LIPIDS OF THE FRUIT OF Pyrus communis

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The compositions of the various groups of liposoluble compounds in the peel and flesh of the fruit Pyrus communis of the varieties Williams and Bere Ardanpon have been established and their amounts have been determined by chromatographic and chemical methods. The qualitative compositions have been shown to be identical and characteristic quantitative differences have been found in the lipids of individual elements of these pairs. The fatty acid compositions of the lipids have been studied.

The fruit of the common pear is used in foods in fresh and preserved forms [1]. At the present time, new regimes for the technological treatment of pears are being developed which take into account the chemical compositions of the various groups of biologically active substances of the whole fruit and their individual elements, and also the transformation of the compounds during preservation and storage. It is known [2] that the lipids and pigments of the fruit, in spite of their small amount, exert a substantial influence on the organoleptic indices, stability, and storage time of the products.

We have studied the composition and amounts of lipids and liposoluble pigments of the flesh and peel of the fruit of Pyrus communis of the widely grown varieties Williams (variety I – summer) and Bere Ardanpon (variety II – winter) gathered in the plantations of the Kuba zone of the Azerbaidzhan SSR in 1986.

According to the experimental results, the total amount of liposoluble compounds, determined as described in [3] amounted for pear samples of the variety Williams to 6850 mg/kg (peel) and 2674 mg/kg (flesh, and for the variety Bere Ardanpon to 9980 and 1587 mg/kg, respectively. It must be mentioned that the lipids content of the fruit Pyrus communis substantially exceeded that of applies [4], persimmons [5], citrus fruits [6], and grapes [7]. The considerably higher level of lipids in the peel as compared with the flesh is due to the fact that the dense cuticular membrane of the fruit is usually coated with a waxy bloom (pruinescence) and contains a larger amount of liposoluble pigments than the flesh.

The total lipids were separated into neutral lipids (NLs), glycolipids (GLs), and phospholipids (PLs) by column chromatography on silica gel [8]. The individual groups of lipid compounds were obtained by TLC. The lipids were identified and determined quantitatively as in [5]. The results of the analysis are given in Table 1.

The neutral lipids were the largest class of lipids of the pear peels in quantitative respect. However, their amount in the flesh was much lower (by a factor of 1.4-2).

When they were separated in system 1, the neutral lipids were found to contain more than ten groups of different compounds.

The compositions of the NLs of varieties I and II were qualitatively identical but the ratios of the groups in the individual varieties and elements of the fruits of Pyrus communis were different. Thus, the total amount of NLs in the peel exceeded their amount in the flesh 5- to 10-fold, which is characteristic for fruits having a waxy bloom on their surface. In addition, the amount of pigments, monoacylglycerols, hydrocarbons, and free fatty acids in the peel was greater than their amount in the flesh. The winter variety Bere Ardanpon had a considerably larger amount of sterols and pigments than the summer variety Williams.

The largest group of NLs in the flesh of the fruit of both varieties in the quantitative respect proved to be the free sterols. A determination of the composition of the sterols

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TABLE 1. Composition and Amounts of the Classes (mg/kg of the mass) and Group (% of the total) Lipids of the Fruits of the Varieties William (I) and Bere Ardanpon (II) of Pyrus communis

