THERMAL BEHAVIOUR OF DIFFERENT HOG AND CATTLE TISSUE LIPIDS BY DSC ANALYSIS

D. SKALA, M. BASTIĆ, Lj. BASTIĆ[1], G. REMBERG[2] and J. JOVANOVIĆ

Faculty of Technology and Metallurgy, Belgrade, Karnedžijeva 4; [1]Yugoslav Institute of Meat Technology, YU-11000 Belgrade, Kaćanskog 13; [2]Institute of Organic Chemistry, D-3400 Göttingen, FR Germany

INTRODUCTION

DSC analysis was successfully applied for the determination of various characteristics of natural substances, such for example, the polymorfic transformation of fats[1], total heat of fusion of different samples of intramuscular lipids and changes during storage at +4°C, or after forced oxidation by UV-irradiation[2,3]. An attempt was made to improve thermal methods and DTA techniques for the study of oil and oil products proposing that a correlation exists between the composition of hydrocarbons present in the oil with the shapes of the DTA curves[4]. The location of the peak maximum in the DTA or DSC curve could be explained by the composition of the oil or fat[2,4], using a very simple additive rule.

In the recent past DSC studies (Schlichter[5] and Garti et al[6]) concerning the effects of chemical structure and composition on phase transitions in triglycerides have been published. It has been shown that thermal methods can be applied very effectively in estimating the extent and mechanism of a polymorphic transformation which is strongly dependent on thermal history and rate of scanning.

The polymorphic and thermal behaviour of lipids varies according to the chemical structure of the key components present in lipids (triglycerides) and the presence of other compounds (hydrocarbons, di- and monoglycerides, cholesterol and its derivatives, free fatty acids) as constituents of neutral lipids, as well as on the quantity of glucolipids and phospholipids[2,5,6]. From such a point of view, lipids originating from different animal tissues (muscle, liver, fatty tissue, brain and spinal cord) is very interesting as a sample with quite different compositions and weight percentages of neutral lipids, glucolipids and phospholipids. While heat effects, during the heating of lipid samples, is the consequence of a polymorphic transformation from the metastable toward the stable form followed by the melting primarily of triglycerides, the heat effects during the heating of pure phospholipids or glucolipids can be neglected[1]. Thus, such a constituent of the total lipids extracted from different hog and cattle tissues can be treated as an inert[2], or as inhibiting agent which can considerably alter the crystallization of different structural arangements of triglycerides (α, β´and β forms) as was shown in the case of pure

saturated monoacid triglycerides in the presence of a small quantity of surfactant[6].

Following the investigation we started a few years ago on thermal behaviour of intramuscular lipids by DSC analysis, in the present study the goal was to show the difference in the total heat effects during the heating of different lipid samples and to correlate it with their composition.

EXPERIMENTAL

Materials and methods

The preparation of samples of total lipids from different hog and cattle tissue is given in detail elsewere[7]. DSC analysis was performed using samples held at +4°C for 1 and 2 years after their preparation. The total lipids from muscle and fatty tissues (held at +4°C for 18 months) were fractionated on a Silica Gel 60 (70-230 mesh) column to neutral lipids, glucolipids and phospholipids according to the procedure described by Johnston[8]. The neutral lipid fractions were used for DSC analysis and for further processing by column chromatography (Florisil 100-200 mesh)[8] with the aim of only separating triglyceride fractions which were further analysed by DSC.

DSC experimental investigations were performed using a PERKIN ELMER DSC-2 unit. The heating rate was always 5°/min in the temperature range 233-363 K, with a 25 ccm/min flow of dry nitrogen through the DSC sample holder. The sample weights were always app. 50 mg (s.s. pan and an empty pan as a reference).

RESULTS AND DISCUSSION

The obtained typical polymorfic curves for five different hog and cattle tissues (muscle-*M. Longissimus dorsi*, liver, fatty tissue, brain and spinal cord) are shown in Figure 1. The curves of hog and cattle lipids from muscle and fatty tissues have several peaks indicating the specific structural arrangement of different triglycerides in which tri- and diunsaturated triglycerides (trioleate, dioleopalmitate and dioleostearate) are dominant[2,9,a] lower temperatures, while at higher temperatures the polymorfic structural change corresponds to monounsaturated or saturated triglycerides. However, the curves of hog and cattle liver, brain and spinal cord lipids are different in shape indicating the existance of only a small heat effect and much more complex structure. These samples are characterized only with a relatively small quantity of triglycerides, i.e. neutral lipids.

