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Thermochimica Acta 370 (2001) 135–140

thermochimica acta

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Comparative studies of oxidative stability of linseed oil

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Received 9 October 2000; received in revised form 8 December 2000; accepted 13 December 2000

Abstract

The oxidative stability of linseed oil was studied using classical method based on determination of peroxide value (PV), the Rancimat method based on conductometric measurements and thermoanalytical methods, i.e. the differential scanning calorimetry (DSC) and thermogravimetry (TG) in oxygen atmosphere.

The onset temperatures $T_{onset,DSC}$ and $T_{onset,TG}$ were determined from dynamical DSC and TG curves, respectively. From isothermal DSC curves times t_{onset} were determined.

The effect of two antioxidants was also studied. An antioxidant blend containing α-tocopherol, ascorbyl palmitate, citric acid, ascorbic acid, and ethoxylated ethylene glycol proved more effective than butylated hydroxy anisole for protection of linseed oil against process, in good agreement with results obtained by the classical titration and the Rancimat methods.

Keywords: Linseed oil; Thermal analysis; Oxidative stability

1. Introduction

Unsaturated oils and fats are easily susceptible to auto-oxidation process [1,2]. Traditionally, in edible oil industry classical method used for determining oxidative stability of oils is the active oxygen method (AOM), also known as the Swift method [1,3]. In this method, the purified air is bubbled through a sample held in a heated oil bath at 97.8°C, and peroxide values (PV) are determined at certain time intervals. Most newer methods are based on oxygen adsorption and the formation of volatile oxidation products, e.g. the Rancimat method [3]. The Rancimat method developed by Hadorn and Zürcher is based on the conductometric determination of volatile degradation products. Nevertheless, it has been sought by the edible oil industry the rapid and precise analytical methods to predict the oxidative stability of oils due to limitations of these methods [3,4].

Recently, thermoanalytical methods are more commonly used for characterization of fats and oils, as well as for investigation of their thermal auto-oxidation process. For example, the differential scanning calorimetry (DSC) technique was used to characterize oils extracted from macademia nuts and peanuts for country of origin [5,6]. The specific heats of some edible oils, pharmaceutical oils, and a fat were measured by DSC at 70–140°C [7]. The DSC method was also used for thermal characterization of edible fats and oils (melting, crystallization, and oxidation processes) [8]. It was found that a high content of unsaturated fatty acids leads to reduced oxidation stability. Thermal-oxidative decomposition of vegetable oils and fats was studied by DSC method [9,10].

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0040-6031/01/$ – see front matter
PII: S0040-6031(00)00781-4

The effects of flavonoids on the thermal auto-oxidation of palm oil and other vegetable oils were determined by DSC [11]. Thermogravimetry (TG) method was applied to study thermal decomposition of rancid oils [12,13].

The aim of this work was to compare the classical methods of determination of oxidative stability of vegetable oils (determination of PV and the Rancimat method) with thermoanalytical methods, i.e. DSC and TG. For this study, the linseed oil was used.

Linseed oil containing essential fatty acids (EFA), phytosterols, phospholipids, and vitamins are considered as bio-active cosmetic substrate. In comparison with other vegetable oils, linseed oil is distinguished by the highest content of α-linolenic acid, i.e. 26–60%, which since recently has been found as especially important for human organism. Unfortunately, a high content of α-linolenic acid influences a poor oxidative stability of linseed oil. In this study, we used the different antioxidants in order to protect the linseed oil against oxidation process.

2. Experimental

2.1. Materials

In this work, linseed oil pressed at temperature lower than 40°C in nitrogen was used. Oil was not then refined or bleached.

The following antioxidants were used:

- butylated hydroxy anisole (BHA) in amounts of 0.01 and 0.02%;
- blend containing α-tocopherol, ascorbyl palmitate, citric acid, ascorbic acid, and ethoxylated ethylene glycol (M) in amounts of 0.05, 0.1, and 0.2%.

2.2. Procedures

PV was determined according to the standard ISO 3960:1977 (E). The method is based on the iodometric titration, which measures the iodine produced from potassium iodide by the peroxides present in the oil. The result is reported in milli-equivalents of oxygen per kilogram of fat.

