SUMMARY

A series of analogs of natural isoflavones has been synthesized from 2,4-dihydroxydeoxybenzoins. The yields amounted to 63-96%.

All the isoflavones synthesized possess a pronounced hypolipidemic activity.

LITERATURE CITED

1. G. N. Dorofeenko, A. L. Shinkarenko, A. L. Kazakov, A. I. Pyshchev, and V. V. Mezheritskii, Khim. Prir. Soedin., 160 (1974).
2. A. L. Kazakov, Khim.-Farm. Zh., No. 1, 58 (1979).
3. A. L. Kazakov and S. F. Dzhumyrko, Rast. Res., No. 3, 344 (1979).
4. M. S. Luk'yanchikov, Khim. Prir. Soedin., 43 (1984).
5. A. L. Kazakov and N. I. Kokovkii-Shcherbak, "The prediction of the biological activities of isoflavones as functions of their structures with the aid of an additive model," in: Abstracts of Lectures at the IIIrd All-Union Congress of Pharmacists of the USSR [in Russian], Kishinev (1980).
6. P. E. Spoerri and A. S. DuBois, Organic Reactions, Coll. Vol. 5, 387-412 (1949).

DYNAMICS OF THE ACCUMULATION OF THE MONOTERPENOIDS OF *Citrus limon*

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The amounts and compositions of the essential oils in the leaves and fruit of Meyer's lemon in the various vegetation periods have been studied. It has been established that as the fruit ripens the amount of essential oils and of monoterpene hydrocarbons in its peel and in the leaves increases.

We have studied the amount and composition of the essential oils of the leaves and fruit of Meyer's lemon [*Citrus limon*] in the various vegetation periods. The leaves and fruit were collected from normally developed fruit-bearing plants from the middle, with respect to height, parts of the crown from all sides in the morning in dry weather on experimental-production plots of the Sukhumi Zonal Experimental Station of Essential-Oil Crops and the Sukhumi Experimental Station of Subtropical Crops of the All-Union Institute of Plant-Growing.

The leaves were collected every month for a year, beginning with the flowering period. The collection of the fruit was begun in July when its size had reached 5-7 mm. The essential oils were isolated by the steam distillation method 30-40 min after the material under investigation had been gathered. The oils were isolated from the distillate by extraction with methylene chloride and were analyzed by gas-liquid chromatography.

Results on the amount of essential oils are shown in Fig. 1. The biosynthesis of the essential oil in the peel of the fruit intensified as the fruit ripened and reached a maximum in the period of full ripeness. The amount of essential oil in the leaves increased from the flowering period up to September. In October, i.e, at the beginning of the ripening of the fruit, the biosynthesis weakened considerably, and then, in the period of full ripeness of the fruit, the process of oil-formation intensified and reached a maximum. In winter, in the period of forced dormancy, the amount of essential oils scarcely changed. From the beginning of the growth of the shoots to the flowering period, the amount of oil in the leaves increased.

Analysis of the results on the change in the monoterpenoids in the leaves during the year (Table 1) shows that from the flowering period to September there is an intensive bio-

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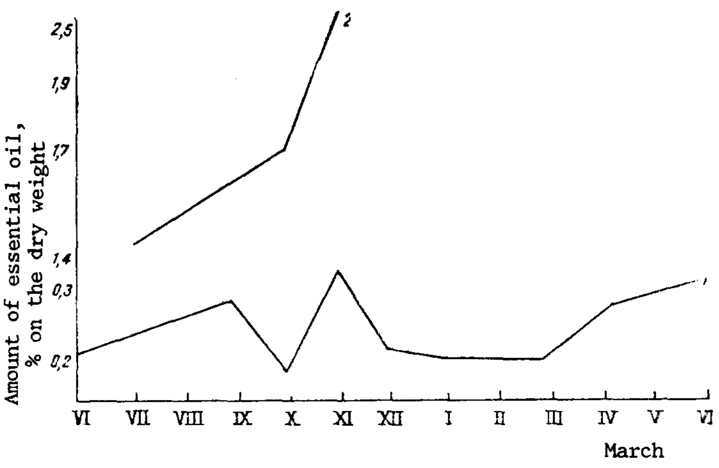

Fig. 1. Change in the amount of essential oil in the leaves (1) and peel (2) of the fruit of Meyer's lemon according to the stages of vegetation.

