High Pressure Differential Thermal Analysis (HPDTA) of Fatty Acid Methyl Esters and Triglycerides

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ABSTRACT

When using high pressure differential thermal analysis to study the stability of a fatty methyl ester or triglyceride in an atmosphere of air, a departure from the base line in the exothermic curve is observed. The point where an extension line from the base line intersects a tangent line to the departure curve was selected as the transition point in the exothermic curve. For each sample studied, temperature at this transition point showed good reproducibility. The influence of sample container and air pressure upon the temperature of the transition point in the exothermic curve (TTE) was examined. A linear correlation between the number of double bonds in the sample and TTE was observed.

INTRODUCTION

Thermal analysis is generally applied to investigate the physical and chemical changes which may occur when certain materials are heated. These changes are usually observed by measuring the temperature, form, weight or electrical resistance of the material being heated. Thermal analytical techniques are widely used in the field of oil chemistry; i.e., in the fusion of edible fats and oils (1), solidification behavior, quality control in the process of manufacturing edible oil (2-5), crystal transition (6), detection of adulterant (7,8) and examination of glyceride composition (9,10). Furthermore, DTA may be applied as an alternative method of measuring oil stability (11,12).

When an oil is heated and oxidized in an atmosphere of either air or oxygen using differential thermal analysis techniques, an exothermic curve is generally observed. This curve at atmospheric pressure shows a gradual ascent which makes it difficult to locate where the transition point is on the curve. However, under high pressure, this departure in the base line is more abrupt and the transition point is more easily defined. We carried out HPDTA on the methyl esters of palmitic, oleic, linoleic and linolenic acid as well as triglycerides composed of the above single fatty acids. The effects of sample container and air pressure on the observed TTE were studied.

The present paper also describes the relationship between TTE and the number of the double bonds in the fatty ester or triglyceride.

MATERIALS AND METHODS

Methyl esters of palmitic, oleic, linoleic and linolenic acid as well as tripalmitin, triolein, trilinolein and trilinolenin were provided by Sigma Chem. Co. The purity of each material was 99% as determined by GLC.

HPDTA was carried out on a Rigaku High Pressure Differential Thermal Analyzer R-I, manufactured by Rigaku Co., Tokyo.

The sample was weighed and placed in the cup holder. An empty cup was used as the reference standard. After the

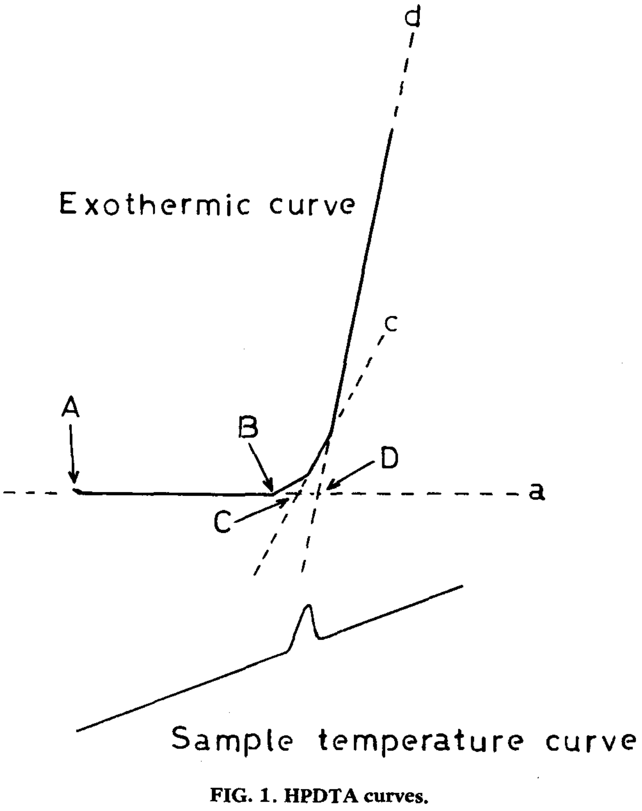

FIG. 1. HPDTA curves.

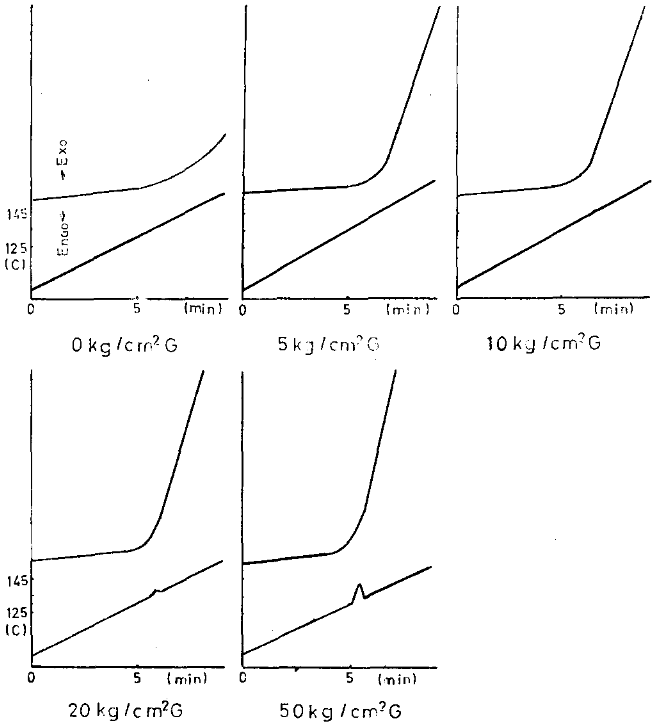

FIG. 2. Exothermic and sample temperature curves of methyl linolenate in HPDTA. Sample size, 5 mg; atmosphere, air; container, and aluminum cup.

