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CHARACTERIZATION OF FATTY ACID METHYL ESTERS BY THERMAL ANALYSIS

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The thermal stability of selected straight-chain (C_6–C_{14}) esters of fatty acids has been studied by TG-DTG and DTA analysis. In DTG, a peak is detected between 84° and 125°C followed by a main effect in the range 105°–215°C, whereas in DTA only an exothermic peak appears in the range of 126.5° to 187°C (onset temperatures). The temperatures of these effects have been related with ignition points, molecular weights and boiling points.

The characteristics of melting and recrystallization of the above fatty acid methyl esters and those with carbon numbers between C_{14} and C_{24} have been established by DSC along the melting range between –83° and 50°C. Polymorphism appears in caproic, heptanoic, palmitic and stearic acid methyl esters.

Keywords: fatty acid methyl ester, TG/DTG and DTA, thermal stability, polymorphism

Introduction

Boiling, melting and ignition points and crystallization degree are among the most important properties of fats and their derivatives. Systematic reliable measurements were only published in the last two decades on the main classes of fatty compounds, although isolated studies had been made earlier.

In a review of the state-of-the art of these compounds we have detected that the fatty acid methyl esters have received little attention [1–3]. This fact is unexpected because the fatty acid methyl esters are nearly ideal in their behaviour, boiling points are lower than those of the corresponding acids, and they are more stable thermally.

In this paper, TG, DTG, DTA and DSC curves were successfully used to obtain useful information on the above thermal properties for the fatty acid methyl esters containing 6 to 24 carbon atoms.

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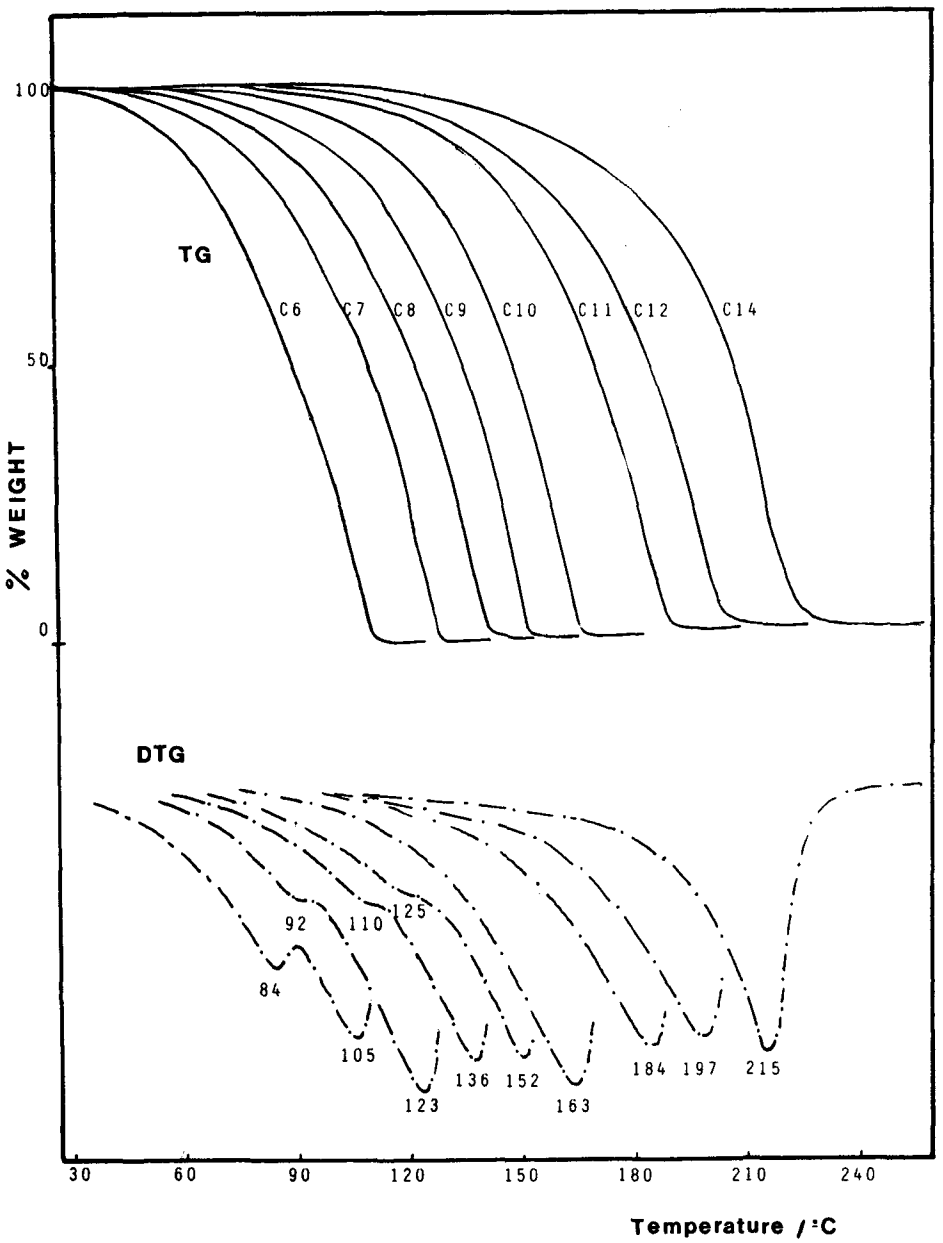

