Chemistry of Natural Compounds, Vol. 47, No. 2, May, 2011 [*Russian original No. 2, March-April, 2011*]

ISOLATION OF REPIN FROM THE AERIAL PART OF *Centaurea scabiosa*

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UDC 547.972

Centaurea scabiosa L. (Asteraceae) is of great scientific and practical interest among the flora of Siberia. Its chemical composition includes various groups of compounds, of which sesquiterpene lactones (SL) have special significance. The guaiane-type SLs grosshemin and cynaropicrin were previously isolated for the first time from *C. scabiosa* and identified [1, 2].

Herein we report the isolation from the aerial part of *C. scabiosa* of another guaianolide, repin.

The total SLs were separated over a column of silica gel (sorbent:compound ratio 30:1) with elution by petroleum ether and a gradient of petroleum ether:EtOAc with increasing fraction of the latter.

Elution of the column by petroleum ether:EtOAc (90:10) afforded a brownish-yellow oil that was a mixture of eight compounds according to TLC. It was rechromatographed over a column of silica gel (sorbent:compound ratio 50:1) with elution by hexane and hexane:EtOAc.

Removal of solvent from fractions eluted from the column by hexane afforded a colorless oil with crystalline inclusions that was soluble in benzene and $CHCl_3$; partly soluble in EtOH, EtOAc, Et_2O, and hexane; and practically insoluble in H_2O.

Purification of the fraction with hexane followed by work up of the residue with EtOH (80%) isolated colorless crystals, mp 153–155°C (EtOH). IR spectrum (KBr, ν, cm^{-1}): 3500 (OH), 1767 (γ-lactone CO), and 1730 (ester).

The PMR spectrum of the isolated compound (Table 1) showed doublets at 2.77 and 3.21 ppm with SSCC 6.0 Hz in addition to a singlet for methyl protons CH_3 (19) that were characteristic of epoxymetacrylic acid in the C-8 position of the guaiane skeleton.

Resonances of exocyclic methylene protons conjugated to a γ-lactone ring carbonyl were also found as a pair of doublets at 6.15 and 5.55 ppm. Resonances of protons of a second exocyclic methylene were observed as broad singlets at 5.12 and 4.96 ppm. A resonance at 4.90 ppm belonged to a hemiacyl proton. Table 1 presents the PMR and ^{13}C NMR spectra.

The compound was identified as the guaiane-type SL repin based on the physicochemical properties and spectral data [3]. It was isolated from the first time from *C. scabiosa*.

Thus, column chromatography over silica gel isolated for the first time the guaianolide repin from the aerial part of *C. scabiosa*. Repin was characterized before as having pronounced antibacterial and antifungal activity against *Entamoeba histolytica* and *Trichomonas vaginalis* [4].

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TABLE 1. ^{13}C NMR and PMR Spectra of Repin

Atom, group	δ_C, ppm	δ_H, ppm (J/Hz)	Atom, group	δ_C, ppm	δ_H, ppm (J/Hz)
C-1, H-1	47.72 d	3.28 (ddd, J = 10.0, 9.0, 9.0)	C-10	138.57 s	–
C-2, H-2	38.80 t	1.99 (ddd, J = 15.0, 10.0, 5.0)	C-11	142.69 s	–
		2.36 (ddd, J = 15.0, 9.0, 7.0)	C-12	169.03 s	–
C-3, H-3	75.25 d	4.22 (dd, J = 7.0, 5.0)	C-13, H-13	121.09 t	5.55 (d, J = 3.5); 6.15 (d, J = 3.0)
C-4	69.11 s	–	C-14, H-14	117.99 t	4.96 (br.d, J = 1.0); 5.12 (br.d, J = 1.0)
C-5, H-5	55.03 d	2.21 (dd, J = 11.5, 9.0)	C-15, H-15	48.90 t	3.20 (d, J = 5.0); 3.38 (d, J = 5.0)
C-6, H-6	77.40 d	4.90 (dd, J = 11.5, 9.5)	C-16	170.18 s	–
C-7, H-7	45.93 d	3.12 (dddd, J = 9.5, 9.0, 3.5, 3.0)	C-17	54.1 s	–
C-8, H-8	75.43 d	5.24 (ddd, J = 9.0, 5.0, 3.5)	C-18, H-18	53.01 t	2.77 (d, J = 6.0); 3.21 (d, J = 6.0)
C-9, H-9	36.31 t	2.40 (dd, J = 15.0, 3.5)	C-19, H-19	17.44 q	1.55 (3H, s)
		2.82 (dd, J = 15.0, 5.0)			

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