# THE FLAVONOIDS OF THE FLOWERS OF Cirsium oleraceum

V. L. Shelyuto, V. I. Glyzin,
A. I. Ban'kovskii, and N. T. Bubon

UDC 547.972

TABLE 1. Chemical Shifts of the Protons of the Silylated Flavonoids

| Protons | δ, ppm, substance | | |
|---|---|---|---|
| | 1 | 2 | 3 |
| 2′6′ | 7,88 | 7,68 | 7,34 |
| 3′5′(5′) | 6,80 | 6,82 | 6,82 |
| 8 | 6,26 | 6,26 | 6,26 |
| 6 | 6,14 | 6,12 | 6,14 |
| 3 | | 6,42 | 6,38 |
| $OCH_3$ | 3,87 | | |

Linarin, pectolinarin, and luteolin 7-glucoside have been isolated previously from various species of the genus Cirsium [1]. On studying the flavonoids of Cirsium oleraceum L. growing in Belorussia, we found no less than 12 substances of flavonoid nature in the leaves of this plant. The present paper gives the results of a study of the flavonoid aglycones present in them.

The leaves of C. oleraceum were extracted with ethanol, the ethanol was distilled off, the residue was treated with hot water, and the aglycones were extracted with ethyl ether. The ethereal extract, after the elimination of the ether, was chromatographed on a column of polyamide sorbent. The substance was eluted with mixtures of chloroform and ethanol containing from 1 to 20% of ethanol. Three substances of flavonoid nature were isolated.

Substance 1. $C_{16}H_{12}O_6$, mp 290-292°C, $\lambda_{max}$ 268, 351 nm, $R_f$ 0.23 (15% $CH_3COOH$), 0.75 (60% $CH_3COOH$), 0.93 [in the butan-1-ol–acetic acid–water (4:1:5) system]. The NMR spectrum of silylated substance 1 (Table 1) [2] had the signals of 2′ and 6′ protons (2H) and 3′ and 5′ protons (2H), and also two doublets with an intensity of 1H each of protons located in the meta position, J = 2.5 Hz. These signals we assigned to protons in positions 8 and 6 of ring A. A signal in the 3.87 ppm region (3H) is due to a methoxy group. Thus, on the basis of NMR spectroscopy, the flavonoid concerned has substituents in positions 3, 5, 7, and 4′. The results of UV spectroscopy – $\lambda_{max}$ ($CH_3COONa$) 275, 355 nm; $\lambda_{max}$ ($CH_3ONa$) 276, 400nm; $\lambda_{max}$ [$Zr(NO_3)_2$] 282, 312, 406 nm; $\lambda_{max}$ [$Zr(NO_3)_2$ + citric acid] 272, 314, 352 nm – showed that there are free hydroxy groups in positions 5, 7, and 4′. The methoxy group in the compound can be only in position 3, which was confirmed by our isolation of kaempferol on demethylating substance 1. On the basis of the UV, IR, and NMR spectra, the demethylation products, and alkaline degradation, substance 1 was identified as 3-O-methylkaempferol [3].

Substance 2. $C_{15}H_{10}O_5$, mp 349-351°C, $\lambda_{max}$ 268, 337 nm, acetate 183-185°C. From its UV, IR, and NMR spectra and the products of alkaline degradation, the substance corresponded to apigenin.

Substance 3. $C_{15}H_{10}O_6$, mp 328-330°C, $\lambda_{max}$ 253, 268, 350 nm, acetate 224-226°C. By the methods used for substance 2 and by a direct comparison with an authentic sample, this was identified as luteolin.

## LITERATURE CITED

1. V. A. Bandyukova, Rast. Res., 4, 429 (1968).
2. W. Olechnowicz-Stepien et al., Herba Polonica, 1968, No. 3, 179.
3. K. Egger, M. Tissut, and E. Wollenweber, Phytochemistry, 8, No. 12, 2425 (1968).

Vitebsk Medical Institute. All-Union Scientific-Research Institute for Medicinal Plants. Translated from Khimiya Prirodnykh Soedinenii, No. 3, p. 371, May-June, 1971. Original article submitted January 25, 1971.