Fig. 1 TG and DTG curves of esters of C_6–C_{14} fatty acids. Heating rate: 20 deg·min^{-1}; Atmosphere: air, 20 cm^3·min^{-1}

Table 1 DTG, DTA and DSC effects and physical properties of esters of fatty acids

Methyl ester		Thermal effects				Physical properties			
		DTG peaks/°C		DTA onset/	DSC peak/	Flash point[a]/	Boiling point[a]/	Melting pointa/	Molecular weight/
		I	II	oC		°C			(amu)
C_6	Hexanoate	84	105	126.5	(-81.0) -76.1	45	151	-71	130.1
C_7	Heptanoate	92	123	148.1	(-71.0) -56.4	52	172	-56[c]	144.2
C_8	Octanoate	110	136	167.3	-41.8	72	194	-40[c]	158.2
C_9	Nonanoate	125	152	175.1	-37.0	84	213	n.r.	172.3
C_{10}	Decanoate	-	163	190.0	-16.2	94	223[b]	(-18)	186.3
C_{11}	Undecanoate	-	184	212.0	-12.9	109	246[b]	n.r.	200.3
C_{12}	Dodecanoate	-	197	188.0	7.8	110	262	4.8	214.4
C_{14}	Myristate	-	215	187.0	18.5	110	323	18.4	242.4
C_{16}	Palmitate	-	-	-	22.3 (30.6)	110	163[d]	33.0	270.5
C_{18}	Stearate	-	-	-	(24.8) 30.5	110	181[d]	41.0	298.5
C_{22}	Docosanoate	-	-	-	(44.9) 50.3	110	-	55.0	354.6

[a]see Ref. 4; [b]see Ref. 5; [c]see Ref. 6 [d]/4 mm

Experimental

The C_6 to C_{24} straight-chain fatty acid methyl esters were obtained from Aldrich Chemical Co. Thermal analysis was carried out using a Perkin Elmer equipment: a 3600 data station and the TGS2, DTA 1700 and DSC-7 apparatus. Instrument calibration was performed by standard indium and *n*-heptane samples of known temperatures and enthalpies of fusion. In TG-DTA investigations, the material (approximately 10 μl) was weighed in platinum (TG) or ceramic crucibles (DTA) containing aluminium oxide; the atmosphere was air (20 ml/min) and the heating rate was 20 deg·min^{-1}. In DSC experiments the material was weighed in closed aluminium crucibles and the measurements were carried out in N_2 atmosphere at a heating rate of 10 deg·min^{-1}.

