THE INFLUENCE OF EXTRACTION ON VITAMIN C DETERMINATION IN CHERRY AND SOUR CHERRY

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Abstract

Fruits are an important part of human diet because of their benefits for health. Cherries and sour cherries have a large consumption rate both in fresh state and conserved and are cultivated on large areas. They contain a lot of phytonutrients: fibres, microelements, polyphenols, antocianins and vitamins. The aim of this study was to evaluate the influence of extraction on vitamin C determination in two different species of cherries and sour cherries using iodometric titration. Cherries have vitamin C content between 10.41 and 13.55 mg/100g and sour cherries between 20.90 and 24.95 mg/100g and there were no significant differences between the results obtained by using methaphosphoric acid, aqueous solution 5% or chlorhidric acid, aqueous solution 2% as extraction solvent. Direct and indirect method does not significant affect the determination of vitamin C.

Key words: Vitamin C, cherry, sour cherry

INTRODUCTION

Fruits are an important part of human diet with great influence on health, due to their chemical constituents. Among stone fruits, cherries and sour cherries have a large consumption rate both in fresh state and conserved in different ways. More than hundred species, cultivated or savages are known derivated from *Prunus avium* (cherry) and *Prunus cerasus* (sour cherry or tart cherry). Originated from Anatolia, they are cultivated nowadays on large temperate areas in Europe, Asia, Northern America and Australia. Turkey is the major producer with 480,748 to for cherry and 187,941 to for sour cherry meanwhile Romania was on eleventh position in world cherry production in 2012 (https://en.wikipedia.org/wiki/Cherry).The harvesting period is short, mostly early summer so the storage conditioning is important as well as the conservation techniques (Poiana et al., 2010, Grigoraş and Gavrilă, 2009, Wang, 2006).

They are rather sour fruit with low glycemic index (22 compare to 40 on blueberries) that has great importance in diabetes prevention. The ratio between sugars and malic acid is the most important in consumer acceptance (Crisosto et al., 2003) even if cherry's sugar content is higher than sour Cherrie's (Banu, 2010). The health benefits of cherries consumption derive from their chemical composition. Fibbers and phytonutrients with antioxidant capacities contribute to anti-cancer and anti-inflammation properties. Polyphenols and antocianins are responsible for this action (Ferreti et al, 2010, Chaovanalikit, 2003). Cherries contains several microelements such are calcium and magnesium (14 mg/100 g, 10 mg/100 g respectively), but the main mineral in their composition is potassium with 200 mg/100g (Ferretti et al., 2010). Some cherry cultivars (Balaton and Montmorency) were found to be rich in melatonin, from 2.06 to 13.46 ng/g, so sleep can be improved (Burkhard et al., 2001). Between many other benefits it was proofed that consuming cherries or cherry extract lowers the risk of gout attack (Zhang et al., 2012).

Cherry and sour cherry contain both hydro (C, B) and liposoluble vitamins (A, E and K). Except for K vitamin, sour cherries vitamin content is superior to cherries. Only choline content is in the same domain as vitamin C (6.1 mg/100g), all the other vitamins range in mg (B group) or even µg/100g (A, K). Vitamin C content is significant, from 7 mg/100g in cherries to 10 mg/100g in sour cherries (Ferretti et al, 2010, (http://nutritiondata.self.com/facts/fruits-and-fruit-juices/1867/2, http://nutritiondata.self.com/facts/fruits-and-fruit-juices/1861/2).

Vitamin C determination is performed by two types of analytical method: chemical and instrumental. The last one requires a HPLC device and DAD detection (Gündoğdu, M. and U. Bilge, 2012) which is not always available. The chemical determination is a redox titration based on the reduction of ascorbic acid to dehydroascorbic acid. Several oxidising agent are used: 2,6-Dichloroindophenol (AOAC Official Method 967.21**),** iodine (Purcărea, 2015, http://chemistry.tutorvista.com), brommat/bromine (Răşanu et al, 2005). No matter the analytical method, before the determination the critical step is to separate the vitamin C from the matrix.
The aim of this study is to verify the influence of two different extraction solvent, methaphosphoric acid and chlorhidric acid, on the determination of vitamin C content in cherry and sour cherry.

MATERIALS AND METHODS

Materials

The tested materials ware:

- sweet cherry (*Prunus avium* L.), two cultivars: Gersmerdorf (CG) and Van (CV)
- sour cherry (*Prunus cerasus L.*), two cultivars: Ujfert (VU) and spontaneous (SV)

The samples ware picked from a private orchard in Oradea area during summer 2014. The determination took place in food control laboratory of the Environmental Protection Faculty in June-July 2014.