Lipids	Variety I		Variety II	
	peel	flesh	peel	flesh
1. Neutral lipids				
Total amounts, mg/kg	4110,0	812,9	5469,0	514,2
Hydrocarbons	5,0	1,4	4,8	0,8
Sterol esters	3,6	1,1	2,4	1,0
Fatty acid esters	8,4	3,8	9,0	3,6
Triacylglycerols	1,4	0,9	1,8	1,3
Tocopherols	0,3	0,1	0,1	0,1
Free fatty acids	2,9	0,4	3,1	0,2
Fatty alcohols	4,3	3,6	4,5	3,0
Diacylglycerols	6,9	8,2	6,4	8,6
Free sterols	9,8	8,3	10,7	16,7
Pigments (chlorophyll, carotenoids)	0,1	0,05	0,7	0,3
Monoacylglycerols	17,3	2,6	11,3	3,8
Total natural lipids	60,0	30,4	54,8	39,4
II. Glycolipids				
Total amount, mg/kg	1753,6	751,4	2455,0	625,3
Acylmonogalactosyldiglycerides	3,9	1,1	4,7	0,9
Esterified sterol glycosides	3,3	1,7	2,7	1,3
Monoglactosyldiglycerides	4,2	7,2	4,8	11,8
Sterol glycosides	2,7	3,4	1,8	6,5
Cerebrosides	2,1	2,5	1,4	2,5
Ceramide oligosides	3,6	3,5	4,1	4,7
Digalactosyldiglycerides	2,9	4,0	2,3	6,9
Ceramide phosphate inositol oligosides	1,7	2,5	1,1	2,3
Sulfoquinovosyldiglycerides	1,2	2,2	1,7	2,5
Total glycolipids	25,6	28,1	24,6	39,4
III. Phospholipids				
Total amount, mg/kg	986,4	1109,7	2 56,0	447,5
Diphosphatidylglycerols	0,5	2,9	—	—
Phosphatidic acids	0,3	1,3	—	—
Phosphatidylethanolamines	5,7	14,7	9,0	7,5
Phosphatidylglycerols	4,2	12 4	5,6	6,8
Phosphatidylcholines	2,4	4,7	4 6	5,2
Phosphatidylserines	0,6	2,2	0,5	0,8
Phosphatidylinositols	0,4	1,4	0,4	0,5
Lysophosphatidylethanolamines	0,2	1,0	0,3	0,3
Lysophosphatidylcholines	0,1	0,9	0,2	0,1
Total phospholipids	14,4	41,5	20,6	21,2

by GLC showed that the predominant (86.7%) component was β-sitosterol. Stigmasterol, campesterol, and brassicasterol were present in small amounts. A feature of the composition of the NLs of the flesh of the fruit Pyrus communis was the low amount of triacylglycerols and the comparatively high level of mono- and diacylglycerols (DAGs). In the DAGs the bulk (74.5%) consisted of the 1,2-isomers.

The glycolipids of the fruit Pyrus communis consisted of nine groups of compounds (see Table 1). The Gls were separated in systems 2 and 3 and were determined quantitatively from their carbohydrate components [10].

The predominating groups of glycolipid compounds in the fruit of the varieties of Pyrus communis studied were the monogalactosyldiglycerides, acylmonogalactosyldiglycerides, ceramide oligosides, esterified sterol glycosides and digalactosyldiglycerides. The glycolipids of the flesh differed by a higher amount of mono- and digalactosyldiglycerides and sterol glycosides. In the peel, in contrast to the flesh, a considerable proportion of the GLs consisted of acylmonogalactosyl diglycerides and esterified sterol glycosides. The ratios of the other groups of GLs in the flesh and the peel of the fruit were similar.

According to PC, in the carbohydrate components of the GLs galactose, glucose, and arabinose predominated.

Nine groups of compounds were found in the PLs of the fruit of Pyrus communis. The proportion of PLs in the total lipids of the flesh of variety I was considerably greater (~3-fold) than in its peel. However, these differences were only slight for variety II.