Results

TG and DTG curves of the C_6–C_{14} methyl esters are shown in Fig. 1. The first thermal decomposition process (I) in the DTG curves takes place in the range of 84°–125°C, and it is followed by a second and most important process (II) at 105°–215°C. The corresponding temperatures of effects I and II are presented in Table 1.

In Fig. 1 it is observed that as the molecular weight increases the intensity of the first peak decreases: for C_7 it becomes a shoulder of peak-II and for C_{10} it does not appear.

Search for a relationship between the DTG effects and other known physical properties in order to justify the goodness of our experimental data allowed the following conclusions to be drawn:

(a) The DTG peak-I temperatures for the fatty acid esters C_6 to C_9 are correlated with the tabulated ignition points, *IP* (or flash points, *Fp*) by a linear relationship:

$$T(\text{peak-I}) = 40.77 + 0.98\,IP \quad (r^2 = 0.997;\ p < 0.001)$$

Thus, although the determination of the ignition points for esters by 'Setaflash' (D3278 ASTM methodology) or by DSC high pressure cell measurements is more adequate than their estimation through the measurements of the above DTG peak-I temperatures, this latter procedure may be applied in lack of specific instrumentation.

(b) Also a good correlation was found to exist between the DTG peak-II temperature and the molecular weight (*MW*) for all the methyl esters studied:

$$T(\text{peak-II}) = -22.58 + 1.00\,MW \quad (r^2 = 0.990;\ p < 0.001)$$

This good agreement is expected because the parameters in comparison are intrinsically associated: the dependent variable put as a function of molecular masses is the temperature that in DTG corresponds to the weight losses.

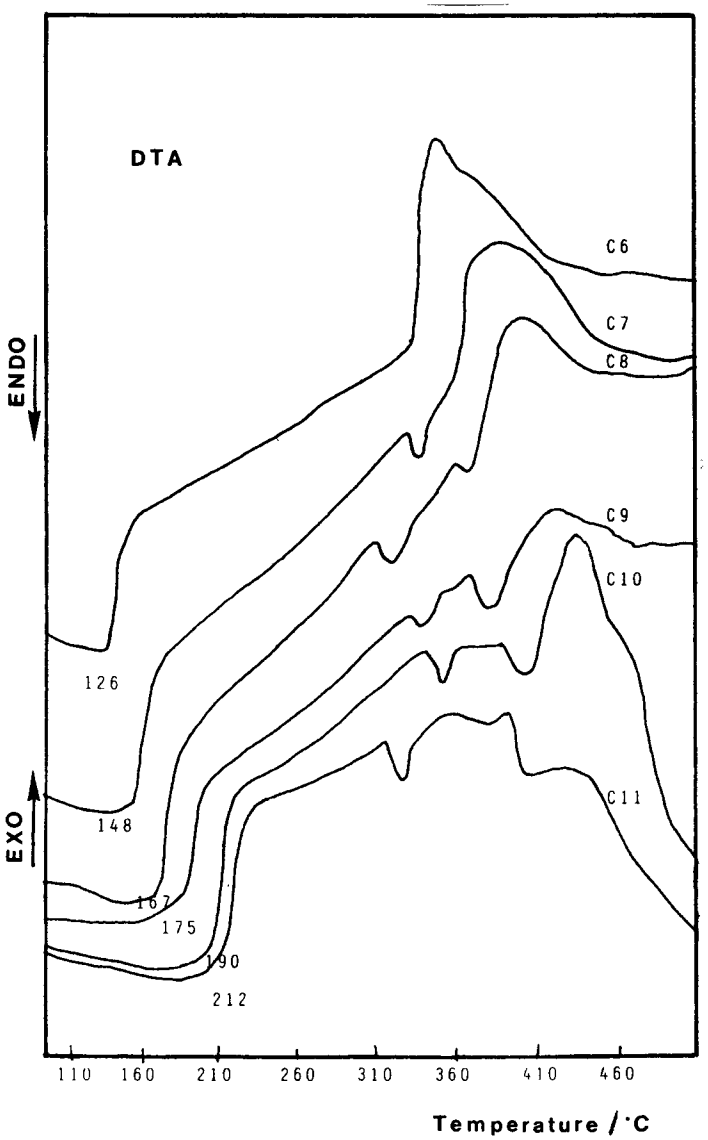

Fig. 2 DTA curves of esters of C_6–C_{11} fatty acids. Atmosphere: air, 20 $cm^3 \cdot min^{-1}$

