LIPIDS OF THE FRUIT OF Feijoa sellowiana

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The composition and amounts of liposoluble substances in the flesh and peel of feijoa fruit has been investigated. About 30 groups of lipid substances have been identified. The main groups of lipids in the flesh were triacylglycerols, sterols, cerebrosides, ceramide phosphate inositol oligosides, sulfoquinovosyldiacylglycerols, phosphatidic acids, phosphotidylglycerols and phosphatidylcholines. In the peel, hydrocarbons, sterols, esters of fatty acids and lower alcohols, cerebrosides, digalactosyldiacylglycerols, ceramide oligosides, phosphatidylglycerols, and phosphatidylinositols predominated. The fatty acids of the flesh were found to include 15 representatives ($C_{12:0}$–$C_{28:0}$), and those of the flesh 11 representatives ($C_{12:0}$–$C_{18:3}$).

Feijoa fruit is a useful dietetic product recommended for medicinal-prophylatic nutrition in diseases of the thyroid gland (its iodine content is about 0.6 mg/100 g), atherosclerosis, pyelonephritis, and diseases of the cardiovascular system and of the gastrointestinal tract [1]. An original combination of various vitamins, pectins, amino acids, and essential oils is responsible for the antiinflammatory and tonic action of feijoa and the product of its processing on the organism.

The chemical composition of feijoa fruit has been studied inadequately, and there is no information in the literature on the liposoluble substances. In view of this, to evaluate its nutritional and biological significance we have studied the chemical composition of the lipids of the fruit of Feijoa sellowiana (family Myrtaceae) of the Syuperb variety grown in industrial plantations of Azerbaidzhan (1989 harvest).

We used freshly gathered fruit that had reached physiological ripeness. The dark-green dense peel with a waxy bloom was separated from the flesh. The component parts of the fruit (flesh and peel) were ground and lipids were extracted by a modified Bligh-Dyer method [2]. The lipids were freed from impurities by washing chloroform extracts with a 0.5% solution of $CaCl_2$.

According to the experimental results, the total amount of lipids in the flesh was 2514 mg/kg, and in the peel 10,407 mg/kg. We have observed a similar great difference in the amounts of lipids in the component elements of the fruit (a fairly characteristic phenomenon due to the presence of the waxy bloom on the fruit) previously in such fruit as persimmons, pears, grapes, and mandarins [3].

The sum of the lipds was separated into neutral lipids (NLs), glycolipids (GLs), and phospholipids (PLs) by the method of column chromatography on silica gel [4]. The group composition of each class of lipids was studied by TLC in various solvent systems.

The compounds were identified by a comparison of the chromatographic mobilities of the substances under investigation and of model preparations on the basis of literature information about R_f values in concrete systems and also from qualitative reactions and spectral characteristics. In the identification of polar lipids of complex structure we used the results of the chemical analysis of the water-soluble and liposoluble fragments isolated after the performance of severe acid hydrolysis.

The classes of lipids in the component elements of the feijoa fruit were present in the following ratios (wt. %):

	Flesh	Peel
Neutral lipids	48.9	44.4
Glycolipids	19.1	38.1
Phospholipids	32.0	17.6

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With respect to their NL contents, the flesh and peel of the fruit studied differed only slightly. The concentration of GLs in the peel was twice as great as in the flesh, while, conversely, the amount of PLs was little more than half. Thus, the neutral lipids in feijoa fruit form the largest class in the quantitative respect. Their group compositions (% of the total) in the peel and flesh of the fruit of Feijoa sellowiana are shown below:

Neutral lipids	Flesh	Peel
Hydrocarbons	5,0	24,6
Carotenoids	0,3	0,5
Sterol esters	3,2	2,0
Wax esters	1,2	3,8
Esters of fatty acids and lower alcohols	2,5	11,4
Triacylglycerols	61,3	5,6
Tocopherols	0,1	0,4
Fatty acids (free)	4,3	7,9
Lipoquinones		5,9
Fatty alcohols		7,2
1,3-Diacylglycerols		
Sterols	3,1	3,8
1,2-Diacylglycerols	13,7	18,0
Hydroxy acids	4,4	1,3
Chlorophills		6,9
Monoacylglycerols	0,9	0,7

The compositions of the NLs of the flesh and peel had substantial differences. Thus, the amount of triacylglycerols in the flesh was 11 times greater than in the peel. Hydrocarbons, waxes, esters of fatty acids and lower alcohols, free fatty acids, hydroxy acids, and sterols were the predominating groups of the NLs of the peel, which is extremely characteristic for the tissues of plants coated with a waxy bloom. At the same time, the above-mentioned groups, apart from the sterols, were also present in the flesh, mainly in small or trace amounts.

The group compositions of the glycolipids (% on the total) of the fruit of Feijoa sellowiana were as follows:

Glycolipids	Flesh	Peel
Monogalactosyldiacylglycerols	0,8	2,7
Sterol glycosides	1,3	4,4
Unidentified (X_1)	2,2	3,2
(X_2)	—	4,3
(X_3)	—	2,2
Cerebrosides	27,2	24,7
Ceramide oligosides	7,3	17,5
Digalactosyldiacylglycerols	13,2	21,2
Ceramide phosphate inositol oligosides	22,9	9,4
Sulfoquinovosyldiacylglycerols	25,1	10,4

In the composition of the GLs, cerebrosides, digalactosyldiacylglycerols, ceramide oligosides (flesh), sulfoquinovosyldiacylglycerols, and ceramide phosphate inositol oligosides (flesh) predominated. A distinguishing feature of the GLs of feijoa is the predominance of digalactosyldiacylglycerols over monogalactosyldiacylglycerols, since in other fruit the opposite relationship of galactodiacylglycerols, since in other fruit the opposite relationship of galactodiacylglycerols is usually observed [3, 4]. According to PC, in the sugar fragments of the GLs galactose predominated (60-70%). Glucose, arabinose, mannose, and uronic acids were also detected.

