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Volatiles of quince fruit and leaf (*Cydonia oblonga* Mill.) from Serbia

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***Abstract*:**

Veličković, D.T., Ristić, M.S., Milosavljević, N.P., Davidović, D.N., Milenović, D.M. Veličković, A.S.: *Volatiles of quince fruit and leaf (Cydonia oblonga Mill.) from Serbia. Biologica Nyssana, 7 (2), December 2016: 145-149.*

The subject of this study is the chemical composition of volatile fractions from the fruit and leaf of quince (*Cydonia oblonga* Mill.). Dominant components were ethyl 2-methylbutanoate, (*E*,*E*)-α-farnesene, ethyl-(2*E*,4*Z*)-decadienoate, pentadecanol, β-acoradienol, ethyl decanoate, ethyl octanoate, (*E*)-nerolidol, ethyl dodecanoate, 14-hydroxy-9-epi-(*E*)-caryophyllene, (2*Z*,6*E*)-farnesol, β-cedrene. Volatile fraction of the fruit was also characterized by ethyl-(4*Z*)-decenoate, ethyl 9-dodecenoate, ethyl hexanoate, ethyl nonanoate and β-cyclocitral, where in the leaf *n*-octanal, *n*-hexanol, *n*-nonanal and benzaldehyde were present.

Key words: Quince fruit, Quince leaf, Volatiles, 2-methylbutanoate, ethyl-(2*E*,4*Z*)-decadienoate

***Apstrakt*:**

Veličković, D.T., Ristić, M.S., Milosavljević, N.P., Davidović, D.N., Milenović, D.M. Veličković, A.S.: *Isparljive supstancije ploda i lista dunje (Cydonia oblonga Mill.) iz Srbije. Biologica Nyssana, 7 (2), Decembar 2016: 145-149.*

Predmet ove studije je hemijski sastav isparljivih frakcija ploda i lista dunje (*Cydonia oblonga* Mill.). Dominantne komponente su bile etil 2-metilbutanoat, (*E*,*E*)-α-farnezen, etil-(2*E*,4*Z*)-dekadienoat, pentadekanol, β-akoradienol, etil dekanoat, etil oktanoat, (*E*)-nerolidol, etil dodekanoat, 14-hidroksi-9-epi-(*E*)-kariofilen, (2*Z*,6*E*)-farnezol, β-cedren. Isparljivu frakciju ploda karakterišu etil-(4*Z*)-decenoat, etil 9-dodecenoat, etil heksanoat, etil nonanoat i β-ciklocitral, dok su u listu bili prisutni *n*-oktanal, *n*-heksanol, *n*-nonanal i benzaldehid.

Key words: plod dunje, list dunje, isparljive supstancije, 2-metilbutanoat, etil-(2*E*,4*Z*)-dekadienoat

Introduction

Quince fruit and its products (jam, marmalade, compote, juice, quince-brandy) are highly appreciated in the market. Some studies have shown that the quince is an excellent natural source of polyphenols and flavonoids (Oliveira et al., 2007; Silva et al., 2008), giving it a very important role and position in traditional medicine.

The fruit is used in the treatment of dysentery, the leaf can be used as a sedative and seed as an emulsifying agent in hair-fixing lotions (Elandsen & Magney, 1992; Bergman et al., 1996). In addition to fructose, glucose and sorbitol, malic, tartaric, citric, phytic and quinic acids, and crude fiber (Oliveira et al., 2008; Rodriguez-Guisado et al., 2009; Szychowski et al., 2014), as main phenolic components in the extract of quince leaf were found 5-O-caffeoylquinic acid and 3-O-caffeoylquinic acid (Costa et al., 2009). Latest studies show that *C. oblonga* is a rich source of chlorogenic acids, proanthocyanidins and flavonol C and O-glycosides (Karar et al., 2014), as well as the volatile components (Schmarr & Bernhardt, 2010). In the seeds of quince linoleic, palmitic, oleic, stearic, eicosanoic, palmitoleic and arachidonic acids were identified (Daneshvand et al., 2012; Szychowski et al., 2014). Among a large number of metabolites isolated from the quince fruit skin, a few have been identified and tested on radical-scavenging and antioxidant activities (Alesiani et al., 2010). Al-Snafi (2016) states antioxidant potential, immunological, antiallergic, cardiovascular, reproductive, dermatological, anticancer, antiinflammatory, antidiabetic, protective effects, as well as effect on respiratory smooth muscle contraction.

