The detailed study of the hydrolysis products and the results of polarimetric analysis gave information on the structure of the carbohydrate moieties of the substances under investigation and characterized substance (III) as luteolin 4'-O-β-D-glucopyranoside 7-O-β-rutinoside, and substance (IV) as luteolin 4'-O-β-D-glucopyranoside 7-O-β-neohesperiodoside. The first luteolin trioside was isolated under the name of cynarotrioside by L. I. Dranik from *Cynara Scolymus* L. [3]. This is the second case of its detection in plant raw material. The second luteolin glycoside has not been described in the literature, and we have called it persiciloside.

The epigeal part of the plant contained the substances (III) and (IV) in a ratio of 10:1, and their total amount determined by a chromato-spectrophotometric method was 0.15%.

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FLAVONOIDS OF THE LEAVES OF THE COTTON PLANT OF VARIETY TASHKENT. I

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We have investigated the composition of the flavonoids of the cotton plant of variety Tashkent 1 grown in the laboratory to the state of five true leaves. The nutrient medium was Knop's medium.

The freshly gathered leaves were extracted with methanol at room temperature. The aqueous methanolic extract was concentrated in vacuum and the residue was extracted repeatedly with chloroform. Then 1/3 volume of water was added to the residue and it was exhaustively extracted with ethyl acetate. The combined substances from the ethyl acetate extract were separated by adsorption partition chromatography on a column of Kapron [nylon-6] powder. The column was washed with chloroform and with chloroform–methanol mixtures with a gradient increase in the amount of the latter. Subsequent rechromatography of the fractions obtained yielded three individual flavonoids.

Flavonoid (I) – $C_{15}H_{10}O_7$, mp 308-310°C (decomp.). UV spectrum, λ_{max}, nm: 376, 258 (ethanol + acetone). Acetyl derivative: $C_{25}H_{25}O_{12}$, mp 194°C. UV spectrum, λ_{max}, nm: 303, 215 (ethanol). Alkaline cleavage gave phloroglucinol and protocatechuic acid, which was identified by its R_f value and its behavior with diagnostic reagents in comparison with markers.

According to the results obtained, flavonoid (I) was identical with quercetin.

Flavonoid (II) – $C_{12}H_{20}O_{12}$, mp 245-246°, $[\alpha]_D^{20}$ –89.0° (c 0.1; methanol). UV spectrum, λ_{max}, nm: (+CH_3OH) 370, 256; (+CH_3COONa) 385, 257; (+CH_3COONa + H_3BO_3) 395, 260; (+$AlCl_3$) 479, 278. In a study of the products of acid hydrolysis (2 N HCl), quercetin and D-glucose were detected. The size of the oxide ring of the sugar residue and the form of the bond were determined from the results of IR spectroscopy and polarimetric analysis (II), and also by enzymatic hydrolysis.

From the results obtained, flavonoid (II) was identified as quercetin 7-O-β-D-glucopyranoside. This flavonoid has been identified previously from the flowers of the cotton plant of variety 108-F [2].

Flavonoid (III) – $C_{27}H_{30}O_{16}\cdot 2H_2O$, mp 188-190° $[\alpha]_D^{25}$ –37.6° (c 0.1; methanol). UV spectrum, λ_{max}, nm: (+CH_3OH) 360, 257; (+CH_3COONa) 381, 272; (+CH_3COONa + H_3BO_3) 375, 257; (+$AlCl_3$) 420, 270; (+CH_3ONa) 415, 272. Qualitative diagnostic reactions showed that the flavonoid (III) was a 3-glycoside. The products of acid hydrolysis were shown to contain quercetin (46.7%), D-glucose, and L-rhamnose. The position of the bond between the sugar residues was

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determined by oxidative degradation with hydrogen peroxide, and it was found that the carbohydrate substituent of the substance was identical with rutinose [3]. The sizes of the oxide rings of the sugar residues and the forms of the bonds were determined from the results of IR spectroscopy and polarimetric analysis.

