

A GERMACROLIDE GLUCOSIDE FROM *LACTUCA TATARICA*

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(Received 27 October 1997)

Key Word Index—*Lactuca tatarica*; Asteraceae; Lactuceae; sesquiterpene lactone; germacrolide; glucoside.

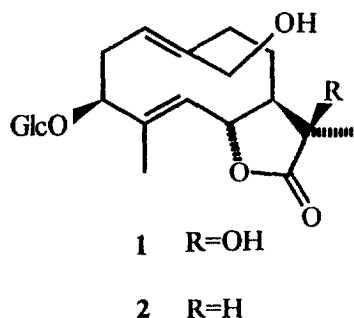
Abstract—Tataroside, a new germacrolide glucoside, was isolated from the roots of *Lactuca tatarica* and characterized as 3 β ,11 β ,14-trihydroxy-11,13-dihydrocostunolide-3- β -glucopyranoside on the basis of mass and ^1H NMR spectra, including ^1H - ^1H COSY experiments. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

In our earlier study on the root constituents of *Lactuca tatarica* C. A. Meyer [1], 11 sesquiterpene lactone aglycones and glycosides were characterized after successive fractionation of the ethanol extract on silica gel. Careful analysis of the most polar fractions of the chromatogram has now allowed the isolation of a new germacrolide glucoside, named tataroside (**1**), whose structural assignment we report herein.

RESULTS AND DISCUSSION

Tataroside (**1**) was the most polar of the above mentioned sesquiterpene lactone constituents. Its ^1H NMR and mass spectral data strongly suggested that the compound was an oxygenated analogue of **2**, a germacrolide glucoside previously reported by us from roots of *Lactuca virosa* [2]. The ESMS of **1** showed a $[\text{M} + \text{Na}]^+$ peak at m/z 467 consistent with the molecular formula, $\text{C}_{21}\text{H}_{32}\text{O}_{10}$, containing one oxygen more than that of **2**. Since in the ^1H NMR spectrum of **1** the H-11 signal was absent and the Me-13 signal appeared as a singlet at δ 1.66, the remaining oxygen atom of the empirical formula had to be attached to C-11 in the form of hydroxyl group. The configuration assignment of this hydroxyl followed from the chemical shift of the H-6 signal, which was deshielded by 0.61 ppm when compared with that of **2** (Table 1). This



deshielding effect indicated a 1,3-diaxial relationship between H-6 and the C-11 hydroxyl group and therefore a β -orientation of this group. The signals of the C-7 and C-8 protons were less affected. ^1H - ^1H COSY experiments confirmed that the H-1 and H-3 signals partially overlapped with those of H-5 and glucose H-1, respectively, while the H-8 β signal overlapped with that of H-9 α . The above data allowed the formulation of **1** as 3 β ,11 β ,14-trihydroxy-11,13-dihydrocostunolide-3- β -glucopyranoside.

Costunolide-3- β -glucopyranoside and its analogues were reported earlier from *Lactuca* [1, 2], *Picris* [3], *Youngia* [4], *Sonchus* [5], *Cichorium* [6] and *Hypochoeris* [7] species of tribe Lactuceae.

EXPERIMENTAL

Plant material and the procedures for the extraction and fractionation of Et-OH extract of the fresh roots

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Table 1. ^1H NMR data of compound **1** (500.13 MHz, pyridine- d_5 , TMS as int. standard, δ -values)

H	1	2 [Ref. 2]
1	4.94 <i>br d</i> *	4.88 <i>dd</i>
2 α	2.54 <i>br dd</i>	2.52 <i>br ddd</i>
2 β	2.71 <i>ddd</i>	2.68 <i>ddd</i>
3	4.84 <i>dd</i> †	4.81 <i>dd</i>
5	4.96 <i>br d</i> *	4.90 <i>br d</i>
6	5.37 <i>dd</i>	4.76 <i>dd</i>
7	1.84 <i>m</i>	1.66 <i>m</i>
8 α	1.95 <i>m</i>	1.66 <i>m</i>
8 β	2.22 <i>m</i> ‡	1.81 <i>m</i>
9 α	2.22 <i>m</i> ‡	1.81 <i>m</i>
9 β	3.23 <i>br d</i>	3.10 <i>br dd</i>
11	—	2.31 <i>dq</i>
13	1.66 <i>s</i>	1.23 <i>d</i>
14	4.49 <i>br d</i>	4.47 <i>br d</i>
14'	4.16 <i>br d</i>	4.16 <i>br d</i>
15	1.90 <i>s</i>	1.93 <i>s</i>
Glucose moiety		
1	4.85 <i>d</i> †	4.83 <i>d</i>
2	4.08 <i>br dd</i>	4.08 <i>dd</i>
3	4.18–4.27 <i>m</i>	4.18–4.27 <i>m</i>
4	4.18–4.27 <i>m</i>	4.18–4.27 <i>m</i>
5	3.91 <i>m</i>	3.91 <i>m</i>
6	4.40 <i>dd</i>	4.40 <i>dd</i>
6'	4.60 <i>br d</i>	4.60 <i>br d</i>

*, †, ‡ Overlapped signals.

$J(\text{Hz})$ compound **1**: 1, 2' = 12.2; 2, 2' = 12.2; 2, 3 = 5.9; 2', 3 = 10.6; 5, 6 = 6, 7 = 9.6; 14, 14' = 12.1; glucose moiety: 1, 2 = 7.8; 5, 6 = 5.1; 6, 6' = 11.7.

(490 g) of *L. tatarica* were described in the previous paper [1]. The most polar CHCl_3 –MeOH (17:3) frs

from CC on silica gel were further purified by prep. TLC (Merck, Art. 5553) using CHCl_3 –MeOH (4:1) to give 8.6 mg of **1**.

Tataroside (**1**)

Colourless gum. ESMS m/z (rel. int.): 467 $[\text{M} + \text{Na}]^+$ (100); ^1H NMR: Table 1.

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