TABLE I

The Temperatures at Point A, B, C and D Illustrated in Fig. 1

Sample	Temp. at A[a]	Temp. at B	Temp. at C	Temp. at D
Methyl palmitate				
1	26	180	198	210
2	57	172	199	210
3	100	186	200	210
Methyl linolenate				
1	53	92	129	138
2	41	106	133	141
3	41	83	130	138

[a] All temperatures °C.

introduction of compressed air into the HPDTA apparatus giving a high pressure atmosphere of air and setting of the temperature programmed rate, HPDTA was started.

The transition points C and D in the exothermic curves were located where the base line intersected the tangent lines c and d (Fig. 1).

TABLE II

The Influence of the Sample Containers on TTE[a]

Sample weight (mg)	Sample container	Point C	TTE point D
5.60	Al	130	138
5.07	Pt	121	133
5.44	Fe	118	126
5.09	Cu	115	125

[a] Sample, methyl linolenate; pressure, 50 kg/cm^2 (air); program, 20 C/min.

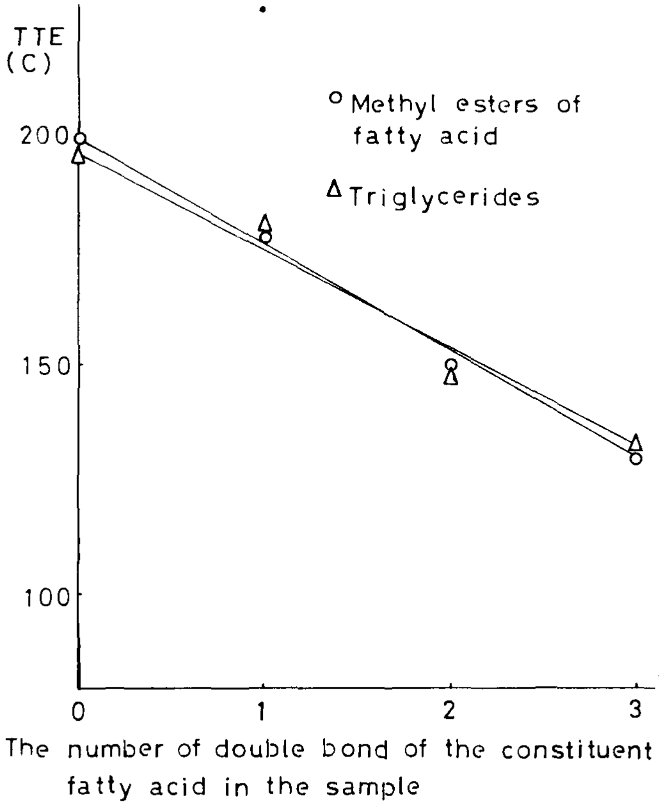

FIG. 3. The relationship between the number of double bond of constituted fatty acid in the sample and the TTE. (Point C) Sample size, 5 mg; program 20 C/min; container, an aluminum cup; pressure, 50 kg/cm^2 G (air).

RESULTS AND DISCUSSION

Using methyl linolenate as a sample, effects of air pressure on the exothermic curve were examined at air pressure 0, 5, 10, 20 and 50 kg/cm^2 g, respectively. Figure 2 indicates the result of HPDTA at different air pressures.

At 0 kg/cm^2 g air pressure, the exothermic curve ascended slowly, whereas under high pressure, the departure points on these curves were more distinct. Furthermore, the departure line had a sharper angle as the air pressure increased. The sample temperature curve gave a distinct peak at an air pressure of 50 kg/cm^2 g.

Methyl esters of palmitic and linolenic acid (ca. 5 mg) were used for the determination of the transition point and the reproducibility of TTE in HPDTA and analyzed under the condition of the programmed temperature of 20 C/min and the air pressure of 50 kg/cm^2 g. The temperature of the starting point A, the departure B from the base line and the intersection of points C and D illustrated in Figure 1 were measured. As shown in Table I, no reproducibility was observed for point B. On the other hand, points C and D showed good reproducibility, and thus they were chosen as the transition points on the exothermic curve. The temperature difference at starting point A in HPDTA had little influence on the TTE.

Aluminum, iron, copper and platinum cups were used as sample containers to examine their influence on TTE in HPDTA. Methyl linolenate was used as the sample. TTE was observed to be influenced by the sample container (Table II). This effect decreased in the order of copper, iron, platinum and aluminum. An aluminum cup was used as the sample container for obtaining the data in this study.

The relationship between the number of double bonds in the fatty methyl ester or triglyceride and TTE was examined. Figure 3 shows TTE at point C tends to increase, when the number of double bonds in the sample decreases and there exists a nearly linear correlation.

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