(c) In a similar manner, the correlation found for C_6–C_{11} esters of fatty acids between DTG peak-II temperature and the boiling point, BP, can be expressed as follows:

$$T(\text{peak-II}) = -20.28 + 0.82\ \text{BP}\ (r^2 = 0.994;\ p < 0.001)$$

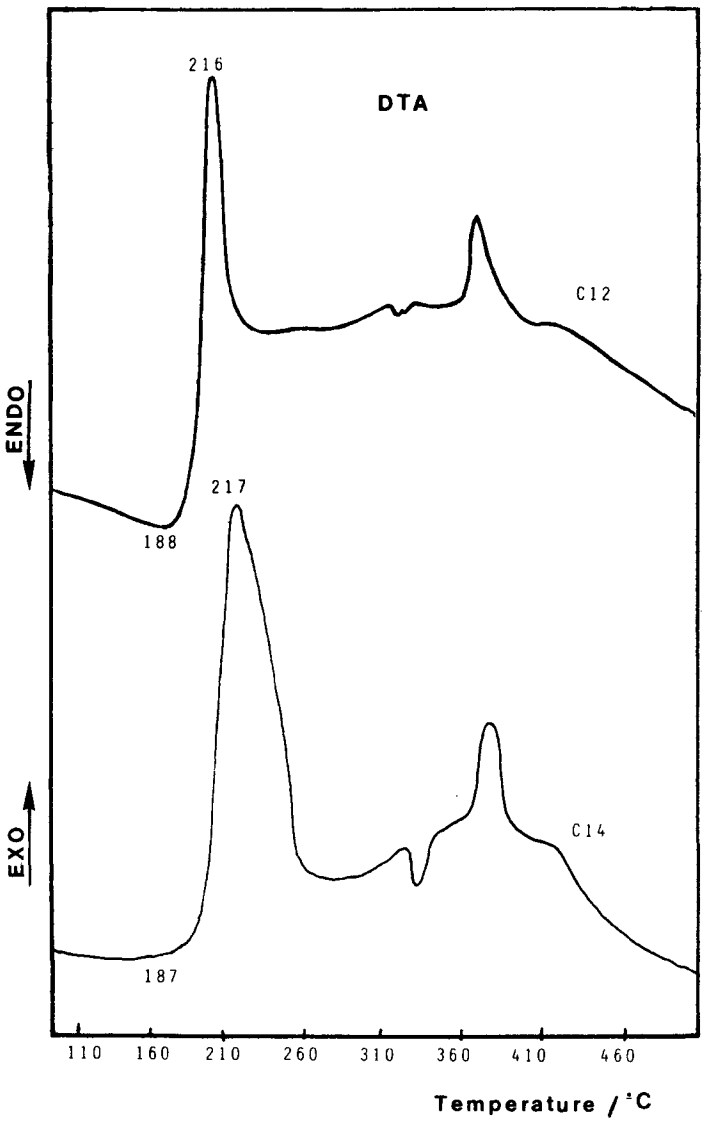

Fig. 3 DTA curves of esters of C_{12}–C_{14} fatty acids. Atmosphere: air, 20 $cm^3 \cdot min^{-1}$

The second group of results are related to the thermal stability of the methyl esters. The information has been obtained in oxidation experiments through DTA curves (Figs 2 and 3). It can be observed that the samples between C_6 and C_{11} show analogous features but when the hydrocarbon chain length increases, the curves pattern is altered. In fact, the exothermic effect is clearly more marked in the case of long chain fatty acid esters than for the lower members of a fatty acid methyl ester series. (Thus, the combustion heats of C_{12} and C_{14} esters have been estimated as 95 and 206 cal/g, respectively, whereas for C_6 and C_7 it was not possible).

