LITERATURE CITED

1. N. S. Fursa, Khim. Prir. Soedin., 124 (1980).
2. M. S. Fursa and V. I. Litvinenko, Farmats. Zh., 83 (1970).
3. V. G. Zaitsev, N. S. Fursa, and L. E. Belyaeva, Khim. Prir. Soedin., 527 (1983).

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, λ_{max}^{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, λ_{max}^{MeOH} 292, 335 sh., nm. PMR spectrum in deuteroacetone, 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, λ_{max}^{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 $B^{+\cdot}$ with m/z 153 (28) and 150 (11). The PMR spectrum of this compound (deuteroacetone) 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',5-5',7-pentahydroxyflavone (tricetin) [1].

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Compound (VI) — yellow crystals with mp 174-176°C.

Compound (VII) — yellow crystals with mp 225-227°C.

Compound (VIII) — yellow crystals with mp 258-261°C.

On acid and enzymatic hydrolysis, compounds (VI), (VII), and (VIII) gave the same carbohydrate moiety, glucose, and the aglycones kaempferol (M^+ 286), quercetin (M^+ 302), and myricetin (M^+ 318), respectively. The 3-glycosylation of these substances followed from the results of UV spectroscopy with diagnostic reagents, and their monoglycosidic nature was confirmed by the results of NMR spectroscopy. On the basis of the facts presented, compounds (VI), (VII), and (VIII) were identified as astragalin, isoquercitrin, and myricetin 3-O-glucoside, respectively.

Compound (IX) — yellow crystals with mp 181-184°C.

Compound (X) — yellow crystals with mp 189-191°C.

On acid hydrolysis, the two compounds gave the same carbohydrate fragments — glucose and rhamnose — and also the aglycones kaempferol and quercetin, respectively. Enzymatic hydrolysis led to the formation of rutinose and the corresponding aglycones. The PMR spectra of (IX), (X), and their acetates in combination with the results of hydrolysis permitted these compounds to be identified as kaempferol 3-O-rutinoside (IX), and rutin (X).

Thus, the investigations performed have confirmed the presence in the tea plant of compound (III), (IV), and (VI-X) isolated previously [2-6].

This is the first time that naringenin (I), dihydrokaempferol (II), and tricetin (V) have been isolated from *Camellia sinensis*. It is interesting that no flavanonols have previously been known for tea, and of flavanones only naringenin fructoside has been described [7].

LITERATURE CITED

1. S. Beckmann and H. Geiger, Phytochemistry, 7, 1667 (1968).
2. E. A. H. Roberts, R. A. Cartwright, and D. I. Wood, J. Sci. Food Agric., 7, 637 (1956).
3. Y. Takino, H. Imagawa, and H. Yoshida, J. Agric. Biol. Chem. 26, 699 (1962).
4. K. G. Mikaberidze and I. I. Moniava, Khim. Prir. Soedin., 835 (1971).
5. K. G. Mikaberidze and I. I. Moniava, Khim. Prir. Soedin., 519 (1972).
6. K. G. Mikaberidze and I. I. Moniava, Khim. Prir. Soedin., 439 (1974).
7. F. Imperato, Phytochemistry, 15, 439 (1976).