Journal of Thermal Analysis and Calorimetry, Vol. 97 (2009) 1, 309–313

THERMAL ANALYSIS OF SOME PHYTOTHERAPEUTIC PRODUCTS IRRADIATED WITH ELECTRON BEAM

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The purpose of the present work deals with the evaluation of the electron beam irradiation effects on some natural products based on thermal analysis. Some natural products with therapeutic contributions (artichoke, sea buckthorn, common sage, stonebreaker and cloves) were irradiated with doses up to 9 kGy using accelerated electron beam. The thermal profiles lead to identify three phenomena: dehydration – volatilization, irreversible degradation – molecular reorganization and residue decomposition. The radio-induced degradations determine slight shifts of the temperatures where these phenomena occur. The energetic value of the studied products is affected by e-beam treatment depending on irradiation dose.

Keywords: *adiabatic combustion calorimetry, DSC, irradiation, medicinal plants*

Introduction

The natural products with therapeutic properties are widely used lately both as drugs and food ingredients. There is a trend worldwide that people come back to the traditional remedies because the chemical constituents of plants having a biological active role are able to cure different illness or to improve merely the health.

The plants chosen to be investigated in the present work are very used in different regions of the world with therapeutic purpose and thus we will briefly present them further. Artichoke (*Cynara scolymus L.*), a plant with Mediterranean origin belonging to *Asteraceae* family, is used as a food and, at the same time, as a medicine due to its choleretic, diuretic and antidiabetic properties [1] provided by the rich content of phenolic acids, flavonoides, phytosterols, unsaturated fatty acids and vitamins (A, B2 and C) [2, 3]. Sea buckthorn (*Hippophae rhamnoides L.*) belongs to *Elaeagnaceae* family and grows in regions with temperate climate of Asia, Europe and Russia [4, 5]. It has a strong curative capability for diseases including cardiovascular problems, cancer, and acute mountain sickness [4, 5] as a consequence of the compounds with biological activity such as antioxidants, carotenoids, tocopherols, flavonoids, fatty acids, sterols and phytosterols [6, 7]. Common sage (*Salvia officinalis*), popular plant that belongs to the family of *Labiatae* and native to the Mediterranean region [8], possesses special antioxidant, antiseptic, antispasmodic activity and free radicals capture ability [9, 10]. It is well known mainly for its essential oil that is rich in thujone, cineole and caryophyllene [8]. Stonebreaker (*Phyllantus niruri L.*) of *Euphorbiaceae* family is a widespread tropical plant commonly found in coastal areas and used widely in traditional medicine for the treatment of flu, dropsy, diabetes, jaundice, gall and bladder calculus, liver disease [11–14]. Its pharmacological properties are due to its remarkable active phytochemicals such as flavonoids, alkaloids, terpenoids, lignans, polyphenols, tannins, coumarins and saponins [15]. Cloves (*Eugenia caryophyllata*) are the aromatic dried flowers of a tree in the family *Myrtaceae*. Cloves are native to Indonesia and well known rather as a spice in cuisine because of the wonderful aroma and great taste. However, cloves are used as a phytotherapeutic product to treat kidney, spleen and stomach diseases. The therapeutic characteristics of cloves are conferred by the presence of the important chemical compounds such as eugenol, tannins, flavonoids, triterpenoids and several sesquiterpenes [16].

All these plants are susceptible to carry different undesirable microorganisms derived from soil, water or air and consequently they may be treated by ionizing radiation treatment to decontaminate them. Electron beam (e-beam) irradiation could be an efficient and rapid method to improve microbio-

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1388–6150/$20.00

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logical quality of medicinal plants without significant changes in the active and nutritional principles of plants depending on irradiation dose [17, 18]. The irradiation dose required for microbial decontamination of foodstuffs depends on several factors such as biological load (type and number of microorganisms), chemical composition of product, irradiation conditions as well as the desired degree of decontamination (reduction of microorganism level or complete removal of all microorganisms – sterilization). *Codex Alimentarius* [19] limits the applications of irradiation up to an overall average dose of 10 kGy while the Joint FAO/IAEA/WHO Study Group [20] suggested that any dose above 10 kGy can be considered both safe to consume and nutritionally adequate if it is appropriate to achieve the intended technological objective. However, characteristics of practical importance during technological production as thermal stability of irradiated medicinal plants received less attention until present time. There are very few reports on thermal analysis of irradiated phytotherapeutic materials [18, 21] which indicate that some changes of thermal behavior, especially at higher temperatures, could occur in products by irradiation as a function of the irradiation dose.

DSC is known as a suitable characterization or screening tool of thermal aspects both for bioproducts or their components like food or their components (proteins, lipids, carbohydrates) [22–25] and medicinal plant [26] or different other biological systems [27].

Bomb calorimetry is generally used to evaluate the energetic (caloric) and nutritional value of foods [28]. There are no reports related to the evaluation of caloric value of the irradiated medicinal plants in the literature up to now.

