Thermochimica Acta 617 (2015) 21–27

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Thermal behavior of raspberry and blackberry seed flours and oils

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ARTICLE INFO

Article history:
Received 28 April 2015
Received in revised form 23 July 2015
Accepted 11 August 2015
Available online 14 August 2015

Keywords:
Blackberry seed
Raspberry seed
Seed oil
DSC
TG

ABSTRACT

This survey was conducted on thermal properties of flours obtained by grinding of blackberry (*Rubus fruticosus* L., Čačak Thornless cultivar) and raspberry (*Rubus idaeus* L., Willamette cultivar) seeds, as well as oils extracted from berry seeds. Thermal behavior and stability of berry seed flours were investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TG). Crystallization and melting points of oils were determined using a conventional and modulated DSC techniques. Oils present in the blackberry and raspberry seeds start melting (T_{on}) at −24.02 and −26.44 °C, respectively. Both berry seeds thermo-oxidatively decompose at temperatures above 210 °C. Thermo-oxidative decomposition of these seed flours takes place in two stages, as TG/DTG curves have two thermal decomposition steps. Polymorphism was detected in both seed oils during heating.

1. Introduction

Lately, utilization of byproducts and wastes from the food industry, as well as under-utilized agricultural products has been focused by food processing. This kind of waste processing would contribute to maximizing available resources and result in the production of various new foods which are mostly with high nutritional value. Simultaneously, a major contribution to avoiding waste disposal problems could be made [1].

The processing of berry fruits for juices and puree typically removes the seeds as a byproduct. Developing value-added utilization of berry seeds will significantly expand the market for berry products as well as improve benefit berry producers and, possibly, consumers. A practical approach to developing value-added uses of berry seeds is to determine and screen for the value adding factors in the seeds. For instance, red raspberry seed was reported to contain 12.2% protein and 11–23% oil [2]. Juranic et al. [3] showed that water extracts of seeds of five different raspberry cultivars possess the potential for antiproliferative action against human colon carcinoma cells in vitro. The antiproliferative action of seed extracts was correlated with their content of ellagic acid. Ellagic acid was reported to be more abundant in red raspberry and blackberry than in other fruits and nuts [4]. Oomah et al. [5] found considerable amounts of tocopherols in the red raspberry oil, mainly of γ-tocopherol. Tocopherols are common lipophilic antioxidants abundant in some oils and nuts, but their presence in raspberry and blackberry seeds [6] could provide vitamin E activity and antioxidant potential as well [7]. These characteristics of berry seeds suggest possible roles in human nutritional products.

One of the possible products from berry seeds is edible oil. 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. Recently, the properties of some berry seed oils have been reported in the literature [8,9]. Significant amounts of α-linolenic acid, tocopherols, polyphenols and carotenoids was found in marionberry, boysenberry, red raspberry and blueberry seed oils [10,11]. Based on anti-inflammatory activity, raspberry seed oil was incorporated in cosmetics and pharmaceutical products for the prevention of gingivitis, rash, eczema, and other skin lesions [5]. Our previous investigation [12] has shown that blackberry and raspberry seed oils are rich in essential fatty acids (linoleic (18:2) and linolenic (18:3) acid). Especially, usage the raspberry seed oil for human consumption may provide potential health benefits because this oil has a low ratio n-6:n-3 fatty acids (2:1) [13–15].

Processing and using of berry seed flours and oils in the food and pharmaceutical industries generally includes a thermal treatment, so that knowledge of the thermal properties of flour and oil is essential for designing the parameters of processing in order to obtain the desired product quality. Since thermal decomposition, melting and crystallization require the intake or release of heat, differential scanning calorimetry (DSC) is eminently suitable technique to

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http://dx.doi.org/10.1016/j.tca.2015.08.017
0040-6031/

determine these physical properties of oil samples [16–21]. Previous investigations of thermal characteristics of edible oils and fats, using DSC, have shown that complex features appear in melting and crystallization curves, such as shoulders, which were not easy to interpret. This is a consequence of the thermal history, chemical composition and the known phenomenon polymorphism of natural oils and fats. These results illustrate the complex nature of triacylglycerides (TAGs) in oil samples [22].

The aim of this paper is to investigate the seed flours and oils of blackberry (*Rubus fruticosus* L., Čačak Thornless cultivar) and raspberry (*Rubus idaeus* L., Willamette cultivar) for their thermal characteristics by mean of conventional differential scanning calorimetry (DSC), modulated differential scanning calorimetry (MDSC) and thermogravimetric analysis (TG). Modulated DSC offers a solution to overcome many of the analytical limitations of conventional DSC. The operating principle of MDSC differs from standard DSC in that MDSC uses two simultaneous heating rates—a linear heating rate that provides information similar to standard DSC, and a sinusoidal or modulated heating rate that permits the simultaneous measurement of the sample's heat capacity. MDSC measures the total heat flow (as well as conventional DSC), plus its heat capacity component (reversible heat flow) and the kinetic component (non-reversible heat flow). Its ability to resolve complex transitions into specific components improves data interpretation [23].

