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PHYSICO-CHEMICAL ANALYSIS OF CRANBERRY USING FT-IR SPECTROSCOPY

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Abstract

In the last years several wild fruits were considered as valuable sources of bioactive molecules as vitamin C, benzoic acid, anthocyanins etc. These compounds have a series of health benefits. For better pharmaceutical use of the plants, it is important to study them from the chemical and compositional point of view. Cranberry species are largely represented in the European, Asia and North America flora and various parts of the fruits are used in traditional medicine. The fruits are rich in anthocyanin, flavonoids, polyphenol, vitamin C and acids such as ascorbic acid. In the last year, FT-IR spectroscopy has been introduced as a very efficient and non-destructive analytical tool for the reliable way to determine the functional groups of three compenents

Key words*: cranberry fruit (Vaccinium macrocarpon), FT- IR (Fourier transform spectroscopy).*

INTRODUCTION

Increased interest in medicinal plants has been demonstrated a plethora of valuable resources of naturally occurring polysaccharide-polyphenolic conjugates with many health benefits (Veskoukis et al., 2019). Shrub genus Vaccinium which belongs to Ericaceae family is comprised from over 450 species and mainly commercially varieties are known as *Vaccinium macrocarpon*, *Vaccinium oxycoccos* and *Vaccinium vitis-idaea* (Brown et al., 2012). Cranberry (*Vaccinium macrocarpon*) is categorized as small northern fruit, historically native to North American and Northern Europe. Fruits are red-colored having spherical shape berries (Narwojsz et al., 2019).

These barriers have been traditionally processed into various products such as juice, sauce, sweetened dried cranberries and also for medicinal use. Cranberry berries reported being rich in sugar (4-7%), citric acid, malic acid, provitamin A, vitamin B1, B2, vitamin C, benzoic acid and anthocyanins comprising peonidin-3-galactoside, which have been implicated in health benefits associated with the consumption of cranberry (Narwojsz et al., 2019).

Despite chemical composition of fruits, cranberry leaves are rich in tannins, flavonoids which are considered strong antibacterial, antimycotic, antioxidant substances, and can be used for their antiseptic properties because of high arbutin content (Ahmad et al., 2019; Nebu and Walsh 2019). The antiseptic and antifungal properties of the fruits may be due to polyphenols, benzoic acid derivates and anthocyanins, which efficacy was proved in vitro and in vivo studies (Kraus et al., 1979; Stambergova et al., 1985; Veskoukis et al., 2019). Plants are the primary source of dietary phenolic compounds (Vinson et al., 2008) that have been suggested to be responsible for many health benefits including anticancer activity (Sun and Liu 2006), antioxidant capacity that can prevent low-density lipoprotein oxidation, thrombocytes platelet aggregation and confer protection against cardiovascular diseases (Abbaszadeh et al., 2019). The consumption of cranberry fruits has been associated with reduced risks of chronic diseases including lung dysfunctions and thrombotic strokes (Manganaris et al., 2014). Cranberry phenolic profile includes simple phenolic acids, flavonoids which containing anthocyanins, proanthocyanidins (PACs) as well as flavonols

(Gregoire et al., 2007). Polyphenolic-rich Vaccinium macrocarpon extracts provide antibacterial activity against numerous *listeria* species (Diarra et al., 2020).

Cranberry leaves and fruits are suggested for treating all forms of renal infections and consumption of cranberry juice (CBJ) is reputed to be effective against urinary tract infections (UTI) (Foo et al., 2000). This phenomenon is attributed to the ability of cranberry phenolics, A-type proanthocyanidin (PAC) oligomers to inhibit adhesion of *Escherichia coli* which is usually responsible for UTI cases (Howell et al., 2005). Moreover, *in vitro* study shows that propolis and cranberry powders sufficiently extended the anti-adherent activity of the proanthocyanidins by reducing the adherence of *E. coli* towards epithelial cells (Lavigne et al., 2011). Association of cranberry and propolis supplementation significantly decreases the occurrence of UTIs during the first 3 months and delays the onset of cystitis episode (Bruyère et al., 2019).

