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THE STUDY OF FATTY AND ORGANIC ACIDS COMPOSITION IN QUINCE LEAVES AND FRUITS (*CYDONIA OBLONGA* MILL)

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Abstract

The composition of fatty and organic acids in quince leaves and fruits (*Cydonia oblonga* Mill.) of selection of M. M. Grishko National Botanical Garden of National Academy of Sciences of Ukraine sorts was determined by gas chromatography-mass spectrometry method. Six sorts of quince were examined: "Academichna", "Kashchenka N18", "Studenrka', "Oranzheva", 'Maria", "Darunok onuku". The presence of 36 fatty acids and 32 organic acids in leaves and fruits of the quince were identified and determined their content. Therefore, main acids are oxalic, citric, palmitic and linolenic acids in quince leaves and malic, palmitic and linoleic acids in quince fruits. The highest content of all acids were identified in the quince leaves of sort "Maria". Moreover, a quite high content of succinic acid in the quince leaves was detected.

Keywords: quince, fatty acids, organic acids, gas chromatography-mass spectrometry method.

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1. Introduction

The quince (*Cydonia oblonga* Mill.) is recognized as a raw material for gelling products, due to the high content of pectin substances which are natural sorbents and they main function is removing body toxins and radio nuclides. The quince has known from ancient times, but unfortunately, is not always sufficiently evaluated. Now quince plays an important role in the economy of some countries and in other countries it is used only to meet domestic needs. Natural habitat of quince is Eastern and Southern Transcaucasia, Asia Minor, Iran. In other parts of the world the wild quince has not been discovered. The quince is cultivated in more than 40 countries, mainly in the humid continental and subtropical climates. But mainly in many countries its plantations are small and the quince may only be found in private gardens.

Study of the chemical composition and pharmacological activity of quince has shown positive prospects of quince fruits and leaves usage for drugs creation [1–15].

In Ukraine, quince is grown in small amounts; mainly in the south-western and southern regions with an average temperature from 10 ºC to 15 ºC and the length of growing season

240–245 days. The part of quince among horticultural crops planting in Ukraine is 0.33 %. Productivity of quince in Ukraine is 1–2.5 kg/m^2 and depends on the climatic conditions, the sort and agronomic properties. Currently the quince is mainly grown in Ukrainian private households. In recent years, the cultivation of the quince is possible in the northern regions of Ukraine with an average temperature from 7 ºC to 10 ºC. Assortment of quince in Northern Ukraine is represented by some local forms and sorts mainly breeding by M. M. Grishko National Botanical Garden (NBG). Those objects are highly perspective for cultivation in the northern regions of Ukraine. In addition, some sorts of quince tolerating for the temperature decrease to –30–35 ºC were bred. This achievement was possible due to the work of the NBG. In conclusion, the border of the quince cultivation was moved for about 500 km from its original cultivation area to north. Works with the quince are the realization of academician Kashchenko ideas about the possibility of quince cultivation in Northern Ukraine. Furthermore, the sorts "Darunok Onuku", "Studentka", "Maria", "Kashchenka № 18", "Mria Shaydarovoy' resisting to critically low temperatures were created. Five sorts of the quince were listed in the Register of Plant Sorts of Ukraine [16].

The study of quince biologically active substances [17–22] and quince pharmacological activity [23–26] of NBG sorts have been studied during the last five years. Those studies showed that quince leaves of the sort "Oranzheva" may be used as a hepatoprotector and the sort "Academichna" as an antiulcer drug.

2. Aim

Study of the fat and organic acids composition in quince leaves by gas chromatography-mass spectrometry method.

3. Materials and methods

Leaf samples were collected from 6 sorts of quince breeding by NBG: "Academichna", "Kashchenka N18", "Studenrka", "Oranzheva", "Maria", "Darunok onuku". Leaves were collected in June and fruits were collected in September of 2013. Raw materials were ground to 1–3 mm particles and used for receiving chloroform-forming fractions by gas chromatography-mass spectrometry method.

