XANTHONES AND FLAVONOIDS OF Gentiana barbata

O. Pureb, Ya. Zhim'vansan,
and Kh. Oyuun

UDC 547.972

Barbed gentian Gentiana barbata Froel. (family Gentianaceae) is a valuable medicinal plant which is a component of numerous drugs of Mongolian-Tibetan medicine, used for the treatment of diseases of the liver, the gall bladder, and the gastro-intestinal tract [1]. The plant growing in the Mongolian Peoples' Republic has been little studied chemically.

In order to isolate the γ-yrone derivatives, the comminuted air-dry raw mateial (0.5 kg) collected in August, 1987 in the environs of Ulan-Bator was exhaustively extracted with ethanol at room temperature. The concentrated extract was diluted with water in a ratio of 1:1 and filtered, and the filtrate was treated successively with chloroform, ethyl acetate, and butanol. By column chromatogrpahy on silica gel in a gradient chloroform—methanol system, the chloroform and ethyl acetate fractions yielded the known xanthones decussatin, gentiacaulein, 1-β-D-glucopyranosyloxy-3,7,8-trimethoxyxanthione, 1-β-D-glucopyranosyloxy-7-hydroxy-3,8-dimethoxyxanthone, and 1-primeverosyloxy-7-hydroxy-3,8-dimethoxyxanthone, and also the flavonoid luteolin. These compounds have been isolated previously from barbed gentian [2, 3].

In the present paper we give the results of a study of the chemical structure of three substances isolated from the ethyl acetate fraction.

Substance (I) – $C_{21}H_{22}O_{11}$, mp 150-152°C (from methanol) was, according to its UV spectrum (λ_{max}^{MeOH}, nm: 244, 256, 302, 365) a 1,3,7,8-tetrasubstituted xanthone [4]. This was confirmed by a study of its PMR spectrum (DMSO-d_6, δ scale), which showed the signals of protons at (ppm) 7.36 and 7.20 (both d, 9 Hz, H-6 and H-5, respectively), 6.86 and 6.72 (both d, 2.5 Hz, H-4 and H-2), 3.30 (d, 6.0 Hz, H-1' of a carbohydrate residue), and 3.94 (s, 8-OCH_3), while a signal at 13.12 ppm showed the presence of free phenolic hydroxy group at C-1 or C-8.

The PMR spectrum of the acetyl derivative obtained by the acetylation of compound (I) with acetic anhydride in pyridine contained the signals of the protons of four acetoxy groups in the carbohydrate moiety at 1.90-2.10 ppm and of one Ar—$OCO\underline{H}_3$ group at 2.40 ppm. Consequently, substance (I) was a monoglycoside.

In actual fact, the acid hydrolysis of glycoside (I) gave an aglycon with the composition $C_{15}H_{12}O_6$, mp 154-155°C, identical with gentiacaulein (1,7-dihydroxy-3,8-dimethoxyxanthone) and D-glucose.

The UV spectrum of glycoside (I) taken with the addition of solutions of $AlCl_3$ and HCl showed the presence in it of a chelate hydroxy group [4]. This agreed with the PMR spectrum (δ 13.12 ppm).

The SSCC of the doublet signal of the anomeric proton (δ 5.30 ppm, J = 6.0 Hz) showed a β-glycosidic bond of D-glucose with the aglycon.

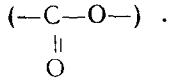
Thus, substance (I) had the structure of 7-β-D-glucopyranosyloxy-1-hydroxy-3,8-dimethoxyxanthone and was a new natural compound.

Substance (II) ($C_{16}H_{12}O_5$, mp 252-254°C (from methanol)) gave a mass spectrum with peaks of ions having m/z 300 $(M)^+$, 152 (A_1), and 148 (B_1), and, according to its UV spectrum λ_{max}^{MeOH}, nm: 253, 267, 340) was a flavone derivative. UV spectra with diagnostic reagents showed the presence of free hydroxy groups in the C-5 and C-7 positions of the flavone nucleus and the absence of an ortho-dihydroxy grouping [5].

