ANALYSIS OF *FICUS CARICA* L. – VOLATILE COMPONENTS AND MINERAL CONTENT

Emese Ficsor[a], Klára Szentmihályi[b], Éva Lemberkovics[a], Anna Blázovics[a], Andrea Balázs[a]

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Ficus carica L. is a well-known Mediterranean plant, its fructus - the fig- is consumed widely, mostly in the southern region of Europe. It's a member of the Moraceae family, one of the earliest crops. It can be consumed raw, dried or even as jam as a part of the Mediterranean diet. One part of our research was to determine the volatile components of *Ficus carica* L. The composition of volatile components are important for the determination of fruit quality. We compared two extraction methods, examined by SPME-GC/MS. Two preparation methods were used: directly measured by SPME, and also samples made by steam distillation. Figs has an important role as phytonutrition. Mineral element content was determined by ICP. Fig is a good source of elements for Ca, Cr, Cu, Fe, K, Mg, Mn and Mo, since eating 5 dkg of dried fig covers more than 15% of the Recommended Dietry Allowances.

* Corresponding Authors
E-Mail: fiemes@indamail.hu

[a] Semmelweis University, Department of Pharmacognosy, H-1086 Budapest, Üllői street 26, Hungary

[b] Institute of Materials and Environmental Chemistry Research Centre for Natural Sciences of the HAS, H-1025 Budapest, POBox 17, Hungary.

Introduction

As Hippocrates said: "Let food be thy medicine and medicine be thy food", phytonutritions role are becoming more important. Many researches are carried out to determine the active components of plants of traditional medicine and nutrition.

Ficus carica L. is part of the Moraceae family, it has been cultivated since ancient times. It requires wasp pollination of a particular species of wasp to produce seeds. *Ficus carica* L. is a widely known and consumed Mediterranean plant. Its fruit is without fat and cholesterol, it contains lots of vitamins, good source for dietary fiber. It's also a good source for mineral elements. In medicine, it is internally used to control digestion. As a part of the Mediterranean diet, it's little laxative effect is quite useful. Fresh *Ficus carica* L. fructus contains lots of pectin, which influences the human body to reduce the cholesterol amount. It contains a lot of antioxidants, a good source of polyphenols and flavonoids.[1]

One of the essential parameter of fruit quality is the aroma, which is determined by the volatile components. They can be derived from amino acids, fatty acids and carbohydrate compounds.[2] Volatile compounds present in the fresh and processed fruits affect the flavour and food quality which is formed by a complex mixture of chemical substances like aldehydes, alcohols, ketones, esters, terpenes and other compounds.[3] The variability of aroma components depend on climatological conditions, cultivar, maturity and technological factors, like harvest, post-harvest treatments, processing and storage conditions. [4,5]

Traditional methods used for determine volatile components are time consuming and require several steps. Methods using solid phase micro extraction (SPME) technique save preparation time, solvent and can improve the detection limits.[6] This type of extraction is a solventless extraction alternative and no modifications occur in the components due to the solvent or the temperature effect. SPME technique has been widely used for the analysis of volatile and semi-volatile components from environmental, biological and food samples.[7]

Mineral elements (macro-, meso- and trace-) play an important role in effecting the proper mechanism in the human body.[8] These components usually obtained from nutrition, but usually not enough is gained. The improper dietetic culture and the unhealthy food consumption play part in prelatent, latent or manifested metal deficiency. Nowadays lots of supplements are commercially sold, but hardly any of them contains the needed elements in the right natural form, therefore their absorption or bioavailability in the human body is not as it is expected.[9,10] Nutrition is the best for gaining these elements by natural form. Previous studies indicate that *Ficus carica* L. is a good source of minerals, vitamins and dietary fibre. [7,11]

The aims of our research was to examine the volatile components in extracts obtained by different extraction methods and determine the mineral element content of the *Ficus carica* L. fructus and folium as well as evaluate as a phytonutrient.

Experimental

Ficus carica L. samples

The *Ficus carica* L. folium and fructus from Hungarian origin was used. The fructus was obtained from the Hungarian trade in order to examine what would get into the human organ by randomly bought fruit, while the folium was collected from Budakeszi under Hungarian weather conditions. The Italian origin folium and cortex were collected in Latina (Italy). The fructus was lyophilised, the folium and cortex were both air-dried.