The thermal data of DTA curves are presented in Table 1. Analogously as with DTG peak-II temperatures, two relationships between the DTA onset temperatures and the boiling points, and between the DTA onset temperatures and the molecular weights, can be established:

$$T(\text{DTA onset}) = -4.20 + 0.87\ BP\ (r^2 = 0.989;\ p < 0.001)$$

$$T(\text{DTA onset}) = -18.80 + 1.14\ MW\ (r^2 = 0.984;\ p < 0.001)$$

It must be mentioned that both equations can only be extended from C_6 to C_{11} because when the hydrocarbon chain is longer than C_{11} the well known polarity effects take place. The last equation justifies that the onset of the exothermic peaks is a marker of the fatty acid ester stability.

The third group of results comes from the DSC investigations and they give information on melting points, crystallization and polymorphism.

Figures 4 and 5 show separately the DSC curves for fatty acid methyl esters C_6 to C_{12} and C_{12} to C_{22}. In Fig. 4 and especially in the case of methyl caproate (C_6) and methyl heptanoate (C_7) esters, the polymorphism can be easily detected by the appearance of a first endothermic peak attributable to softening or early melting, followed by the exothermic peak corresponding to the definite melting. (This effect can be observed when working either with closed or open crucibles.) In the DSC curves (Fig. 5) for methylpalmitate (C_{16}), methyl stearate (C_{18}) and methyl docosanoate (C_{22}) the polymorphism is less evident, perhaps due to contamination (ageing) of the samples.

Table 1 summarizes the temperatures of the DSC endothermic peaks for the above esters. As previously observed with the DTG-DTA data, good relationships have been found between the maxima of the DSC thermal effects (in this case, corresponding to the melting points) and the molecular weights:

$$T_{\text{DSC peak}}(\text{from } C_6 \text{ to } C_{11}) = -188.49 + 0.90\ MW\ (r^2 = 0.965;\ p < 0.001)$$

$$T_{\text{DSC peak}}(\text{from } C_{12} \text{ to } C_{22}) = -54.86 + 0.29\ MW\ (r^2 = 0.984;\ p < 0.001)$$