TABLE 1. Dynamics of the Quantitative Change in the Monoterpenoids of Meyer's Lemon Leaves during the Year (% on the total oil)

Component	Month												
	VI	VII	VIII	IX	X	XI	XII	I	II	III	IV	V	VI
α-Pinene	0.05	0 2	0,1	0 1	0,1	0,1	0 05	0.1	0,1	0,2	0,2	0 2	0,1
Sabinene	0 6	0,2	0 3	0.2	0,3	0 2	0,4	0.5	0.5	0,6	0 5	0 5	0,2
Myrcene	0.4	0.1	0.8	0 4	0 4	0,4	1 1	1.2	1,4	1,5	1,2	1,4	0,3
Limonene	28,4	50,5	55.1	40.2	64.0	75.4	68,8	70 7	69,9	68,3	69,2	65.4	53,3
1,8-Cineole	5,0	2 8	2.8	2 2	1.2	1 3	1,4	1,3	1.1	1,6	1 6	1.5	1,4
γ-Terpinene	2,1	4,4	2 6	0,7	0,3	1.8	3.1	2,8	0 4	1,8	3,0	1 1	1,4
p-Cymene	0,6	0,6	0 8	0,9	1,1	1,3	1,0	0,9	0.9	0,3	0 3	0,5	0,6
Citronellal	2,5	3,5	7 6	8 9	2,9	5,3	5,9	3,3	4,4	4,7	5,6	5,9	6,0
Methylheptanone	0,2	0,3	0,4	0 2	0.2	0.1	0,1	0,2	0,1	0.1	0,1	0,1	0.2
Linalool	3.6	3 1	3,9	8 1	4,3	2.2	3.8	2,7	2.8	2 9	2,5	3,3	4,3
Terpinen-4-ol	0,8	1 7	1 0	1,7	0,8	0.5	0 6	0 5	0,4	0.5	0.7	0,8	0,7
Isopulegol	8,5	3 3	3,0	11,4	4.8	1 7	2 4	1,8	3,5	2.9	2,6	3,7	5 1
α-Terpineol	12,5	5 5	1 3	3,0	2,5	1,1	1,2	1,2	1.2	1 1	1.9	2,3	4,0
Neral	11 1	0,9	1,3	2.5	2,2	0.4	0,5	0,5	0,7	1,2	1.2	0,8	0,8
Geranial	5,7	2,4	2,3	1.8	0,8	1.0	0 7	0 3	0,3	1,4	1,5	1,5	1.8
Nerol	5,6	4 2	4,1	7 6	5.1	1.8	1,9	2,1	2,1	2 2	2.4	2 2	2,5
Citronellol	0 4	0,6	0 6	0.2	0,1	0 1	0,1	0.1	0,1	0.2	0.3	0,4	0,6
Geranyl acetate	0,2	0 2	0.3	0,3	0 4	0 2	0,2	0.3	0,2	0,2	0.5	0 7	0,9
Neryl acetate	0 2	0.3	0,4	0.4	0,4	0 6	0,2	0,2	0,2	0,6	0 6	0,7	0,9
Thymol	0,06	0 06	0,05	0.08	0.2	0.4	0 7	0,7	0,8	0,9	1.0	1.1	1,0

synthesis of limonene and a corresponding fall in the amount of α-terpinol, isopulegol, neral, and geranial. In September, the biosynthesis of limonene weakens considerably and its intensifies again with the beginning of the ripening of the fruit, reaching a maximum in the period of complete ripeness. From the period of forced dormancy to flowering, the quantitive level of monoterpenoids scarcely changes. In the flowering period, the amount of limonene again falls.