One of the basic goals of this study was to confirm the assumption, presented in some of our previous papers, that thermal effects and corresponding structural arrangements, especially characteristic for intramuscular lipids and fatty tissue lipids, originate exclusively from neutral lipids, i.e. triglycerides. Thus, neutral lipids were extracted from the total lipids

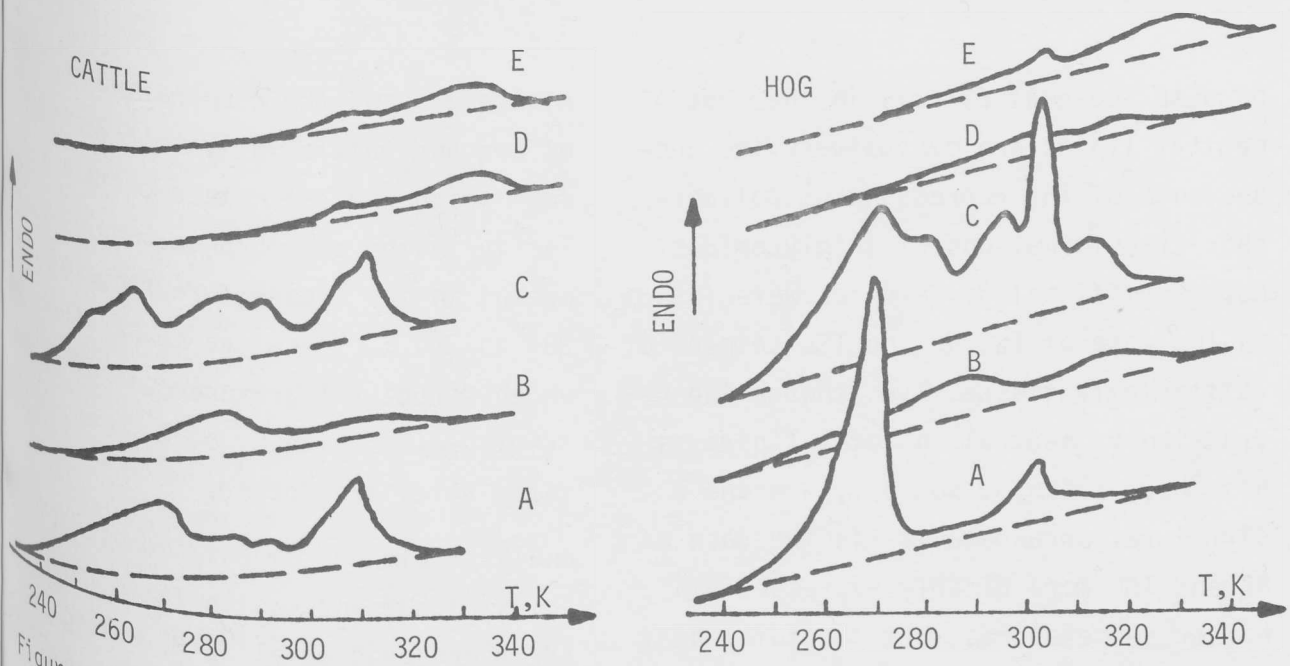

Figure 1. DSC curves of lipids from: A-muscle tissue (*M. Longissimus dorsi*); B-liver; C-fatty tissue; D-brain, and E-spinal cord

of fatty and muscle tissues, and , in turn, from them only triglycerides. Such a series of samples (total lipids-neutral lipids-triglycerides) from hog and cattle fatty tissue was analysed by means of DSC and the results presented in Figure 2.