In the Rancimat method, the volatile degradation products are trapped in distilled water, measured conductometrically, and the induction times were determined from curves of the conductivity against time. The measurements were conducted using Model 679 Rancimat (Metrohm AG, Herisau, Switzerland) at 100°C, with sample size of 2.5 g and purified air flow rate of 10 l/h.

Thermoanalytical measurements were carried out using a Perkin-Elmer TGA 7 thermogravimetric analyzer and DSC 7 differential scanning calorimeter. Thermogravimetric measurements were performed at a heating rate of 5°C/min. Samples of approximately 10 mg were heated from 30 to 300°C. TG measurements were carried out in pure oxygen flow of 30 ml/min.

The DSC measurements were carried out in open Al crucibles with a sample mass of approximately 4 mg. The instrument was purged with pure oxygen at a flow rate of 60 ml/min. Samples were heated from 30 to 220°C at a heating rate 20°C/min. Isothermal DSC measurements were performed at 130°C for 2 h also in pure oxygen flow of 60 ml/min.

3. Results and discussion

In Fig. 1, the dynamic DSC curve of linseed oil sample is given. The exothermic peak in the range of 150 to 320°C related to auto-oxidation process of unsaturated fatty acids is observed [8]. From the DSC curve, the onset temperature ($T_{onset,DSC}$) at which the auto-oxidation process begins is determined. The onset temperature is usually taken as a parameter characterizing the oxidative susceptibility of oils [8,9,11].

In Fig. 2, the dynamic TG curve is shown. The increase in mass in the temperature range 190–220°C followed by a rapid mass loss is observed. The first change in the TG curve may be attributable to the beginning of oxidation process, then the thermal-oxidative decomposition proceeds more rapidly [14]. As an indicator of the auto-oxidation process, the onset temperature ($T_{onset,TG}$) at the beginning of the mass increase is determined.

The results of both DSC and TG dynamical measurements are summarized in Table 1.

It is found that the linseed oil sample without antioxidants exhibit the lowest onset temperatures determined by TG as well as by DSC. It indicates

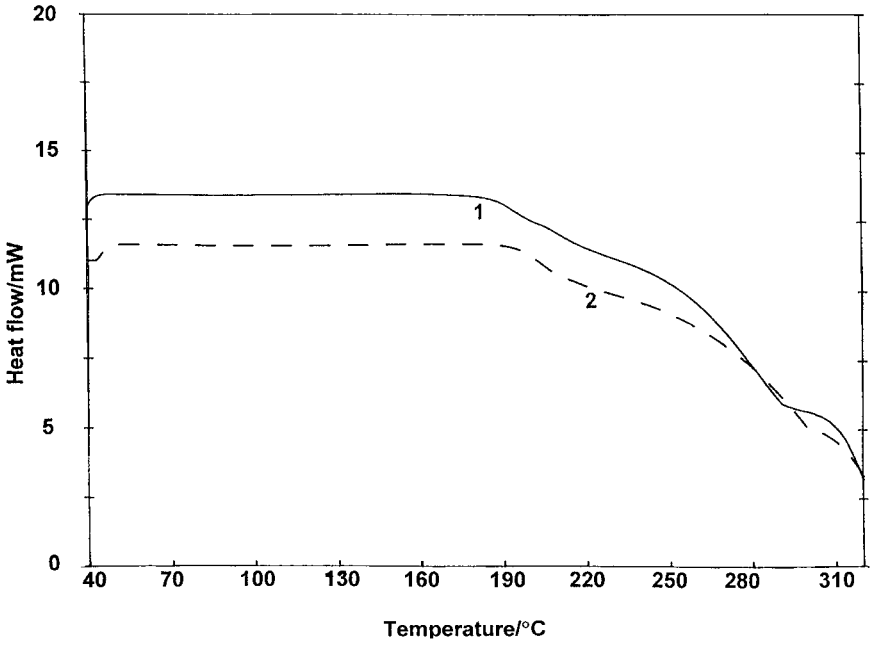

Fig. 1. Dynamic DSC curve of linseed oil in oxygen atmosphere: curve 1: linseed oil without antioxidant; curve 2: linseed oil with 0.2% M.