The main goal of this study was to determine quince volatiles of Serbian origin, and compare our results with accessible publications.

Material and methods

Plant material

For this study, it was used the quince *Cydonia oblonga* Mill. var. Leskovačka, from locality Džigolj, municipality Prokuplje, central Serbia (Jovanović, 1972). The authors are very grateful to Prof. Jugoslav Trajković (College of Agriculture and Food Technology) for botanical identification of the plant. Ripe fruits were collected in October 2013.

Isolation of volatiles (VS)

Volatiles were isolated from small pieces of quince fruit and cut fresh leaves. The materials were put into a round-bottom flask of 2 l, and hydrodistillation process was performed using a Clevenger-type apparatus (Ph. Eur. 4, 2002), with hydromodule 1 : 10. The VS were taken up in cyclohexane (1 ml), which was inserted in a graduated tube of the apparatus. Solutions were stored for a few hours at 4 °C in the dark until being analyzed by GC.

Identification of volatiles (VS)

Analytical gas chromatography (GC-FID) and combination of gas chromatography and mass spectrometry (GC-MS) were used for the characterization of volatiles trapped in graduated tube of the Clevenger type apparatus used.

GC-FID analysis was carried out on an Agilent Technologies, model 7890A gas chromatograph, equipped with split-splitless injector and automatic liquid sampler (ALS), attached to HP-5MS column (30 m × 320 μm, 0.25 μm film thickness) and fitted to flame ionization detector (FID). Carrier gas flow rate (H_2) was 1 ml/min, split ratio 1:30, injector temperature was 250 °C, detector temperature 300 °C, while column temperature was linearly programmed from 40 °C to 260 °C (at a rate of 4 °C/min), and then kept isothermally at 260 °C for 15 min. Sample solutions were prepared in cyclohexane (in conc. of approximately 10 g/l), and injected by ALS (2 μl).

The same analytical conditions as those mentioned for GC-FID were employed for GC-MS analysis, along with column HP-5MS (30 m × 250 μm, 0.25 μm film thickness), using HP G 1800C Series II GCD system [Hewlett-Packard, Palo Alto, CA (USA)]. Helium was used as a carrier gas. Transfer line was heated at 260 °C. Mass spectra were acquired in EI mode (70 eV) in m/z range 40-450. The amounts of 0.2 μl of sample solutions were injected.

Constituents were identified by comparison of their mass spectra with those stored in MS libraries (Wiley 275, NIST05 and Adams 2007), using different search engines (PBM, NIST 2.0), as well as using calibrated AMDIS (ver. 2.64) for determination and comparison of retention indices (Adams, 2007). Similarly, quantification of present constituents was achieved by normalization method, based upon the area percent report obtained by GC-FID. Statistics has been covered by FID specification (results with a range of deviation for the level 1%).

Table 1. Volatiles of different parts of quince (%, w/w)

