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OXIDATION OF LIPIDS STUDIED BY ISOTHERMAL HEAT FLUX CALORIMETRY

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ABSTRACT

The exothermic reaction of the autoxidation of lipids has been studied by isothermal heat flux calorimetry at temperatures between 80°C and 160°C. A number of lipid samples have been kept in the calorimeter under excess of oxygen for 1 or 2 hours. The capabilities of the method are illustrated by examples exhibiting different thermal behaviour, where the influence of temperature and the role of unsaturation and of antioxidants are presented for selected lipids.

INTRODUCTION

Numerous aspects of lipid oxidation have been studied in the past, and a great number of excellent reviews are now available in this field (ref. 1).

Lipid oxidation is a subject of primordial importance in many different aspects of the life sciences. Biologists dealing with the highly unsaturated phospholipids of membranes are very much concerned with their oxidative degradation (ref. 2), and a particularly great effort has been made to better characterize these lipid degradation products (ref. 3).

In food science and technology, the oxidative degradation of lipids in foods is of great concern to the chemist (ref. 4). Many methods have been developed for following oxidation reactions by determining individual primary or secondary oxidation products in different circumstances: in particular many attempts have been made to develop systems for accelerating the oxidation reactions (ref. 5). All of these tests have one point in common: they introduce an artificial condition such as high temperature, light, exogenous catalyst (metal ions, peroxides, etc. ...) or oxygen pressure. It is therefore often advisable to combine several test systems and compare results of complementary measurements in order to attenuate the problems of artefacts introduced by the accelerating condition.

A priori, thermal analysis techniques seem ideal tools for studying accelerated oxidation of lipids as they are based on the detection of thermal parameters such as heat flux which are directly linked to the autoxidation of the analyzed substance. It is therefore not surprising that a number of studies have emerged in this field: differential scanning calorimetry (DSC) (ref. 6), thermogravimetry (ref. 7) and especially high pressure DSC (refs. 8-12) have been proposed for studying oxidation reactions of food and non food oils.

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EXPERIMENTAL

The instrument was a conventional heat flux differential scanning calorimeter (ref. 13) DSC 111 from Setaram (69300 Caluire, France); it was used in the isothermal mode. The gas flow system was built in such a way that the sweeping gas was distributed equally between reference and sample channel (0.5l/hour in each).

Samples of 5mg were weighed on an analytical balance in open aluminium or fused alumina crucibles. The lipids studied were of commercial origin with the exception of deodorized chicken fat which was prepared according to a procedure already described (ref. 14). Propyl gallate (Fluka AG, CH - 9470 Buchs, Switzerland) was dissolved in ethanol before addition to the lipids.

The cells containing the lipid samples in the form of thin layers were introduced into the calorimeter which was kept under argon flow at a temperature chosen between 80° C and 160°C. The reference was an identical empty cell. Once thermal equilibrium was reached (after approximately 15 min), the gas suppply was switched from argon to a constant flow of oxygen, furnishing the lipid sample with an excess of oxygen.

Conventional induction times were determined according to published procedures (ref. 15) using the Rancimat (Metrohm AG, CH-9100 Herisau, Switzerland). As there is no ICTA definition in this matter, we have arbitrary considered 2 types of induction times from the calorimetric data. Induction time A is the time lag between switching over to oxygen and beginning of exothermic heat flow, induction time B is the time necessary to reach the maximum heat flow.

RESULTS

Fig. 1 presents the calorimetric curves of the series methyl stearate, methyl oleate, methyl linoleate and methyl linolenate, which were oxidized at 120°C for 2 hours. The induction times of these methyl esters determined from

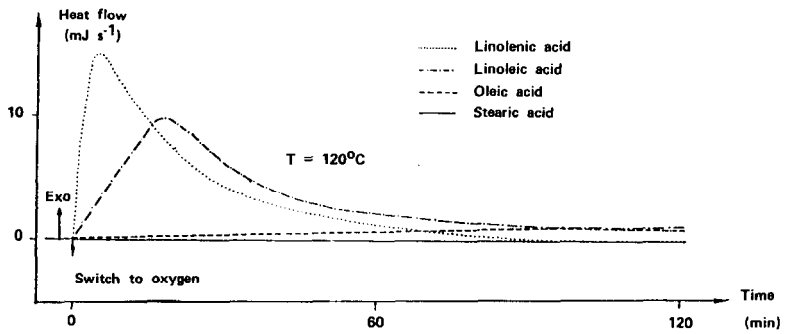

Fig. 1 Calorimetric curves of the serie of methyl esters ranging from methyl stearate to methyl linolenate, oxidized at 120°C.

such calorimetric data are reported in Table 1.

Fig. 2 shows the calorimetric curves of three oils with very different stabilities: they were analyzed at 130°C. Nujol is shown here as an inert standard. Results obtained with vegetable oils of different stabilities are summarized in Table 2.

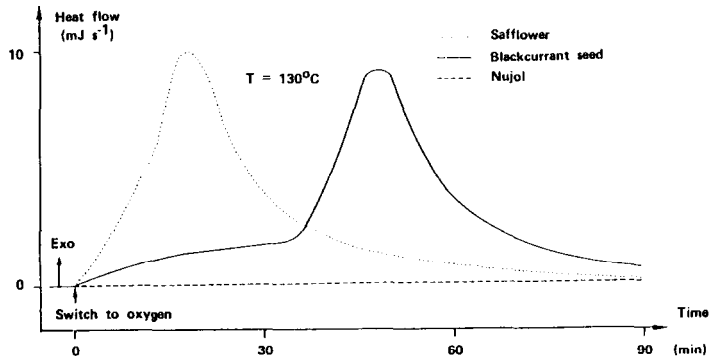

Fig. 2 Calorimetric curves of three oils with different stabilities, oxidized at 130°C.

