5. Y. Takino and H. Imagawa, J. Agric. Chem. Soc. Jpn., 28, 186 (1954).
6. Y. Sakamoto, J. Agric. Biol. Chem., 31, 1029 (1967).
7. Y. Sakamoto, J. Agric. Biol. Chem., 34, 919 (1969).

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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The essential oils of these varieties differ mainly with respect to the amounts of the components.

LITERATURE CITED

1. J. W. Kesterson and R. Hendrickson, Am. Perf. Cosmet., 79 (1964).
2. J. W. Kesterson and R. Hendrickson, Am. Perf. Cosmet., 82 (1967).
3. M. G. Moshonas, J. Agric. Food Chem., 19 (1971).
4. C. W. Wilson and P. E. Shaw, J. Agric. Food. Chem., 26 (1978).
5. N. A. Kekelidze and G. M. Fishman, Subtropicheskie Kul'tury, 6 (1973).
6. N. A. Kekelidze, M. I. Dzhanikashvili, and V. V. Kutateladze, Khim. Prir. Soedin., 803 (1981).

BIOMIMETIC SYNTHESIS OF 7α-HYDROXYSANDARACOPIMARINOL — THE ANTISPASMATIC PRINCIPLE OF *Iboza riparia*

V. A. Raldugin and V. A. Pentegova

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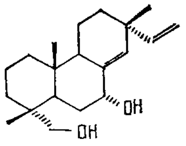
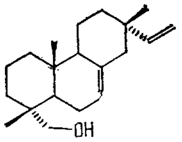
7α-Hydroxysandarcopimarinol (isopimara-8(14),15-diene-7α, 18-diol)* (I) has been isolated from the leaves of the Central African plant *Iboza riparia* (Hochst) N. E. Br., which is used in folk medicine [1]. Continuing studies on biomimetic syntheses [2] and the photooxidation of natural terpenoids [3], we have performed the synthesis of this compound from isopimarinol (II) [4] by sensitized photooxidation. The conditions of photooxidation and of the subsequent working up and separation of the products were similar to those used previously [3] except that the time of the reaction was increased to 8 h. Under these conditions, from 2.20 g of isopimarinol 1.95 g of combined products was obtained the chromatography of which led to the isolation of 1.66 g of the initial compound, 0.05 g of a mixture of by-products, and 0.22 g of the diol (I) with mp 76-82°C (from acetone), $[\alpha]_D^{20}$ −82° (c 8.37; methanol) (according to the literature [1]: mp 76-81°C (from acetone), $[\alpha]_D$ −87.1° (methanol)). By drying *in vacuo* at 100°C, acetone of solvation was eliminated from the crystals obtained [1] and the product was recrystallized from pentane to give fine needles of the diol (I) with mp 96-98°C. The PMR spectrum (in C_6D_6) corresponded to that given in the literature [1].

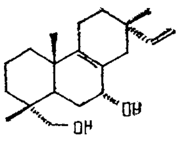
Mass spectrum (70 eV, 100°C, direct introduction): *m/z* 304 (M^+, 65), 286 ($(M-H_2O)^+$, 4), 255 (22), 164 (26), 151 (85), 123 (100), 81 (41). As has been shown by Fourrey [6], on photooxidation methyl isopimarate gives the corresponding 7α-hydroxy ester.



I



II



III

The mixture of by-products contained ~80% of the isomeric diol (III) (PMR spectrum), which it was possible to isolate by crystallization from a mixture of acetonitrile and diethyl ether. The PMR spectrum of this diol, which had mp 118-120°C, differed qualitatively from that for the diol (I) (solutions in $CDCl_3$) only by the absence of the signal of a proton at a trisubstituted double bond. The methyl groups in them gave singlets at 0.70, 0.92, and 0.95 ppm, and the components of a AB system formed by the protons of the CH_2—OH group were observed at 2.89, 2.94, 3.46, and 3.51 ppm. The H_7 signal (3.78 ppm) had the form of a

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*The name of compound (I) given in [1] does not agree with the accepted nomenclature of cyclic diterpenoids [5].

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