Constituents	KIL	Fruit	Leaf
Ethyl 2-methylbutanoate	864	1.4	23.4
n-Hexanol	863	0.3	1.3
2-Methylbutyl acetate	875	tr.	-
2-Heptanol	896	0.7	0.7
n.i.	-	-	0.4
n.i.	-	-	0.3
Ethyl pentanoate (ethyl valerate)	901	tr.	-
Cumene	924	tr.	0.7
Ethyl tiglate	929	0.5	0.2
Benzaldehyde	952	-	1.0
6-Methyl-5-hepten-2-one	981	0.2	tr.
Ethyl hexanoate (ethyl caproate)	997	2.0	tr.
n-Octanal	998	tr.	2.0
(2*E*,4*E*)-Heptadienal	1005	-	tr.
Hexyl acetate	1007	tr.	-
β-Phellandrene	1025	tr.	-
1,8-Cineole	1026	tr.	-
Ethyl 2-hexenoate	1038	0.1	-
γ-Terpinene	1054	tr.	-
n-Octanol	1063	0.1	-
cis-Linalool oxide	1067	tr.	-
Fenchone	1083	tr.	-
Linalool	1095	-	tr.
Ethyl heptanoate (ethyl enanthate)	1097	0.8	tr.
4-Ethyl-2-hexynal	n.a.	-	0.6
n-Nonanal	1100	tr.	1.1
(*Z*)-Isocitral	1160	0.9	0.6
Ethyl 3-(methylthio)-(*Z*)-2-propenoate	n.a.	0.3	-
Camphor	1141	tr.	-
Ethyl-(4*E*)-octenoate	1184	0.2	-
α-Terpineol	1186	-	tr.
Ethyl octanoate (ethyl caprilate)	1196	4.3	1.9
n-Decanal	1201	-	0.3
β-Cyclocitral	1217	1.2	0.6
Ethyl-(2*E*)-octenoate	1245	0.5	-
Ionene	1258	0.6	0.3
Vitispirane	1272	1.0	0.6
Ethyl nonanoate (ethyl pelargonate)	1294	1.4	0.7
(2*E*,4*E*)-Decadienal	1315	0.3	-
n.i.	-	0.5	-
n.i.	-	0.1	-
Ethyl-(4*Z*)-decenoate	1380	2.7	1.9
Ethyl-(4*E*)-decenoate	1388	0.5	-
Ethyl decanoate (ethyl caprinate)	1395	6.3	3.9
(*E*)-β-Damascone	1413	0.9	0.6
β-Cedrene	1421	2.5	1.5
(*E*)-β-Farnesene	1454	tr.	-
Ethyl-(2*E*,4*Z*)-decadienoate	1467	8.3	4.2
(*E*)-β-Ionone	1487	tr.	tr.
Ethyl undecanoate	1498	0.7	0.7
(*E*,*E*)-α-Farnesene	1505	18.4	16.1
α-Dehydro-ar-himachalene	1516	0.6	-
Megastigmatrienone **	n.a.	0.2	-
(*E*)-Nerolidol	1561	4.1	2.7
Ethyl 9-dodecenoate	n.a.	2.2	-
Ethyl dodecanoate (ethyl laurate)	1594	3.2	3.8
β-Atlantol	1608	tr.	-
n.i.	-	3.0	1.7
n.i.	-	0.4	-
Himachalol	1652	0.5	0.3
Lyral	1665	tr.	-
14-Hydroxy-9-epi-(*E*)-caryophyllene	1670	3.8	2.3
n.i.	-	0.4	-
n.i.	-	0.2	-
(2*Z*,6*Z*)-Farnesol	1698	0.5	-
(2*E*,6*Z*)-Farnesal	1713	0.6	0.5
(2*Z*,6*E*)-Farnesol	1722	3.2	1.7
Ethyl 3-hydroxydodecanoate	n.a.	0.2	-
β-Acoradienol	1762	7.6	5.1
Pentadecanol	1773	7.8	5.2
n.i.	-	0.1	-
Ethyl tetradecanoate (ethyl myristate)	1795	tr.	-
Hexahydrofarnesyl acetone	1838	-	0.5
n-Hexadecanol	1874	0.3	-
Nonadecane	1900	0.3	-
Methyl hexadecanoate (methyl palmitate)	1922	0.5	-
n.i.	-	0.2	-
Ambrettolide	n.a.	0.2	-
Ethyl hexadecanoate (ethyl palmitate)	1992	tr.	-
Eicosane	2000	tr.	0.5
Octadecanol	2077	0.1	-
Heneicosane	2100	0.3	1.0
Ethyl oleate (ethyl (*Z*)-9-octadecenoate)	2179	0.7	0.7
Docosane	2200	0.2	-
n.i.	-	-	0.8
Tricosane	2300	0.2	0.9
Tetracosane	2400	0.2	1.1
n.i.	-	-	0.6
Pentacosane	2500	0.3	1.4
Hexacosane	2600	0.2	1.2
Heptacosane	2700	0.3	2.4

% w/w - mass percent defined by peak area percent determined by integration (GC-FID)

KIL - Kovats (retention) index (Adams, 2007)
n.a. - not available
n.i. - not identified
tr. - traces (< 0.1%)
** - tentative identification

Results and discussion

Table 1. shows a comparative overview of volatiles in the quince fruit and leaf, where 94.8% and 96.2% of the components were identified from the total mass, respectively.