TABLE 2. Composition and Amounts of Liposoluble Pigments of the Fruit of Pyrus communis of the Williams I and Bere Ardanpon II Varieties

Pigment	Variety I		Variety II	
	peel	flesh	peel	flesh
Chlorophylls, % on the total:				
chlorophyll a	70,1	61 8	65,6	50,7
chlorophyll b	29.9	18,4	19,4	15,1
chlorophyllide a	Tr.	15,3	10.4	23,2
chlorophyllide b	Tr.	6 5	4,1	11,0
total amount, mg/kg	4.9	0,3	17,7	1,4
Carotenoids, % on the total:				
phytoene	0.9	2,9	0,5	2,0
phytofluene	1,7	3,1	1,1	2,3
α-carotene	7,2	5,0	4,8	6,1
β-carotene	11,5	38,1	7,7	16.6
hydroxy-α-carotene	4,5	0.9	6,0	0,4
cryptoxanthin	2,0	2.8	0,7	1,1
lutein	47 1	30.0	56.0	38,2
zeaxanthin	3,8	1,6	6.4	3,0
lutein monoepoxide	2,7	3.5	2.4	4,9
mutatoxanthin	1,7	1.1	Tr.	3,7
violaxanthin	7,8	4,9	9,0	6,5
luteoxanthin	2,4	1,5	—	—
neoxanthin	6 7	4.0	5.4	5,2
total amount, mg/kg	0.7	0,1	19,2	0,2

The phospholipids were separated by two-dimensional TLC in system 4 and were determined quantitatively from their phosphorus contents [11]. A characteristic feature of the composition of the PLs was the predominating (about 90%) amount of phosphatidylethanolmines, phosphatidylglycerols, and phosphatidylcholines.

The eluate containing the NLs was also used to study the liposoluble pigments – chlorophylls and carotinoids. An aliquot part of the NL eluate intended for the isolation of the carotenoids was freed from chlorophylls and lipids by saponification and was fractionated into carotenes and xanthophylls by the use of a sucrose column [12]. Part of the extract was freed from lipids and carotenoids by column chromatography on silica gel [13] and was used for determining chlorophyll. The bands of the pigments separated by TLC were removed from the plates and eluted with acetone, and their absorption spectra were studied in the visible and ultraviolet regions, their absolute and relative amounts (% on the mass) being determined on the basis of their molar extinction coefficients [14].

The pigment complexes of the varieties of pear studied had similar compositions, on the whole (Table 2). However, the total amount of pigments in the variety Bere Ardanpon proved to be considerably higher than in the variety Williams.

Particularly large differences (~27-fold) were found in the amounts of carotenoids in the peel of the fruit of both varieties of pears. In the flesh of the fruit, the amount of chlorophylls was higher than in the peel, which is obviously due to the greater activity of the enzyme chlorophyllase in the flesh. The relative amounts of xanthophylls in the peel was substantially higher (~1.5-fold) than in the flesh.

On the whole, with the exception of the peel of the winter variety Bere Ardanpon, the pears were characterized by comparatively low amounts both of chlorophylls and of carotinoids.

The amounts of vitamin-active pigments were 43.1 and 32.7% of the total carotenoid complex in the flesh and 18.5 and 12.5%, respectively, in the peel.

Among the fatty acids of the lipids of the flesh, palmitic, oleic, and linoleic acids predominated (Table 3). In addition, in the lipids of the flesh of variety II there were comparatively large amounts of an eicosadienoic ($\Delta^{11,14}$) and an eicosatrienoic ($\Delta^{5,8,11}$) acid.

The lipids of the peel contained a high level of an eicosatrienic acid and linoleic acid.

On the whole, the lipids studied were characterized by high levels (80-90%) of unsaturated fatty acids, which may explain the susceptibility to oxidative loss of pear raw material and the products of its processing.