Linseed oil and methyl linolenate were analyzed at different temperatures ranging from 80°C to 140°C. A summary of these results showing the temperature dependance of the induction time is given in Table 3 and the calorimetric curves obtained for linseed oil are presented in Fig. 3.

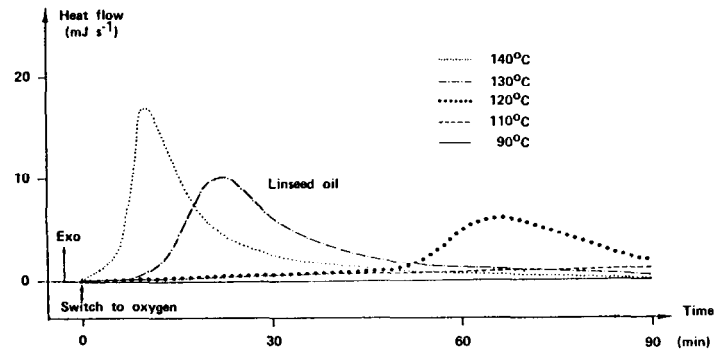

Fig. 3 Calorimetric curves of linseed oil oxidized at different temperatures.

The influence of antioxidants on the calorimetric curves at 120°C and on the induction times was studied using deodorized chicken fat and adding increasing quantities of propyl gallate dissolved in a small amount of ethanol. In parallel to these measurements, a conventional induction time determination was run using the automated A.O.M. procedure (Rancimat) at a temperature of 120°C. Both results are summarized in Table 4.

DISCUSSION

It has been suggested (ref. 6,9) that studies of oxidation by DSC were difficult to carry out because of imprecise reaction initiation and unstable base lines. The set up proposed here overcomes these problems by introducing the samples under argon, thus preventing oxidation before thermal equilibrium is attained at the chosen temperature. Switching to oxygen then allows the autoxidation to begin. Thus, stable base lines and precise reaction initiations can be obtained.

In order to verify that the observed phenomena were really due to oxidation, some samples were kept for extended periods under argon flow at elevated temperatures: the corresponding calorimetric curves were only straight lines, thus showing that decomposition, evaporation, polymerisation and/or isomerisation were not relevant in the temperature and time range of interest.

The results indicated in tables 1 and 2 are in good agreement with the generally expected behaviour of methyl esters of individual unsaturated fatty acids and the fatty acid composition of the vegetable oils analyzed. However the difficulties associated with the use of type A induction times are clearly shown in Table 1 and in the corresponding Fig. 1 where the fatty acids are relatively unstable: the type A parameter is of particular value for acids with stable structures. The induction times listed in Table 3 for linseed oil and methyl linolenate show the influence of temperature; as was expected, induction times decrease with increasing temperatures.

In the evaluation of the antioxidants effect, chicken fat was chosen as the substrate for the following reasons: it does not contain any antioxidants - interactions with added antioxidants could therefore be avoided - and it is of high unsaturation (> 54%). The induction times listed in table 4 for comparison between calorimetry and the Rancimat were obtained at 120°C: the trend of both indications is correct as induction times increase similarly as a function of propyl gallate addition (from 0 to 500 ppm).

CONCLUSION

Even if other techniques are available to follow edible lipid oxidation, thermal analysis should bring valuable complementary information in this field. The method described here is promising firstly because it is more convenient to study lipids under oxygen flow than under oxygen pressure as is usually done, and secondly because the temperature range of interest for these experiments is far below the self-ignition temperature found for fats and oils, therefore allowing autoxidation rather than combustion studies (ref. 16).

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TABLE 1 Induction times determined by heat flow calorimetry for methyl esters of selected saturated and unsaturated fatty acids.

Methyl esters	Induction times at 120°C (min)		Induction times at 140°C (min)	
	A	B	A	B
Methyl stearate	n.d.[1]	n.d.	n.d.	n.d.
Methyl oleate	1	117	1	36
Methyl linoleate	1	18	1	13
Methyl linolenate	1	5	1	7

1) too stable for a determination

TABLE 2 Induction times determined by heat flow calorimetry for oils with different stabilities.

Oils	Induction times at 120°C (min)		Induction times at 130°C (min)	
	A	B	A	B
Palm	n.d.	n.d.	173	213
Olive	108	175	17	105
Blackcurrant seed	95	118	32	50
Corn	78	99	35	50
Peanut	68	92	39	54
Sunflower	69	87	1	22
Linseed	50	65	11	21
Safflower	43	63	1	18

TABLE 3 Induction times of linseed oil and methyl linolenate between 80°C and 140°C.

Temperature (°C)	Induction times for linseed oil (min)		Induction times for methyl linolenate (min)	
	A	B	A	B
80	n.d.	n.d.	1	50
100	186	231	1	25
120	50	65	1	5
130	11	23	1	4
140	5	13	1	3

TABLE 4 Induction times of deodorized chicken fat stabilized with propyl gallate.

Amount of propyl gallate ppm	Induction times from calorimetry at 120°C A (min)	B (min)	Induction times from Rancimat at 120°C (min)
0	15	53	16
50	81	125	93
100	109	157	144
200	255	303	195
350	317	385	318
500	489	555	438

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