Table 2 gives information on the quantitative levels of the monoterpenoids identified in the peel of the fruit in the period of its development. As can be seen from Table 2, as the fruit ripens the amounts of linalool, α-terpineol, and thymol fall sharply, which is accompanied by a corresponding increase in the level of limonene.

Thus, the monoterpenoids of the leaves and peel of the fruit of Meyer's lemon undergo considerable changes during the vegetation period.

EXPERIMENTAL

All the gas–liquid chromatographic work was performed on a Varian Aerograph 1860 instrument with a flame-ionization detector. Helium was used as the carrier gas.

Analytical GLC was performed on the column described in [1] and on a 0.2 × 300 cm column with 20% of the stationary phase DEGS on Chromosorb W 80/100 mesh. The rate of flow of He was 30 ml/min, and the column temperature 80-180°C. IR spectra were recorded on a UR-10 instrument.

TABLE 2. Dynamics of the Quantitative Change in the Amounts of Monoterpenoids in the Peel during the Period of the Development of the Fruit of Meyer's Lemon (% on the total oil)

Component	Month				
	VII	VIII	IX	X	XI
α-Pinene	0.5	1,0	1.3	1.4	1,4
Sabinene	0.7	1,0	1.1	1.2	1,8
β-Pinene	0,1	0,1	0,2	0,3	0,3
Myrcene	0,8	1,0	0,8	0,8	0,9
Limonene	51,2	62.8	70.3	74,9	77.4
γ-Terpinene	1,2	1,6	1,9	3,8	5,8
p-Cymene	0,9	1,0	0,9	0,5	0.5
Terpinolene	0,1	0,2	0,2	0,1	0.1
Citronellal	0,4	0,3	0.4	0,2	0.1
Linalool	11,1	7.3	3,2	1,0	0,7
Terpinen-4-ol	1.1	0,9	0,5	0,2	0,1
α-Terpineol	7,3	4.6	2,3	0.9	0,4
Neral	0.5	0,2	0,2	0,2	0,1
Geranial	0,3	0,2	0,1	0,2	0,1
Citronellol	0,3	0,2	0,2	0.1	0.1
Nerol	0.3	0.3	0,2	0.2	0.1
Geranyl acetate	0,8	0,7	0,7	0.5	0,4
Neryl acetate	0.4	0.2	0.2	0,1	0,1
Thymol	11,1	8.8	7,2	6,1	5.3

The quantitative levels of the monoterpenoids were determined by the internal-standard and internal-normalization method. As the internal standard for hydrocarbons we used naphthalene [2], and for thymol we used eugenol.

The phenols were isolated from the essential oils by the usual procedure [3]. The phenolic fractions were analyzed by GLC (2 × 450 cm column, 5% of SE-30 on Chromosorb W 80/100 mesh, 180°C). Thymol was identified in the oils from its retention time. The fractions of the essential oils remaining after the extraction of the phenols were chromatographed on Al_2O_3 (activity grade II). Petroleum ether eluted hydrocarbons, and ethanol eluted oxygen-containing monoterpenes.

The hydrocarbons were subjected to vacuum distillation to eliminate sesquiterpene hydrocarbons. Limonene, γ-terpene, and 1,8-cineole were isolated from the monoterpene fraction by preparative GLC (0.9 × 600 cm column, 30% of FFAP on Chromosorb W 80/100 mesh, 140°C). They were identified by comparing their IR spectra with those given in the literature [3]. α- and β-Pinenes, sabinene, myrcene, and terpinolene were identified by the addition of known substances to the sample under investigation and by chromatographing them on columns with the stationary phases FFAP (column temperature 90°C, rate of flow of He 40 ml/min), SE-30 (column temperature 80°C, rate of flow of He 35 ml/min), and DEGS (column temperature 80°C, rate of flow of He 35 ml/min).

Carbonyl compounds were isolated from the fraction of oxygen-containing compounds by a known procedure [4]. Citronellal, neral, and geranial were isolated by preparative GLC (0.9 × 600 cm column, 20% Carbowax 20 M on the weight of the Chromosorb W 60/80 mesh, 170°C), and they were identified by comparing their constants and IR spectra with those of known samples.

