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THERMAL BEHAVIOR OF RASPBERRY AND BLACKBERRY SEEDS OILS FOLLOWED BY DSC

TERMALNE OSOBINE ULJA IZ SEMENA MALINE I KUPINE PRAĆENE DSC METODOM

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ABSTRACT

Studies were conducted on thermal properties of oils extracted from raspberry and blackberry seed as well as flours obtained by grinding of seed. Crystallization and melting points of oils were measured with a Differential Scanning Calorimetry (DSC), using TA Instruments DSC Q1000, under N_2 purge flow of 50 ml/min. DSC scans were conducted in temperature range of 40 °C to -90 °C. A programmed cycle was followed in which the sample was cooled from 40 °C to -90 °C and heated back to 40 °C with rate of 2 °C/min. The raspberry and blackberry seeds oils presented a crystallization peak at -66 °C and -61 °C with enthalpy of 25.10 J/g and 29.04 J/g, respectively. Polymorphism was detected in both oils during heating.

Key words: *oil, seed, raspberry, blackberry, DSC.*

REZIME

U ovom radu izučavana su termalna svojstva ulja dobijenih iz semena kupine i maline kao i brašna dobijena mlevenjem ovog semena. Temperature kristalizacije i tačke topljenja određene su metodom diferencijalne skenirajuće kalorimetrije (DSC), pomoću DSC kalorimetra TA Instruments, DSC Q1000, pri protoku N_2 od 50 ml/min. DSC eksperimenti sprovedeni su u temperaturskom opsegu od of 40°C do -90°C. Programirano je ciklično hlađenje uzorka od 40°C to -90°C i ponovno grejanje do 40°C brzinom od 2°C/min. Određena temperatura kristalizacije ulja iz semena maline i kupine je -66°C i -61°C, a entalpija kristalizacije 25,10 J/g i 29,04 J/g. Nađen je polimorfizam kod oba ulja.

Ključne reči: *ulje, seme, malina, kupina, DSC.*

INTRODUCTION

Recently, more attention has been focused on the utilization of food processing byproducts and wastes, as well as under-utilized agricultural products (*Đević et al., 2008; Hodúr et al., 2009*). Obviously, such utilization would contribute to maximizing available resources and result in the production of various new foods (*Radovanović et al., 2011*). Simultaneously, a major contribution to avoiding waste disposal problems could be made. The processing of berry fruit for juices and puree typically removes the seed as a byproduct. The development of a value-added use of seeds could expand the market for berry products and increase grower profit margins. For instance, red raspberry seed was reported to contain 12.2 % protein and 11-23 % oil (*Bushman et al., 2004*). Considerable amounts of tocopherols were found in the red raspberry oil, mainly of γ-tocopherol (*Oomah et al., 2000*). Tocopherols are common lipophilic antioxidants abundant in some oils and nuts, but their presence in red raspberry seed could provide vitamin E activity and antioxidant potential as well (*Bramley et al., 2000*). Ellagic acid was reported to be more abundant in red raspberry and blackberry than in other fruits and nuts (*Daniel et al., 1989*). Occurring primarily in the seed, ellagic acid has shown chemopreventative activity in animal models (*Stoner and Morse, 1997, Xue et al., 2001*). These characteristics of red raspberry seed suggest possible roles in human nutritional products. Additional research is required to investigate fruit seed flours for their contents of health beneficial factors to promote their value-added utilization as beneficial food ingredients.

High-value vegetable oils (like berry seed oils) are gaining attention owing to their health benefits which are linked to their high content of polyunsaturated fatty acids and antioxidants. All berry seed oils have a high content of polyunsaturated fatty acids in common, providing essential fatty acids (*Hoed et al, 2009*). Recently, the properties of some berry seed oils have been reported in the literature. *Parry and Yu (2004), Parry et al. (2005)* found significant amounts of α-linolenic acid, tocopherols, polyphenols and carotenoids in marionberry, boysenberry, red raspberry and blueberry seed oils.

The present study was conducted to investigate the seed flours and oils of raspberry (*Rubus idaeus L., sort Willamette*) and blackberry (*R. fruticosus L., sort Čačak Thornless*) for their thermal characteristics by mean of Modulated Differential Scanning Calorimetry (MDSC), conventional Differential Scanning Calorimetry (DSC) and Thermogravimetric analysis (TGA). Modulated DSC (MDSC) offers a solution to overcome many of the analytical limitations of conventional DSC. MDSC differs from conventional DSC wherein the sample is subjected to a more complex heating program incorporating a sinusoidal temperature modulation accompanied by an underlying linear heating ramp. It provides the total heat flow, the non-reversible (kinetic component) and the reversible (heat capacity component) heat flows (*Cao, 1999*).