Very similar polymorphic effects were registered in the case of total lipid (TL), neutral lipid (NL) and triglyceride (TGL) samples from hog and cattle tissue. That could have been expected on the basis of the fraction of neutral lipids in total lipids (99.6%) and

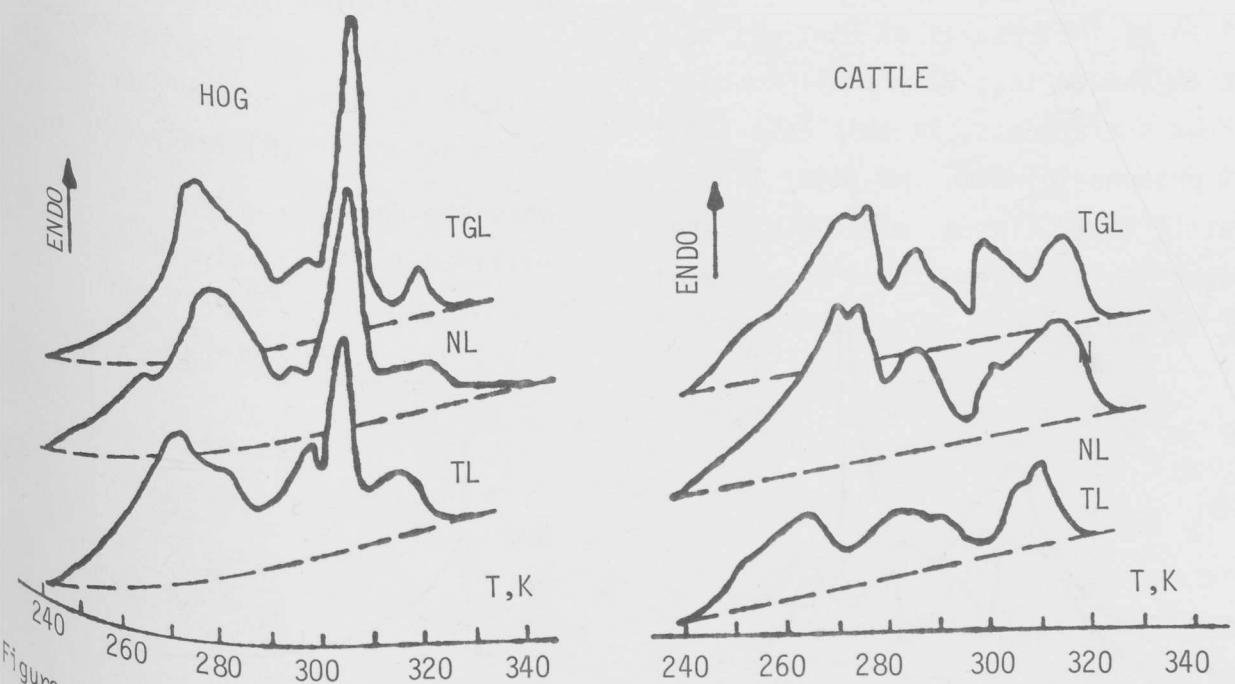

Figure 2. DSC curves of total lipids (TL), neutral lipids (NL) and triglycerides (TGL) of hog and cattle fatty tissue.

because the heat effects in the case of neutral lipids are exclusively the consequence of the corresponding polymorphic transformations of triglycerides. More significant differences were found in the case of TL, NL and TGL samples of cattle fatty tissue. Even though the fraction of neutral in total lipids is also high (96.6%), not only are the β structural arrangements in the case of NL and TGL more clearly expressed at higher temperatures, but the total heat effects are disproportionately greater than those to be expected on the basis of the corresponding composition. These results are in contradiction with the assumption that the total lipid fusion enthalpy of each sample may be correlated by the additive rule on the basis of fractions and fusion enthalpies of the triglyceride fractions. An explanation for such a phenomena is partially given by the results of Garti et al[6] which showed that very small amounts of added surfactants, in this case about 3% phospholipids in the total lipids of cattle fatty tissue, may inhibit the formation of β structural arrangements of triglycerides.

