Chemistry of Natural Compounds, Vol. 42, No. 4, 2006

ISOLATION OF GROSSHEMIN FROM THE SIBERIAN POPULATION OF *Centaurea scabiosa*

E. A. Krasnov,[1] V. A. Raldugin,[2] T. V. Kadyrova,[1] and I. P. Kaminskii[1]

UDC 547.914

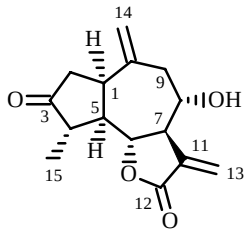
Centaurea scabiosa (Asteraceae) has a wide range in the northern hemisphere and is common in Siberia, Europe, and Scandinavia [1]. This plant has long been interesting for its polyacetylene derivatives [2-4], after which Czech researchers discovered in it the germacranolide scabiolide [5, 6], which is structurally similar to cnicin [7].

We investigated the chemical composition of the air-dried aerial part of *C. scabiosa* from Tomsk District using extraction by diethylether and did not isolate scabiolide as reported earlier [6].

Isolation of Lactone 1. Raw material (0.5 kg) was soaked in $CHCl_3$ (3 × 2 L) at room temperature. Filtration and removal of solvent produced a syrupy extract in 2% yield. The resulting product (10 g) was chromatographed over SiO_2 with elution by $CHCl_3$ and then $CHCl_3$:$(CH_3)_2CO$ mixtures with an increasing gradient of the latter. Removal of solvent from the $CHCl_3$:$(CH_3)_2CO$ (9:1) eluent produced a precipitate that had mp 200-201°C and R_f 0.13 ($CHCl_3$) after washing with Et_2O.

Lactone 1 was a white with a cream tint finely crystalline powder, mp 200-201°C, lit. mp [10] 205°C. The IR spectrum had the following absorption bands (ν, cm^{-1}): 3475 (OH), 1740 (C=O of a 5-membered ring conjugated to an unsaturated bond), 1650 (C=O), 1450 and 1410 (=CH_2).

Chromatography of the $CHCl_3$ extract isolated grosshemin (**1**), which has been known since 1964 [8]. Its correct structure was established by Breton et al. [9]; the stereochemistry, by Samek et al. [10]. The latest publication did not completely assign the signals for H-1 and H-4 in the PMR spectrum and did not describe the signals for H-2 and H-5 (in DMSO-d_6 solution).



1

Herein we report these data, which are necessary for rapid and reliable identification of this important germacranolide. Furthermore, the ^{13}C NMR spectrum is described and interpreted using two-dimensional ^{13}C—^{1}H and ^{1}H—^{1}H NMR spectra (Table 1).

The absence of scabiolide in the Siberian population of *C. scabiosa* may indicate that a separate race of this species is present in which lactone **1** is synthesized instead of scabiolide. Lactone **1** was found for the first time in a plant of the genus *Centaurea*.

1) Siberian State Medical University, 634050, Tomsk, fax (3822) 53 33 09, e-mail: krasnov.37@mail.ru; 2) N. N. Vorozhtsov Novosibirsk Institute or Organic Chemistry, Siberian Division, Russian Academy of Sciences, 630090, Novosibirsk, fax (3832) 34 47 52, e-mail: raldugin@nioch.nsc.ru. Translated from Khimiya Prirodnykh Soedinenii, No. 4, p. 397, July-August, 2006. Original article submitted March 23, 2006.

0009-3130/06/4204-0495

TABLE 1. ^{13}C NMR and PMR Spectra of **1** (DMSO-d_6, δ, ppm, TMS)

C atom	δ_C	δ_H
1	39.33 d	2.62 dt
2	42.69 t	1.88 (2A, ddd); 2.03 (2B, dd)
3	218.76 s	-
4	46.11 d	1.73 m
5	49.78 d	1.84 dt
6	82.34 d	3.56
7	48.82 d	2.58
8	71.82 d	3.18
9	47.36 t	1.69 (9A, dd); 2.21 (9B, dd)
10	144.62 s	-
11	137.90 s	-
12	169.56 s	-
13	123.56 t	4.19 (13A, br.m); 4.48 (13B, m)
14	114.07 t	5.60 (14A, dd); 5.71 (14B, dd)
15	14.47 d	0.60 (3H, d)

REFERENCES

1. *Flora of the USSR*, Vol. XXVII [in Russian], Moscow and Leningrad (1963), p. 503.
2. N. Lofgren, *Acta Chem. Scand.*, **3**, 82 (1949).
3. F. Bohlmann, S. Portulka, and J. Ruhnki, *Chem. Ber.*, **91**, 1642 (1958).
4. A. A. Andersen, J. Lam, and P. Wrang, *Phytochemistry*, **16**, 1829 (1977).
5. M. Suchy, V. Herout, and F. Sorm, *Collect. Czech. Chem. Commun.*, **27**, 1905 (1962).
6. M. Suchy, Z. Samek, V. Herout, and F. Sorm, *Collect. Czech. Chem. Commun.*, **33**, 2238 (1968).
7. S. M. Adekenov, Yu. V. Gatilov, I. Yu. Bagryanskaya, and V. A. Raldugin, *Sib. Khim. Zh.*, No. 2, 76 (1993).
8. K. S. Rybalko, A. M. Ban′kovskii, and P. N. Kibal′chich, *Zh. Obshch. Khim.*, **34**, 1358 (1964).
9. J. L. Breton, G. B. Marrero, and G. A. Gonsalez, *An. Quim.*, **64**, 1015 (1968).
10. Z. Samek, M. Holub, K. Vokac, B. Drozdz, G. Jommi, P. Gariboldi, and A. Corbella, *Collect. Czech. Chem. Commun.*, **37**, 2611 (1972).