The group compositions of the phospholipids (% on the total) of the fruit of Feijoa sellowiana were as follows:

Phospholipids	Flesh	Peel
Phosphatidic acids	36,7	8,4
Diphosphatidylglycerols	8,1	7,6
Unidentified	1,5	—
Phosphatidylethanolamines	7,2	10,1
Phosphatidylglycerols	19,3	42,0
Phosphatidylcholines	16,4	12,6
Phosphatidylinositols	10,8	19,3

The predominating components of the phospholipids of the flesh were phosphatidic acids, phosphatidylglycerols, and phosphatidylcholines, and in the peel phosphatidylglycerols and phosphatidylinositols. The predominance of these groups of phospholipids is not characteristic for fruits, as a rule [3], since in the majority of cases ~50% of the PLs is represented by phosphatidylethanolamines and phosphatidylcholines.

Below we give the fatty acid compositions of the total lipids (% by weight) of the component parts of the fruit of Feijoa sellowiana

Fatty acid	Flesh	Peel
12:0	2,1	0,2
14:0	0,3	0,8
15:0	—	0,6
16:0	20,0	21,2
16:1	0,6	1,8
16:2	1,1	—
17:1	1,0	2,1
18:0	2,0	3,9
18:1	18,6	12,8
18:2	45,6	26,4
18:3 (Δ6,9,12)	0,8	—
18:3 (Δ9,12,15)	8,0	21,2
20:0	—	1,3
23:0	—	1,9
24:0	—	1,0
26:0	—	2,2
28:0	—	2,6
Total saturated	24,4	35,7
Total unsaturated	75,6	64,3

Among the fatty acids, four predominated: linoleic, palmitic, oleic, and linoleic. The unsaturation index (U/S) of the lipids of the flesh was fairly high at 3.1, while in the peel this index was considerably lower (1.8), which agrees well with information on the predominance of saturated lipids in the composition of the waxes of fruit blooms [5]. Attention is attracted by the extremely high level of readily oxidized polyunsaturated acids (>50%) in the feijoa flesh, which demands a certain care in the storage and processing of the fruit.

EXPERIMENTAL

Column chromatography was conducted on silica gel L 100/160, and thin-layer chromatography on Silufol and silica gel L 5/40 with gypsum in the following solvent systems: 1) for NLs – heptane–methyl ether ketone–acetic acid (47.5:7.5:0.5), two runs; 2) for GLs – chloroform–methanol-water (65:25:4); 3) acetone–toluene–acetic acid–water (60:60:2:1); and 4) chloroform–acetone–methanol–acetic acid–water (6:8:2:2:1); and 5) for PLs – chloroform–methanol–7 N ammonia (65:30:4) in the first direction, and chloroform–methanol–acetic acid–water (170:25:25:6), in the second direction.

Neutral lipids were determined spectrophotometrically by Amenta's method based on the oxidation of the lipid compounds with the dichromate reagent [6], PLs from their phosphorus content [7], and CLs from their carbohydrate components [8]. The water-soluble products obtained after severe acid hydrolysis (2 N HCl, 125°C, 48 h) of the polar lipids were separated and identified with the aid of paper chromatography as described by Kates [9].

Paper chromatography of the carbohydrate components of the GLs was carried out by the descending method in the benzene–butan-1-ol–pyridine–water (1:5:3:3, upper phase) system. Quantitative determination was carried out by the colorometric method using the aniline phthalate reagent [10]. The methylation and the GLC of the methyl esters of the fatty acids were carried out as described in [4].

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CRYSTAL AND MOLECULAR STRUCTURE OF HYATOQUINONE HYDRATE FROM A MARINE SPONGE Hyatella sp.

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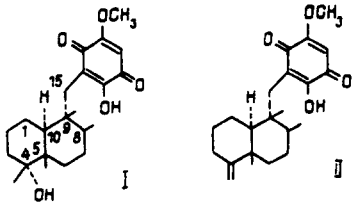
The crystal and molecular structures of hyatoquinone hydrate have been established by x-ray structural analysis. The existence of a difference in the spatial orientation of the quinoid fragment in hyatoquinone and in the ilimaquinone studied previously has been shown.

In [1] the isolation of a new quinone from the marine sponge Hyatella sp., which was called hyatoquinone, was reported. On the basis of the results of NMR spectroscopy it was concluded in this paper that a hydroxy group in hyatoquinone was present at C-5. We have made an x-ray structural investigation of this compound, as a result of which the structure of hyatoquinone has been established as (I).



The spatial structure of the molecule of (I) is given in Fig. 1. The coordinates of the nonhydrogen atoms are given in Table 1, the lengths of the bonds in Table 2, and the valence angles in Table 3. The general conformation of the (I) molecule differs substantially from that of ilimaquinone (II) an x-ray structure study of which was performed previously by a group of American scientists [2]. The main difference consists in the mutual orientation of the quinoid ring and the sesquiterpenoid backbone of the molecule relative to the C-9–C-15 bond. While in compound (II) the substituent at this bond occupies the trans position relative to the C-8 in compound (I) it is turned by 120° and is present in the trans position relative to the C-16 methyl group. This shows the considerable conformational possibilities of molecules with such a structure.

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