Components which dominate in the quince fruit and leaf are (*E*,*E*)-α-farnesene (18.4% and 16.1%), ethyl-(2*E*,4*Z*)-decadienoate (8.3% and 4.2%), pentadecanol (7.8% and 5.2%), β-acoradienol (7.6% and 5.1%), ethyl decanoate (6.3% and 3.9%), ethyl octanoate (4.3% and 1.9%), (*E*)-nerolidol (4.1% and 2.7%) and ethyl dodecanoate (3.2% and 3.8%). The above components are more present in the fruit, with the exception of ethyl dodecanoate. One of the essential components of the leaf is ethyl 2-methylbutanoate with 23.4%, which is present in the fruit with only 1.4%.

Some more components that characterize the volatile fraction of the fruit are 14-hydroxy-9-epi-(*E*)-caryophyllene (3.8%), (2*Z*,6*E*)-farnesol (3.2%), ethyl-(4*Z*)-decenoate (2.7%), β-cedrene (2.5%), ethyl 9-dodecenoate (2.2%), ethyl hexanoate (2.0%), ethyl nonanoate (1.4%) and β-cyclocitral (1.2%). The leaf is characterized by 14-hydroxy-9-epi-(*E*)-caryophyllene (2.3%), *n*-octanal (2.0%), (2*Z*,6*E*)-farnesol (1.7%), β-cedrene (1.5%), *n*-hexanol (1.3%), *n*-nonanal (1.1%), benzaldehyde (1.0%), as well as the compounds of the cosane group.

The presence of fatty acid esters is obvious, especially in the quince fruit: ethyl decanoate (6.3%) > ethyl octanoate (4.3%) > ethyl dodecanoate (3.2%) > ethyl hexanoate (2.0%) > ethyl nonanoate (1.4%) > ethyl heptanoate (0.8%) > ethyl undecanoate (0.7%) > ethyl oleate (0.7%). Ethyl pentanoate, ethyl tetradecanoate and ethyl hexadecanoate occur only in traces.

Schmarr & Bernhardt (2010) identified esters in the quince fruit (ethyl butanoate, ethyl 2-methylbutanoate, 2-methylbutyl acetate, butyl acetate, hexyl acetate), alcohols (butanol, 2-methylbutanol, hexanol, (*E*)-2-hexenol), carbonyls (hexanal, (*Z*)-3-hexenal, (*E*)-2-octenal, (*E*/*Z*)-2-nonenal, 1-octen-3-one), and terpenes ((*E*)-β-damascenone, limonene, farnesene, linalool, eugenol). The authors assume that (*E*,*Z*)- and (*E*,*E*)-ethyl 2,4-decadienoate could be characteristic esters responsible for flavor. Sousa et al. (2007) identified *trans*-9-amino-8-hydroxy-2,7-dimethyl-nona-2,4-dienoic acid glucopyranosyl ester, homo-monoterpenic compound which could be chemical marker. Also, main volatiles of quince fruit were *trans*-α-farnesene, furfural, megastigma-4,6,8-trien-3-one, *trans*-marmelo lactone and *cis*-marmelo lactone (Tsuneya et al., 1983). The results of Umano et al. (1986) showed that main volatile constituents of quince fruit peel were ethyl propionate, ethyl acetate, ethyl dodecanoate, ethyl octanoate, ethanol, 2-methyl-1-propanol. The newest chemical analysis of *C. oblonga* showed that it contained phenolics, pectin, essential and volatile oils. The analysis of the leaves essential oils (Al-Snafi, 2016) showed that it contained aromatic aldehyde, fatty acid, oxygenated monoterpene, and sesquiterpene hydrocarbon (benzaldehyde, hexadecanoic acid, linalool, (*E*)-β-ionone, germacrene D).

We have also identified some of those substances, especially regarding the ethyl 2-methylbutanoate, ethyl-(2*E*,4*Z*)-decadienoate, (*E*,*E*)-α-farnesene, ethyl octanoate, and ethyl dodecanoate.

Conclusion

The presented results show that the quince fruit and leaf are an extraordinary source of substances, which from the chemical standpoint, belong to different groups of compounds. Quince fruit was rich in fatty acid esters. Among the volatiles, ethyl 2-methylbutanoate and ethyl-(2*E*,4*Z*)-decadienoate were the most abundant which could be responsible for flavor.

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References

Adams, R.P. 2007: Identification of Essential Oil Components by Gas Chromatography / Mass Spectrometry. 4th ed. Allured Publishing Corp., Carol Stream, IL 60188 USA.

