Acetylation of patuloside gave a hexaacetate with the composition $C_{32}H_{30}O_{16}$, mp 229-231°C, $[\alpha]_D^{20}$ −45.4° (c 0.528; chloroform), ν_{CO} 1780, 1760, 1660 cm^{-1}.

The pyranose form of the sugar is shown by the multiplicity of the signals of the methylene protons in the NMR spectrum of the acetate (Fig. 1) and by the large shift between the H-5"a and the H-5"e signals. The spin–spin coupling constants of the anomeric proton in the TMS ether and of the proton at C-5" in patuloside acetate agree well with the $^4C_1$ conformation of D-xylopyranose in these compounds.

To confirm the pyranose form of the sugar, the glycoside residue was methylated by Hakomori's method [2] and the full methyl ether obtained was subjected to hydrolysis, which gave 2,3,4-tri-O-methyl-D-xylose, identified by TLC on silica gel and by GLC in the presence of a marker.

Thus, the results obtained show that patuloside has the structure of luteolin 7-O-β-D-xylopyranoside.

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DZHAMIRONE — A NEW KETONE FROM THE ROOTS OF *Ferula dshaudshamyr*

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UDC 547.913.5:668.5.918

From a methanolic extract of the roots of *Ferula dshaudshamyr* Eug. Kor., by chromatography on a column of type KSK silica gel we have isolated an oily substance with the composition $C_{23}H_{32}O_3$, M^+ 356, R_f 0.78 [petroleum ether–ethyl acetate (4:1)], readily soluble in organic solvents and insoluble in water which we have called dzhamirone. Its UV spectrum [λ_{max} 230, 275, and 312 nm (log ε 3.90, 4.16, and 3.85, respectively)] is characteristic for a 2,4-dihydroxybenzoyl chromophore. IR spectrum, ν_{max}, cm^{-1}: 3350 (phenolic hydroxy group), 1630 (carbonyl of an aryl alkyl ketone) [1], and 1610 and 1520 (aromatic nucleus). The molecule of this substance contained two phenolic hydroxyls, which was confirmed by the formation of a diacetate (M^+ 440).

The NMR spectrum of the substance has the signals of three aromatic protons — doublet at 7.50 ppm (J = 10 Hz, 1 H), quartet at 6.22 ppm (J_1 = 10 Hz, J_2 = 2 Hz, 1 H), and doublet at 6.25 ppm (J = 10 Hz, 1 H), and also a singlet at 12.86 ppm (1 H), corresponding to the proton of a phenolic hydroxy group bound by a hydrogen bond with a ketone carbonyl [1]. A multiplet in the 5.00-ppm region (3 H) corresponds to three olefinic protons. In the strong field there are signals at 1.54 (6 H), 1.56 (3 H), and 1.58 ppm (3 H), corresponding to four methyl groups on double bonds.

Thus, dzhamirone is an aryl alkyl ketone the terpenoid part of which has the composition $C_{15}H_{25}$.

On hydrogenation over PtO_2 in ethanol, dzhamirone absorbed three moles of hydrogen. This showed that the terpenoid part of the molecule contains three double bonds. In the NMR spectrum of the hydrogenation product (M^+ 362), the signals of the three olefinic protons and of the methyl groups on double bonds had disappeared, and a doublet had appeared at 0.86 ppm (J = 7.5 Hz, 12 H). With the given composition and with three double bonds, the terpenoid substituent can only have an acyclic structure.

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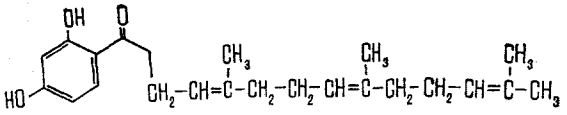
The mass spectrum of the substances had the peak of the molecular ion M^+ 356, m/e 287 ($M - C_5H_9$), 219 ($M - C_7H_5O_3$), 204 ($M - C_8H_8O_3$), 152 ($C_8H_8O_3$), 127 ($C_7H_5O_3$). The mass spectrum of the fragment corresponding to the terpenoid substituent of dzhamirone coincided completely with that of the coumarin umbelliprenin, which contains a farnesane residue. The NMR spectra of umbelliprenin and dzhamirone also coincided in the region from 5.00 to 1.0 ppm, which shows the presence of a farnesane residue in dzhamirone. In dzhamirone the aliphatic part substitutes the methyl group of acetophenone, while in umbelliprenin it substitutes the phenolic hydroxyl in position 7. To confirm what has been said above, we performed a comparative oxidation of umbelliprenin and dzhamirone under the same conditions with periodate-permanganate [2]. The same carboxylic acid was formed from the terpenoid part in the two cases.

On the basis of the facts presented, we propose the following structure for dzhamirone:



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CYNAROSIDE FROM THE LEAVES OF *Digitalis ciliata*

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Luteolin, apigenin, and dracocephaloside have been obtained from the leaves of *Digitalis ciliata* Trautv. previously [1, 2]. When an ethanolic-chloroformic extract of the leaves of the plant was separated on a column of silica gel, in addition to cardenolides we isolated a yellow crystalline substance giving a reaction for flavonoids [3].

After recrystallization from dilute ethanol, this compound melted at 255-257°C and had the composition $C_{21}H_{20}O_{11}$, $[\alpha]_D^{20}$ −58° [c 0.53; methanol–pyridine (3:2)]. On PC in various solvent systems it appeared that the level of an authentic sample of cynaroside, $\lambda_{max}^{C_2H_5OH}$ 355, 255 nm; $\lambda_{max}^{+CH_3COONa}$ 355, 255 nm; $\lambda_{max}^{+CH_3COONa+H_3BO_3}$ 370, 257 nm; $\lambda_{max}^{+AlCl_3}$ 395, 280 nm [1].

Bryant's reaction [3], the results of acid hydrolysis, and a comparison of absorption intensities in the shortwave region of the UV spectrum of this glycoside and of dracocephaloside [2] indicated their monoside nature.

Acid hydrolysis of the flavone glycoside with Kiliani's mixture [4] yielded the aglycone (60%) with mp 325-328°C which was identified by UV and IR spectroscopy, a mixed melting point, and comparative PC as luteolin [5]. D-Glucose was found in the carbohydrate moiety of the glycoside. The flavone glycoside was also cleaved by 0.5% KOH.

The absence of a shift of the shortwave maximum in the UV spectrum of the glycoside and its appearance in the aglycone on the addition of fused sodium acetate showed that the carbohydrate substituent was attached to position 7 of the luteoline [5].

The β configuration of the glycosidic bond and the pyranose form of its oxide ring were established by comparing molecular rotations of the glycoside under investigation and simple phenyl glycosides [6].

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