All the used reagents were p.a. grade: Iodine, metaphosphoric acid, ultra pure sand, and starch from Merck Germany, Ascorbic acid from ROTH, potassium iodide and chlorhidric acid from Chemopar.

Precision glass pipettes (0.01ml) were used for titration purposes. The laboratory device used in the present study was Hettich centrifuge Rotina 620.

Methods

Prior to determination the stone was gently removed taking care to not lose juice. Then 10 g of each fruit sample was mixed for 10 minutes in a ceramic mortar with ultrapure sand and 10 ml of each of the extraction media used in this experiment:

a- methaphosphoric acid, aqueous solution 5%

b- chlorhidric acid, aqueous solution 2%

Then the mixtures are passed quantitatively in a 50 ml glass jar and separated by centrifugation, 10 minutes at 1500 rot/min.

Vitamin C (ascorbic acid) was determinate by redox method based on the quantitative oxidation of ascorbic acid by iodine to dehydroascorbic acid. Two variants of iodometric titration ware used, as follows:

Direct iodometry is based on titration of the sample and ascorbic acid standard solution ($1mg\cdot ml^{-1}$) with 0.004N iodine solution, until blue, in starch presence. Aliquot of the sample were diluted with distillate water in order to observe properly the end-point (Purcărea, 2015). The volume used for standard was ten ml and for the sample two ml diluted to ten ml with distillate water.

Indirect iodometry – The oxidising iodine agent is formed "in situ" by the reaction between 0.6M potassium iodine solution and 0.002M potassium iodide solution in acidic environment (1M chlorhidric acid solution). A blue-black colour appears in starch presence. The originate method(http://www.outreach.canterbury.ac.nz/chemistry/documetnts/vitaminc iodate.pdf) was modified regarding the sample volume due to the intense colour of the sample; no more than 2 ml (dilute to 20 ml) can be titrate in order to obtain an enough bright solution, that mean ten time less that in the originate method.

Statistical analysis - All tests were performed as duplicate and are presented as mean ± SD. The results of different experimental variants were compared by T-test for independent samples. Differences between means at 95% ($p<0.05$) confidence level were considered statistically significant.

RESULTS AND DISCUSSIONS

Table 1 present the results of the experiment as mean and standard deviation for all applied variants. Cherries have vitamin C content between 10.41 and 13.55 mg/100g and sour cherries between 20.90 and 24.95 mg/100g. These values comply with those already reported for cherry from 6.01 to 11.44 mg/100g (Gündoğdu and Bilge, 2012) and 9.16 mg/100g (Poiană et al, 2010) as well as for sour cherry: 20.94 mg/100g (Răşanu et al,) and 17.5 to 28.23 mg/100g (Poiană et al, 2011). Filimon et al, 2011 found lower values for sour cherry (10.3 to 12 mg/100g) but vitamin C determination has a lot of variables regarding the extraction solvent and the titrimetric method so variations are expected as well as for both cherry and sour cherry a lot of botanical types.

Table 1

Vitamin C content, mg/100g

Sample		**Extraction solvent**				**General mean±SD**
		MFA		**HCl**		
		ID	**IDI**	**ID**	**IDI**	
CG	Mean	9,64	12,22	8,58	11,23	10,41±1,40
	SD	0,20	1,21	1,12	0,36	
CV	Mean	12,82	15,84	10,48	15,06	13,55±2,09
	SD	0,74	0,24	0,99	0,85	
VS	Mean	21,07	25,19	17,46	20,25	20,99±2,77
	SD	0,77	1,64	0,58	0,82	
VU	Mean	24,80	27,47	22,37	25,17	24,95±1,81
	SD	0,81	0,71	1,32	0,66	

MFA **-** methaphosphoric acid

ID – direct iodometry
IDI – indirect iodometry

At first sight methaphosphoric acid allows a superior recovery for vitamin C than chlorhidric acid and indirect iodometry lead to higher values than indirect iodometry. However, from the statistical point of view there are not significant differences between the results obtained by direct iodometry or indirect iodometry at $p<0.05$ as well as between results obtained using different extraction solvents.

CONCLUSIONS

The experiment leads to some conclusions, as follows:

- The sour cherry types tested has higher vitamin C content that the cherries with the lowest for Gersmerdorf Cherry and the higher for Spontaneous Sour Cherry;
- There use of chlorhidric acid 2% solution instead of more expensive methaphosphoric acid 5% doesn't lead to significant differences on the determination of vitamin C;
- Both titrimetric methods can be used but the end-point is more difficult to observe in the indirect method;
- For so deep coloured fruits, the observation of titration end-point is depending of the dilution which can affect the results, moreover different dilution were applied in the used methods;
- An instrumental parallel determination could show the limitation of the volumetric method.

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