Microscopical preparations

The fructus and folium samples with Hungarian origin were examined. Due to the regulation of the eighth Pharmacopoea Hungarica, cross sections and powder preparations were made to determine the microscopic features.[12]

GC analytical procedures

The analysis was carried out with an Agilent 6890N/5973N GC-MSD (Santa Clara, CA, USA). Separations were performed using an Agilent HP-5MS capillary column (30 m × 250 μm × 0.25 μm). The GC oven temperature was programmed from 60 ºC (3 min isothermal) to 200 ºC at 8 ºC min^{-1} (2 min isothermal), 200-230 ºC at 10 ºC min^{-1} (5 min isothermal) and finally 230-250 ºC at 10 ºC min^{-1} (1 min isothermal). Helium was the carrier gas at 1.0 mL min^{-1} (37 cm s^{-1}) in constant flow mode.

The mass selective detector was equipped with a quadrupole mass analyzer and was operated in electron ionization mode at 70 eV. The MS was operated in full scan mode (41-500 amu at 3.2 scan s^{-1}), and data were evaluated by MSD ChemStation D.02.00.275 software (Agilent).

Volatile extraction

Samples from the Hungarian folium and fructus were created by steam distillation described by the Pharmacopoeia Hungarica VIII.[12] These results were compared by samples measured directly by SPME.

Measurement of element concentrations

The element concentration (Al, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, S, Si, Sn, Sr, Ti, V, Zn) of the fig fruit and folium from Hungarian trade and Italian origin plant was determined with an ICP-OES (inductively coupled plasma optical emission spectrometer). Type of instrument: Spectro Genesis ICP-OES (Kleve, Germany). The samples were measured three times.

Results and Discussion

Microscopic examination

First the microscopic features of folium and fructus were determined. Several Ca-oxalate rosettas and covering trichomes on the folium were found by cross section, these are good identification signs in the powder preparations as well. In the folium cross section the porous and columned parenchyma can be easily observed next to the many trichomes. In the fructus powder preparations oil drops and oil beads were present with several covering trichomes and Ca-oxalate rosettas.

GC-analytical measurements

One part of our research was to determine the volatile components of *Ficus carica* L. For the examination of volatile components, SPME method connected to GC-MS (SPME-GC/MS) was used beside the traditionally applied extraction methods (solvent extraction and steam distillation). For these experiments *Ficus carica* L. samples of Hungarian origin was applied. The results of samples made by steam distillation were compared with the results obtained from direct examination by SPME (no extraction methods were used).

Examining the *Ficus carica* L. fructus directly with SPME, only one volatile compound, 2,3-butane-diol, was found. In the other side, when used steam distillation first and measured by SPME-GC-MS, the sample contained many other components. These components were mainly hydrocarbons, like the tetramethyl-decane, trimethyl-undecane, octadecane and one terpene, which was carvacrol. ß-Caryophyllene, caryophyllene-oxid and apiol were also present. Carvacrol is a monoterpenoid phenol, it has a characteristic, purgent odor. It inhibits the the growth of several bacteria strains like *Escherichia coli* and *Bacillus cereus*.[13] It also activates PPAR and suppresses COX-2 inflammation.[14] ß- Caryophyllene is known for its antibacterial properties.[15] Sesquiterpenes, like ß-caryophyllene, are released in response to the attack by *Spodoptera exigua* larvae in cotton plantlets. This confirm the hypothesis that these components play part in the defence against insects.[16] β-Caryophyllene has been shown to selectively bind to the cannabinoid receptor type-2 (CB_2) and to exert significant cannabimimetic antiinflammatory effects in mice. It doesn't have psychomimetic effects because it doesn't bind to the centrally expressed cannabinoid receptor type-1.[17] In the fructus damascenone is present, which is derived from the degradation of carotenoids. It belongs to a family of chemicals known as rose ketones, and has an important role in creating the rose aroma.[18]

Examined the folium volatile compounds directly by SPME, the main components were 3,5-octadiene-2-on and trimethyl-methylene-vinilbicyclononane. Other components were like aldehyde (hexanal), hydrocarbons (undecane, dimethyl-undecane) and alcohol (ethyl-cyclohexanol). Hexanal is an alkyl-aldehyde, which is used by the flavor industry to produce fruity flavour. Undecane has affects on moths as a mild sex attractant, and also as an alert signal for ants.[19] Benzaldehyde is one of the simplest aromatic aldehyde, which is used by the industry because it has an almond-like odor. It is the primary component of bitter almond oil, and can be extracted from other natural sources as well. Limonene is also present in the folium, it is a cyclic terpene. Mainly the D isomer is present, which gives a natural citrus smell like orange. It can be found in many citrus fruits.[20]

The samples made from the folium by steam distillation and measured by SPME-GC-MS contained well known substances, like hydrocarbons (methyl-undecane, dimethyl-undecane and nonadecane), sesquiterpenes - which are present in the fructus as well- like ß- caryophyllene and caryophyllene-oxid. Ionones are a series of closely related chemical substances, mostly aroma compounds found in the many essential oils, like in rose oils. β-ionone contributes to the aroma of roses, it is present in a low concentration, and also used in parfumery.[18]

Examining the folium and fructus by different extraction methods the data show that great variety can be observed in the determined components.