MATERIAL AND METHOD

Fruit seed flours and oils preparation

Fruit seeds were the solid residues from the cold-pressing fruit pulp. Seeds were drayed at room temperature, to the constant moisture of 6-7 % and grinded immediately before thermal analysis. Examined oils were obtained by extraction from milled raspberry (*Rubus idaeus L., sort Willamette*) and blackberry (*R. fruticosus L., sort Čačak Thornless*) seeds using hexane as described in literature (*Oomah et al., 2000).*

Thermal analysis

All measurements have been performed on TA Instruments DSC Q1000, Differential Scanning Calorimeter and TA Instruments TGA Q500, Thermogravimetric Analyzer with TA Universal analysis 2000 software, under N_2 purge flow of 50 ml/min and 60 ml/min, respectively. DSC was calibrated with a high-purity indium standard.

Thermal analysis of blackberry and raspberry seed flours - flour samples were placed in sealed aluminium pans and into the equipment's sample chamber and their weight was (5.0 ± 0.5) mg. An empty sealed aluminum pan was used as the reference. MDSC scans were conducted in temperature range from -90 °C to 300 °C, with heating rate of 5 °C/min with modulation of ±0.50 °C amplitude and 40 s period of modulation. TGA scans were performed in temperature range of 25 °C to 700 °C with heating rate of 5 °C/min. The initial mass of the flour samples was been about 12 mg in TGA measurements. Thermal analysis of blackberry and raspberry seed oils - oil samples were placed in sealed aluminium pans and into the equipment's sample chamber and their weight was (3.0 ± 0.3) mg. An empty open aluminum pan was used as an inert reference to balance the heat capacity of the sample pan. DSC scans of blackberry and raspberry seed oils were conducted in temperature range of 40 °C to -90 °C. A programmed cycle was followed in which the sample was cooled from 40 °C to -90 °C with cooling rate of 2 °C/min, maintained at this low temperature for 5 min and heated back to 40°C with same rate.

RESULTS AND DISCUSSION

On the Figures 1.a) and 1.b) are presented MDSC curves of blackberry and raspberry seed flours. It is evident that the curves quite similar for both seed flours. Total DSC curve (curve 1) is characterized with overlapping effect in low-temperature region caused by the freezing and unfreezing of large-amplitude motion (*Pyda and Wunderlich, 2005*). It was shown that thermal transitions, observed in the range of −80 °C to −10 °C were independent on water content, and they were mainly attributed to lipid melting transitions (*Matiacevich et al., 2006*) Broad endothermic peak with T_m at about 93 °C corresponds to protein denaturation (*Matiacevich et al., 2006*). Thermal decomposition is happened above 200 °C. Using MDSC, the reversing (curve 3) and nonreversing (curve 2), thermal events in the low temperature region of seed flour have been approximately separated (*Pyda and Wunderlich, 2005*). Reversing curve is suggesting that there are two independent thermal processes.

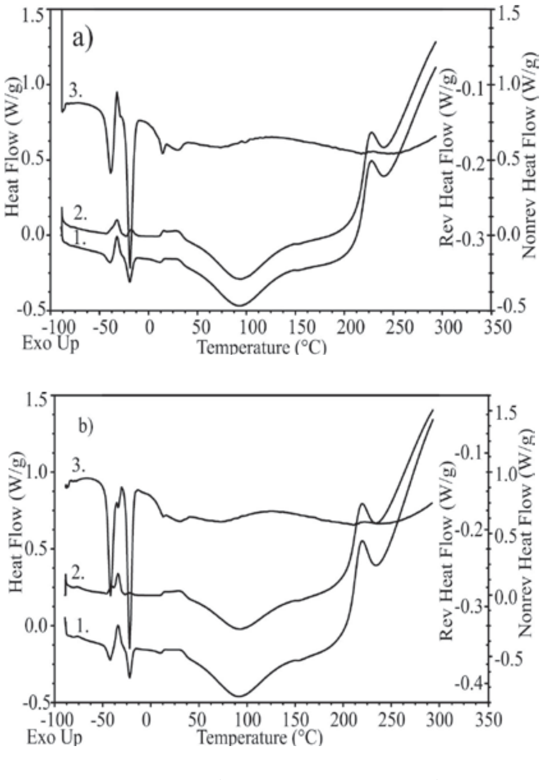

Fig. 1. MDSC curves of: a) blackberry seed flour; and b) raspberry seed flour. (1-total heat flow, 2-nonreversing heat flow and 3-reversing heat flow)

