3.67 *s*	3.67 *s*

J (Hz): Compound **5b**: 5,7 = 2.5; 6,7 = 10; 13,14 = 7; 13,14′ = 8; 14,14′ = 14; 13,16 = 7; compound **7b**: 5,6 = 4.5; 6,7 = 4.5; 6,17 = 6,9 = 7,17 = 9,17 = 1.5; 7,9 = 2; 12,13 = 13,14 = 13,16 = 7; compound **8b**: 8,17 = 6; 13,14 = 6.5; 13,14′ = 8; 13,16 = 6.5; compound **8c**: 1,2 = 9.5; 1′,2 = 7; 2,3 = 1; 8,17 = 6; 13,14 = 6.5; 13,14′ = 8; 13,16 = 6.5.

the same group. Only a *Carphephorus* species [6] has so far been investigated, but no typical compounds were isolated. Euparin and similar compounds are present in *Liatris* species too, but these compounds are also not very characteristic.

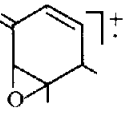
EXPERIMENTAL

The air dried plant material (voucher H.W. R 6420) was extracted with Et_2O–petrol (1:2) and the resulting extracts were separated first by column chromatography (SiO_2) and further by repeated TLC (SiO_2). The roots (30 g) afforded 8 mg α-pinene, 12 mg germacrene D, 50 mg **1** and 30 mg **2**, while the aerial parts (200 g) gave 85 mg germacrene D, 200 mg lupeyl acetate, 30 mg **1**, 4.5 mg **3** (Et_2O–petrol, 3:1), 3 mg **4** (Et_2O–petrol, 3:1), 4 mg **5a**, 4 mg **6a**, 30 mg **7a** and 100 mg **8a** (**5a**–**8a** were transformed to their methyl esters and separated by TLC (Et_2O–petrol, 1:1 and Et_2O–CH_2Cl_2–C_6H_6, 1:4:4).

15,5′-Bis-deoxypunctatin (**3**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1775 (γ-lactone), 1730, 1650 (C = CCO_2R); MS *m/e* (rel. int.): 344.162 (M^+, 6) ($C_{20}H_{24}O_5$), 244 (M − AngOH, 10), 83 ($C_4H_7CO^+$, 90), 55 (83 − CO, 100).

15-Deoxypunctatin (**4**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620 (OH), 1780 (γ-lactone), 1730, 1655 (C = CCO_2R); MS *m/e* (rel. int.): 360.157 (M^+, 3), 244 (M − RCO_2, 12), 99 (RCO^+, 100), 81 (99 − CO, 51).

Methyl-ent-*labda*-6,8(17)-*diene*-15-*oate* (**5b**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740 (CO_2R), 3040, 1640, 890 (C = CH_2); MS *m/e* (rel. int.): 318.256 (M^+, 34) ($C_{21}H_{34}O_2$), 287 (M − OMe, 5), 190 ($C_{14}H_{22}$, 58), 189 ($C_{14}H_{21}$, 46), 119 (100). $[\alpha]_D$ + 1.1 (*c* = 0.36, $CHCl_3$).

*A = 

Hartwrightia acid methyl ester (**7b**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1775 (γ-lactone), 1740 (CO_2R), 1650 (C=C); MS *m/e* (rel. int.): 348.230 (M^+, 1) ($C_{21}H_{32}O_4$), 333 (M − Me, 1), 317 (M − OMe, 3), 264 (M − $MeCO_2Me$, 8), 109 (C_8H_{13}, 100).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{+0.9 \quad -0.2 \quad -1.7 \quad -15.1} \quad (c = 0.53,\ CHCl_3).$$

Methyl-3,4-β-*epoxy-kolavan*-2-*on*-15-*oate* (**8b**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740 (CO_2R), 1710 (C = O); MS *m/e* (rel. int.): 350.246 (M^+, 1) ($C_{21}H_{34}O_4$), 335 (M − Me, 2), 319 (M − OMe, 4), 303 (335 − MeOH, 6), 137 (**A***, 47), 109 (137 − CO, 100).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{+72.8 \quad +76.5 \quad +89.5 \quad +190.9} \quad (c = 2.2,\ CHCl_3).$$

To 20 mg **8b** in 1 ml MeOH 10 mg $NaBH_4$ were added. After 15 min dil H_2SO_4 was added. The products were extracted with Et_2O. Evapn afforded 20 mg **8c**, colourless gum, ^{1}H NMR see Table 2.

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