Mineral elements

Mineral element content was determined by ICP method. The fig fruit and folium from Hungarian trade and also Italian origin *Ficus carica* L. folium and cortex was measured.

The Italian origin *Ficus carica* L. samples (folium and cortex) contain the following mineral elements in about average plant concentration[21,22]: Al, B, Ba, Ca, Cd, Co, Cu, Mg, Mo, Na, Ni, Sn, V (Table 1). The concentrations of P (<3000 μg g^{-1}), S (<1000 μg g^{-1}) and (<20 μg g^{-1}) in both samples was low. The amount of Fe (<100 μg g^{-1}), K (< 20 000 μg g^{-1}) and Mn (<10 μg g^{-1}) was also found to be low in the folium and in the cortex as well.

Table 1. Mineral concentration ± standard deviation (μg g^{-1}) of Italian origin *Ficus carica* L.

Elements	Folium	Cortex
Al	131.8±5.1	34.36±3.60
B	84.57±4.30	66.50±4.37
Ba	13.46±0.06	10.70±0.30
Ca	27531±137	18623±712
Cd	0.65±0.01	0.63±0.01
Co	0.41±0.01	0.39±0.01
Cr	2.46±0.31	1.44±0.40
Cu	4.84±0.21	4.21±0.00
Fe	153.22±5.14	28.12±4.60
K	24786±280	13902±879
Mg	3519±70	2202±285
Mn	22.69±0.61	5.06±0.82
Mo	0.87±0.01	0.49±0.10
Na	239.4±8.3	87.40±18.32
Ni	1.44±0.19	0.73±0.01
P	945.9±3.1	960.7±107.5
Pb	1.12±0.17	2.90±2.66
S	819.3±37.6	356.7±26.4
Si	183.6±31.6	169.4±6.3
Sn	0.91±0.22	1.49±0.49
Sr	142.4±8.2	70.44±4.71
Ti	4.70±0.38	0.66±0.33
V	0.82±0.01	0.38±0.01
Zn	14.37±0.28	6.33±0.68

In the Hungarian origin *Ficus carica L.* samples, mineral elements like Al, B, Ba, Cd, Co, Cu, Mg, Mo, Na, Pb, Sn, V and Ti are present in average concentration compared to other plants as it can be seen in Table 2. The amount of Ca and Fe in the Hungarian folium was higher than usually available in other plants.[21] Relatively low concentration was found in the Hungarian origin fructus for Ca (<10000 μg g^{-1}), Fe (<100 μg g^{-1}), K (< 20 000 μg g^{-1}), Mn (<10 μg g^{-1}), and S (<1000 μg g^{-1}), while the Cr concentration was high (>1 μg g^{-1}) compared to the average plant concentration determined by other authors. [21,22] In the Hungarian samples the amount of P (<3000 μg g^{-1}) and Zn (<20 μg g^{-1}) was also low.

Comparing the macro element content of folium samples the amount of Ca is almost the same in the Italian and Hungarian folium. The amount of Na in the folium of Italian origin was much higher than in the folium of Hungarian origin, but it was also the same in the cortex and in the fructus. Regarding the K content, the Italian folium contains higher concentration than the others, since it is almost the same in them. The amount of Mg in the two foliums was almost the same, but it was less in the fructus.

Table2. Mineral concentration ± standard deviation (μg g^{-1}) of Hungarian origin *Ficus carica* L.

Elements	Fructus	Folium
Al	24.24±14.72	105.5±1.98
B	50.44±11.28	130.1±5.29
Ba	6.60±1.09	7.97±0.09
Ca	6006±613	27611±152
Cd	0.61±0.01	0.64±0.00
Co	0.69±0.33	0.41±0.01
Cr	1.34±0.49	1.25±0.07
Cu	5.66±0.00	8.57±0.13
Fe	41.62±3.47	182.6±3.06
K	13892±415	16000±234
Mg	1381±186	3565±174
Mn	7.76±0.01	27.02±1.31
Mo	0.54±0.17	0.84±0.09
Na	88.49±10.83	136.6±7.9
Ni	1.74±0.07	1.70±0.03
P	1054±44	1285±31
Pb	<detection limit	0.99±0.27
S	536.1±7.5	1150±67
Si	157.4±40.4	106.9±16.3
Sn	1.24±0.51	0.72±0.21
Sr	20.12±2.89	64.37±4.20
Ti	1.03±0.66	3.43±0.24
V	0.38±0.02	0.58±0.00
Zn	9.80±0.39	14.27±0.80

