

fitted with a SS-100 MS computer data-processing system under identical conditions: energy of the ionizing electrons 70 eV; accelerating voltage 3 kV; temperature of the evaporation of the sample 100°C; temperature of the ionization chamber 120°C. The conditions for recording and processing the DADI and defocusing spectra were similar to those described previously [3, 4]. The names of the fatty acids are given in accordance with the IUPAC nomenclature [5].

SUMMARY

Using mass-spectrometric methods, cholesterol, docosanoic, heneicosanoic, eicosanoic, octadecanoic, cis-octadec-9-enoic, heptadecanoic, hexadecanoic, and pentadecanoic acids have been found in the odoriferous secretions of the pre-anal glands of females and males of the common adder and of the saw-scaled viper and of females of the mamushi.

It has been established that the chemical compositions of the secretions of the pre-anal glands of the females of the adder, the viper, and the mamushi and of the males of the adder and the viper are not identical.

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LIPIDS OF THE FRUIT OF *Ficus carica*

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By chromatographic methods, about 30 groups of various lipid compounds belonging to the classes of neutral lipids, glycolipids, and phospholipids have been identified from the fruit of the fig tree. The main groups are triacylglycerols, free and esterified sterols, mono- and digalactosyldiglycerides, ceramide oligosides, cerebrosides, esterified sterol glycosides, and phosphatidylglycerols. In the fatty acid composition, linoleic, linolenic, oleic, and palmitic acids predominated (>90%).

In spite of their small amount in fruits, lipids have a fundamental influence on their times of storage, organoleptic properties, and nutritional and biological value [1]. At the present time, within the framework of the Feed Program, it is planned to increase agricultural production and to develop new technologies for storing and preserving various fruits, including figs, which are a valuable and perishable product. However, there is no information on the chemical composition of the lipids of the fruit of *Ficus carica* L.

We have investigated the lipids of the fruit of *Ficus carica* (family *Moraceae*) - the fig of the widely distributed technical varieties Smena (I) and Turetskii korichnevyi (II).

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The total lipids were isolated with mixtures of chloroform and methanol in volume ratios depending on the moisture content of the sample and determined from a ternary diagram [2].

According to the experimental results, the total lipid content amounted to 7655 mg/kg for variety I and 3255 mg/kg for variety II, which appreciably exceeds their levels in a number of other fruits (citrus fruits [3], apples [4], grapes [5]). To all appearances, this is due to the fact that a considerable part of the bulk of the fruit of Ficus carica consists of small seeds rich in oil, and the cuticular membrane is copiously impregnated with lipid substances.

The combined lipids were separated into neutral lipids (NLs), glycolipids (GLs), and phospholipids (PLs) by column chromatography on silica gel [6]. Individual types of lipid compounds were obtained by the TLC method.

The assignment of the chromatographically individual zones of substances to different groups of lipids was made on the basis of a comparison of the chromatographic mobilities of the substances under investigation with the mobilities of model preparations, and also by qualitative reactions [6, 7] and spectral characteristics. In the identification of a number of lipids of complex structure, the results of chemical analysis of the water-soluble and liposoluble fragments of the molecules isolated after the performance of severe acid hydrolysis were used.

For their quantitative determination, the lipids were eluted from a plate and their amounts were estimated. The ratio of the groups of neutral lipids (NLs) was evaluated by a universal method based on the oxidation of the lipid compounds with a dichromate reagent, followed by spectrophotometric determination [8].

The NLs were quantitatively the largest fraction of the lipids of the fig, and amounted to 84.5 and 47.5%, respectively, for varieties I and II.

