

Substance (IV), $C_{25}H_{26}O_{15}$, mp 261-262°C, $[\alpha]_D^{20}$ 36° (c 0.15; CH_3OH), $\lambda_{max}^{CH_3OH}$ 275, 327, 372 nm ν_{CO} 1665 cm^{-1} , R_f 0.14 and 0.45. Quantitative acid hydrolysis yielded equimolar amounts of herbacetin, L-arabinose, and D-xylose. From the changes in the UV spectra of the flavonoid caused by ionizing and complex-forming reagents, it was established that in the glycoside there were substituents at the C_6 and C_4 atoms of herbacetin.

Stepwise acid hydrolysis formed a mixture of two monosides: herbacetin 4'-xyloside and herbacetin 8-arabinoside. Treatment of the diglycoside with β -hydrolase led to the splitting out of D-xylose. On the basis of its physicochemical properties, chemical transformations, and UV and IR spectra, for substance (IV) we suggest the structure of 3,4',5,7,8-pentahydroxyflavone 8-O- α -L-arabinopyranoside 4'-O- β -D-xylopyranoside and the name rhodalide.

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DIDYMIN FROM THE BLOSSOMS OF THE SATSUMA ORANGE

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We have investigated the blossoms of the satsuma orange (*Citrus unshiu* Marc., syn, *C. nobilis* Lour. var. *unshiu* Swingle), which is widely cultivated on the Black Sea slopes of the town of Batumi.

The blossoms were extracted with 70% ethanol and the presence of flavonoid compounds in the alcoholic extracts was found by two-dimensional chromatography on paper in the butan-1-ol- $CH_3COOH-H_2O$ (4:1:5) and 30% CH_3COOH systems and by the revelation of flavonoid spots by chromogenic reagents.

Not less than five flavonoid compounds were found in the blossoms, of which two were flavanone glycosides (chromatogram stained with a saturated solution of sodium tetrahydroborate in isopropanol and with hydrochloric acid vapor) [1].

To isolate the individual compounds, the blossoms were dried at +60°C and were exhaustively extracted first with chloroform and then with 60% ethanol. The alcoholic extracts were concentrated, one third of a volume of water was added, and the mixture was cooled to +5°C. After a week, the light-colored precipitate that had deposited was separated off and washed with cold water, and after four recrystallizations from 70% acetic acid colorless crystals of substance (I) with mp 212°C were obtained. UV spectrum (C_2H_5OH), nm: λ_{max} 287, 332 sh. No bathochromic shift was observed in the presence of sodium acetate. The acetyl derivative, obtained by a method described previously [2], had mp 118°C, λ_{max} (C_2H_5OH), nm: 268, 311 sh.

Acid hydrolysis with 5% sulfuric acid for three hours gave a hydrolysate containing D-glucose and L-rhamnose (paper chromatography, spots revealed with the aniline phthalate reagent). On partial hydrolysis with 85% formic acid in cyclohexanol, only L-rhamnose was split out.

The aglycone — colorless crystals with mp 193°C — gave a brown coloration with a solution of ferric chloride and a pink-violet coloration with sodium tetrahydroborate in the presence of hydrochloric acid.

UV spectrum, nm: $\lambda_{max}^{C_2H_5OH}$ 291, 330 sh; $+AlCl_3$: $\Delta\lambda$ + 16 nm; CH_3COONa ; $\Delta\lambda$ + 37. Its R_f values corresponded to those of isosakuranetin (5,7-dihydroxy-4'-methoxyflavanone).

The PMR spectrum of the acetyl derivative of the glycoside in $CDCl_3$ (internal standard

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TMS) showed that 8:4 ratio of the sugar protons that is typical for rutinose in the regions $\delta = 4.5$ and 5.5 ppm (8 H) and $\delta = 3.4-4.4$ ppm (4 H). At 4.72 ppm ($J = 1.0$ Hz) there was the signal of the C-1 proton of an acetylated rhamnose residue [3] on the basis of which it was concluded that substance (I) was isosakuranetic 7-rutinoside, which has been described under the name didymin [4].