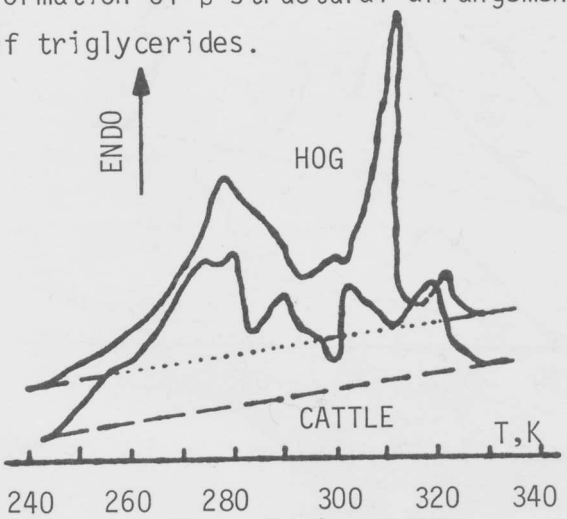

Figure 3. DSC analysis of TGL

Figure 3 shows the comparative analysis of hog and cattle fatty triglycerides from which one can note a certain similarity in the polymorphic behaviour, except in the temperature range of about 304 to 320 K. These are temperatures at which structural arrangements of mixed triglycerides with C_{16}^{o}, C_{18}^{o} and $C_{18}^{=}$ fatty acids are formed.

Analysis of the composition of fatty acids of hog and cattle fatty tissue TL (V. Djordjević et al[10]; M. Bastić et al[7]) which, for the sake of further interpretation of heat effects, is presented in Table 1, indicates that the fraction of monounsaturated fatty acids in the case of hog fatty tissue lipids is about 10% higher than in that of cattle lipids. The opposite holds for the content of polyunsaturated fatty acids (PUFA). Both facts also indicate why different values of heat effects were determined because β structural arrangement is favoured by a higher content of monounsaturated (M) fatty acids.

When the data presented in Table 1 are utilized for the analysis of the dependence of ΔH_t on the PUFA/S ratio, presented

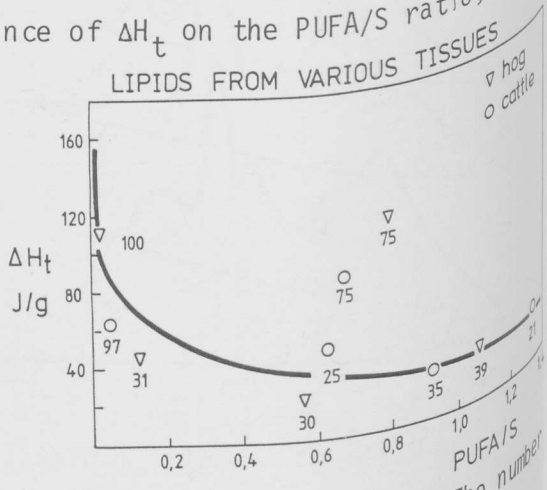

Figure 4. ΔH_t versus PUFA/S. The number coresponds to NL content.

TABLE 1. Total heat effects determined by DSC analysis: HOG/(CATTLE)*[10,7]

TISSUE	ΔH_t, J/g	Lipids % NL	Phosph.	S	M	PUFA	PUFA/S
MUSCLE	109.2	74.9	24.4	47.3	15.4	37.1	0.79
	82.2*	75.1*	22.8*	45.1*	7.6*	31.1*	0.68*
LIVER	42.9	31.0	64.2	84.4	4.9	10.8	0.13
	43.3*	24.8*	72.0*	43.6*	6.8*	28.0*	0.64*
FATTY	111.9	99.6	0.3	34.5	53.8	0.8	0.02
	64.4*	96.6*	3.0*	38.6*	44.2*	2.2*	0.05*
BRAIN	19.8	29.7	60.8	58.6	12.4	31.0	0.55
	20.8*	34.5*	58.4*	17.2*	4.5*	15.8*	0.92*
SPINAL CORD	24.6	39.0	56.6	35.1	27.6	37.4	1.07
	22.4*	21.0*	71.4*	30.2*	17.6*	39.7*	1.31

ted in Figure 4, it may be concluded that regardless of the lipid origin (hog and cattle tissue), there exists a corresponding exponential dependence between the fusion effects and the ratio of polyunsaturated and saturated fatty acids (PUFA/S). The higher the value of PUFA/S, the lower the heat effect and vice versa which is also in agreement with the work of Peron[11] who analysed the influence of unsaturation on triglyceride polymorphism.

