2. K. S. Rybalko, Natural Sesquiterpene Lactones [in Russian], Meditsina, Moscow (1978).
3. A. I. Shreter, The Medicinal Flora of the Soviet Far East [in Russian], Meditsina, Moscow (1975), p. 287.
4. S. L. Vichkanova, M. A. Rubinchik, and A. I. Shreter, Rast. Res., 5, No. 2, 224 (1969).
5. M. A. Rubinchik, "The trichomonadal properties of higher plants," in: Phytoncides [in Russian], Naukova Dumka, Kiev (1972), p. 128.
6. K. S. Rybalko, O. A. Konovalova, N. D. Orishchenko, and A. I. Shreter, Rast. Res., 12, No. 3, 387 (1976).
7. I. D. Sham'yanov, A. Mallabaev, and G. D. Sidyakin, Khim. Prir. Soedin., 788 (1983).
8. A. K. Singhal, P. K. Chowdhury, R. P. Sharma, J. N. Bawah, and W. Herz, Phytochemistry, 21, No. 2, 462 (1982).
9. I. D. Sham'yanov, N. D. Abdullaev, G. P. Siyakin, and K. O. Taizhanov, Khim. Prir. Soedin., 667 (1981).
10. A. G. Gonzalez, V. Derias, G. Alonso, and E. Estevez, Planta Med., 40, No. 2, 179 (1980).
11. L. D. Modonova, A. A. Semenov, Ts. Zhapova, N. D. Ivanova, A. K. Dzhaparova, A. P. Fedoseev, E. P. Kirdei, and T. I. Malkova, Khim.-farm. Zh., No. 12, 1472 (1986).
12. P. Piacentini, R. Benzi Cipelli, E. Zizzi, G. Gorini, L. Ciardelli, and F. Castelli, Planta Med., No. 6, 548 (1986).

COUMARINS OF Physochlaina physaloides

G. Daandai, R. Naran, G. Gantimur, A. I. Syrchina, M. F. Larin, and A. A. Semenov

UDC 547.814:582.925

The air-dry roots of the plant Physochlaina physaloides (L) Don, family Solanaceae, which is used in Indo-Tibetan and traditional Mongolian medicine, that had been gathered in September, 1984, were extracted with 80% ethanol. The extract was concentrated in vacuum to small volume (1.5 liters from 10 kg of roots) and was extracted successively with hexane, chloroform, ethyl acetate, and butanol. By column chromatography on silica gel [chloroform–methanol (99:1)] the combined chloroform and ethyl acetate extracts yielded umbelliferone (I), $C_9H_6O_3$, mp 234-235°C [$\lambda_{max}^{CH_3OH}$ 256 and 325 nm] and scopoletin (II), $C_{10}H_8O_4$, mp 206-207°C [$\lambda_{max}^{CH_3OH}$ 230, 256, 298, and 343 nm] [2].

In the cold, the aqueous residue deposited a crystalline mixture of two coumarin glycosides (III and IV), which were separated by preparative chromatography on silica gel [chloroform–methanol (4:1)]. Compound (III), with the composition $C_{16}H_{18}O_9$, mp 210-211°C, and

TABLE 1. Chemical Shifts of the C Atoms of Fabriatrin (δ, ppm, relative to TMS, DMSO-d_6)

C atom	δC	C atom	δC	C atom	δC
2	160,6	9	149,0	5g	76,7
3	113,4	10	112,4	6g	68,3
4	144,3	OCH_3	56,1	1x	104,2
5	109,9	1g	99,6	2x	73,1*
6	146,1	2g	73,4*	3x	76,7
7	149,9	3g	75,5	4x	69,3
8	103,2	4g	69,6	5x	65,7

Note. g, glucose; x, xylose; *, assignment ambiguous.

Institute of Chemistry of the Mongolian People's Republic, Ulan-Bator. Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR. Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 130-131, January-February, 1988. Original article submitted July 20, 1987.