Phenolics from CBJ previously showed a rich antioxidant capacity regulating cholesterol and other biochemical parameters, also cranberry juice polyphenolics stimulate nitric oxide synthase mediated in vasodilatation in a rat model system and have been implicated in the human lipoprotein profile regulation (Ruel et al., 2006). Cranberry flavonols, anthocyanins, and proanthocyanidins have been previously characterized via HPLC (White et al., 2010). Some attempts for cranberry compounds isolation such as flavonol glycosides by semi-preparative –HPLC have been reported as not quantitatively technique (Yan et al., 2002; Gregoire et al., 2007). However, other reports to our knowledge regarding cranberry chemical analysis provide quantitative yields (Wilson et al., 2008) including Fourier transform infrared spectroscopy (FT-IR) analysis (Andronie et al., 2019). FT-IR spectroscopy proved to be a suitable and efficient method for the analysis of biologically active molecules derived from plant powders (Namiesnik et al., 2013; Galarraga-Vinueza et al., 2018).

Therefore, the scope of this study was to analyze and obtain comparisons among molecular structures of *Vaccinium macrocarpon* after application of different drying temperatures. The berries from Romanian flora were analyzed by using vibrational spectroscopy techniques (FT-IR) and Photochem assay. Tools that recently have been described as useful for food and pharmaceutical industries due to the qualitative description of secondary metabolites and polysaccharide – polyphenolic conjugates derived from plant extracts.

MATERIALS AND METHODS

Biological material

The samples were obtained from fresh cranberry fruits at full maturity harvested from four points (1 - 46°40'54.6"N 23°05'46.1"E; 2 - 46°40'48.9"N 23°05'32.2"E; 3 - 46°40'32.1"N 23°05'48.3"E; and 4 - 46°41'19.3"N 23°05'27.2"E), located in Mărișel commune, Cluj County, Romania. The fruits were harvested in early September and preventively washed with water. The samples were dried in the air-oven at different temperatures for different periods of time at 40 °C for 4 days (sample 1), 70 °C for 3 days (sample 2) and 90 °C for 2 days (sample 3), respectively. For the liquid samples, we used juice from fresh cranberries and from frozen cranberries at -15 C° for 2 days.

FT-IR spectroscopy

The powdered forms of the fruit samples were prepared from cranberries dried at different temperatures.

The sample from the FT-IR spectrum was obtained from 0.005g of fruits used without further purification. FT-IR spectra were performed in the absorbance whit a Jasco FT-IR-4100 spectrophotometer using KBr pellet technique. When radiant energy is equal to the vibrational frequency of the molecule, it realizes the absorption and vibration. Absorption intensity for each frequency of vibration is monitored by a detector. Specific footprint is a specific combination between molecular vibration and rotational vibration and has a great significance to identify specific molecules.

The sample was prepared using calcinated potassium bromide as a matrix material and was mixed at a proportion of 3 mg of the sample to 200 mg KBr. Then the mixture was condensed in 15 mm die at a pressure equal to 10 t till 2 min.

Measurements were carried out on the infrared scale of 650-4000 cm^{-1} and a spectral resolution was set at 4 cm^{-1} and all spectra were acquired over 256 scans.
The spectral data were analyzed using Origin 6.0 software (Figures 1 and 2). These spectra were analyzed by comparing the obtained vibrational bands with those of similar functional groups from the literature.

RESULTS

The FT-IR spectrum was used to identify the functional groups of the active components present in the sample, based on the peak's values in the region of IR radiation.
The presence of flavonoids, pectin, proanthocyanidins, tannins, carotenoids, sugars, fruit acids such as ascorbic acid, malic acid, and citric metabolites which possess antioxidant activity was reported, according to FT-IR analysis. The peak characteristics for asymmetric stretching vibration of $–CH_2$ is corresponding to 2927 cm^{-1} (Santana et al., 2016) and the absorption bands for the carboxyl group may be found at 1742 cm^{-1} (Pancerz et al., 2019). Moreover, these groups are presented in all obtained spectra showing clear intensity for al samples. Significant discrepancies in intensity between all of the samples were observed in the area 1650-1220 cm^{-1}, corresponding to the oscillation of the carbonyl C=O group of fructose and aldehyde CH=O of glucose (Saha et al., 2007; Vardin et al., 2008).