Institute of Chemistry, Academy of Sciences of the Mongolian Peoples' Republic, Ulan-Bator. Translated from Khimiya Prirodnykh Soedinenii, No. 2, pp. 284-285, March-April, 1991. Original article submitted October 14, 1988; revision submitted November 2, 1990.

0009-3130/91/2702-0245$12.50

By studying its UV, mass, and PMR spectra and also by direct comparison with an authentic sample, substance (II) was identified as diosmetin (3',5,7-trihydroxy-4'-methoxyflavone) [5].

Substance (III) – $C_{30}H_{48}O_3$, mp 304-305°C (from ethanol) $[\alpha]_D^{20}$ + 72° (methanol); ν_{max}^{KBr}, cm^{-1}: 3500-3400 (OH group, 3030 (>CH.); 1700  $(-\underset{\underset{O}{\|}}{C}-O-)$. Mass spectrum: m/z 456 (M^+), 240, 233, 203, 196, 133 – was identified as oleanolic acid.

LITERATURE CITED

1. Ts. Khaidav, B. Altanchimeg, and T. S. Varlamova, Medicinal Plants in Mongolian Medicine [in Russian], Ulan-Bator (1985).
2. G. G. Nikolaeva, V. I. Glyzin, D. K. Fesenko, and A. V. Patudin, Khim. Prir. Soedin., 255, 841 (1980); 392 (1981).
3. V. D. Galinskaya, "Flavonoid content of some Siberian species of gentian," in: Plant Resources of Siberia and Their Use [in Russian], Novosibirsk (1978), p. 50.
4. V. I. Glyzin, G. G. Nikolaeva, and T. D. Dargaeva, Natural Xanthones [in Russian], Nauka, Novosibirsk (1986), p. 174.
5. T. J. Mabry, K. R. Markham, and M. B. Thomas, The Systematic Identification of Flavonoids, Springer, New York (1970), p. 354.

CHEMICAL COMPOSITION OF Potentilla fruitcosa

III. FLAVONOIDS AND FREE STEROLS

T. V. Ganenko, A. L. Vereshchagin,
and A. A. Semenov

UDC 547.972-547.926

Continuing investigation begun previously [1], from the chloroform-soluble part of an aqueous-methanolic extract of <u>Potentilla fruticosa</u> L. we have obtained two fractions. Fraction (I), containing the total free sterols, was separated on a column of silica gel with elution by hexane–acetone (10:1).

The free sterols were identified by chromato-mass spectrometry. As a result of the analysis we identified components with M^+ 414 – β-sitosterol, M^+ 412 – stigmasterol, and M^+ 400 – campesterol.

In fraction (II) a substance with m/z M^+ 344, $C_{18}H_{16}O_7$, mp 176-178°C, was identified as 3',4',7-trimethylquercetin [2].

From the butanol-soluble fraction of the aqueous methanolic extract, by chromatography on silica gel in the solvent system chloroform–methanol–water (80:35:7) we isolated a flavonoid glycoside $C_{28}H_{16}O_{15}$, mp 200-203°C, $[\alpha]_{546}$ – 59.8° (c 1.17; pyridine). The glycoside obtained was identified as quercetin 3-β-D-galactopyranoside 6"-gallate [3]. The position of attachment of the acyl residue followed from the chemical shifts of the C6" and C5" carbon atoms by +2.4 and –2.3 ppm, respectively, as compared with quercetin galactoside.

The individual compounds were identified by the use of NMR spectroscopy.

This is the first time that any of these compounds have been detected in this plant.

LITERATURE CITED

1. T. V. Ganenko and A. A. Semenov, Khim. Prir. Soedin., 856 (1989).
2. A. G. Valesi, R. Rogrigez, G. V. Velse, and T. J. Mabry, Phytocheistry, <u>11</u>, 2821 (1982).
3. A. Nahrstedt, K. Dumkow, and B. Janistyn, Tetrahedron Lett., 559 (1974).

Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR, Irkutsk. Translated from Khimiya Prirodnykh Soedinenii, No. 2, pp. 285-286, March-April, 1991. Original article submitted May 28, 1990.