

Substance (7) —  $C_{21}H_{20}O_{11}$ , mp 185–187°C,  $\lambda_{\max}$  355, 257 nm,  $[\alpha]_D^{20}$  –118.6° (c 0.87; methanol). On hydrolysis with 2%  $H_2SO_4$ , quercetin and rhamnose were formed. A mixture of the substance obtained and quercitrin gave no depression of the melting point. The results obtained permit the substance to be identified as quercitrin (quercetin 3-O- $\alpha$ -L-rhamnoside) [7].

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#### FLAVONOL 3,7-DIGLYCOSIDES OF *Lepidium syvaschicum*

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The flavonol biosides rutin and nicotiflorin have been isolated previously from the epigeal part of *Lepidium syvaschicum* Kleop [1]. We have subsequently investigated the inflorescences of this plant. An ethanolic extract obtained from them was subjected to separation by absorption-partition chromatography on polyamide, and two flavonoid substances (I and II) were isolated in the individual state which fluoresced dark brown on paper chromatograms in UV light before treatment and lettuce-green (substance I) and orange (II) after treatment with a 3% solution of zirconyl chloride and ammonia vapors. Substance (I) had the composition  $C_{33}H_{40}O_{19}$ , mp 205–207°C; and (II)  $C_{33}H_{40}O_{20}$ , mp 208–211°C. The results of spectral investigations in the UV region permitted the assumption that the carbohydrate components of both substances were present in positions 3 and 7. Kaempferol (substance (I)) and quercetin (substance (II)), D-glucose, and L-rhamnose were detected by paper chromatography in the products of the acid hydrolysis of the glycosides with 5%  $H_2SO_4$  solution. On acid hydrolysis of each of the substances under investigation with 10%  $CH_3COOH$  or a 0.04 N solution of HCl, the formation of three intermediate substances provisionally designated (Ia, Ib, and Ic) (substance (I)) and (IIa, IIb, and IIc) (II) was observed. Substances (Ia) and (IIa) on PC, before treatment, fluoresced yellow in UV light, and substances (Ib, IIb, Ic, and IIc) fluoresced dark brown. The results of investigations in the UV regions of the spectrum using ionizing and complex-forming reagents made it possible to establish that the carbohydrate components in the first two of the intermediate substances mentioned above were present in position 7, and in the other four they were in position 3. In the products of acid and enzymatic hydrolyses, PC showed the presence L-rhamnose (substances (Ia and IIa)), D-glucose (IIb and Ib), L-rhamnose and D-glucose (Ic and IIc), and kaempferol and quercetin, respectively. On comparison with substances isolated previously [1–3], the intermediate compounds were identified as the 7-O- $\alpha$ -L-rhamnosides (substance Ia and IIa), 3-O- $\beta$ -D-glucosides (Ib and IIb), and 3-O-rutinosides (Ic and IIc) of kaempferol and quercetin.

Consequently, substances (I) and (II) were characterized as the 7-O- $\alpha$ -L-rhamnoside 3-O-rutinosides of kaempferol and of quercetin.

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FLAVONOIDS OF *Camellia sinensis*

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To eliminate lipophilic substances and caffeine, air-dry young shoots (flushes) of the tea plant of the Georgian variety (*Camellia sinensis* L.) collected in August 1982 on the plantation of the variety-testing section of the Chakva branch of the All-Union Scientific Production Amalgamation for Tea and Subtropical Crops were subjected to extraction with chloroform-benzene (1:1), after which the flavonoids were extracted with ethyl acetate. The evaporated ethyl acetate extract was freed from the bulk of the catechins on a column of silica gel (Silpearl). For this purpose, the column was washed exhaustively with diethyl ether, and the residual flavonoids were desorbed with methanol.

On repeated chromatography on the evaporated methanolic eluate on silica gel and polyamide (with mixtures of water and methanol), ten individual compounds of flavonoid nature were isolated.

Compound (I) — colorless crystals with the composition  $C_{15}H_{12}O_5$ ,  $M^+$  272 (100%), mp 248–249°C,  $\lambda_{\text{max}}^{\text{MeOH}}$  227 sh., 291, 334 nm. The mass spectrum of (I) included fragmentary ions characteristic for flavonones: an oxonium ion with  $m/z$  179 (26),  $(A + H)^+$  with  $m/z$  153 (64), and ions of ring B with  $m/z$  121 (6) and 120 (33), which, in combination with the results of UV spectroscopy, permitted compound (I) to be identified as naringenin.

Compound (II) — colorless crystals with the composition  $C_{15}H_{12}O_6$ ,  $M^+$  288 (43%), mp 224–225°C,  $\lambda_{\text{max}}^{\text{MeOH}}$  292, 335 sh., nm. PMR spectrum in deuterioacetone, ppm: 1.57 (s, 5-OH), 7.40 (d, 9 Hz, H-2',6'), 6.88 (d, 9H, H-3',5'), 6.01 (d, 2.5 Hz, H-8), 5.96 (d, 2.5 Hz, H-6), 5.07 (d, 12 Hz, H-2), 4.59 (d, 12 Hz, H-3). The mass spectrum of (II) included fragmentary ions characteristic for flavanonols:  $(M - 29)^+$  and  $(A + H)^+$   $m/z$  259 (55) and 153 (100), and also ions of ring B with  $m/z$  136 (33), 121 (4). The spectral characteristics presented permitted compound (II) to be identified as dihydrokaempferol.

Compound (III) — yellow crystals with the composition  $C_{15}H_{10}O_6$ ,  $M^+$  286 (100), mp 285–287°C, was identified as kaempferol.

Compound (IV) — yellow crystals with the composition  $C_{15}H_{10}O_7$ ,  $M^+$  302(100), mp 307–310°C, was identified as quercetin.

Compound (V) — light yellow crystals with the composition  $C_{15}H_{10}O_7$ ,  $M^+$  302(100), decomposed without melting at 290°C,  $\lambda_{\text{max}}^{\text{MeOH}}$  261 sh., 270, 256 nm.

The mass spectrum of compound (V) contained ions from the retro-Diels-Alder reaction that are characteristic for flavones:  $(A + H)^+$  and  $B^+$  with  $m/z$  153 (28) and 150 (11). The PMR spectrum of this compound (deuterioacetone) contained the signals of the C-6 and C-8 protons in the form of two doublets with a constant of 2.5 Hz at 6.47 and 6.23 ppm, the two-proton singlet signal of the C-2' and C-6' protons (7.08 ppm), and the singlet signal of the C-3 proton at 6.46 ppm. The facts given permitted compound (V) to be characterized as 3',4',5',7-pentahydroxyflavone (tricetin) [1].

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