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AN ACYLPYRROLE DERIVATIVE AND FURTHER CONSTITUENTS FROM JAMAICAN REPRESENTATIVES OF THE TRIBE SENECIONEAE

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Key Word Index—*Odontocline glabra*; *O. hollickii*; *O. laciniata*; *Jacmaia incana*; Senecioneae; Compositae; syringenin esters; acylpyrrole derivative.

So far no chemical investigations of the small genus *Odontocline* [1, 2] and the monotypic genus *Jacmaia* [1, 2], both growing only in Jamaica, are available. We therefore have investigated three *Odontocline* species and the *Jacmaia* species.

The aerial parts of *Odontocline glabra* (Sw.) B. Nord. afforded germacrene D, selina-4(15),11(13)-diene, bisabolene and a new ester of syringenin, the isovalerate **3** as clearly indicated from the ^{1}H NMR data (Table 1), which were further supported by the MS. The symmetrical aromatic substitution could be deduced from the aromatic proton singlet, while the chemical shift of this signal was in agreement only with the vicinal position of the oxygen functions. The aerial parts of *O. hollickii* (Britt. ex Greenm.) B. Nord. afforded β-farnesene, germacrene D, α-humulene, caryophyllene and senaetnin (**6**) [3], while the aerial parts of *O. laciniata* (Sw.) B. Nord. gave only caryophyllene, selina-4(15),11(13)-diene, liguloxide (**2**) [4] and the carbinol **1** [5].

The aerial parts of *Jacmaia incana* (Sw.) B. Nord. afforded β-farnesene, germacrene D, caryophyllene, α-humulene, bisabolol and two further esters of syringenin, the senecioate **4** and the angelate **5**, which, however, could not be separated. Their structures could be deduced from the ^{1}H NMR data (Table 1), which were very similar to those of **3**. Furthermore a new acylpyrrole was present. The ^{1}H NMR data (Table 2) showed that we are dealing with a derivative of dehydroheliotridinone, where the two hydroxyl groups are esterified with senecioyloxyangelate and senecioate. Although partial saponification was not successful, the MS data strongly suported structure **7**, as the base peak of the CI spectrum was $M^+ + 1 - C_4H_7CO_2H$, which only seemed to be reasonable if the senecioate is placed at C-7, and because of the optical rotation [3, 6] most probably in the β-configuration. Although several acylpyrrole derivatives have been isolated before [3] this type is a new one, as the macrolide part is missing.

Table 1. ^{1}H NMR spectral data of compounds **3**–**5** (270 MHz, CDCl$_3$, TMS internal standard)

	3	4		5
2,6-H	6.63 *s*		6.66 *s*	
7-H	6.60 *br. d*		6.62 *br. d*	
8-H	6.23 *dt*		6.27 *dt*	
9-H	4.73 *br. d*		4.76 *dd*	
OCOR	2.47 *d*	5.75 *qq*		6.20 *br. q*
	2.24 *m*	2.21 *d*		2.03 *br. s*
	1.07 *d*	1.93 *d*		
	0.98 *d*			
OMe	3.82 *s*		3.82 *s*	

J (Hz): 7, 8 = 16; 7, 9 = ; 8, 9 = 7; OiVal: 2′, 3′ = 3′, 4′ = 3′, 5′ = 7; OSen: 2′, 4′ = 2′, 5′ = 1; OAng: 3′, 4′ = 7.

Table 2. ^{1}H NMR spectral data of compound **7** (270 MHz, CDCl$_3$)

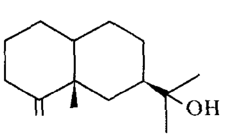
2-H	6.54 *d*	OSen	5.63 *qq*
3-H	7.08 *d*		2.14 *d*
6-H	3.54 *dd*		1.88 *d*
6′-H	2.97 *dd*	OCOR	6.41 *tq*
7-H	6.19 *dd*		2.07 *tq*
9-H	5.19 *d*		4.74 *br. s*
9′-H	5.07 *d*		5.67 *qq*
			2.19 *d*
			1.91 *d*

J (Hz): 2, 3 = 3.5; 6, 6′ = 19; 6, 7 = 7; 6′, 7 = 2; 9, 9′ = 12; OSen: 2, 4 = 2, 5 = 1; OCOR: 3, 4 = 7.5; 3, 5 = 0.7.