Experimental procedure

Methyl esters of fatty acids were obtained by a Peysker modified method. A mixture of chloroform with methanol and sulfuric acid in a ratio 100:100:1 was used for methylation. 30–50 ml of lipophilic extract was placed in a glass vial and 2.5 ml of a mixture was added for methylation, and ampoules were sealed. Ampoules were placed in a thermostat with a temperature of 105 ºC for 3 hours. Ampoules were opened after the end of the methylation, their contents were transferred to a test tube, and powdered zinc sulphate was added on the tip of a scalpel as well as 2 ml water and 2 ml of hexane for methyl esters extraction. After careful shaking, hexanoic extracts were filtered and used for chromatographic analysis.

Injection into the chromatographic column was carried out in splitless mode. The speed of a sample injection is 1.2 ml/min for 0.2 minutes. Chromatograph Agilent Technologies 6890 with a mass spectrometer detector 5973. Chromatography column – capillary DB-5 with interne diameter 0.25 mm and a length of 30 m. Speed of carrier gas (helium) is 1.2 ml/min. Temperature of sample introduction heater is 250 ºC. Temperature of thermostat is programmed from 50 to 320 ºC with a speed of 4 ºC/min.

The mass spectra library NIST05 and WILEY 2007 with a total of more than 470.000 specters were used for components identification, as well as identification programs AMDIS and NIST. Internal standard method was used for quantitative calculations.

4. Results

In quince leaves were identified 36 fatty and organic acids, whereas 29 among them are common to all of the samples (**Table 1**).

Table 1
Fatty and organic acids of quince leaves

Name of the acid	Content in leaves of sorts, mg/kg dry plant					
	Academichna	Kashchenko N18	Studentka	Oranzheva	Maria	Darunok onuku
Capronic	52.2	42.3	52.7	68.2	79.2	54.2
2-Hexenic	53.1	29.1	58.9	92.5	53.2	37.8
3-Hexenic	145.3	109.5	182.7	232.0	213.2	126.4
Oxalic	3049.8	2495.6	2696.5	2650.6	2757.6	2010.9
Malonic	255.8	173.0	175.0	182.1	274.6	235.2
Succinic	502.4	417.5	281.7	557.1	472.7	208.0
Glutaric	10.9				21.5	8.2
Adipic	9.1	6.7	12.5	12.8	14.1	8.1
Azelaic	71.1	67.6	71.0	105.6	95.0	20.8
Fumaric	42.2	38.7	29.9	60.2	56.7	30.2
Benzoic	184.5	198.1	212.7	583.3	267.7	174.3
Phenylacetic	10.6	7.0	8.3	9.7	13.4	15.6
Salicylic	29.6	26.8	22.8	29.5	23.5	21.6
Vanillic	18.9	14.9	21.5	23.4	19.6	11.0
Malic	444.7	523.5	260.4	418.9	41.2	5.9
3-Oxy-2-methylglutaric				118.1	69.9	
Citric	1274.7	924.5	687.1	1062.0	2255.1	724.2
Cinnamic			101.5	96.5	109.2	10.3
p-Coumaric	13.4	13.3	17.0			
Ferulic		6.2	5.8	9.6		
Lauric	37.3	28.9	34.0	32.4	35.3	34.0
Myristic	88.2	110.2	96.6	53.3	90.6	70.8
Pentadecanoic	18.5	15.9	20.8	28.9	33.1	65.2
Palmitic	2330.9	2078.6	2620.7	2517.0	3484.6	2582.0
Palmitoleic	177.5	178.7	221.9	172.0	338.0	253.5
Heptadecanoic	19.6	16.8	22.3	23.9	26.8	27.3
Stearic	137.8	139.2	148.8	152.0	291.3	150.9
Oleic	120.9	144.9	121.4	123.2	231.9	123.9
Linoleic	492.6	411.6	513.8	360.2	561.5	628.1
Linolenic	1086.4	1021.3	1236.4	809.8	1688.3	1547.6
Arachinic	48.9	46.3	48.1	49.1	86.4	65.4
Heneicosanoic	9.2	7.1	8.6	8.4	12.7	14.3
Begenic	32.3	38.8	33.2	34.4	56.2	49.0
Tricosanoic					6.9	10.6
Tetracosanoic	16.4	18.2	15.5	8.3	18.2	24.5
Hexacosanoic	7.8	10.7	10.1	9.3		

In quince fruits were identified 32 fatty and organic acids, whereas 22 among them are common to all of the samples (**Table 2**).

