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RAPESEED OIL IN MARGARINE AND OTHER PRODUCTS

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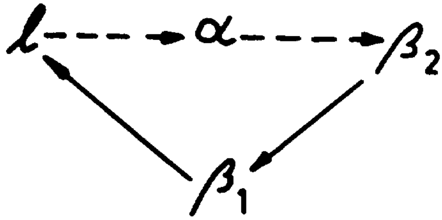
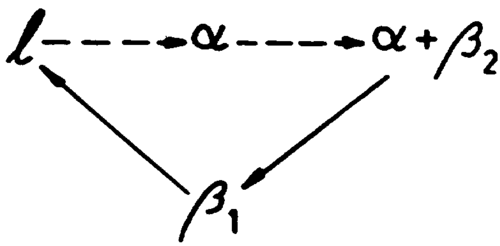
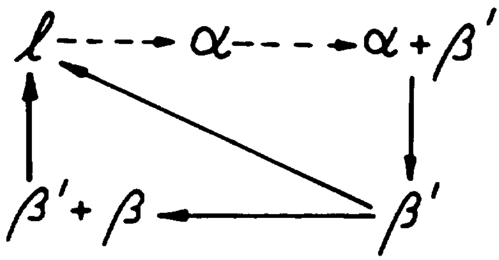
Since the Second World War the cultivation of rapeseed has become established in Europe on a more permanent basis, and some countries are giving it a measure of governmental assistance. In Canada the production was erratic until about 1956. In Europe and Canada rapeseed oil is used mainly as a component of margarine, shortenings or table oils. Let us first look at the physical properties of rapeseed oil, whether hydrogenated or not, and compare it with soybean oil and other competing oils.

MELTING AND SOLIDIFICATION OF RAPESEED OIL

The high content of erucic acid in rapeseed oil would imply a high melting point for this oil. The melting point of the most stable polymorphic form of trierucin is about 30°C. It has, however, been shown that erucic and eicosenoic acids are preferentially situated in the 1- and 3- positions of the glycerol residue, thus leading to mixtures of molecules containing oleic, linoleic and linolenic acids in the 2-position. These compounds have not yet been characterized, but melting points between 4°C and 5.8°C have been reported for rapeseed oils from West Pakistan, Sweden and Canada. Riiner investigated a number of Cruciferae seed oils by X-ray and thermal methods and found generally the same polymorphic behaviour for oils containing between 8 percent and 63 percent of erucic acid (Figure I). Below a level of 8 percent the polymorphism was no longer determined by the glycerides containing erucic acid. The behaviour on melting and crystallization was shown to vary regularly with the erucic acid content and thus the phase behaviour of a certain oil can be predicted from its fatty acid composition (Figure II). This would be of importance for oils which are used in foods that have to be stored and used at low temperatures. It was thus concluded, that for a Cruciferae oil to remain clear at 0°C, the erucic acid content should be below about 39 percent in the case of *Brassica napus* oils and below about 43 percent for *Sinapis alba* oils.

The connection between the polymorphic transitions on crystallization of hydrogenated rapeseed oil and the thermal effects were investigated by Riiner and Melin. Figure III shows the thermal cooling curves for two of the oils, determined according to Wilton and Wode. The temperature T_1 indicates