The experimental results and also a comparison with an authentic sample indicated that flavonoid (III) was identical with rutin.

In view of the fact that the conditions of growth affect the synthesis and amount of organic compounds in plants, we determined the sum of the flavonoids quantitatively. In the plants that we investigated it was 9 μg/g of raw mass of the leaves. This is the first time that the flavonoids of the leaves of the cotton plant of variety Tashkent 1 have been studied.

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SESQUITERPENE LACTONES OF *Pyrethrum pyrethroides*. PYRETHROIDININ

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From the total chloroform extract of *Pyrethrum pyrethroides* (Kar. et Kir.) B. Fedtsch. [1] we have isolated a new sesquiterpene lactone with the composition $C_{15}H_{20}O_4$, mp 170-172°C (ethyl acetate–hexane) $[\alpha]_D^{22}$ +850° (c 0.8; ethanol), which we have called pyrethroidinin. Its IR spectrum had absorption bands at 3360-3460 cm^{-1} (OH group), and 1770, 1670, and 1630 cm^{-1} (C=O, α,β-unsaturated γ-lactone conjugated with an isolated C=C bond). The UV spectrum was characterized by a maximum at $\lambda_{max}^{C_2H_5OH}$ 204 nm (log ε 4.27). The circular dichroism spectrum of this compound (C_2H_5OH) showed a negative Cotton effect at 261 nm ($\Delta\varepsilon$ = −0.57) and a positive one at 208 nm ($\Delta\varepsilon$ = 14.7).

The mass spectrum of pyrethroidinin had the peak of the molecular ion with m/z 264 (M^+ −34%), and the peaks of ions with m/z 246 [M − H_2O] (365) and 228 [M − $2H_2O$] (8.4%), due to the ejection of 1 and 2 molecules of water, and also fragments with m/z (%): 249 [M − CH_3] (3), 229 (3.9), 223 (6.9), 218 [M − CO − H_2O] (6.4), 213 [M − $2H_2O$ − CH_3] (23.5), 206 (8.9), 205 (8.4), 204 (9.9), 203 [M − H_2O − CH_3 − CO] (34.6), 194 (5), 193 [M − C_4H_7O] (18), 191 [M − C_4H_9O] (6.9), 190 (5.9), 189 [$C_{12}H_{13}O_2$] (20), 188 [$C_{12}H_{12}O_2$] (50), 185 [M − $2H_2O$ − CH_3 − CO] (15), 177 (54), 176 (14), 175 [$C_{11}H_{11}O_2$] (25), 173 [$C_{11}H_9O_2$] (8), 149 (100), etc, which are characteristic for the fragmentation of guaianolides under electron impact [2, 3].

The PMR spectrum of pyrethoidinin (C_5D_5N, O − HMDS) was characterized by the following signals (ppm): 1.00 (3 H, s, CH_3 − C − OH at C-10); 2.06 (3 H, br.s, CH_3–C=C); 3.39 (1H, m, H-7); 4.60 (1 H, br.d, H-6); 5.32 and 6.14 (1 H each, d, ^4J = 3.1 and 3.4 Hz, respectively, 2 H-13); 5.75 (1 H, s, tertiary OH group); 6.24 (1 H, d, ^3J = 6 Hz, secondary OH group). At 4.80 ppm there was a considerably broadened singlet which was converted in the presence of CD_3OD into a doublet with broadened lines having ^3J = 7.4 Hz. Consequently, this signal belongs to a proton (H-3) located geminally to a secondary OH group.

The presence of a methyl group on a double bond, of a CH_3–C–OH grouping, of doublet splitting of the signal of the lactone proton with ^3J = 10.9 Hz, and the absence of an olefinic proton unambiguously showed the position of the isolated double bond in the guaiane structure of pyrethroidinin at C-4 and C-5, of a tertiary OH group at C-10, and of a trans-linked lactone ring at C-6 and C-7.

The values of the chemical shifts of the protons of the exocyclic methylene group of the lactone ring indicated the absence of a hydroxy substituent at C-8. The broadening of the

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