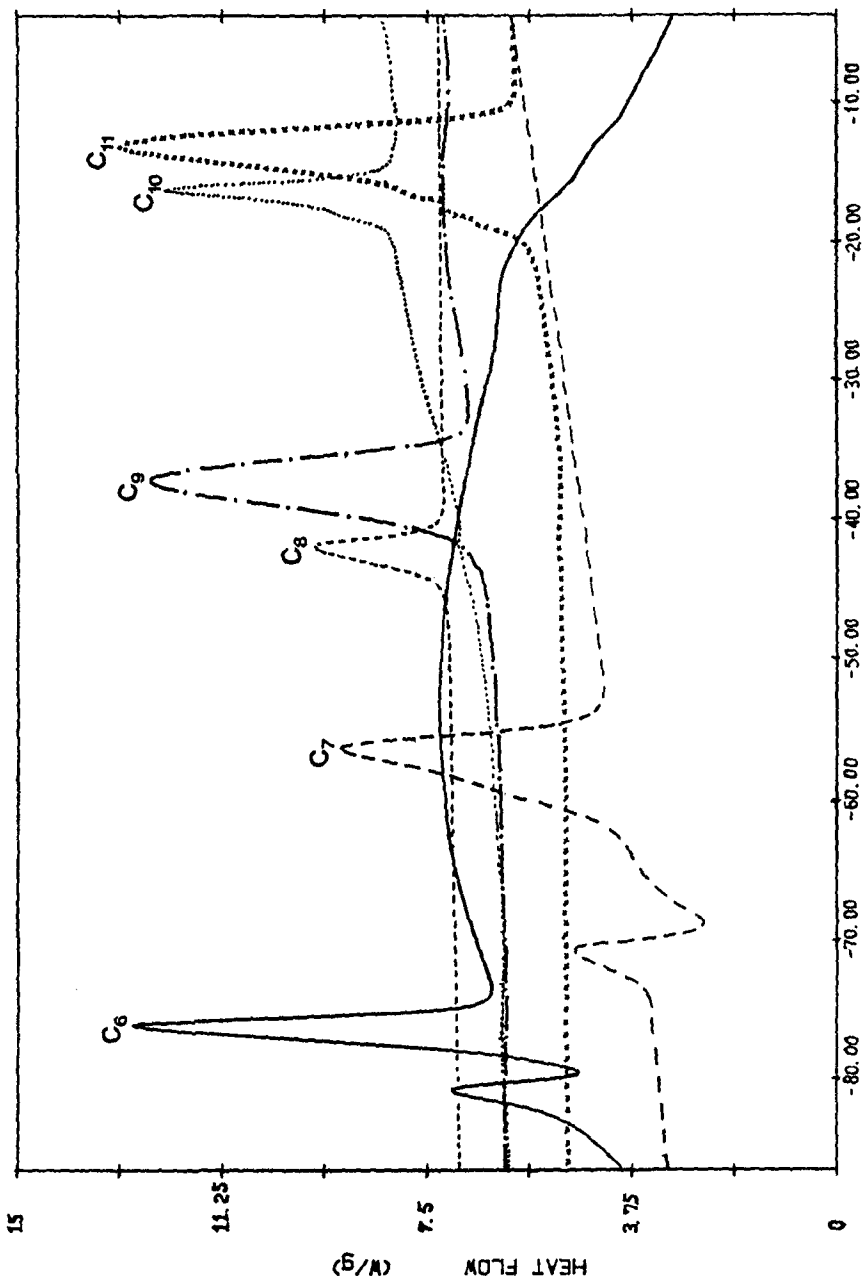

Fig. 4 DSC curves of esters of C_6–C_{11} fatty acids

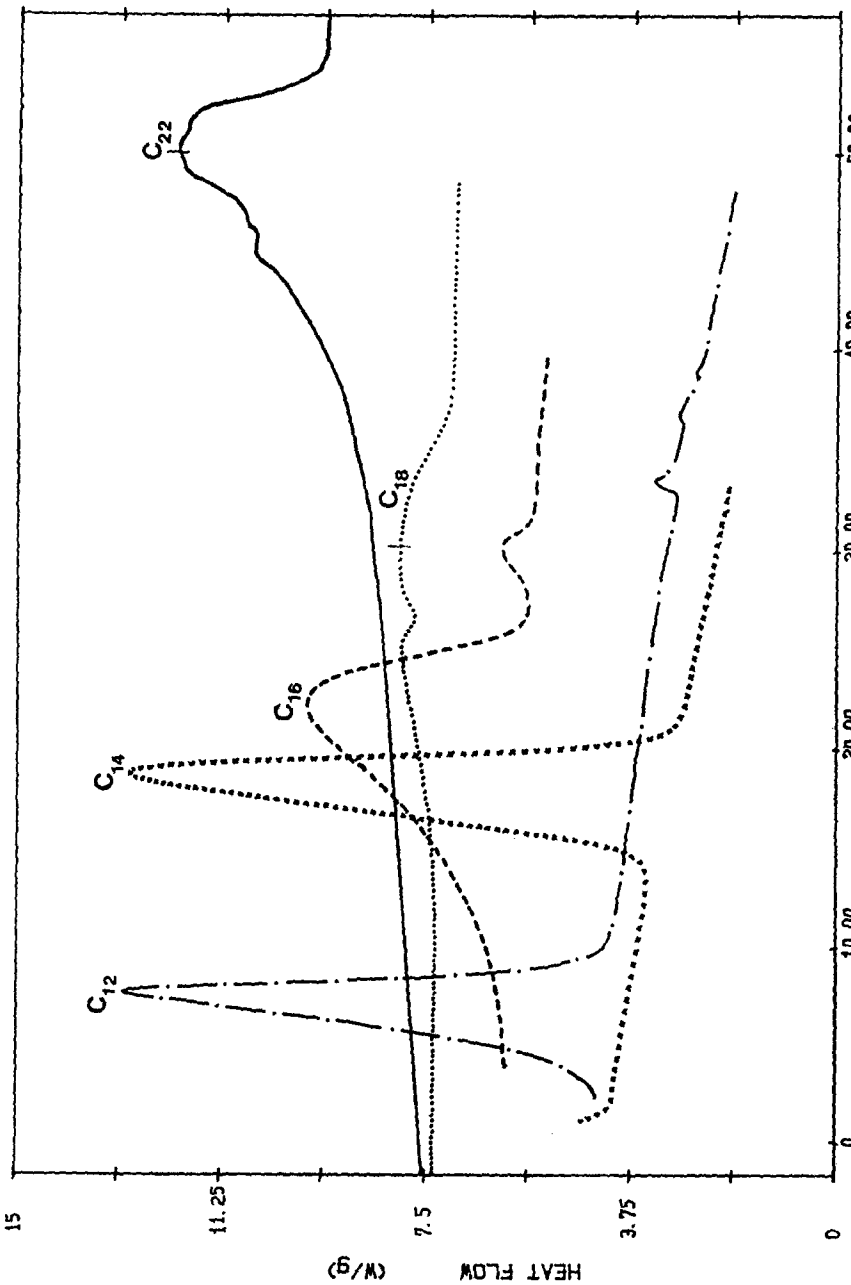

Fig. 5 DSC curves of esters of C_{12}–C_{22} fatty acids

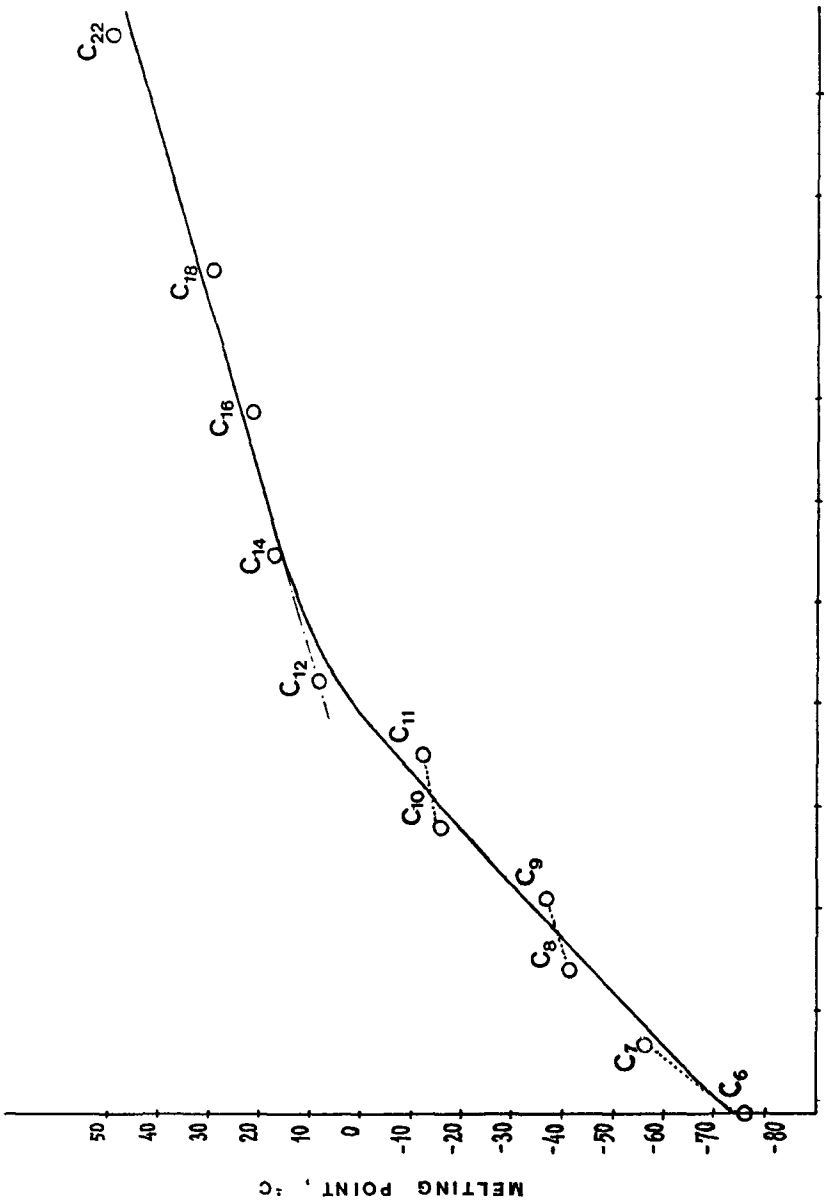

Fig. 6 Melting points *vs.* molecular weights for esters of fatty acids

Figure 6 in which the DSC maximum temperatures are plotted *vs.* molecular weights, shows a change of slope with increasing length of the hydrocarbon chain from C_{12} to C_{22}. (This loss of linearity have also been observed between DTA onset temperatures and physical properties.) In Figs 4 and 6 it is possible to recognize an association between the members of the pairs C_6–C_7, C_8–C_9 and C_{10}–C_{11}. This feature can be described in another way by saying that the melting points alternate according to whether the molecule contains an even or odd number of carbon atoms; the melting