

11 β ,13-DIHYDROLACTUCIN, A SESQUITERPENE LACTONE FROM *LAUNAEA MUCRONATA**

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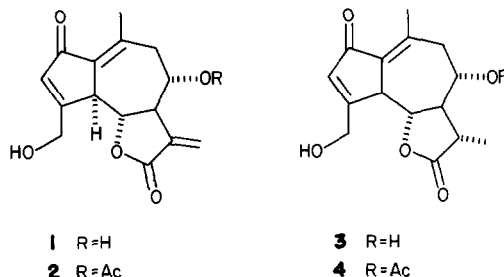
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Key Word Index—*Launaea mucronata*; Compositae; sesquiterpene lactone; guaianolides.

Abstract—The roots of *Launaea mucronata* afforded, in addition to lactucin, lactucin-8-*O*-acetate and the corresponding dihydro derivative, 11 β ,13-dihydrolactucin.

So far little is known of the chemistry of the genus *Launaea*, only some widespread triterpenes are reported [1]. The roots of *L. mucronata* Forssk. afforded lactucin (1) [2], the acetates 2 [3] and 4 [3] as well as the corresponding diol 3, not isolated previously. The structure followed from the molecular formula (C₁₅H₁₈O₅), the ¹H NMR spectral data (Table 1) and spin decoupling. Irradiation of a narrowly-split double quartet at δ 6.43 caused a sharpening of two broadened doublets at 4.86 and 4.53, which therefore were the signals of H-15, as the downfield shift of the former signal was typical for a H-3 proton of lactones like lactucin. Irradiation of the triplet at δ 3.65 collapsed the broadened doublet at 3.57 to a doublet and the three-fold doublet at 2.13 to a double doublet, thus allowing the assignment of the H-5 and H-7 signals. The latter was further coupled with a three-fold doublet at δ 3.75 and a double quartet at 2.57. Since the latter was coupled with the methyl doublet δ 1.44 and the signal at 3.75 with two double doublets at 2.71 and 2.32, all signals could be assigned. The coupling $J_{7,11}$ indicated the α -orientation of the C-11 methyl group. Compound 3 therefore was 11 β ,13-dihydrolactucin. Consequently the ¹H NMR spectral data were close to those of the corresponding acetate isolated from a *Lactuca* species [3].

The chemistry of the *Launaea* species supports its placement in the subtribe Crepidinae [4], as several typical genera of this group contain lactucin and closely related lactones [5].



EXPERIMENTAL

Fresh roots of *L. mucronata* (1 kg) were extracted with 95% EtOH. The filtered and concd extract was diluted with H₂O and extracted with CHCl₃. The extract was separated by prep. TLC (Si gel) (CHCl₃-MeOH, 9:1) affording 1-4 as major compounds. The identity of 1, 2 and 4 was established by comparing their ¹H NMR spectra with those of authentic material.

11 β ,13-Dihydrolactucin (3). Colourless crystals, mp 91°, IR $\nu_{\text{CHCl}_3}^{\text{max}}$ cm⁻¹: 3410(OH), 1770 (γ -lactone), 1680, 1635, 1620 (C=CCOC=C); MS m/z (rel. int.): 278.115 [M]⁺ (60)(C₁₅H₁₈O₅), 260 [M - H₂O]⁺ (19), 231 [260 - CHO]⁺ (35), 187 [231 - CO₂]⁺ (100). [α]_D + 8.7 (CHCl₃; c 0.63).

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Table 1. ¹H NMR spectral data of compound 3 (400 MHz, CDCl₃, TMS as int. standard)

H-3	6.43 dq	H-9 β	2.39 dd
H-5	3.57 dbr	H-11	2.57 dq
H-6	3.65 t	H-13	1.44 d
H-7	2.13 ddd	H-14	2.44 br s
H-8	3.75 ddd	H-15	4.86 br d
H-9 α	2.71 ddb	H-15'	4.53 br d

J (Hz): 3,5 = 3,15 = 1.5; 5,6 = 6,7 = 7,8 = 10; 7,11 = 11.5; 8,9 α = 11; 8,9 β = 1; 4 α , 9 β = 14; 15,15' = 18.

*Part 402 in the series "Naturally Occurring Terpene Derivatives". For Part 401 see Bohlmann, F., Wegener, P. and Jakupovic, J. (1982) *Phytochemistry* **21**, 1109.