When the neutral lipids were separated in system 1, the presence of more than 10 groups of different compounds was established (% on the total NLs):

| <u>Lipids</u> | <u>Variety I</u> | <u>Variety II</u> |
|--------------------------------------|------------------|-------------------|
| Hydrocarbons | 1.7 | 0.6 |
| Sterol esters | 15.4 | 12.2 |
| Fatty acid esters | 11.5 | 9.6 |
| Triacylglycerols | 44.5 | 51.0 |
| Tocopherols | 0.2 | 0.3 |
| Free fatty acids | 7.3 | 4.1 |
| Diacylglycerols | 5.6 | 2.2 |
| Free sterols | 8.9 | 10.5 |
| Pigments (carotenoids, chlorophylls) | 0.8 | 2.7 |
| Monoacylglycerols | 4.1 | 6.8 |
| Total, mg/kg weight of the fruit | 6468.5 | 1532.1 |

The group compositions of the NLs of varieties I and II were identical and their quantitative ratios were similar. However, a profound influence of variety features on the amounts of NLs in the fruit of Ficus carica must also be mentioned. Thus, the amounts of NLs in the samples of varieties I and II grown under similar soil and climatic conditions differed by a factor of 4.2.

The predominating component (~50%) of the NLs consisted of triacylglycerols. Sterol esters, fatty acid esters, and free sterols were also present in substantial amounts.

In the quantitative respect, the glycolipids were the second fraction of the lipids of the fruit Ficus carica, amounting to 9.5 and 45.5%, respectively, for varieties I and II. The quantitative determination of the GLs was performed on the carbohydrate component [9], separation being carried out in systems 3 and 4. We give the composition of the glycolipids (% on the total GLs) below:

| <u>Glycolipids</u> | <u>Variety I</u> | <u>Variety II</u> |
|---|------------------|-------------------|
| Acylmonogalactosyldiglycerides | 5.1 | 5.2 |
| Esterified sterol glycosides | 15.3 | 14.4 |
| Monogalactosyldiglycerides | 17.4 | 19.1 |
| Sterol glycosides | 6.1 | 8.4 |
| Cerebrosides | 11.5 | 12.3 |
| Ceramide oligosides | 12.0 | 13.8 |
| Digalactosyldiglycerides | 13.4 | 11.3 |
| Ceramide phosphate inositoligosides | 7.2 | 9.0 |
| Sulfoquinovosyldiglycerides | 6.6 | 4.5 |
| Unidentified diglycerides (two compounds) | 5.4 | 4.0 |
| Total amount, mg/kg weight of the fruit | 727.2 | 1467.4 |

The predominating types of compounds in the fruit of the varieties of F. carica studied were mono- and digalactosyldiglycerides, esterified sterol glycosides, cerebrosides, and ceramide oligosides.

The main carbohydrate components of the GLs according to PC were galactose, glucose, and arabinose (1:1:1), making up more than 90% of all the monosaccharides.

The smallest fractions of the fig lipids in the quantitative respect were the phospholipids, amounting to 6 and 7%, respectively, for varieties I and II.

In the PLs of the figs, 10 types of compounds were detected (% on the total PLs):

| <u>Phospholipids</u> | <u>Variety I</u> | <u>Variety II</u> |
|--------------------------------------|------------------|-------------------|
| Diphosphatidylglycerols (DPGs) | 1.8 | 3.0 |
| Phosphatidic acids (PAs) | 7.1 | 18.4 |
| Phosphatidylethanolamines (PEs) | 3.6 | 1.9 |
| Phosphatidylglycerols (PGs) | 45.6 | 28.3 |
| Unidentified PLs | 3.8 | 11.1 |
| Phosphatidylcholines (PCs) | 18.2 | 10.5 |
| Phosphatidylserines (PSs) | 4.8 | 21.9 |
| Phosphatidylinositols (PIs) | 4.5 | 1.9 |
| Lysophosphatidylethanolamines (LPEs) | 8.5 | 1.8 |
| Lysophosphatidylcholines (LPCs) | 2.1 | 1.2 |
| Total PLs, mg/kg weight of the fruit | 459.3 | 225.7 |

The quantitative determinations of the PLs were made from their phosphorus content [10], separation being carried out by two-dimensional TLC in system 5. A characteristic feature of the PLs was the predominating amount of PGs and the comparatively small amount of the types of phospholipids most widely distributed in fruit - PCs and PEs [3-5]. The PLs of variety II differed from the PLs of variety I by a higher amount of PSs, PAs, and unidentified PLs (R_f 0.39 - two-dimensional TLC, system 5, second direction; R_f 0.42 - system 2).