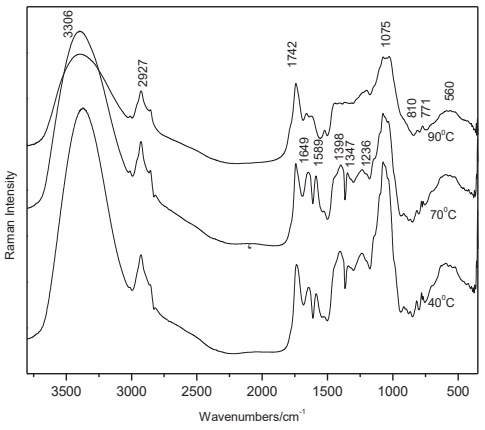

Figure 1. FT-IR spectrum of cranberry fruits (*Vaccinium vitis idaea*) dried at different temperatures

The band located at 1236 cm^{-1}, it is more intense for samples with lower drying temperature and this seems to be linked to the prediction of the presence of ester carbonyl groups.
The analysis of FT-IR spectra showed that each particular polysaccharide has a specific band, with a maximum detected within 1200-1000 cm^{-1} region, which is assigned to stretching vibration of (C-OH) side groups, and the glycoside bond (C-O-C) vibrations in polysaccharide chains, as it can be observed in Figure 1 (Pawlaczyk et al., 2008). The bands identified at 1075 cm^{-1} specific to this group are much more intense in the case of the spectra from sample were fruits was dry a temperature at 90^0 compared to the one obtained for 70^0 and 40^0 .This finding may suggest that the cranberry have a lower polysaccharide content when was dry for more temperature (90^0C).
Another interesting region is a characteristic of various types of fruits, and it is represented by bands in the range from 850-760 cm^{-1}, which correspond to the specific oscillation of the anomeric region of carbohydrates, or C-H deformation. The region is described by considerable differences between particular samples, which evidences a significant change of bond conformation (glycoside bond) (Samborska et al., 2018).
The absorbance of bands at 553-633 cm^{-1} indicates C-O-O and P-O-C bending of aromatic compounds such as phosphates.
Anthocyanin is an integrated molecule, which particularly eases the transport of electrons through its structure (Cramer et al., 2011).
It can be seen that the absorption peaks of the wild fruits at around 560 cm^{-1} are demonstrating the presence of three anthocyanin pigments (Ramamurthy and Kannan, 2007).
Figure 2 shows a comparison between fresh cranberry juice and fruits which were frozen at a temperature of 15 °C over 2 days. It can be observed that both FT-IR spectra showed a band at a location of 1650 cm^{-1} that is attributed to the vibrational C = O bond from amide I. In addition, this region was more intense in the spectrum obtained from the fresh juice sample.
Furthermore, the band from the 1075 cm^{-1} region is specific to the polysaccharides and showed an elevated vibrational intensity in

fresh cranberry juice compared to the frozen fruits. This suggests that the polysaccharides content decreases after exposure of the fruits to the thermal processes.

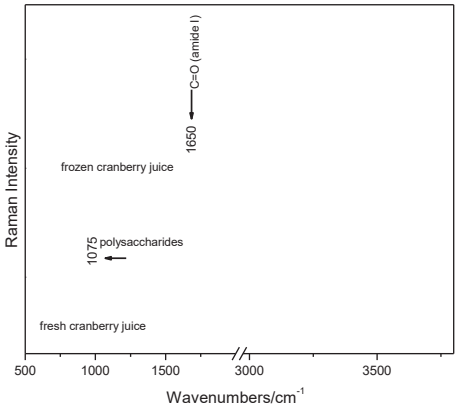

Figure 2. FT-IR spectrum from fresh and frozen cranberry juice (CBJ)

CONCLUSIONS

The acquired FT-IR spectral data is suggesting that the curative and protective properties of the fruits begin to decrease due to the physical-chemical changes occurred in the fruits as the temperature increases (the drying process).

Based on the obtained results, it can be concluded that the FT-IR spectroscopy is a reliable instrumental technique for the determination of mean components in wild fruits.

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