Intramuscular lipids

The thermal behaviour of intramuscular lipids extracted from the *M. Longissimus dorsi* of hog and cattle (12th to 14th verterba) does not fit into the dependance presented in Figure 4. These samples are characterized by a high value of PUFA/S and also by a high content of neutral lipids. This indicates that unsaturated fatty acids, mostly PUFA, present the main constituents of neutral lipids and not phospholipids, as was the case for total lipids of other tissues (liver, brain, spinal cord).

Figure 5 presents the DSC curves of samples of hog and cattle intramuscular lipids (*M. Longissimus dorsi*), as well as the corresponding extracted fractions (neutral lipids from cattle tissue and triglycerides from hog muscle tissue).

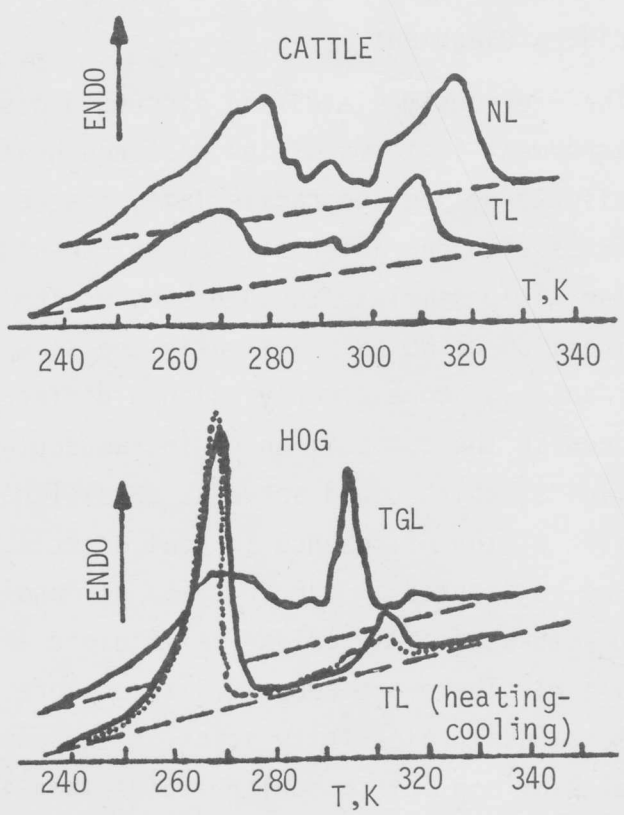

Figure 5. DSC anal. of intramuscular l.

Table 2. Total heat effects of fusion and polymorphic transformation ΔH_t, J/g

TISSUE	DSC analysis performed		ΔH_t calculated
	May 1988	April 1989	
Muscle-HOG			
TL	109.2	116.1	-
TGL	-	158.2	145.8
Fatty-HOG			
TL	111.9	131.2	-
NL	-	140.2	112.3
TGL	-	132.8	-
Muscle-CATTLE			
TL	82.2	-	-
NL	-	10.7	100.9
Fatty-CATTLE			
TL	64.4	73.5	66.7
NL	-	112.6	-
TGL	-	112.0	-

Table 2 gives certain values of heat effects in separated analysis performed in an interval of one year. The results confirm some previous ones[2,9] that the larger storage of lipid samples at + 4°C enables more complete β´and β triglyceride arrangement.

The previously stated and discussed disagreement in terms of the measured heat effects of hog and cattle fatty tissue TL is also characteristic of intramuscular lipid samples. In both samples the fraction of NL is practically the same (Table 1). More clearly defined differences in the composition of intramuscular lipids, which could serve as an explanation of the difference in heat effects, are registered in the fraction of mono-unsaturated fatty acids (palmitoleic and oleic). There are about 2.5 times more mono-unsaturated fatty acids in the samples of hog intramuscular lipids than in the case of cattle ones. The composition of C_{16} and C_{18} (S,M) fatty acids is presented in Table 3, where both the fraction of these acids in the hog *M. Semimembranosus* muscle NL and TGL fractions is shown[12].