2. Materials and methods

2.1. Berry seed flours and oils preparation

Blackberry (*R. fruticosus* L., Čačak Thornless cultivar) and raspberry (*R. idaeus* L., Willamette cultivar) were obtained from the Fruit Research Institute, Čačak, Serbia. Fresh berries were frozen at −20 °C and stored for one month until processing. Berry seeds were obtained by fruit pulp cold-pressing. Seeds were dried at room temperature to the constant moisture of 6–6.5% and milled by laboratory grinder immediately before thermal analysis. Berry seed flours contained: moisture 6–6.5%, oil 16–18%, ash 1.3–1.7%, proteins + carbohydrates 74–76%. Examined oils were obtained by extraction from milled raspberry and blackberry seeds using hexane (Sigma-Aldrich, Missouri, USA) as described in literature [5]. The oil was stored at −20 °C until analysis. All chemicals and reagents used were of the highest purity (p.a.). Fatty acids percentage contribution (% w/w) in berry seed oils was determined in our previous work [12]: blackberry seed oil—(16:0) palmitic 3.65, (18:0) stearic 2.27, (18:1) oleic 12.53, (18:2) linoleic 66.33 and (18:3) linolenic acid 14.62% w/w; raspberry seed oil—(16:0) palmitic 3.47, (18:0) stearic 1.06, (18:1) oleic 11.55, (18:2) linoleic 55.29 and (18:3) linolenic acid 27.80% w/w.

2.2. Physicochemical characterization

The ISO Standard Methods were used for determinations of the free fatty acid content (FFA), acid, peroxide and saponification values [24–26], and Wijs Method was used for determinations of iodine value in the oil samples. Both oil samples were analyzed in triplicate.

2.3. Thermal analysis

All measurements have been performed on TA Instruments DSC Q1000, Differential Scanning Calorimeter and TA Instruments TGA Q500, Thermogravimetric Analyzer (Delaware, USA), with TA Universal analysis 2000 software, under air flow of 50 ml/min and 60 ml/min, respectively. DSC was calibrated with a high-purity indium standard. Characteristic points were determined from DSC curves: onset temperature (T_{on}), offset temperature (T_{off}) (as the intersection of the extrapolated baseline and the tangent line (leading edge) of the endothermic/exothermic peak), and the peak temperature (T_p) (temperatures of a maximum heat flow) between T_{on} and T_{off}. The melting and crystallization enthalpies (ΔH) of both berry seed oils were obtained by the integration of the corresponding DSC peaks (the linear baseline function integration).

Thermal analysis of blackberry and raspberry seed flours–flour samples were placed in sealed aluminum pans and into the equipment's sample chamber, and their mass was 5.0 ± 0.5 mg. An empty sealed aluminum pan was used as the reference. DSC scans were conducted in temperature range from −90 °C to 300 °C, with heating rate of 5 °C/min. The seed flours were immediately cooled to −90 °C and equilibrated for 5 min before heating. For clarifying the thermal transitions of berry seed flours in the low-temperature region, heating rate of 2 °C/min was used (the use of slow scan rates is advisable in that it minimizes instrumental lag in output response and, at a given temperature, the examined reaction is closer to the equilibrium, as well as giving better resolution of the transition which will be important if identification of the data is to be undertaken [18]). The study of thermo-oxidative degradation of berry seed flours was carried out by thermogravimetric measurement. For this purpose the seed flours were heated from 25 to 700 °C at a heating rate of 5 °C/min. Flour samples of 12.0 ± 0.5 mg were weighed into platinum crucible and loaded into the TG furnace. Obtained TG curves as well as its derivative curves (DTG) were used to analyze the thermal stability of berry seed flours. The onset temperature (T_{on}) was used to indicate the resistance of seed flours against thermo-oxidative degradation and it was determined using DTG curve (as the intersection of the extrapolated baseline and the tangent line (leading edge) of the thermal decomposition peak).

Thermal analysis of blackberry and raspberry seed oils—oil samples were placed in open aluminum pans and into the equipment's sample chamber, and their mass 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 a temperature range of −90 to 40 °C. A programmed cycle was followed in which the sample was cooled from 40 to −90 °C with cooling rate of 2 °C/min, equilibrated at this low temperature for 5 min and heated back to 40 °C with the same rate. The modulated DSC (MDSC) procedure was used in heating samples for the clarification of some thermal processes. The modulation amplitude was ±0.5 °C each 40.0 s. The modulated DSC method helped to better understand the melting and recrystallization processes, which took place in the oil during heating. The reversing heat flow indicates the melting and glass transition, while the non-reversing heat flow indicates the recrystallization in the case of oils. The comparison between the reversing and non-reversing heat flow gives the opportunity to split the exothermic recrystallization peaks, when they are overlapping the endothermic melting peaks [27]. Specific heat capacity (C_p) of both berry seed oils was determined in a temperature range of −90 to 40 °C at a heating rate of 2 °C/min using MDSC thermograms.

2.4. Statistical analysis

All data were statistically analyzed by one-way analysis of variance (ANOVA) with the STATISTICA 10.0® (StatSoft Inc., Tulsa, OK, USA) software. Tukey's HSD test was applied to determine significant differences between means, at a level of $p < 0.05$.

3. Results and discussion

DSC curves of heating blackberry and raspberry seed flours from −90 to 300 °C at the rate of 5 °C/min in air flow are