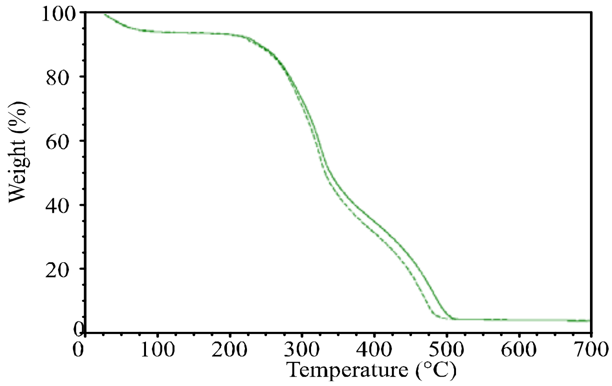

Fig. 2. TGA curves of blackberry (solid curve) and raspberry (dashed curve) seed flour

On the Figure 2. TGA curves of blackberry and raspberry seed flours are presented. And these curves are confirmed the thermal degradation of seed flours at temperatures above 200 °C. Results from TGA analysis are shown in Table 1.

Table 1. Results obtained from TGA curves of blackberry and raspberry seed flours

seed flour	I weight loss (moisture) (%)	II weight loss (%)	III weight loss (%)	Residue (ash) (%)
raspberry	6.09	60.92	31.70	1.29
blackberry	6.22	57.33	35.28	1.16

Results obtained from TGA and DSC curves indicated similarity in thermal behavior of raspberry and blackberry seed flours.

On the Figure 3. DSC curves of blackberry and raspberry seed oils are presented. Oil curves are very similar to the curves of flours. They have similar shape in the same temperature range. It confirms that the overlapping effect in the low temperature regions of flour DSC curves arise due to the presence of oil.

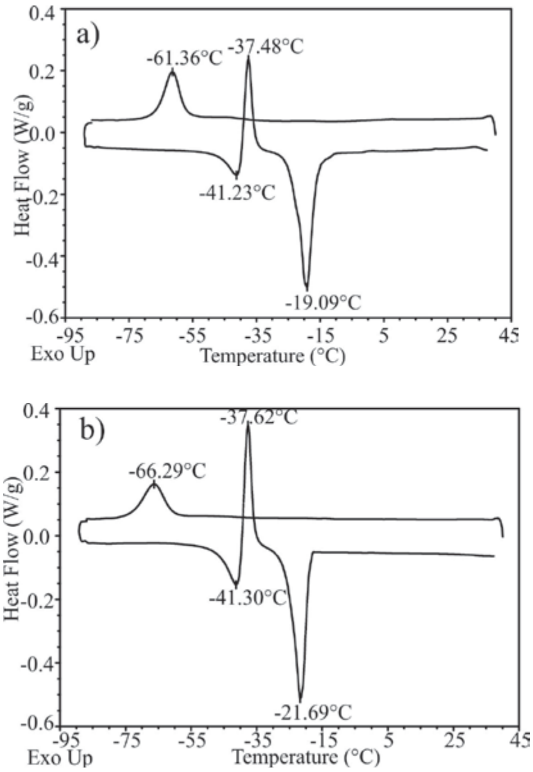

Fig. 3. DSC profile of: a) blackberry seed oil; and b) raspberry seed oil

The blackberry and raspberry seed oils presented a crystallization peak at -61 °C and -66 °C with enthalpy of 29.04 J/g and 25.10 J/g, respectively. Polymorphism was detected in both seed oils: after melting of the low temperature form at -41 °C (for both oils), an additional form crystallized with an exothermic peak at -37 °C (for both oils). At -19 °C and -22 °C (for blackberry and raspberry seed oils, respectively) this forms melted with an originally existing crystallite of the same kind. Similar thermal behavior was observed for grape seed oil by Kaisersberger (*Kaisersberger, 1990*). These polymorphic changes can be hindered by addition of emulsifiers. According to *Garti et al*. (*1988*), the first small endothermic peak at -41 °C represents the melting of the unstable crystal form *a* followed by the crystallization of the more stable form *b* which is characterized by an exothermic peak. The melting enthalpy of blackberry and raspberry seed oils were 72.44 J/g and 63.95 J/g, respectively.

CONCLUSION

Using MDSC, thermal events in low temperature region of seed flour have been approximately separated by reversing heat flow, suggesting that there are two independent thermal processes. It was shown that overlapping effect of flour DSC curves arise due to the presence of oil. In both, blackberry and raspberry seed oils, polymorphism was detected during heating treatment.

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