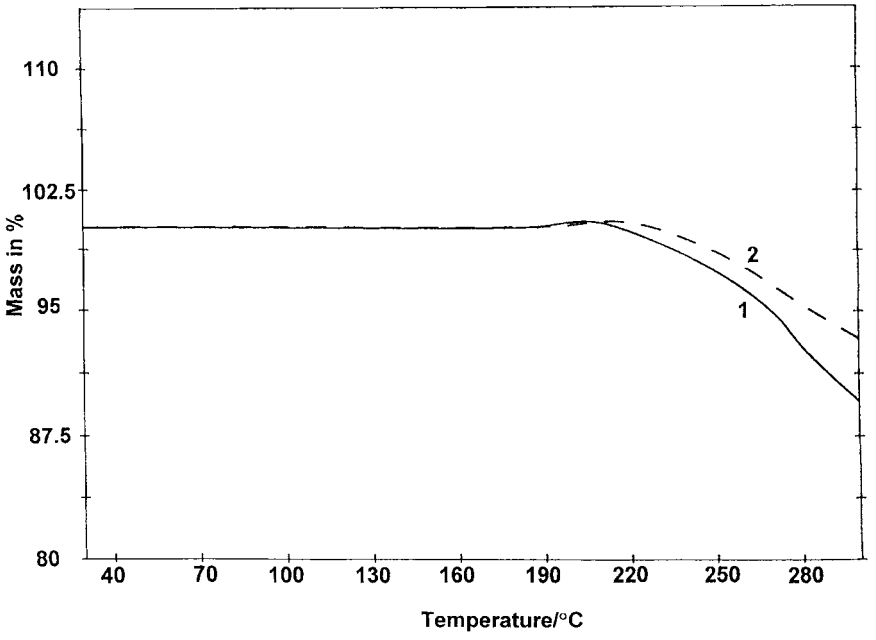

Fig. 2. Dynamic TG curve of linseed oil in oxygen atmosphere: curve 1: linseed oil without antioxidant; curve 2: linseed oil with 0.05% M.

Table 1
Dynamical thermoanalytical measurements of linseed oil samples

Sample	Antioxidant (%)	TG; $T_{onset,TG}$ (°C)	DSC; $T_{onset,DSC}$ (°C)
1	0	177	186
2	0.05 M	192	190
3	0.1 M	197	192
4	0.2 M	210	195
5	0.01 BHA	195	187
6	0.02 BHA	184	191

Table 2
Isothermal DSC measurements of linseed oil at 130°

Sample	Antioxidant (%)	t_{onset} (min)
1	0	23.1
2	0.05 M	25.1
3	0.2 M	33.1
4	0.01 BHA	24.0
5	0.02 BHA	30.1

the poorest oxidative stability of unprotected linseed oil sample.

The onset temperatures of linseed oil samples containing antioxidants are shifted to higher temperatures as compared with that one without antioxidant. It proves that the presence of antioxidants improves the oxidative stability of linseed oil. It is confirmed by both TG and DSC (see Table 1). The antioxidative activity of butylated hydroxy anisole (BHA) and a mixture consisting of α-tocopherol, ascorbyl palmitate, ascorbic acid, and ethoxylated etylene glycol (M) is associated with the ability of phenolic compounds to scavenge reactive free radicals [15]. The antioxidant M, however, proves more effective as antioxidant than BHA. It may be explained by the presence of α-tocopherol in the blend M which is known as one of the most effective natural antioxidant [2,16]. It is also observed that the increase in the antioxidant content increases both onset temperatures, e.g. $T_{onset,TG}$ and $T_{onset,DSC}$.

Isothermal DSC measurements were performed at 130°C. A typical isothermal DSC curve is given in Fig. 3. The exothermic peak attributable to the autooxidation process of linseed oil is observed. The time