Table 3. Fatty acid composition for muscle tissue (1-hog and 2-cattle *M. Longissimus dorsi*; 3-hog *M. Semimembranosus*; 4-hog and 5-cattle fatty tissue)

Acids	1	2	3[12]	4	5
$C_{16}{}^{1=}$	2.6	0.2	4.5	1.2	2.9
$C_{16}{}^{o}$	27.0	24.2	13.1	21.0	23.3
$C_{18}{}^{1=}$	8.0	4.0	37.7	57.3	36.3
$C_{18}{}^{o}$	15.7	17.6	6.6	16.9	10.8

The results lead to the conclusion that there is a great difference between the fraction of PUFA and M in hog and cattle muscular lipids which greatly influence the heat effects and measured fusion of enthalpies of total lipids. It should be emphasized that beside knowing the characteristic PUFA/S values for a lipi sample, in order to properly estimate the sample heat of fusion, one should know in which total lipid fraction (NL or phospholipids) PUFA predominate. Therefore, information on the thermal behaviour of intramuscular lipids of two different hog muscle (fusion effect *M. Longissimus dorsi* 109.2 J/g, *M. Semi membranosus* 56 J/g[2]) is significant for analysing the influence of M and PUFA on oxidation and the formation of volatile compounds.

CONCLUSION

The fusion effect of total lipids of hog and cattle muscle, liver, brain, spinal

cord and fatty tissue lies in the range of 20 to 112 J/g and was measured in the temperature interval 233 to 363 K at a heating rate of 5^{o}/min. It can be correlated with the PUFA/S ratio regardless of its origin (hog or cattle).

In the case of fatty, liver, brain and spinal cord tissue the phospholipid fraction in the total lipids increases with increase of PUFA/S, and therfore, the fusion effect decreases. The contrary holds for muscle tissue lipids where a high value of the PUFA/S ratio is not followed by an adequate increase in phospholipids, the neutral lipid and triglyceride fractions are still dominant. This indicates the complexity of the acid composition of intramuscular lipids and their role in the formation of volatile compounds responsible for meat aroma and taste.

Depending on the complexity of the composition of fatty acids in some samples it is possible to relate the fusion effect of total lipids to the fraction and heat effect of the present triglycerides. The study of the thermal behaviour of total lipids and the corresponding fractions of total lipids enables the derivation of a simple correlation between the total registered heat effects and the composition. This analysis becomes significant when oxidative changes in total lipids are studied.

REFERENCES

1. Le Meste,M., Cornily,G. and D. Simatos, R.F.C.G., 31, No 3 (1984)107.
2. Skala,D., Bastić, Lj., Bastić, M., and J. Jovanović, XXXII EMMRW, Ghent Belgium, Procedings II,p441 (1986).
3. Bastić,Lj., Bastić, M., and D. Skala Food Technology and Biotechnology Review, 25, No 1-2 (1987) 25.
4. Tiunova, I., Thermochimica Acta, 134 (1988) 79.
5. Schlichter,J.A., ibid 134 (1988) 1.
6 Garti,N., Schlichter, J., and S.Sari Fat Sci. Technol., 90, No 8 (1988) 295.
7. Bastić, M., Bastić,Lj., Remberg,G., Skala, D., and J. Jovanović, XXXV International Congress of Meat Science and Technology, Copenhagen, Denmark (in press).
8. Johnston, J.J., Chaubari,H.A., Wheeler, W.B., and Kirk J.R., J. Fd. Science, 48 (1983) 33.
9. Bastić Ljubica, Ph D. Thesis, University of Belgrade (1986).
10. Djordjević,V., Bastić, M., Remberg, G., and J. Jovanović, XXXIV International Congress of Meat Science and Technology, Brisbane, Australia, Procedings II, p595 (1988).
11. Perron, R.R., R.F.C.G., 31, No 4-5 (1984) 171.
12. Bastić, M., Bastić, Lj., Đordjević, V., Remberg, G., Skala, D., and J. Jovanović, J. Serb. Chem. Soc., 52 (1987) 565.