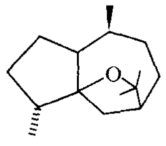
The chemical results on the species investigated showed a close relationship between *Odontocline* and *Jacmaia*. The absence of furanoeremophilanes and the occurrence of acylpyrroles may be an indication of a relationship to special *Senecio* groups [7]. So far, **3** has only been isolated from a *Ligularia* species [4]. Other members of other genera from North and Central America have to be studied to get a clearer picture of the relationships.

EXPERIMENTAL

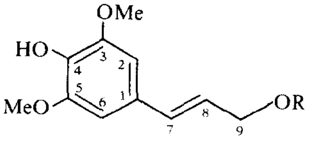
The air-dried plant material, collected at Jamaica (voucher Botanical Museum, Stockholm) was extracted with



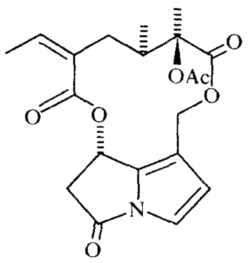
1



2



3 R = *i*-Val
4 R = Sen
5 R = Ang



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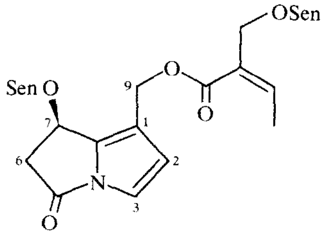

7

Et$_2$O–petrol and the resulting extracts were separated by column chromatography (Si gel, act. grade II) and further by repeated TLC (Si gel). Known compounds were identified by comparing the IR and ^{1}H NMR spectra with those of authentic samples.

O. glabra. The aerial parts (100 g) afforded 100 mg germacrene D, 5 mg selina-4(15),11(13)-diene, 100 mg bisabolene and 50 mg **3** (Et$_2$O–petrol, 1:1).

O. hollickii. The aerial parts (100 g) afforded 10 mg β-farnesene, 15 mg germacrene D, 50 mg α-humulene, 50 mg caryophyllene and 200 mg **6**.

O. laciniata. The aerial parts (250 g) afforded 200 mg selina-4(15),11(13)-diene, 2 mg caryophyllene, 200 mg **1** and 250 mg **2**.

J. incana. The aerial parts (200 g) afforded 60 mg β-farnesene, 20 mg germacrene D, 20 mg caryophyllene, 20 mg α-humulene, 100 mg bisabolol, 15 mg **4** and 15 mg **5** (Et$_2$O–petrol, 1:3) as well as 12 mg **7** (Et$_2$O–petrol, 1:1).

Syringenin-isovalerate (**3**). Colourless oil, IR $\nu_{\max}^{\mathrm{CCl_4}}$ cm^{-1}: 3520 (OH), 1745 (CO$_2$R); MS *m/e* (rel. int.): 294.147 (M$^+$, 100) ($C_{16}H_{22}O_5$), 218 ($M^+ = O{=}C{=}CHCHMe_2$, 11), 193 ($M^+ - O_2CR$, 10), 85 ($C_4H_9CO^+$, 26) 57 (85 – CO, 52).

Syringenin-senecioate respectively angelate (**4** *and* **5**). Colourless oil, IR $\nu_{\max}^{\mathrm{CCl_4}}$ cm^{-1}: 3520 (OH), 1725, 1650 (C=CCO$_2$R); MS *m/e* (rel. int.): 292.131 (M$^+$, 9) ($C_{16}H_{20}O_5$), 192 ($M^+ - RCO_2H$, 3), 83 ($C_4H_7CO^+$, 100), 55 (83 – CO, 61).

7β-Senecioyloxy-9-[5-senecioyloxy angeloyloxy]-5,8-dehydroheliotridin-5-one (**7**). Colourless gum, IR $\nu_{\max}^{\mathrm{CCl_4}}$ cm^{-1}: 1765 (OAc), 1725, 1650 (C=CCO$_2$R); MS *m/e* (rel. int.): 429.179 (M$^+$, 0.1) ($C_{25}H_{27}NO_7$), 329 ($M^+ - C_4H_7CO_2H$, 0.3), 181 (MeCH=C(CH$_2$OSen)CO$^+$, 20), 132 (A*, 11), 83 ($C_4H_7CO^+$, 100); CI (isobutane): 330 ($M^+ + 1 - C_4H_7CO_2H$, 100), 132 (A, 68), 101 ($C_4H_7CO_2H + 1$, 18).

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \qquad 578 \qquad 546 \qquad 436\,\mathrm{nm}}{-12.0 \quad -12.6 \quad -14.0 \quad -20.7} \; (c = 0.9,\ \mathrm{CHCl_3}).$$

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