This is the first time that this substance has been isolated from satsuma blossoms.

The investigation of the flavonoids of the blossoms is continuing.

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FLAVONOID GLYCOSIDES OF *Salix rubra*

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The ether-soluble fraction of a total preparation of polyphenols from the bark of *Salix rubra* was chromatographed on a column with a polyamide sorbent by a method described previously [1]. Fractions of eluate corresponding to the zones on the column fluorescing in UV light were collected.

In the first fractions pyrocatechol, p-coumaric, and naringenin 5-glucoside were detected by paper chromatography. The last two fractions, eluted from the column with a 30% solution of acetone and with pure acetone, yielded two individual glycosides of flavonoid nature.

The first of them formed yellow prisms with mp $170-171^\circ\text{C}$ and $[\alpha]_D^{20} -19.6^\circ$ (ethanol). UV spectra (nm): $\lambda_{\text{max}}^{\text{C}_2\text{H}_5\text{OH}}$ 370; $\lambda_{\text{max}}^{\text{C}_2\text{H}_5\text{OH}+\text{AcNa}}$ 380; $\lambda_{\text{max}}^{\text{C}_2\text{H}_5\text{OH}+\text{AlCl}_3}$ 420; $\lambda_{\text{max}}^{\text{C}_2\text{H}_5\text{OH}+\text{ZrOCl}_2}$ 424. On acid hydrolysis, the glycoside split into glucose and naringenin in equimolar ratio. The elementary analysis corresponded to that calculated for $\text{C}_{21}\text{H}_{22}\text{O}_{10}$. From these properties, the flavonoid proved to be identical with chalcononaringenin 6'-glucoside, which is present in the bark of *S. purpurea* and *S. acutifolia* [3].

The second compound formed bright orange needles with mp $181-182^\circ\text{C}$ and $[\alpha]_D^{20} +151.5^\circ$ (c 0.5, ethanol). UV spectra (nm): $\lambda_{\text{max}}^{\text{C}_2\text{H}_5\text{OH}}$ 319, 372; $\lambda_{\text{max}}^{\text{C}_2\text{H}_5\text{OH}+\text{AcNa}}$ 384; $\lambda_{\text{max}}^{\text{C}_2\text{H}_5\text{OH}+\text{AlCl}_3}$ 425; $\lambda_{\text{max}}^{\text{C}_2\text{H}_5\text{OH}+\text{ZrOCl}_2}$ 425. Glucose, naringenin, and p-coumaric acid were identified as the products of the acid hydrolysis of the glycoside. On alkaline hydrolysis, it formed the chalcononaringenin 6'-glucoside described above and p-coumaric acid. Its elementary analysis corresponded to that calculated for $\text{C}_{30}\text{H}_{28}\text{O}_{12}$.

Thus, on the basis of chemical properties and the results of spectral investigations with ionizing and complex-forming reagents it may be concluded that this compound is an ester of chalcononaringenin 6'-glucoside and p-coumaric acid. The presence of an ester grouping in it was confirmed by the corresponding absorption band in the IR spectrum: 1690 cm^{-1} ($\nu_{\text{C=O}}$ of an Ar-CH=CH-COO-R group), 1290 and 1100 cm^{-1} , and others. These bands were absent from the IR spectrum of the deacylated glycoside. On the basis of the absence of an absorption band of 1050 cm^{-1} ($\nu_{\text{C=O}}$ of a glucose CH_2OH group) from the IR spectrum of the compounds under investigation and its appearance after the splitting out of the p-coumaric acid, we assumed that the acid residue in it substitutes the hydroxyl at C₆ of the glucose. Consequently, the acylated chalcone from the bark of *Salix rubra* is 2',4,4',6'-tetrahydroxychalcone 6'-O-(p-coumaroylglucopyranoside). This compound proved to be identical with the chalcone that we have isolated previously [1] from the bark of *S. acutifolia*.

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