Polymorphic transitions in *Cruciferae* seed oils

Scheme		Erucic acid content
1		> 25%
2		8-25%
3		0-8%

- - - - transition on cooling 0.5°C/min

——— transition on heating 0.5°C/min

FIGURE I

PHASE TRANSITIONS IN CRUCIFERAE OILS

ERUCIC ACID CONTENT 8%

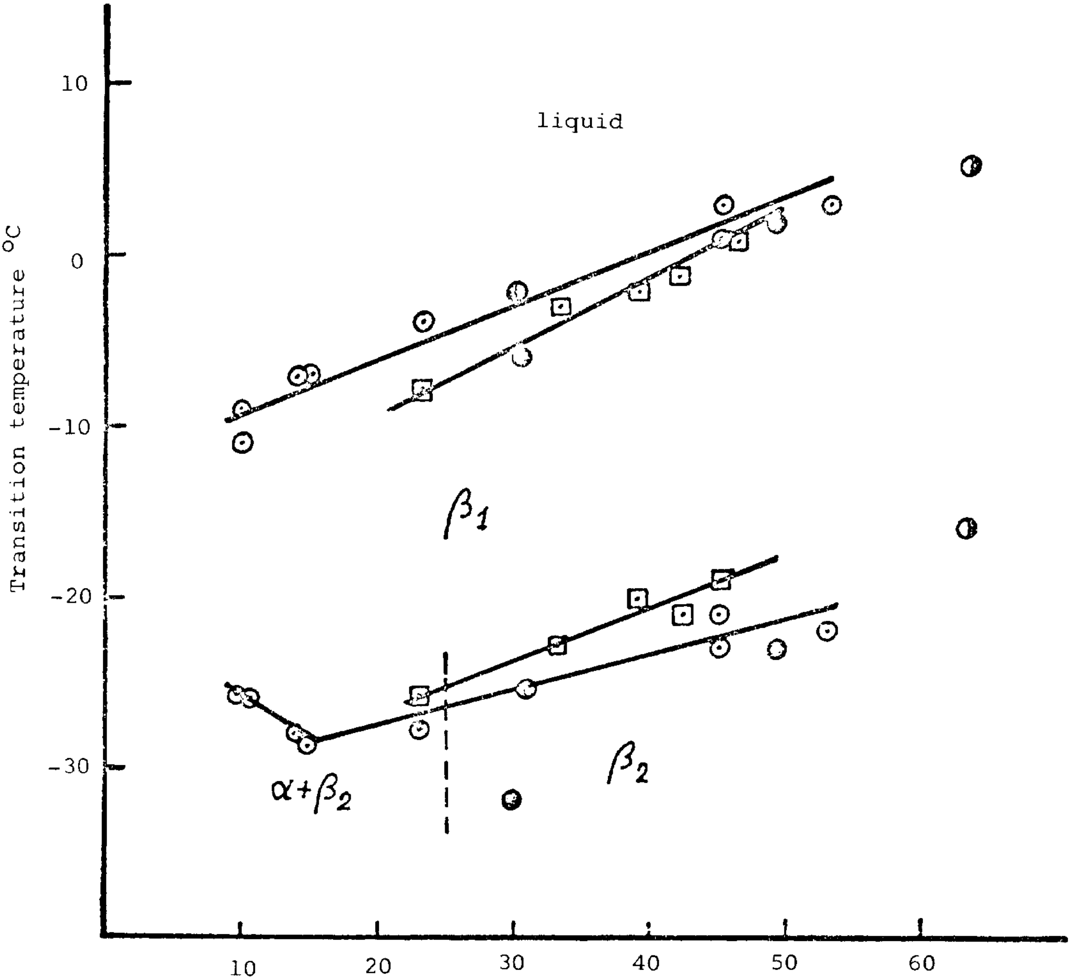


FIGURE II

⊙ Brassica napus

⊡ Sinapis alba

● Brassica campestris

◑ Crambe abyssinica

◐ Conringium orientalis

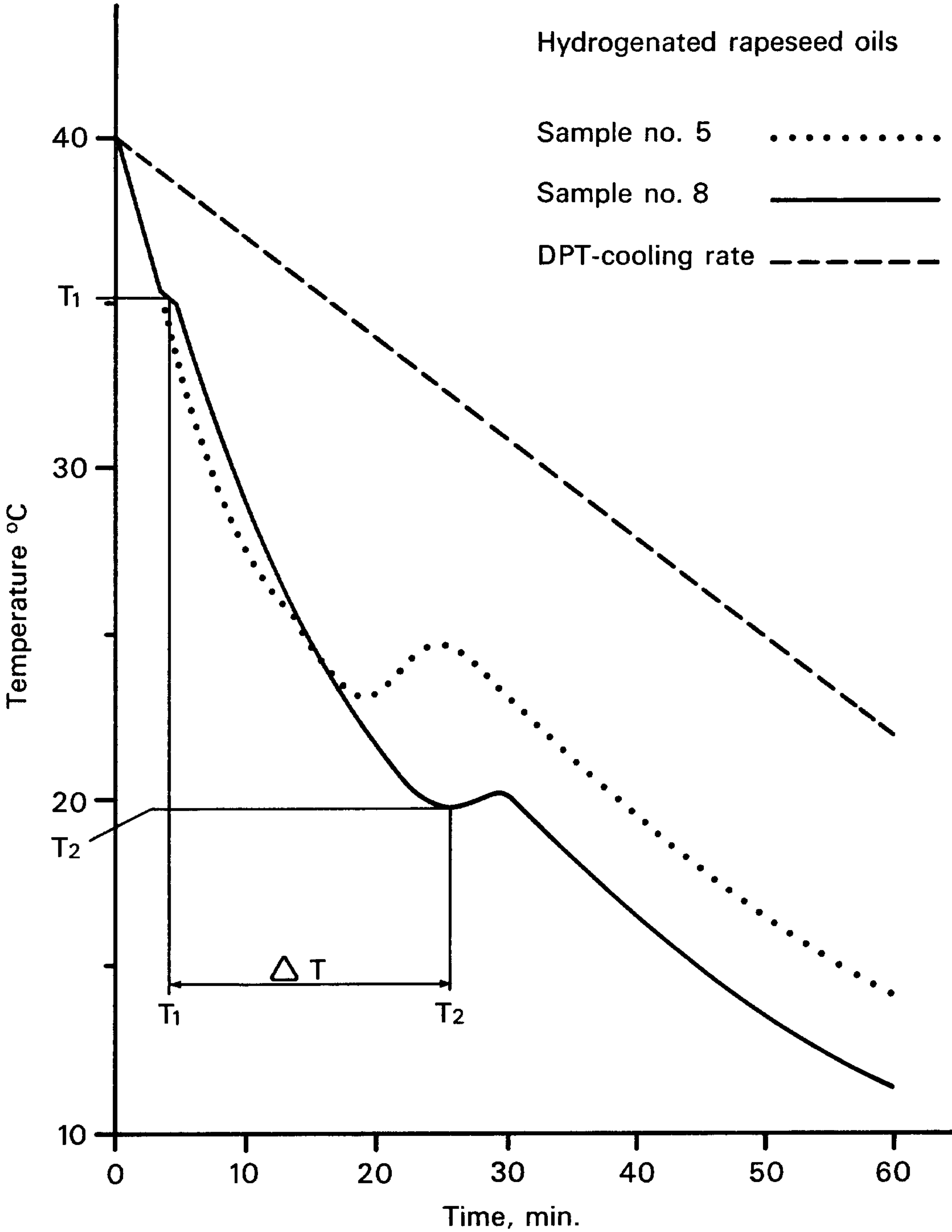

Hydrogenated rapeseed oils
Sample no. 5
Sample no. 8
DPT-cooling rate
40
30
20
10
T1
T2
ΔT
T1
T2
Temperature °C
0
10
20
30
40
50
60
Time, min.

FIGURE III

the point where the time-temperature curve first deviates from the curve for a non-crystallizing glyceride mixture, e.g. soybean oil. The temperature T_2 indicates the temperature for the minimum point. It is seen from Table I that T_1 coincides within 1-2°C with the transition temperature for liquid to α-form indicated by temperature programmed X-ray diffraction, and that T_2 coincides with the transition temperature for α to β' form. The lifetime of the form consequently depends only on the rate of cooling between T_1 and T_2 and, therefore, the difference T_1-T_2 can be regarded as a measure of the α state lifetime under equal rates of cooling. This measure can probably be used in the analysis of the conditions for the large-scale production of crystallized fat products. It should be borne in mind, however, that great differences exist between the conditions of these experiments and actual practice.

In order to know how much hydrogenated rapeseed oil could be used in a margarine blend it is necessary to know something about the solubility of this rapeseed oil in different other kinds of other oils. Two examples are given in Figures IV and V

