FLAVONOID GLYCOSIDES OF Cirsium oleraceum

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Continuing an investigation of the flavonoids of Cirsium oleraceum L., we have isolated four substances of the nature of flavonoid glysocides.

Substance C-8, $C_{21}H_{20}O_{11} \cdot 1/2\ H_2O$, mp 266-268°C, λ_{max} 257, 267, 352 nm, $[\alpha]_D$ −54.7° (c 0.6; *l* 0.7; formamide). When this substance was hydrolyzed with sulfuric acid, luteolin, with mp 349-351°C, and D-glucose were obtained; hydrolysis with emulsin gave the same products. In the NMR spectrum (Table 1) of the silylated glycoside [1], in the region of the protons of the carbohydrate moiety at 3.4-3.8 ppm there were the signals of six protons, which characterizes the compound isolated as a monoglucoside. It was shown by UV spectroscopy that the glucose is attached in position 7. The value of the chemical shift of the anomeric glucose proton of 4.91 ppm, J = 7 Hz, showed the β configuration of the glycosidic bond. The UV, IR, and NMR spectra and the other properties of the substance showed that it was luteolin 7-β-D-glycopyranoside.

Substance C-9, $C_{21}H_{10}O_{10} \cdot 1/2\ H_2O$, mp 222-225°C, $[\alpha]_D$ −142°C (c 0.6; *l* 0.7; dimethylformamide). The hydrolysis of substance C-9 gave apigenin and D-glucose. The position of the glucose in this compound was established as in the preceding case. From its UV, IR, and NMR spectra, substance C-9 was identified as apigenin 7-β-glucoside (cosmosiin).

Substance C-5, $C_{20}H_{32}O_{14}$, mp 267-269°C, $[\alpha]_D$ −121° (c 0.65, *l* 0.7; formamide) λ_{max} 269, 325 nm. The hydrolysis of this substance gave the aglycone acacetin, glucose, and rhamnose. The aglycone was identified on the basis of its demethylation products (apigenin), alkaline degradation (phloroglucinol and anisic acid), and by a direct comparison with an authentic sample. The hydrolysis of substance C-5 with diastase gave the aglycone acacetin and rutinose. The values of chemical shifts of the anomeric protons of the glucose and rhamnose corresponded to those given in the literature for rutinose in position 7 (see Table 1). Thus, substance C-5 is acacetin 7-rutinoside and is identical with linarin [2].

Substance C-6, $C_{29}H_{34}O_{15}$, mp 247-250°C, $[\alpha]_D$ −92.8° (c 0.6; *l* 0.7; formamide), λ_{max} 275, 330 nm. The hydrolysis of substance C-6 with sulfuric acid led to the formation of pectolinarigenin, the demethylation of which gave scutellarein. In C-6 and its aglycone there are two methoxy groups in positions 6 and 4′ [established by UV and NMR spectroscopy (see Table 1)]. The carbohydrate part of glycoside C-6 consists of rutinose in position 7, as was shown in the same way as for substance C-5. The facts given show that the glycoside C-6 is pectolinarigenin 7-rutinoisde (pectolinarin) [2].

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

Protons	δ, ppm			
	C-8, luteolin 7-glucoside	C-9, apigenin 7-glucoside	C-5, linarin	C-6, pectolinarin
2′6′	7,20	7,68	6,74	6,66
3′5′(5′)	6,74	6,80	6,86	6,84
8	6,42	6,60	6,40	6,65
6	6,10	6,26	6,32	
3	6,12	6,32	6,45	6,28
OCH_3			3,83	3,80372
H-1 of glucose	4,91	4,91	5,00	5,12
H-1 of rhamnose			4,37	4,32
Glucose and rhamnose	3,4–3,8	3,4–3,8	3,50	3,56
CH_3 of rhamnose			1,00	0,90

LITERATURE CITED

1. W. Olechnowicz-Stepien et al., Herba Polonica, 1968, No. 3, 179.
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