The amount of Fe was highest in the Hungarian origin folium, followed by the Italian folium. The amount of Fe in the fructus is not high. The Zn content was same in the foliums, while it was a little less in the fructus. The amount of Mn in both foliums was almost the same, nevertheless in the fructus it was less compared to the foliums. In the Hungarian *Ficus carica* L., both in the fructus and in the folium, the concentration of Cu was higher compared to the samples of Italian origin. The concentration of Cr (>1μg g^{-1}) in both Italian samples, of Ti (>2 μg g^{-1}) in the folium and of Pb (>2 μg g^{-1}) in the cortex was high. Comparing the Hungarian and Italian samples it can be seen that the amount of Ca, Cd, Co, Mg, Sn and Zn doesn't differ significantly. These mineral elements are probably specific feature for the species which does not depend on the geological and weather conditions.

Mineral element intake

Fig fruit contains low calorie. Depends on the species of *Ficus*, the weight of one fresh fructus can be around 10-20 dkg. In dry form fig contains 4-5 times more dry matter content, so more precious components can be found. In dried form the fructus contains more calorie, it is around 249 calories counted for 100 g.

Calculating the mineral element intake by fig fruit, it can be stated that fig is a good source of elements for Ca, Cr, Cu, Fe, K, Mg, Mn and Mo, since eating 5 dkg of dried fig covers more than 15% of the Recommended Dietry Allowances (RDA).[23]

The RDA of K for the human body is 2000 mg/70 kg body weight/day and the Dietary Reference Intake (DRI)[24] of Na is also 2000 mg/70 kg body weight/day. The fig eating (5 dkg, 2-3 pieces of dried fruit) covers 34.7% of K requirement (RDA), while 0.2% of Na intake (DRI). The optimal Na:K rate is about 1:4. Usually, this rate is shifted to

Na, because of the used methods in the food industry. In this case, the Na:K rate is greatly shifted to the K side. The RDA of Ca for an adult is 800 mg/70 kg body weight/day. Five dkg of fig contains 37.6% of RDA. The RDA of Mg for the human body is 6 mg kg^{-1} so for a 70 kg person it is 420 mg d^{-1}, 16.4% of which may be ensured by fig. In general the ratio of optimal intake between Ca and Mg is from 2:1 to 1:1, which is about 4:1 in the case if fig. RDA values of Mn are 2.4 mg for men and 1.6 mg for women, that's why calculating for an average 2 mg need, the fig fructus contains 19.4% of the RDA. The RDA value of Cu is 1 mg d^{-1} now, so the fig fructus covers 38.8% of the RDA. According to the calculations relevant element intake can be got for Cr (167.5% of RDA), Fe (15%) and Mo (54%) as well.

In the case of non essential elements, high amount of intake could obtaine for Al with 30.3% of the DRI (DRI: 4 mg d^{-1}), B with 262.7% of the DRI (DRI: 0.96 mg d^{-1}, Ba with 33% of the DRI (DRI: 1 mg d^{-1}), Cd with 17.9% of the DRI (DRI: 0.17)[25], Co with 119% of the DRI (DRI: 0.029 mg d^{-1})[26], Ni with 22.9% of the DRI (DRI: 0.38 mg d^{-1}), Sr with 20.1-100% of the DRI (DRI: 1-5 mg d^{-1}) and V with 105.5% of theDRI (DRI: 0.018 mg d^{-1}).

Conclusion

Fig is consumed widely, as a part of the Mediterranean diet knowing the inner components combination can be useful to determine its role as a phytonutrient. Nutrition is important to gain and preserve human health. Macro- and microelements take part in many enzyme reactions, influencing the normal function from the base.

In our research, we wanted to highlight the importance of knowing what components get into the human body by consuming phytonutrients like *Ficus carica* L.

Since the Ca, Cd, Co, Mg, Sn and Zn concentration doesn't differ significantly between the Hungarian and Italian folium samples it is supposed to be a specific feature for the species which does not depend on the geological and weather conditions.

Fig fruit is a good source of Ca, Cr, Cu, Fe, K, Mg, Mn and Mo, since eating some pieces of dried fig covers more than 15% of the RDA.

References

[1]Balázs, A., Ficsor, E., Győry, H., *Orvosi Hetilap*, **2011**, *152 (2)*, 72-75.