points of the two series lie on two smooth curves which gradually approach one another with increasing molecular weight. This feature can be due to the fact that the molecules are not linear but they display preferably a zig-zag configuration.

In conclusion, TG-DTG, DTA and DSC are useful tools for the study of qualitative and quantitative properties of methyl esters of fatty acids.

* * *

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References

1 P. M. Althouse and H. O. Triebold, Ind. Eng. Chem. (Anal. Ed.), 16 (1944) 605.
2 J. W. Shigley, C. W. Bonhorst, C. C. Liang, P. M. Althouse and H. O. Triebold, J. Am. Oil Chemists' Soc., 32 (1955) 213.
3 A. Rose and W. R. Supina, J. Chem. Eng. Data, 6 (1961) 173.
4 Catalog Handbook of Fine Chemicals Aldrich, Alcobendas (Madrid) 1990–91.
5 Catalog Lancaster of MTM Research Chemicals, Strasbourg 1991–92.
6 H. D. Durst and G. W. Gokel, Experimental Organic Chemistry. McGraw-Hill Book Company (Spanish version ed. Reverté S. A., Barcelona 1985, p. 563.)

Zusammenfassung — Mittels TG-DTG und DTA wurde die thermische Stabilität einiger ausgewählter geradkettiger (C_6-C_{14}) Fettsäureester untersucht. In der DTG-Kurve wird ein Peak zwischen 84° und 125°C beobachtet, gefolgt von einem großen Effekt im Bereich 105°–215°C, wobei in der DTA-Kurve im Bereich 126,5° bis 187° (onset-Temperaturen) nur ein einziger exothermer Peak erscheint. Die Temperaturen dieser Effekte wurden dem Zündungspunkt, den Molekülgewichten und den Siedepunkten zugeordnet.
Mittels DSC wurden im Schmelzbereich zwischen –83° und 50°C die Schmelz- und Rekristallisationsmerkmale obiger Fettsäuremethylester und solcher mit einer Kohlenstoffatomanzahl zwischen C_{14} und C_{24} ermittelt. Polymorphie tritt in den Methylestern von Kapron-, Heptyl, Palmitin- und Stearinsäure auf.