Taking into account the aspects presented above, the aim of our study is to evaluate the possible effects induced in some medicinal herbs by electron beam irradiation using thermal analysis: DSC and adiabatic combustion calorimetry.

Experimental

The materials used in the experiments were: artichoke (Brazil), sea buckthorn (Romania), common sage (Albania), stonebreaker (Brazil), cloves (Brazil). The samples were grounded before packing.

The packed samples were treated in accelerated electron beam (mean energy of 6 MeV) at room temperature and ambient pressure. The irradiation doses checked by ferrous cupric sulphate dosimetry procedure were 1, 3, 6 and 9 kGy.

The DSC measurements have been carried out in a PerkinElmer DSC-2 calorimeter at temperature within 323–673 K in an inert gas (argon). The instrument was calibrated with indium (*m.p.*=429.6 K, ΔH=6.8 cal g^{-1}). The samples of 1–4 mg have been heated in sealed aluminium pans at a heating rate of 10 K min^{-1}. An empty gold pan was used as a reference.

Energetic value was determined at temperature of 298 K in a Gallenkamp calorimetric bomb. The combustion was performed in oxygen at pressure of 30–35 atm using Cr-Ni (335 cal g^{-1}) and cotton (4180 cal g^{-1}) wires.

The reported data are the mean of three different measurements.

Results and discussion

The measuring principle in DSC is to compare the rate of heat flow to the sample and to an inert material that are heated or cooled at the same rate [20].

Our DSC study revealed quite similar thermal behavior for all medicinal products. The first endothermic peak appeared due to the loss of water and volatiles, phenomenon which finished around 415 K for all studied samples (Fig. 1).

The thermal profile of the plants showed the second endothermic peak around the temperature of 450 K, which can be attributed to the degradation process of organic compounds and probably of initial matrix reorganization (e.g. isomerization, breaking of bonds). However, the sample of common sage showed this phenomenon at higher temperature (Fig. 1c) and stonebreaker one presented moderate degradation phenomenon suggested by the flat peak in narrow temperature range (428–457 K) that could be observed in Fig. 1d.

The DSC curves of the studied products presented also an exothermic process that indicated the thermal decomposition of residue. This phenomenon took place at approximately 600 K, excepting sea buckthorn (Fig. 1b) that had the exothermic peak at 480 K. The decrease of the temperature corresponding to the exo process for sea buckthorn can be related to the rich content in oils that decompose at lower temperatures.

It was remarked that common sage showed the second endothermic peak around 600 K, being rapidly followed by the exothermic peak (Fig. 1c), so that the processes of degradation and decomposition have been succeeded very fast.

The irradiated samples suffered no significant changes of the thermal behavior. Nevertheless, slight shifts of the peak positions to lower temperatures than control sample were observed as the irradiation dose increase. For instance, the exothermic peaks of the 9 kGy irradiated artichoke and cloves showed a shift with 6 K (Fig. 1a) and 9 K (Fig. 1d), respectively in

