FLAVONOIDS OF *Camellia sinensis*.

II. COMPONENTS OF A METHANOLIC EXTRACT

I. D. Chkhikvishvili, V. A. Kurkin,
and M. N. Zaprometov

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Ten flavonoid compounds have previously been isolated from an ethyl acetate extract of young shoots of the tea plant *Camellia sinensis* L., family Theaceae of the selection variety "Kolkhid." When the plant material was subsequently extracted with methanol, an additional amount of flavonoid practically free from catechins was obtained.

When the methanolic extract was repeatedly chromatographed on columns of polyamide and silica gel (with water–ethanol and chloroform–methanol), compound (I) was obtained in the individual form. The isolation of compounds (II-IV) required additional purification on a column of Sephadex LH-20 (with the use as eluent of chloroform containing 12% of methanol).

Compound (I) — light yellow crystals with mp 258-260°C, λ_{max}^{MeOH}, nm: 270, 331; +NaOAc 279, 303 sh., 378. On treatment with acid (10% HCl), compound (I) did not decompose, but under the action of Kiliani's mixture it formed apigenin (M^+ 270) and glucose. Compound (I) gave no coloration with the Gibb's reagent [2], which indicates the substitution of the C-8 position in the apigenin molecule.

The mass spectrum of (I) contained the following ions: M — H_2O 414 (20%), the benzyl cation of the algycone with m/z 283 (100), the algycone with m/z 270 (49), and fragments from the breakdown of the benzyl cation with m/z 165 (36) and 121 (28). In combination with the results of PMR and UV spectroscopy, compound (I) was identified as spigenin 8-C-β-D-glucopyranoside (vitexin).

Compound (II) — light yellow crystals with mp 226-229°C, λ_{max}^{MeOH}, nm: 273, 335; +NaOAc, 283, 303 sh., 390. On treatment with acid (10% HCl), compound (II) did not decompose. Under the action of Kiliani's mixture it formed intermediate C-monoglycosides and apigenin, with glucose as the carbohydrate fragment. The PMR spectra of the substance and of its acetate in combination with the facts given permitted compound (II) to be characterized as spigenin 6,8-di-C-glucoside.

Compound (III) — yellow crystals with mp 231-233°C, λ_{max}^{MeOH}, nm: 267, 350.

Compound (IV) — yellow crystals with mp 215-219°C, λ_{max}^{MeOH}, nm: 258, 266 sh., 359.

On acid hydrolysis, compounds (III) and (IV) were cleaved with the formation of identical carbohydrate fragments (rhamnose and 2 moles of glucose) and the aglycones kaempferol and quercetin, respectively. The ratio of the signals of aromatic and aliphatic acetoxy groups in the PMR spectra of the acetates of (III) and (IV) confirmed the trioside nature of the flavonoid glycoside. Consequently, compound (III) was a kaempferol 3-rhamnodiglucoside and (IV) a quercetin 3-rhamnodiglucoside [3-5].

Thus, we have confirmed the presence of compounds (III) and (IV) in the tea plant. The presence of compounds (I) and (II) was shown previously only for a Japanese variety of tea plant [6, 7].

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ESSENTIAL OIL OF THE GRAPEFRUIT *Citrus paradisi* GROWING IN THE GEORGIAN SSR

N. A. Kekelidze, M. I. Dzhanikashvili, and G. M. Fishman

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The chemical compositions of the essential oils obtained by cold pressing from different varieties of grapefruit growing in the USA have been well studied [1-4]. There is a report [5] on the amount of monoterpene hydrocarbons in the essential oil of grapefruit cultivated in the Georgian SSR. There is no information in the literature on oxygen-containing compounds and sesquiterpene hydrocarbons.

We give the results of an investigation of the chemical composition of the essential oils that were isolated by steam distillation from the peel of ripe grapefruit *Citrus paradisi* Macf., of the Duncan and Marsh varieties growing in the Georgian SSR.

The essential oils, consisting of greenish liquids, were distilled *in vacuo* through a fractionating column into low-boiling and high-boiling fractions. The process of distillation was monitored with the aid of the gas—liquid chromatography.

The high-boiling fraction, after saponification, was chromatographed on alumina (activity grade II-III) and the sesquiterpene hydrocarbons, carbonyl compounds, and alcohols were separated by successive elution with petroleum ether, benzene, and diethyl ether. The components were isolated from the fractions obtained on distillation and chromatography on Al_2O_3 and were identified by a procedure described previously [6].

The compositions of the essential oils were determined by the GLC method on a Varian Aerograph 1860 chromatograph with a flame-ionization detector. The best separation of the essential oils was achieved on a 550 × 0.2 mm column with the stationary phase FFAP 10 on Chromosorb W 80/100 mesh. The rate of flow of He was 35 ml/min. The temperature was programmed from 100 to 230°C.

The amounts of the components in the essential oils of the grapefruit of the varieties studied were as follows (% on the total oil):

Component	Duncan	Marsh	Component	Duncan	Marsh
α-Pinene	0.15	0.45	Linalool	0.13	0.08
Sabinene	0.81	0.40	Decyl acetate	0.23	-
Myrcene	0.82	1.40	Neryl acetate	0.34	0.16
α-Phellandrene	0.30	0.50	Neryl formate	0.14	-
d-Limonene	88.5	92.5	α-Terpeneol	0.23	0.12
γ-Terpinene	0.05	0.07	Octanol	0.21	0.12
p-Cymene	0.40	0.10	Terpinen-4-ol	0.20	0.12
Octanal	0.44	0.23	Neral	0.02	0.04
Nonanal	0.12	0.08	β-Caryophyllene	0.23	0.16
Decanal	0.20	0.12	β-Copaene	0.02	0.01
Citronellal	0.12	0.07	Cadinene	0.13	0.05

Institute of Plant Biochemistry, Academy of Sciences of the Georgian SSR, Tbilisi. All-Union Scientific-Research and Experimental-Design Institute for the Storage and Processing of Subtropical Fruits, Batumi. Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 119-120, January-February, 1985. Original article submitted June 11, 1984.

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