TABLE 3. Fatty Acid Compositions of Pyrus communis Fruits, mol %

Fatty acid	Variety I		Variety II		Fatty acid	Variety I		Variety II	
	peel	flesh	peel	flesh		peel	flesh	peel	flesh
9:0	0,1	0,1	Tr.	0,1	17:0	0,2	0,3	0,2	0,1
10:0	0,1	0,1	0,1	0,2	18:0	2,9	6,0	1,1	4,3
12:0	0,2	0,2	0,3	0,1	18:1	12,1	27,4	3,7	17,5
13:0	0,2	0,2	0,1	0,1	18:2	29,5	56,0	19,6	22,8
14:0	0,3	0,2	0,1	0,3	18:3	2,3	1,1	0,4	0,4
14:1	Tr.	0,1	0,2	Tr.	20:1	0,0	12,5	Tr.	5,6
15:0	0,3	0,4	0,2	0,1	20:2	3,5	0,0	5,0	21,9
16:0	12,5	14,8	7,1	11,7	20:3	35,1	0,0	50,1	14,7
16:1	Tr.	0,6	0,2	0,1	Σ sat	16,8	22,3	9,4	17,0
16:2	0,7	0,0	0,2	Tr.	Σ unsat	83,2	77,7	90,6	83,0

EXPERIMENTAL

Column chromatography was performed on silica gel L 100/160 and thin-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–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 method of methylation and the conditions for performing GLC have been described previously [8].

The positions of the double bonds in the methyl esters of the 20:2 and 20:3 fatty acids were determined with the aid of the mass spectrometry of the trimethylsilyl derivatives of the diols obtained by the hydroxylation of the double bonds [15].

The diacylglycerol isomers were isolated by TLC on silica gel impregnated with boric acid [16]. The purity of the DAGs was monitored by the GLCs of their trimethylsilyl ethers in a nonpolar silicone column in the isothermal regime (300°C) [17]. The water-soluble products obtained by severe acid hydrolysis of the GLs and PLs (2 N HCl, 125°C, 48 h) were investigated in accordance with [13]. The compositions of the monosaccharides in the glycosides were determined by PC [18].

Individual representatives of the pigments were obtained by TLC on cellulose (Nagel) using the solvent system heptane–methyl ethyl ketone (5:3) to separate the xanthophylls and chlorophylls, and hexane–acetone (96:4) for the carotenes. The chlorophylls and carotenoids were identified and determined quantitatively on the basis of the nature of their spectra and the density of absorption of the pigments at points corresponding to the characteristic maxima in the 400-700 nm interval (Specord UV-Vis).

SUMMARY

The compositions and amounts of the various groups of neutral lipids, glycolipids, phospholipids, and liposoluble pigments in the peel and flesh of the Williams and Bere Ardanpon varieties of the fruit of Pyrus communis have been investigated for the first time.

The identity of the qualitative compositions has been shown and characteristic quantitative differences in the lipids of the individual elements of the pears have been determined.

About 30 groups of lipids and 17 pigment compounds have been identified, among which free sterols, mono- and diacylglycerols, liposoluble pigments (peel), and mono- and digalactosylglycerides, acylmonogalactosylglycerides, ceramide oligosides, sterol glycosides, phosphatidylethanolamines, phosphatidylglycerols, phosphatidylcholines, chlorophylls a and b, lutein, and β-carotene predominate.

The fatty acids of the lipids were represented by 18 components, of which 80-90% consisted of unsaturated acids – oleic, linoleic, eicosadienoic, and eicosatrienoic (peel).

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LIPIDS OF THE LEAVES OF Brassica oleracea

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The composition of the various groups of liposoluble compounds in the leaves of wild cabbage of early-, middle-, and late-ripening varieties have been identified and their amounts have been determined by chromatographic and chemical methods. About 30 groups of lipid substances have been identified, among which free and esterified forms of sterols, di- and triacylglycerols, hydrocarbons, lipoquinones, mono- and digalactoside glycerides, cerebrosides, phosphatidylethanolamines, phosphatidylglycerols, and phosphatidylcholines predominate. The presence of 13 components has been established among the fatty acids, linolenic acid being present in the greatest amount (~50%). The influence of the time of ripening of the cabbage variety (early-, middle-, or late-ripening) on the composition of the lipid complex has been elucidated.

The lipids are some of the main nutritional components of food products. The organoleptic evaluation of a foodstuff and its calorie content and also its quality and keeping

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