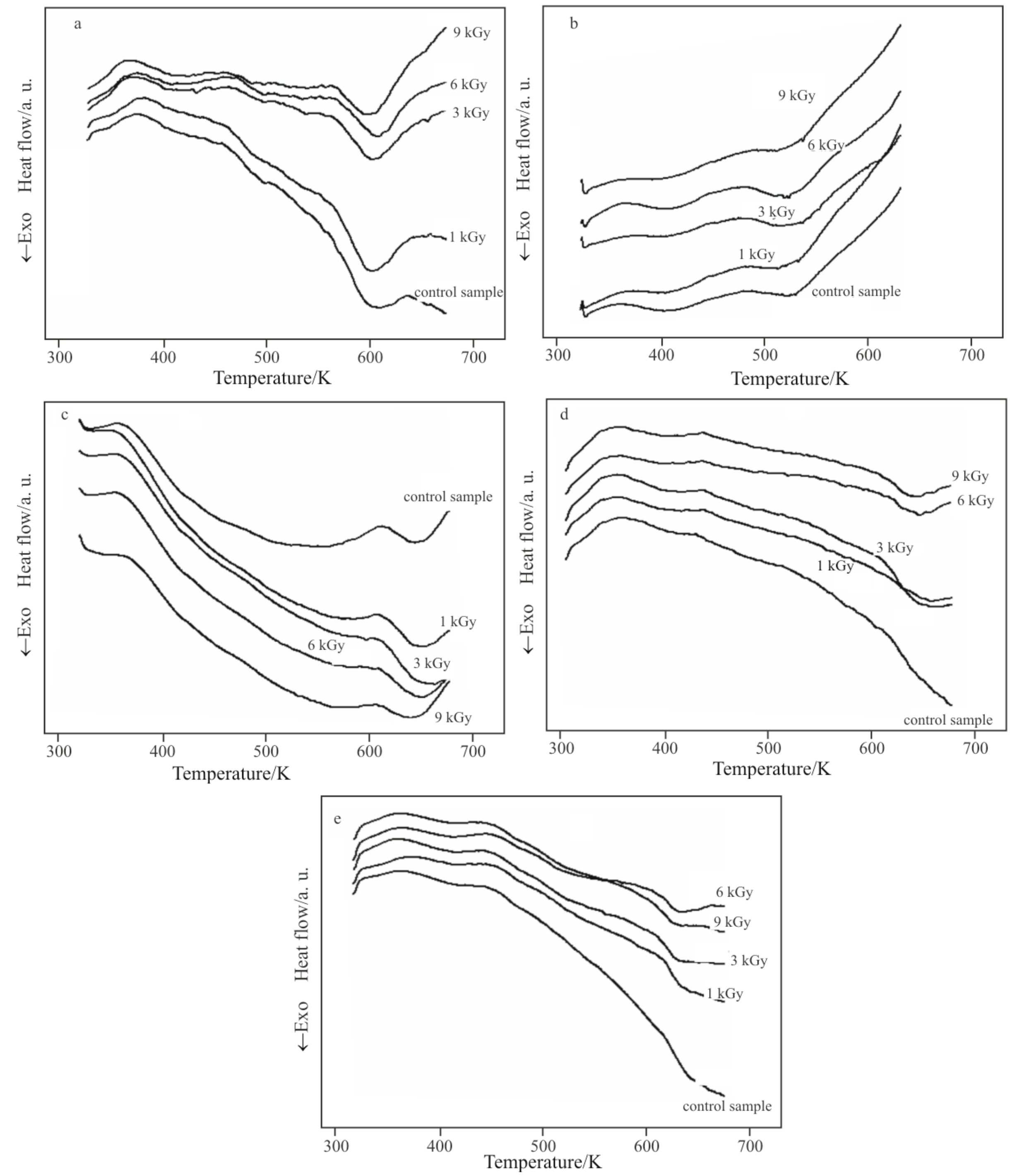

Fig. 1 DSC curves of the phytotherapeutic products: a – artichoke, b – sea buckthorn, c – common sage, d – stonebreaker, e – cloves

comparison to their control samples. These changes can result from some possible radioinduced degradation.

Natural products, generally, and medicinal plants, particularly, are characterized by a complex and varying chemical composition containing both organic and inorganic compounds with various concentrations [29], leading to different thermal behavior. Even so, the obtained results indicate that generally the thermal behavior of the dry medicinal plants presents three events: dehydration – volatilization, irreversible degradation of some organic compounds – molecular reorganization and residue decomposition. This aspect is in agreement with the

Table 1 Energetic value of the phytotherapeutic products before and after irradiation

Irradiation dose/kGy	Energetic value/kJ g^{-1}				
	Artichoke	Sea buckthorn	Common sage	Stonebreaker	Cloves
0	14.34±0.60	22.84±1.28	30.29±2.42	7.36±0.35	42.46±2.97
1	15.08±0.53	21.93±0.21	27.58±2.10	17.16±1.24	36.99±2.96
3	15.79±0.63	25.78±2.27	25.60±2.36	19.17±1.44	32.21±2.09
6	16.58±0.70	20.58±1.52	24.10±2.14	20.50±1.17	29.32±2.11
9	17.67±0.69	23.29±1.16	22.24±1.25	20.28±0.97	28.29±1.50

report of Weselowski *et al.* [29] where the same three stages were identified for inflorescences by other thermal methods – DTA, DTG and TG. The appearance of this phenomenon succession was maintained by irradiation, but the range of their temperature was affected.

Bomb calorimetry measures the heat liberated when ‘food/or a sample’ is combusted in a sealed chamber (the bomb) surrounded by water [30]. This heat of combustion is transposed as energetic value of the studied sample.

The energetic values of each studied plant, irradiated and non-irradiated, are presented in Table 1.

An increase of the energetic value was noticed for artichoke and stonebreaker as the increase of the irradiation dose. This increase was relatively modest for artichoke, while stonebreaker showed a sharp one even after irradiation with 1 kGy. An opposite evolution, meaning a decrease of the energetic value as the increase of the irradiation dose was observed for common sage and cloves. E-beam irradiation had no significant effect on sea buckthorn. The experimental results indicate that the energetic value evolution with the irradiation dose is influenced by the complexity and concentrations of studied product constituents.

Conclusions

The DSC investigation revealed that the studied phytotherapeutic products showed three stages, two endotherm and one exotherm, attributed to the concomitant dehydration and volatilization, degradation associated with molecular reorganization, and thermal decomposition. The complex chemical composition of plants induced different shapes of the DSC curves from plant to plant. E-beam irradiation modified insignificantly the thermal behavior of the studied products. Slight shifts of the peak positions can be attributed to some possible radioinduced degradations. The energetic value of the products was affected by e-beam irradiation.

The performed thermal study of these medicinal plants suggests that the effect of e-beam irradiation was influenced by their complex chemical composition.

Acknowledgements

This work has been performed as a part of the project Nucleu 06.36.05.02/2006.

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ICTAC 2008

DOI: 10.1007/s10973-008-9624-8