The terpene alcohols linalool, α-terpineol, and nerol were isolated preparatively on the same column. They were identified by comparing their IR spectra with those given in the literature [3]. Isopulegol, terpinen-4-ol, and citronellol were identified from their retention times and the increase in the size of the corresponding peaks on the addition of the pure substances to a sample of the fraction.

Nernyl acetate and geranyl acetate were identified by a procedure described previously [1].

SUMMARY

The amounts of essential oils and their qualitative compositions in the leaves and peel of the fruit of Citrus limon (L.) Burm. fil. according to vegetation periods have been established.

It has been shown that as the fruit ripens the amounts of essential oils and monoterpene hydrocarbons in its peel and in the leaves increase. From the period of forced dormancy to flowering, the quantitative levels of the monoterpenoids in the leaves scarcely change.

LITERATURE CITED

1. N. A. Kekelidze, M. I. Dzhanikashvili, A. N. Tatarishvili, and T. P. Bagdoshvili, Khim. Prir. Soedin., 607 (1984).
2. M. I. Goryaev, F. S. Sharipova, L. A. El'chibekova, and V. Yu. Averina, Khim. Prir. Soedin., 560 (1981).
3. M. I. Goryaev and I. Pliva, Methods of Investigating Essential Oils [in Russian], Alma-Ata (1962).
4. W. L. Stanley and R. M. Ikedo, J. Food. Sci., 26, 43 (1961).

THE STRUCTURE OF A NEW GERMACRANOLIDE – SHONACHALIN C – FROM Artemisia fragrans

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UDC: 633.82/88

The structure of the new germacranolide shonachalin C ($C_{15}H_{22}O_4$, mp 203-205°C) isolated from Artemisia fragans has been established on the basis of spectroscopic (IR, ^1H and ^{13}C NMR) results.

Continuing a study of the sesquiterpene lactones of Artemisia fragrans Willd. collected in the village of Shona-chala, Lerik region, Azerbaidzhan SSR, by means of chromatography on a column of alumina we have isolated a crystalline substance with the composition $C_{15}H_{22}O_4$, mp 203-205°C (hexane–ether). The molecular weight, determined mass-spectrometrically, was 266.

In the region of characteristic frequencies of the IR spectrum there were bands of OH groups (3250 cm^{-1}), of the CO of a γ-lactone ring (1770 cm^{-1}), and of double bonds (1675 cm^{-1}).

The presence of two hydroxy groups was shown by acetylation. This gave a diacetyl derivative with the composition $C_{19}H_{26}O_2$, mp 149-151°C (hexane–ether) the IR spectrum of which contained absorption bands at 1770 cm^{-1} (CO of a γ-lactone ring), 1740, 1245, and 1230 cm^{-1} (CO of acetyl groups), and 1670 cm^{-1} (double bonds). There was no band of OH groups.

On comparing the physiochemical properties of the lactone under investigation with those of known sesquiterpene lactones, we came to the conclusion that it was new and we have called it shonachalin C.

In the ^{13}C NMR spectrum of shonachalin C taken with complete suppression of spin-spin coupling, 15 signals corresponding to the 15 carbon atoms of the molecule of the compound were detected, and in the off-resonance spectrum (here and below where the multiplicity of a signal is given, what is in view is the form of the signal under conditions of incomplete uncoupling from protons) these appeared in the form of the two quadruplets, four triplets, six doublets, and three singlets.

Doublets at 124.81 and 128.69 ppm, and singlets at 138.51 and 139.25 ppm observed in the spectrum of the region of sp^2-hybridized carbon atoms showed the presence of two trisubstituted double bonds in the molecule of the substance.

In the region of sp^3-hybridized carbon atoms, in addition to signals of carbon atoms bearing hydroxyls (69.26 ppm, triplet, and 73.90 ppm, doublet), there were three doublets in the spectrum at 41.80, 55.33, and 77.31 ppm relating to methine carbon atoms. Of these, the

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