In the fatty acid composition, determined by the GLC method, four acids predominated - linoleic, linolenic, palmitic, and oleic, making up more than 90% of all the acids (Table 1). The lipids of the fruit of Ficus carica were characterized by a high degree of unsaturation (>68%) of the fatty acid acyls, the bulk of which were polyunsaturated, which, to a certain extent, can explain the high liability to oxidative deterioration of figs and the products of their processing [11].

EXPERIMENTAL

The fruit of the Ficus carica L. was collected in the phase of full physiological ripeness (total sugars 15-70%) from plantations in the Gurdzhaani region of the Georgian SSR, in August 1985. The lipids were isolated [8] from a homogenate of the fresh fruit (flesh, skin) and were freed from nonlipid impurities by washing with extracts of an aqueous solution of $CaCl_2$ and by gel chromatography on Sephadex G-25.

Column chromatography was performed 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) heptane-methyl ethyl ketone-acetic acid (47.5:7.5:0.5), two runs; 2) chloroform-methanol-water (65:25:4); 3) acetone-toluene-acetic acid-water (60:60:2:1); 4) chloroform-acetone-

TABLE 1. Fatty Acid Composition (mol-%) of the Main Fractions of the Lipids of the Fruit of *Ficus carica* L.

| Variety | 12:0 | 13:0 | 14:0 | 14:1 | 15:0 | 16:0 | 16:1 | 17:0 | 18:0 | 18:1 | 18:2 | 18:3 | 20:2 | Σsat | Σunsat |
|----------------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|--------|
| Neutral lipids | | | | | | | | | | | | | | | |
| I | 0,1 | — | 0,4 | 0,1 | 0,2 | 13,4 | 0,5 | — | 2,4 | 16,1 | 27,3 | 37,4 | 2,1 | 16,5 | 83,5 |
| II | 0,3 | — | 0,2 | 0,1 | 0,1 | 9,5 | 0,3 | — | 2,6 | 17,0 | 30,1 | 39,1 | 0,7 | 12,7 | 87,3 |
| Glycolipids | | | | | | | | | | | | | | | |
| I | 0,7 | Tr. | 0,4 | 0,4 | 0,5 | 19,7 | 1,1 | Tr. | 2,1 | 16,1 | 24,5 | 30,7 | 3,8 | 23,4 | 76,6 |
| II | 1,7 | Tr. | 0,7 | 0,9 | 0,4 | 25,7 | 2,1 | — | 3,1 | 17,2 | 22,6 | 21,6 | 4,0 | 31,6 | 68,4 |
| Phospholipids | | | | | | | | | | | | | | | |
| I | 0,7 | — | 0,6 | Tr. | Tr. | 26,3 | Tr. | Tr. | 1,5 | 14,9 | 32,4 | 21,4 | 2,2 | 29,1 | 70,9 |
| II | 0,6 | Tr. | 0,5 | 0,2 | 0,3 | 29,6 | 1,5 | 0,2 | 0,2 | 4,8 | 31,5 | 28,0 | 2,6 | 31,4 | 68,6 |

methanol-acetic acid-water (6:8:2:2:1); and 5) 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.

The methylation procedure and the conditions for performing GLC have been described previously [12].

The water-soluble products obtained after severe acid hydrolysis of the GLs and PLs (2 N HCl, 48 h, 125°C) were separated and identified with the aid of paper chromatography according to Kates [6]. The paper chromatography of the carbohydrate components of the GLs was performed by the descending method in the benzene-butan-1-ol-pyridine-water (1:5:3:3, upper phase) method. The substances were revealed with the aniline phthalate chromogenic agent [13].

SUMMARY

The composition and amounts of various groups of neutral lipids, glycolipids, and phospholipids in the fruit of *Ficus carica* L., *Smena* and *Turetskii korichnevyi* varieties, have been investigated. About 30 groups of lipid substances have been identified, of which the predominating ones were triacylglycerols, free and esterified sterols, mono- and digalactosyldiglycerides, ceramide oligosides, cerebrosides, esterified sterol glycosides and phosphatidylglycerols. The fatty acids of the lipids consisted of 13 components, of which more than 90% was represented by linoleic, linolenic, oleic, and palmitic acids.

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