Alesiani, D., Canini, A., D'Abrosca, B., DellaGreca, M., Fiorentino, A., Mastellone, C., Monaco, P., Pacifico, S. 2010: Antioxidant and antiproliferative activities of phytochemicals from Quince (*Cydonia vulgaris*) peels. *Food Chemistry*, 118: 199-207.

Al-Snafi, A. E. 2016: The medical importance of *Cydonia oblonga* - A review. *IOSR Journal of Pharmacy*, 6 (6): 87-99.

Bergman, R., Afifi, A.K., Heidgerip, P.M. 1996: Text of Histology. 9th ed. Saunders WB, Montréal, 159 p.

Costa, R.M., Magalhães, A.S., Pereira, J.A., Andrade, P.B., Valentão, P., Carvalho, M., Silva, B.M. 2009: Evaluation of free radical-scavenging and antihemolytic activities of quince (*Cydonia oblonga*) leaf: A comparative study with green tea (*Camellia sinensis*). *Food and Chemical Toxicology*, 47: 860-865.

Daneshvand, B., Ara, K.M., Raofie, F. 2012: Comparison of supercritical fluid extraction and ultrasound-assisted extraction of fatty acids from quince (*Cydonia oblonga* Miller) seed using response surface methodology and central composite design. *Journal of Chromatography A*, 1252: 1-7.

Elandsen, S., Magney, J. 1992: Color Atlas of Histology. 6th ed. Mosby, Toronto, 104 p.

European Pharmacopoeia, 2002. 4th edn., Strasbourg.

Jovanović, B. 1972. Genus *Cydonia* Mill. In: Josifović, M. (ed.), Flora SR Srbije. IV: 130-131, SANU, Beograd.

Karar, E.G.M., Pletzer, D., Jaiswal, R., Weingart, H., Kuhnert, N. 2014: Identification, characterization, isolation and activity against *Escherichia coli* of quince (*Cydonia oblonga*) fruit polyphenols. *Food Research International*, 65: 121-129.

Oliveira, A.P., Pereira, J.A., Andrade, P.B., Valentão, P., Seabra, R.M., Silva, B.M. 2007: Phenolic profile of *Cydonia oblonga* Miller leaf. *Journal of Agricultural and Food Chemistry*, 55: 7926-7930.

Oliveira, A.P., Pereira, J.A., Andrade, P.B., Valentão, P., Seabra, R.M., Silva, B.M. 2008: Organic acids composition of *Cydonia oblonga* Miller leaf. *Food Chemistry*, 111: 393-399.

Rodriguez-Guisado, I., Hernández, F., Melgarejo, P., Legua, P., Martínez, R., Martínez, J.J. 2009: Chemical, morphological and organoleptical characterisation of five Spanish quince tree clones (*Cydonia oblonga* Miller). *Scientia Horticulturae*, 122: 491-496.

Schmarr, H.G., Bernhardt, J. 2010: Profiling analysis of volatile compounds from fruits using comprehensive two-dimensional gas chromatography and image processing techniques. *Journal of Chromatography A*, 1217: 565-574.

Silva, B.M., Valentão, P., Seabra, R.M., Andrade, P.B. 2008. Quince (*Cydonia oblonga* Miller): an interesting dietary source of bioactive compounds. In: Papadopoulos, K.N. (ed.), Food Chemistry Research Developments: 243-266, Nova Science Publishers, Inc., New York.

Sousa, C., Silva, M.B., Andrade, B.P., Valentão, P., Silva, A., Ferreres, F., Seabra, M.R., Ferreira, A.M. 2007: Homo-monoterpenic compounds as chemical markers for *Cydonia oblonga* Miller. *Food Chemistry*, 100: 331-338.

Szychowski, J.P., Munera-Picazo, S., Szumny, A., Carbonell-Barrachina, A.Á., Hernández, F. 2014: Quality parameters, bio-compounds, antioxidant activity and sensory attributes of Spanish quinces (*Cydonia oblonga* Miller). *Scientia Horticulturae*, 165: 163-170.

Tsuneya, T., Ishihara, M., Shiota, H., Shiga, M. 1983: Volatile Components of Quince Fruit (*Cydonia oblonga* Mill.). *Agricultural and Biological Chemistry*, 47 (11): 2495-2502.

Umano, K., Shoji, A., Hagi, Y., Shibamoto, T. 1986: Volatile constituents of peel of quince fruit, *Cydonia oblonga* Miller. *Journal of Agricultural and Food Chemistry*, 34 (4): 593-596.