

group of overlapping signals in the 3.3-3.8-ppm region. The other four protons resonate in a weaker field. The greatest paramagnetic shift was undergone by the signal of the anomeric proton (doublet at 5.45 ppm with  $J = 8$  Hz) corresponding to H-1" of  $\beta$ -D-glucopyranose. A two-proton multiplet with its center at 4.32 ppm belongs to a geminal methylene group (2H-6"). Consequently, one of the p-coumaric acid residues esterifies the 6"-OH group. The position of the second residue can be deduced from the presence of a triplet ( $J_1 = J_2 = 9.5$  Hz) at  $\delta$  5.2 ppm, the appearance of which is explained by the acylation of the 3"-OH or the 4"-OH group of the glucose. An unambiguous choice between these two positions is impossible on the basis of the available spectral information. However, it may be assumed that structure (I) (see Fig. 1) with the acyl residues in positions 3" and 6" is preferable on the basis of the analogy with the reliably determined structure of other 3",6"-acylated compounds that we have found in the needles of this species of pine.

#### FLAVONOIDS FROM THE FLOWERS OF *Cirsium oleraceum*

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3-O-Methylkaempferol, apigenin, and luteolin have been isolated previously from the flowers of *Cirsium oleraceum* (L.) Scop. [1]. Continuing a study of the flavonoid composition of this plant, we have isolated and identified another four substances (IV-VII).

Substance (IV),  $C_{28}H_{32}O_{14}$ , mp 267-260°C,  $[\alpha]_D^{20} -120^\circ$  (c 0.65; formamide). From the products of acid hydrolysis we obtained glucose, rhamnose, and an aglycone  $C_{16}H_{12}O_5$  with mp 261-263°C (mp of the acetate 202-204°C) which was identified as acacetin.

Substance (V),  $C_{29}H_{34}O_{15}$ , mp 247-250°C,  $[\alpha]_D^{20} 92.8^\circ$  (c 0.6; formamide). From the products of hydrolysis by sulfuric acid we isolated glucose, rhamnose, and an aglycone  $C_{17}H_{14}O_6$  with mp 219-222°C (mp of the acetate 155-156°C), identified as pectolarigenin.

Substance (VI),  $C_{15}H_{10}O_7$ , mp 308-310°C (mp of the acetate 199-200°C), was identified as quercetin [2].

Substance (VII),  $C_{16}H_{12}O_7$ , mp 255-261°C, was identified as 3-O-methylquercetin [3].

From their elementary composition and the products of acid hydrolysis and of alkaline degradation and their UV, IR, and NMR spectra, substances (IV) and (V) were identified as linarin and pectolarin, respectively.

#### LITERATURE CITED

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