Table 2

Fatty and organic acids of quince fruits

Name of the acid	Content in leaves of sorts, mg/kg dry plan					
	Academichna	Kashchenko N18	Studentka	Oranzheva	Maria	Darunok onuku
Caprinic		13.5	3.4			
Oxalic	12.2	29.6	62.8	8.2	10.4	16.5
Malonic	48.0	54.5	55.2	33.0	47.7	38.0
Succinic	31.9	21.7	40.9	60.5	73.3	45.9
Methoxysuccinic	6.2			9.2	13.4	4.9
Fumaric	22.4	41.0	50.1	40.3	40.4	75.3
Benzoic	6.2	5.9	42.9			
Vanillic	9.1				10.7	
Malic	3052.5	1285.6	3235.1	7302.5	7413.7	3105.6
Citric	105.7	183.6	159.2	82.6	233.6	105.1
Lauric	32.2	27.1	39.8	29.5	31.6	33.3
Myristic	28.0	61.5	55.1	108.8	44.6	39.2
Pentadecanoic	11.3	26.3	29.5	12.0	15.2	17.1
Palmitic	1136.0	1679.5	1379.7	1061.5	1086.3	1130.4
Palmitoleic	19.6	39.8	33.8	16.8	18.8	20.3
Heptadecanoic	25.7	46.1	40.6	25.4	25.8	31.9
Stearic	164.4	243.1	239.2	132.8	140.0	160.3
Oleic	295.7	453.9	338.8	135.0	144.4	150.1
8-Octadecenic	90.8	142.8	100.3	92.8	74.4	83.2
Linoleic	1446.4	2252.6	1399.6	1644.2	1779.7	1577.8
Linolenic	429.7	458.7	391.1	389.8	478.4	432.9
Arachinic	78.5	96.7	98.1	56.4	80.0	66.6
11-Eicosenoic	17.6					
11.14-Eicosadienoic		13.6		8.1	10.9	6.5
Heneicosanoic		23.4	14.1	11.6	12.5	9.2
Begenic	49.4	88.8	112.4	37.6	88.5	36.0
13-Docosenoic	61.4	95.7	78.9	35.6	118.2	21.8
Tetracosanoic	94.1	145.0	157.8	74.8	150.1	54.9
15-Tetracosenoic	54.7	60.3	80.3	45.1	88.6	29.6
Pentacosanoic				9.1	18.8	9.7
Hexacosanoic		138.8	272.4	77.8	147.9	75.6
Hexadecadienoic		40.3				

5. Discussion

As we can see from the **Table 1**, main organic acids of quince leaves were oxalic and citric acid. Palmitic and linolenic acids were dominated in the fat acids composition. The highest content of citric, palmitic and linoleic acid were identified in the quince leaves of sort "Maria". In addition, the highest amount of all acids was determined in the same sort.

Moreover, a quite high content of succinic acid in the quince leaves was detected: from 208.0 mg/kg ("Darunok Onuku") to 557.1 mg/kg ("Oranzheva").

It is known, that the succinic acid with citric acid stimulate redox reactions, respiration processes and ATP synthesis, activate organs and tissues physiological functions (stimulate adaptive, compensatory and protective capabilities of the organism), improve physical efficiency. The malonic acid is an antimetabolite of the succinic acid. Interestingly that the maximum ratio of succinic acid and malonic acid is 3:1 in the sort "Orangeva" quince leaves, which shows hepatoprotective properties (the aqueous extract).

The results in **Table 2** showed that the content of organic acid is higher in leaves than in fruits, except the malic acid which dominates among organic acids in quince fruits. Similar data were received by Portuguese explorers on local sorts of quince. Even though Portuguese quince sorts leaves had insignificant content of oxalic acid, other dibasic acids were not identified in them [27]. According with the **Table 2**, in quince fruits as well as in quince leaves, palmitic acid was the main fatty acid. Moreover, linoleic acid was dominated among of unsaturated fatty acids.

5. Conclusions

1. The presence of 36 fatty acids and 32 organic acids in leaves and fruits of the quince were identified and their content was determined by gas chromatography-mass spectrometry method.

2. Main acids were oxalic, citric, palmitic and linolenic acids in quince leaves and malic, palmitic and linoleic acids in quince fruits.

3. The highest content of all acids were in the quince leaves of sort "Maria".

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