In a margarine blend there is an equilibrium between the solid and liquid phases and it is the amount and type of solid phase that determines the consistency of the product at a given temperature. It is, therefore, essential to have a theroretically correct method for measuring the solid phase percentage, and this has been achieved with the development of NMR. The correlation between the NMR-method and the dilatation method is shown in Figure VI.

OXIDATION TENDENCY OF RAPESEED OIL

With the advent of the first substantial rapeseed crop in Sweden in 1944, there was a marked reduction in the oxidation tendency of margarine. Unfortunately, however, the expected increase in flavour stability of margarine did not occur. Apparently rapeseed oil needed to be handled very carefully.

Laboratory investigation showed, that the tendency of rapeseed oil to oxidize depended partly on the occurrence of secondary oxidation products, which were formed in rapeseed oil as the result of the decomposition of peroxides.

Study of these secondary oxidation products showed, that they consisted in part of unsaturated aldehydes. Some of these could be eliminated by deodorization. Others were decidedly non-volatile, tasteless and odourless and could not be removed. These non-volatile products accelerate both, formation and decomposition of peroxides during storage of the oil.

TABLE I

LIFETIME OF THE α FORM AT THE CRYSTALLIZATION OF HYDROGENATED RAPESEED OILS

Sample No.	I.V.	Dilatation, mm 3/g[a]					DPT-Diagram			Thermal Cooling Curve		
		10	20	30	35	40 (°C)	$t_{\alpha l \rightarrow \alpha}$ min	°C	$\alpha \rightarrow \beta'$ °C	Δt min	T_1 °C	T_2 °C
5	70.2	50	34	13	3.9	0.6	13	26	22	7	26	23
6	68.8	53	44	19	8.5	1.7	21	30	24	10	29	24
7	64.2	61	56	33	19	8.3	28	35	26	12	33	26
8	73.6	41	32	17	12	7.7	50	36	21	21	35	20

a) Dilatation calculated per g of sample.