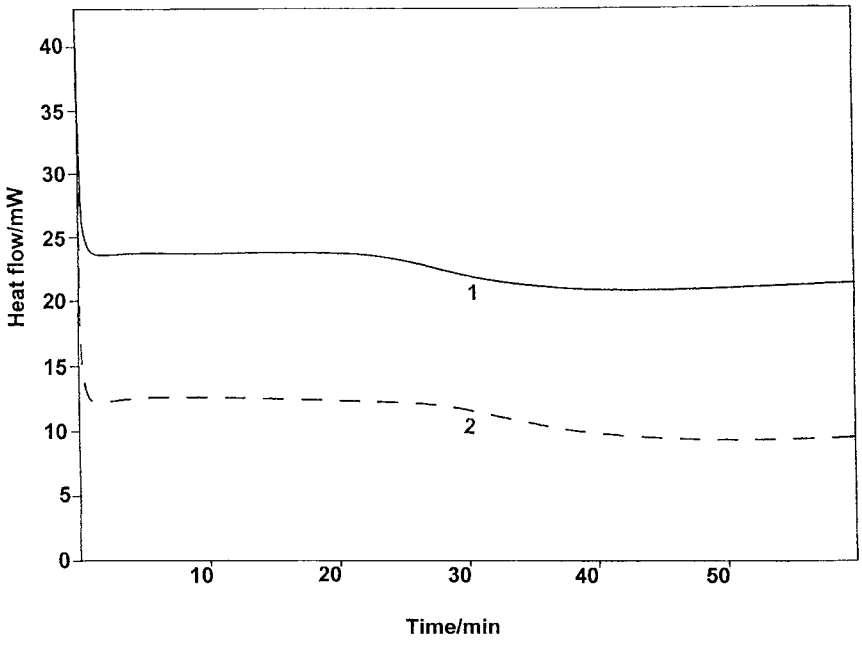

Fig. 3. Isothermal DSC curve of linseed oil in oxygen atmosphere: curve 1: linseed oil without antioxidant; curve 2: linseed oil with 0.02% BHA.

Table 3
Results of ageing of linseed oil/peroxide values

Sample	Antioxidant (%)	Peroxide value after ageing time (months)						
		0	1	2	3	5	7	9
1	0	2.0	2.0	2.2	2.7	3.8	6.2	12.3
2	0.05 M	2.1	2.3	1.7	2.0	2.2	4.0	8.8
3	0.1 M	2.0	2.2	1.6	1.7	1.7	2.5	6.7
4	0.2 M	2.0	2.2	1.5	1.2	1.6	1.9	3.2
5	0.01 BHA	2.1	3.0	2.0	2.1	2.9	4.8	8.0
6	0.02 BHA	2.3	2.4	1.7	2.1	2.7	4.1	7.2

required for the appearance of the first exotherm was taken as the induction time (t_{onset}) [11]. Results are given in Table 2.

Isothermal results agree with those obtained by dynamical DSC and TG measurements. The addition of antioxidant increases t_{onset}. The antioxidant M ensures a better oxidative protection than the antioxidant BHA.

Thermoanalytical results are compared with those obtained by the classical titration method. Results of investigations of oxidative stability of linseed oil during storage obtained by determination of PV are given in Table 3.

It was confirmed that the addition of antioxidants improves oxidative stability of linseed oil samples stored at room temperature. Antioxidant M exhibits the better oxidative protection in comparison with antioxidant BHA. The best antioxidant efficiency characterize the antioxidant M in the amount of 0.2%. In this case, the PV does not exceed value of 5 after 9 months of storage.

The results of the Rancimat test are given in Table 4. Both the antioxidants increased induction time as compared to the sample without antioxidant. The best stabilizing effect has the antioxidant M for which the longest induction time is observed. The results obtained from the Rancimat measurements correspond to those based on thermoanalytical methods.

Table 4
Induction times determined by the Rancimat method

Sample	Antioxidant (%)	Induction time (h)
1	0	6.40
2	0.05 M	8.30
3	0.1 M	8.70
4	0.2 M	12.00
5	0.01 BHA	6.67
6	0.02 BHA	7.18

4. Conclusions

It was found that among two antioxidants studied, i.e. butylated hydroxy anisole and a blend containing α-tocopherol, ascorbyl palmitate, citric acid, ascorbic acid, and ethoxylated ethylene glycol, the latter proved more effective for protection of linseed oil against oxidation.

The results obtained from dynamical DSC and TG measurements correspond with those based on the classical titration method as well as on the Rancimat method.

The thermoanalytical methods (TG and DSC) are useful to study the oxidative stability of linseed oil. They can be suitable for the prediction of oxidative stability of vegetable oils and for the evaluation of the efficiency of antioxidants.

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