$\lambda_{max}^{CH_3OH}$ 230, 283, and 341 nm, was identified from the results of acid hydrolysis and ^1H and ^{13}C NMR spectroscopy as scopoletin 7-O-β-D-glucopyranoside (scopolin) [2, 3].

On acid hydrolysis, compound (IV), with the composition $C_{21}H_{26}O_{13}$, mp 234-236°C, and $\lambda_{max}^{CH_3OH}$ 230, 283, and 340 nm, formed compound (II), D-glucose, and D-xylose. The order of attachment of the carbohydrate residues was determined by means of an analysis of the ^{13}C NMR spectrum of compound (IV). The assignment of the signals, which is given in Table 1, was made on the basis of literature information [3-5] and a comparison with the spectra of (II) and (III) and by the use of the INEPT and off-resonance methods. The downfield shift of the signal of C-6 of the glucose residue of (IV) as compared with its resonance in (III) indicated a 1 → 6 interglycoside bond. Measurements of the carbon-proton SSCCs in spectra without decoupling from protons gave values for J_{C1-H_1} of 160.5 and 159.6 Hz for the glucose and xylose residues, respectively. This shows their β-configuration [5].

Thus, the coumarin bioside from Ph. physaloides has the structure of scopoletin 7-O-β-D xylopyranosyl-(1 → 6)-β-D-glucopyranoside (fabiatrin) [2]. Together with scopolin, the latter has been isolated previously [6] from the species Physochlaina infundibulum growing in China.

LITERATURE CITED

1. Ts. Khaidab, B. Altanchimég, and T. S. Varlamova, Healing Plants in Mongolian Medicine [in Russian], Ulan-Bator (1985), p. 137.
2. R. D. H. Murray, J. Mendez, and S. A. Brown, The Natural Coumarins, Wiley, New York (1982).
3. S. Narantuyaa, D. Batsurén, É. Kh. Batirov, and V. M. Malikov, Khim. Prir. Soedin., 288 (1984).
4. N. Cassan and T. N. Huckerby, Tetrahedron, 33, 2719 (1975).
5. P. Bhandari and R. P. Rastogi, J. Sci. Ind. Res., 42, 437 (1983).
6. Zenai Chen, Xingruo Chan, et al., Zhongcaoyao, 12, No. 7, 1 (1981); Chem. Abstr., 96, 11552 (1982).

DETERMINATION OF COUMARIN IN SWEET CLOVER HERBAGE BY A POLAROGRAPHIC METHOD

Yu. E. Orlov

UDC 541.124.7:547.814.5

Continuing an investigation of coumarin-containing plants [1, 2], we have developed a polarographic method of determining coumarin in sweet clover herbage, in which the amount of this constituent serves as a criterion of the fodder [3] and medicinal [4] properties of the plant.

For analysis we used samples of the herbage of yellow and white sweet clovers (Melilotus officinalis Desz and Melilotus alba, respectively) gathered in Ryazan' province in 1986. The comminuted sweet clover herbage (5 g) was extracted with boiling ethanol (100 ml for 1 h and 50 ml for 30 min). The ethanol was distilled off from the combined extracts and the residue was transferred quantitatively to a 25-ml measuring flask.

To 1 ml of the extract so obtained was added 4 ml of ethanol and 3 ml of a 1% solution of tetraethylammonium iodide (TEAI) and analysis was performed by a polarographic method, as described in [1, 2, 5]. A 0.1% solution of coumarin was used as standard. The amount of coumarin in the sweet clover herbage was calculated from the formula

$$X = \frac{C_{st} \cdot H_x \cdot V_x}{H_{st} \cdot A},$$

Kharkov Scientific-Research Institute of Endocrinology and Hormone Chemistry. Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 131-132, January-February, 1988. Original article submitted July 23, 1987.

0009-3130/88/2401-0118 $12.50