[2]Guedes de Pinho, P., Pereira, D. M., Gonçalves, R. F., Valentão, P., Fernandes, F., Taveira, M. Andrade, P. B., *Functional plant science and biotechnology*. Middlesex: Global Science Books, **2009**, 1-15.

[3]Riu-Aumatell, M., Castellari, M., López-Tamames, E., Galassi, S., Buxaderas, S., *Food Chem.*, **2004**, *87*, 627-637.

[4]Botondi, R., De Santis, D., Bellicontro, A., Vizovitis, K., Mencarelli, F., *J. Agric. Food Chem*., **2003**, *51*, 1189-1200.

[5]Lin, J. M., Rouseff, R. L., Barros S., Naim, M., *J. Agric. Food Chem*., **2002**, *50,* 813-819.

[6]Dong, C., Mei, Y., Chen, L., *J. Chromatogr.A*, **2006**, *1117*, 109-114.

[7]Oliveria, A. P., Silva, L. R., Andrade, P. B., Valentão, P., Silva, B. M., Pereira, J. A., Guedes de Pinho, P., *Food Chem*., **2010**, *121*, 1289-1295.

[8]Anke M., *Elements and their Compounds in the Environment,* Vol.1. General Aspects, Merian, E., Anke, M., Ihnat, M. (eds.), **2002**, 343-367.

[9]Szentmihályi, K., Vinkler, P., Fodor, J., Balla, J., Lakatos, B. *Orv. Hetilap*, **2006**, *147 (42)*, 2027-2030

[10]Szentmihályi, K., Vinkler, P., Fodor, J., Balla, J., Lakatos, B. *Orv. Hetilap*, **2009**, *150 (15)*, 681-687.

[11]Solomon, A., Golubowicz, S., Yablowicz, Z., Grossman, S., Bergman, M., Gottlieb, H., et al., *J. Agric. Food Chem.*, **2006**, *54*, 7717-7723.

[12]*Pharmacopoeia Hungarica* VIII. (Ph.Hg. VIII): Medicina Publisher, Budapest, **2004.**

[13]Du, W. X., Olsen, C. E., Avena-Bustillos, R. J., McHugh, T. H., Levin, C. E., Friedman, M., *J. Agric. Food Chem.*, **2008**, *56 (9),* 3082–8.

[14]Hotta, M., Nakata, R., Katsukawa, M., Hori, K., Takahashi, S., Inoue, H., *J. Lipid Res.,* **2010**, *51*, 132–9.

[15]Kim, Y. S., Park, S. J., Lee, E. J., Cerbo, R. M., Lee, S. M., Ryu, C. H. et al., *J. Food Sci.*, **2008**, *73*, 540-545.

[16]Loughrin, J. H., Manukian, A., Heath, R. R., Turlings, T. C. J., Tumlinson, J. H., *Proc. Natl. Acad. Nat. Acad. Sci. USA*, **1994**, *91*, 11836-11840.

[17]Gertsch J, Leonti M, Raduner S, et al., *Proceedings of the National Academy of Sciences of the United States of America*, **2008**, *105 (26)*, 9099–104.

[18]Sachihiko, I., Shigeo, K., Takeo, S., *Helvetica Chimica Acta* **1973**, *56 (5),* 1514–1516.

[19]Hölldobler B, Wilson E. O., *The Ants*. Harvard University Press, **1990**, p. 287.

[20] Fahlbusch, K. G., Hammerschmidt, F. J.,Panten, J., Pickenhagen, W., Schatkowski, D., Bauer, K., Garbe, D.; Surburg, H. *Flavors and Fragrances*. *Ullmann's Encyclopedia of Industrial Chemistry*, **2003**.

[21]Kabata-Pendias, A., Mukherjee, A. B., *Trace Elements from Soil to Human.* Springer Verlag, **2007**.

[22]Szentmihályi, K., Hajdú, M., Then, M., *Medicinal and Aromatic Plant Science and Biotechnology*, **2008**, *2*, 57-62.

[23]*Recommended Dietary Allowances* (RDA) 10th ed. National Academy Press, Washington D.C., **1989**.

[24]*Dietary Reference Intakes for vitamin A, vitamin K, arsenic, boron, chromium, copper, iodine, iron, manganese, molybdenum, nickel, silicon, vanadium, and zinc.* Food and Nutritional Board, Institute of Medicine. National Academic Press, Boston, **2002**, 772-773.

[25] *EFSA: Summary of option, Cadmium in food*, **2009**.

[26]EFSA, *EFSA J.,* **2009**, *7(12)*, 1383.

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