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A PETASOL DERIVATIVE FROM *HOEHNEPHYTUM IMBRICATUM**

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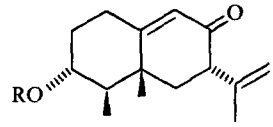
Key Word Index—*Hoehnephytum imbricatum*; Compositae; Senecioneae; eremophilane; petasol ester.

There have been no reports on the chemistry of the small Brazilian genus *Hoehnephytum*. We have now investigated *H. imbricatum* (Gardn.) Cabrera. The roots afforded lupenone, cycloartenone and the petasol esters **1** [1] and **2** [1]. The aerial parts contained a mixture of the olefins **4a**–**4c**, germacrene D, bicyclogermacrene, α-humulene, squalene, lupenone and a further petasol ester, the 3-ethyl crotonate **3**. The structure of **3** followed from the ^{1}H NMR data (Table 1), especially if compared with those of

Table 1. ^{1}H NMR spectral data of compound **3**

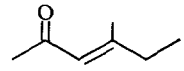
1α-H	2.35 *ddd*	12-H	4.99 *dq*
1β-H	2.53 *dddd*	12′-H	4.83 *br. s*
2α-H	1.49 *m*	13-H	1.75 *br. s*
2β-H	1.62 *m*	14-H	1.25 *s*
3β-H	4.92 *ddd*	15-H	0.97 *d*
4α-H	1.69 *m*	OCOR	5.66 *dq*
6α-H	1.90 *dd*		2.19 *br. q*
6β-H	2.04 *dd*		1.09 *t*
7β-H	3.12 *dd*		2.18 *d*
9-H	5.79 *d*		

J (Hz): 1α, 1β = 14; 1α, 2α = 4; 1α, 2β = 2; 1β, 2α = 14; 1β, 2β = 4; 1β, 9 = 1.5; 2α, 2β = 14; 2α, 3β = 3β, 4α = 11; 2β, 3β = 4; 4, 15 = 6.5; 6α, 6β = 13; 6α, 7β = 14; 7β, 12 = 1; 2′, 4′ = 2′, 6′ = 1; 4′, 5 = 7.5.



1 R = Ang
2 R = Sen

3 R =



$Me(CH_2)_nCH = CH_2$

4a $n = 8$
4b $n = 9$
4c $n = 10$

the corresponding angelate. Its structure was established unambiguously by X-ray analysis [1]. Therefore the isopropenyl group in **1**–**3** has the α-configuration. Consequently in the corresponding petasol esters previously reported [2, 3] the stereochemistry at C-7 has to be changed. The compounds isolated from the *Hoehnephytum* species indicate that this genus is not very closely related to the South American *Senecio* species, but certainly is a typical member of the tribe Senecioneae.

EXPERIMENTAL

The air-dried plant material (voucher RMK 8390) was extracted with Et_2O–petrol (1:2). The extracts obtained were first separated by CC on Si gel and further by repeated TLC (Si gel). The hydrocarbons were identified by their ^{1}H NMR spectra and by GC/MS and the other known compounds by comparing their IR and ^{1}H NMR spectra with those of authentic material. The roots (160 g) afforded 20 mg lupenone, 12 mg cycloartenone,

* Part 317 in the series "Naturally Occurring Terpene Derivatives". For Part 316 see Bohlmann, F., Jakupovic, J., Dhar, A. K., Robinson, H. and King, R. M. (1981) *Phytochemistry* **20**, 843.

15 mg **1** and 15 mg **2**, while the aerial parts (400 g) yielded 200 mg **4a–4c** (*ca* 1:1:1), 50 mg α-humulene, 150 mg germacrene D, 5 mg bicyclogermacrene, 5 mg squalene, 50 mg lupenone, 40 mg **1**, 5 mg **2** and 20 mg **3** (Et_2O–petrol, 1:3).

Petasol-[*3-methyl-pent-*2E*-enoate*] (**3**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1715, 1650 (C=CCO_2R), 1680 (C=CCO); MS *m/z* (rel. int.): 330.220 (M^+, 1.6) ($C_{21}H_{30}O_3$), 216 (M − RCO_2H, 100), 201 (216 − Me, 56), 97 ($C_5H_9CO^+$, 80).

$$[\alpha]_{24°}^{\lambda} = \frac{\begin{matrix}589 & 578 & 546 & 436\,nm\\ +37.2 & +38.6 & +44.1 & +68.6\end{matrix}}{} \quad (c = 0.29).$$

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