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SHORT REPORTS

A NORSESQUITERPENE FROM *SENECIO HUMILLIMUS*[*]

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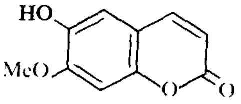
Key Word Index—*Senecio humillimus*; Compositae; norsesquiterpene; noreremophila-dien-one.

The aerial parts of *Senecio humillimus* Sch. Bip. afforded, in addition to isoscopoletin (**1**) and 9,10-dehydrofukinone (**2**) [1], a further ketone, the trinorsesquiterpene **3**. The structure of **3** followed from the molecular formula, the IR data and the ^{1}H and ^{13}C NMR data (Table 1). Spin decoupling and addition of a shift reagent allowed the assignment of nearly all the NMR signals, though some signals were overlapped even in different solvents. Though the absolute configuration was not determined, the proposed one is very likely, as it is the one found in all of the eremophilene derivatives so far isolated from members of the Compositae. **3** is a des-isopropylidene-6,7,9,10-dehydrofukinone. Further investigations of South American *Senecio* species are necessary to establish their relationship to Old World groups, especially those from South Africa.



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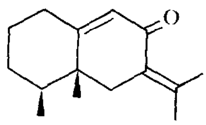

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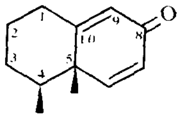

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Table 1. NMR spectral data of **3** (400 MHz, $CDCl_3$, TMS as internal standard)

	^{1}H NMR	Δ*	^{13}C NMR	
1-H	2.49 *ddd*	0.05	C-1	30.4 *t*
1′-H	2.34 *ddd* (*br*)	0.04	C-2	28.1 *t*
2-H	1.98 *m*	0.0	C-3	33.2 *t*
2′-H	1.6–1.4 *m*	0.0	C-4	41.8 *d*
3-H			C-5	41.7 *s*
3′-H			C-6	155.7
4-H	1.50 *m*	0.0	C-7	127.6
6-H	7.06 *d*	0.05	C-8	168.8
7-H	6.24 *dd*	0.22	C-9	124.9
9-H	6.09 *dd*	0.21	C-10	155.7
11-H	1.08 *d*	0.02	C-11	16.2 *q*
12-H	1.15 *s*	0.05	C-12	17.2 *q*

*Δ—values after addition of $Eu(fod)_3$.

J (Hz): 1,1′ = 13; 1,2 = 5; 1,2′ = 13; 1,9 = 1,5; 1′,2 ~ 4; 1′,2′ = 2; 4,12 = 6; 6,7 = 10; 7,9 = 15.

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[*] Part 335 in the series "Naturally Occurring Terpene Derivatives." For Part 334 see Bohlmann, F., Dhar, A. K., Jakupovic, J., King, R. M. and Robinson, H. (1981) *Phytochemistry* **20**, 1425.

EXPERIMENTAL

The air-dried aerial parts, voucher RMK 7407, collected in Bolivia, were extracted with Et_2O–petrol (1:2). The resulting extract, on separation by column chromatography and TLC (Si gel), afforded 7 mg **1**, 228 mg **2** and 15 mg **3** (Et_2O–petrol, 1:10), colourless oil, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1665, 1625, 1605 (C=CCO, C=C); MS m/z (rel. int.): 176.120 (M^+, 100) ($C_{12}H_{16}O$), 161 (M − Me, 41), 147 (M − CHO, 20), 121 (147 − C_2H_2, 68);

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589}{-12.4}\quad\frac{578}{-13.9}\quad\frac{546}{-17.2}\quad\frac{436\,\text{nm}}{-56.3}\ (c = 1.0,\ CHCl_3).$$

REFERENCE

1. Hagashi, K., Nakamura, H. and Mitsuhashi, H. (1973) *Phytochemistry* **12**, 2931.

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THE GERMACRADIENOLIDE ISABELIN FROM *ZEXMENIA VALERII*: STEREOCHEMISTRY AND CONFORMATION OF SCANDENOLIDE AND DEOXYMIKANOLIDE*

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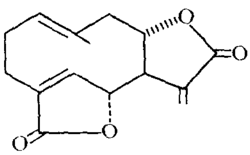
Key Word Index—*Zexmenia valerii*; Compositae; Heliantheae; sesquiterpene lactones; isabelin; germacradienediolide; scandenolide; deoxymikanolide; stereochemistry; conformation.

Abstract—The isolation of the germacradienolide isabelin from *Zexmenia valerii* is reported. In contrast to isabelin, the closely related lactones deoxymikanolide and scandenolide exist in solution in one conformation only, which is similar to that of dihydromikanolide in the solid state. The C-3 stereochemistry of scandenolide is revised.

Several *Zexmenia* species have yielded heliangolides [1–5] or santanolides [6, 7] as well as other terpenoids [6, 7]. We have now isolated the germacradienolide isabelin (**1**) from *Zexmenia valerii* Standl. & Steyerm. Isabelin has been reported previously only from certain small populations of *Ambrosia psilostachya* DC. [8, 9] and *A. artemisiifolia* [10].

In $CDCl_3$ solution, isabelin is a 10:7 mixture of two conformers [8–10] which can be differentiated by NMR spectrometry and give rise to different photochemistry [11, 12]. On the other hand, the ^1H NMR spectra of the very similar dilactones deoxymikanolide (**2a**) and scandenolide (**2b**) in DMSO-d_6 at 90 MHz seemed to indicate only one conformer for each compound [13]. We



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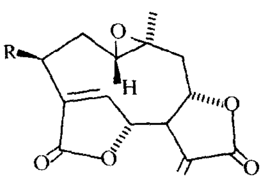
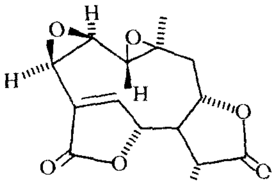


2a R = H
2b R = OAc



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