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# GLYCOFLAVONOIDS OF GYPSOPHILA PANICULATA

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Recently, gypsophilas have been attracting increasing attention from workers as promising plants for the production of saponins [1-4]. However, the other classes of natural compounds that they contain have been studied comparatively little.

In the present paper we give the results of the isolation and identification of the flavonoids of Gypsophila paniculata. In an analysis of various organs, it was found that the roots, where the bulk of the saponins is concentrated, contain a comparatively small amount of flavonoids. However, in the epigeal part, particularly in the leaves and flowers, more than seven components of a flavonoid nature have been found. By extracting the total flavonoids from the herb at 70° C with methanol and separating them on a column of polyamide sorbent, we obtained seven individual compounds. Of these, six were identified on the basis of their physicochemical properties and by comparison with authentic samples as vitexin, saponaretin, orientin, homoorientin, isosaponarin, and adonivernitol.

A substance with the composition $C_{26}H_{28}O_{14}$ and mp 200° C (decomp), on mild hydrolysis and enzymatic cleavage gave vitexin and D-xylose. By a spectroscopic investigation in the UV region [5], free hydroxy groups were found in the 5, 7, and 4' positions. Consequently, the D-xylose must be attached to the C-glycosyl substituent of vitexin. This substance is a new glycoside of vitexin and we have called it kachimoside. ["Kachim" is Russian for gypsophila.]

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# EXTRACTIVE PHENOLIC COMPOUNDS FROM THE HEARTWOOD OF PINUS SIBIRICA

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The composition of the phenolic components of Siberian pine has not previously been studied. From 21.0 g of the benzene-insoluble fraction (0.18% of the dry wood) of an acetone extract of the heartwood of the pine we have isolated

Table 1

| Substance | Ethanol | | | | +$AlCl_3$ | | | | +sodium acetate | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\lambda_{max}$ | | log ε | | $\lambda_{max}$ | | Δλ | | $\lambda_{max}$ | | Δλ | |
| (I) | 312 | 268 | 3.18 | 3.53 | 312 | 280 | 0 | 12 | 312 | 269 | 0 | 1 |
| (II) | 316 | 270 | 3.93 | 4.32 | 330 | 282 | 14 | 12 | 330 | 268 | 14 | −2 |
| Acetate of (I) | 302 | 252 | 3.30 | 3.29 | — | — | — | — | — | — | — | — |
| Diacetate of (II) | 308 | 257 | 4.28 | 4.35 | — | — | — | — | — | — | — | — |
| (III) | 300 | 235 | 4.22 | 4.20 | — | — | — | — | — | — | — | — |

by preparative chromatography on a polyamide sorbent (20 : 1) with elution by chloroform with an increasing content (1-5 vol-%) of methanol three substances: 3-hydroxy-7-methoxyflavone [tectochrysin (I)], 5, 7-dihydroxyflavone (chry-

sin) (II), and 5-hydroxy-3-methoxystilbene (monomethyl ester of pinosylvin) (III). The presence of these substances is characteristic for the subgenus Haploxylon of the genus Pinus.

Table 2

| Chemical shift, ppm | Nature of the signal | No. of protons | Assignment of the signals |
|---|---|---|---|
| 3.75 | Singlet | 3 | Protons of an $OCH_3$ group |
| 6.25 | Doublet, J-3 Hz | 1 | Protons of a benzene ring A |
| 6.40 | " " | 1 | |
| 6.55 | Singlet | 1 | Proton of a pyrone ring |
| 7.27 | " " | — | Solvent $CDCl_3$ |
| 7.4—7.8 | Multiplet | 5 | Protons of benzene ring B |
| 12.7 | Singlet | 1 | OH group with an intramolecular hydrogen bond |

Substance (I) formed yellow crystals with mp 163–163.5° C (chloroform) and its acetate had mp 151–152° C (80% ethanol).

Substance (II) formed yellow crystals which separated from a mixture of chloroform and ethanol (1:1), mp 275–275.5° C, and its diacetate formed white needles melting at 192–194° C (ethanol). By the cleavage of the chrysin with 30% caustic potash, phloroglucinol and benzoic acid were obtained and were identified by paper chromatography.

Substance (III) separated out from benzene in the form of white plates with a pink tinge having mp 118–119° C, mol. wt. 226 (by mass spectrometry). For all the substances isolated, the results of elementary analysis and the content of functional groups agreed well with the results of theoretical calculations. From the frequencies in the IR spectra of the compounds, the presence of the following fragments in them was established:

| Substance | $C_6H_5$, $cm^{-1}$ | C-O, $cm^{-1}$ | OH, $cm^{-1}$ | C-O-C, $cm^{-1}$ |
|---|---|---|---|---|
| (I) | 1455, 1505, 1620 | 1658 | 3610, 3650, 3670 | 1040, 1270 |
| (II) | 1579, 1612 | 1657 | 3600, 3640 | 1169 |
| (III) | 1450, 1490, 1590 | — | 3600, 3650 | 1060, 1240 |

Table 1 gives the results of a spectroscopic study of the compounds in the UV region and Table 2 the assignment of the lines of the NMR spectrum for tectochrysin.

The results that we obtained (melting points of tectochrysin and chrysin and their acetates and of the monomethyl ether of pinosylvin) agree with literature data [1].

The samples were given to us by Prof. Erdtman (Sweden) and A. I. Lisina. Students G. Panteleeva and O. Alekseeva took part in the experimental work.

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# STUDIES OF SUBSTANCES FOUND IN ESSENTIAL OILS. XXXV

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Continuing work on the synthesis of physiologically active substances from terpenoids [1, 2] we have carried out the synthesis of ω-(p-methoxyphenyl) heptanoic acid.