Method C-V 11a(53), DGF-Einheitsmethoden, Stuttgart, 1950-1965.

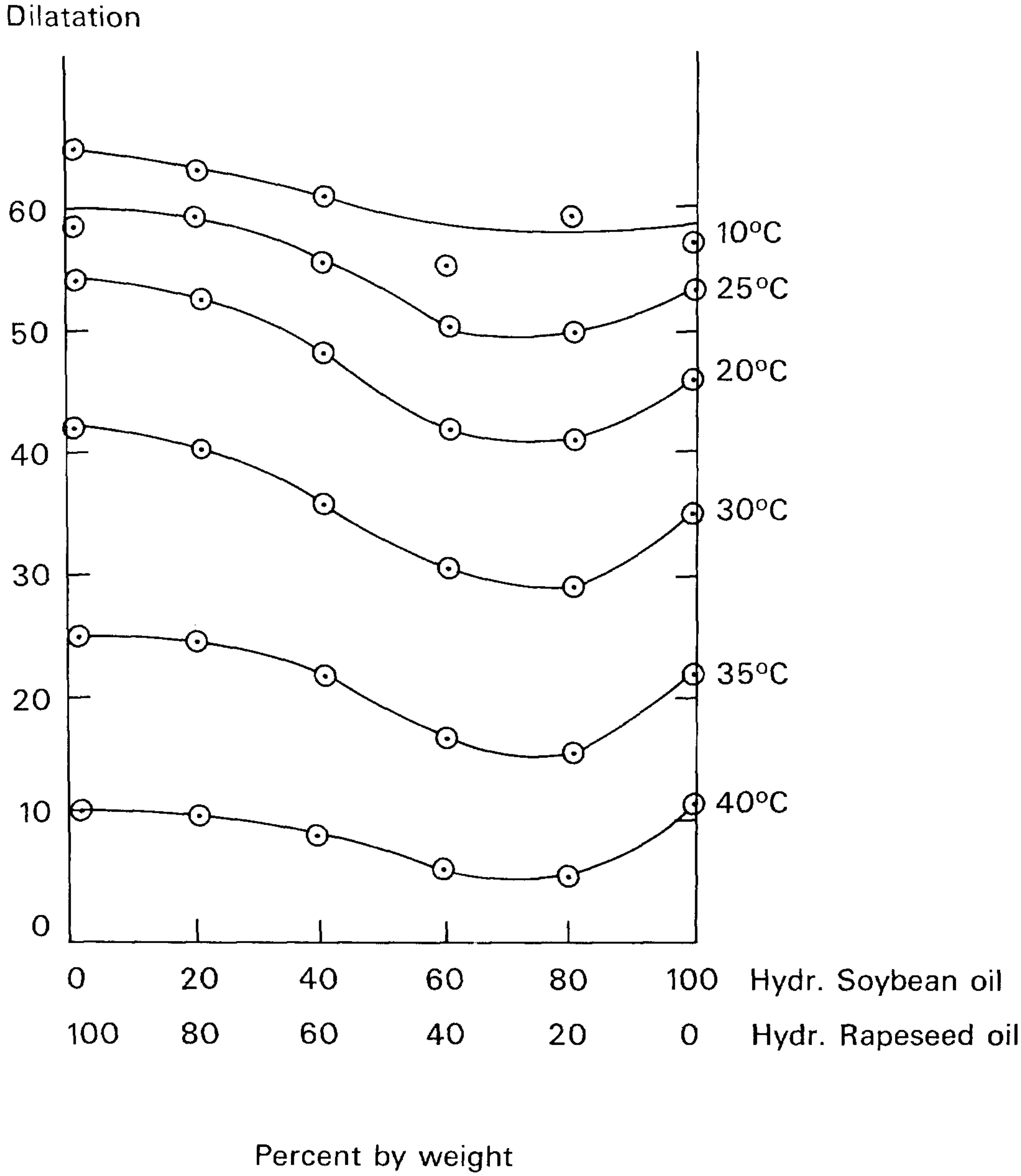

Dilatation
60
50
40
30
20
10
0
10°C
25°C
20°C
30°C
35°C
40°C
0 20 40 60 80 100 Hydr. Soybean oil
100 80 60 40 20 0 Hydr. Rapeseed oil
Percent by weight

FIGURE IV

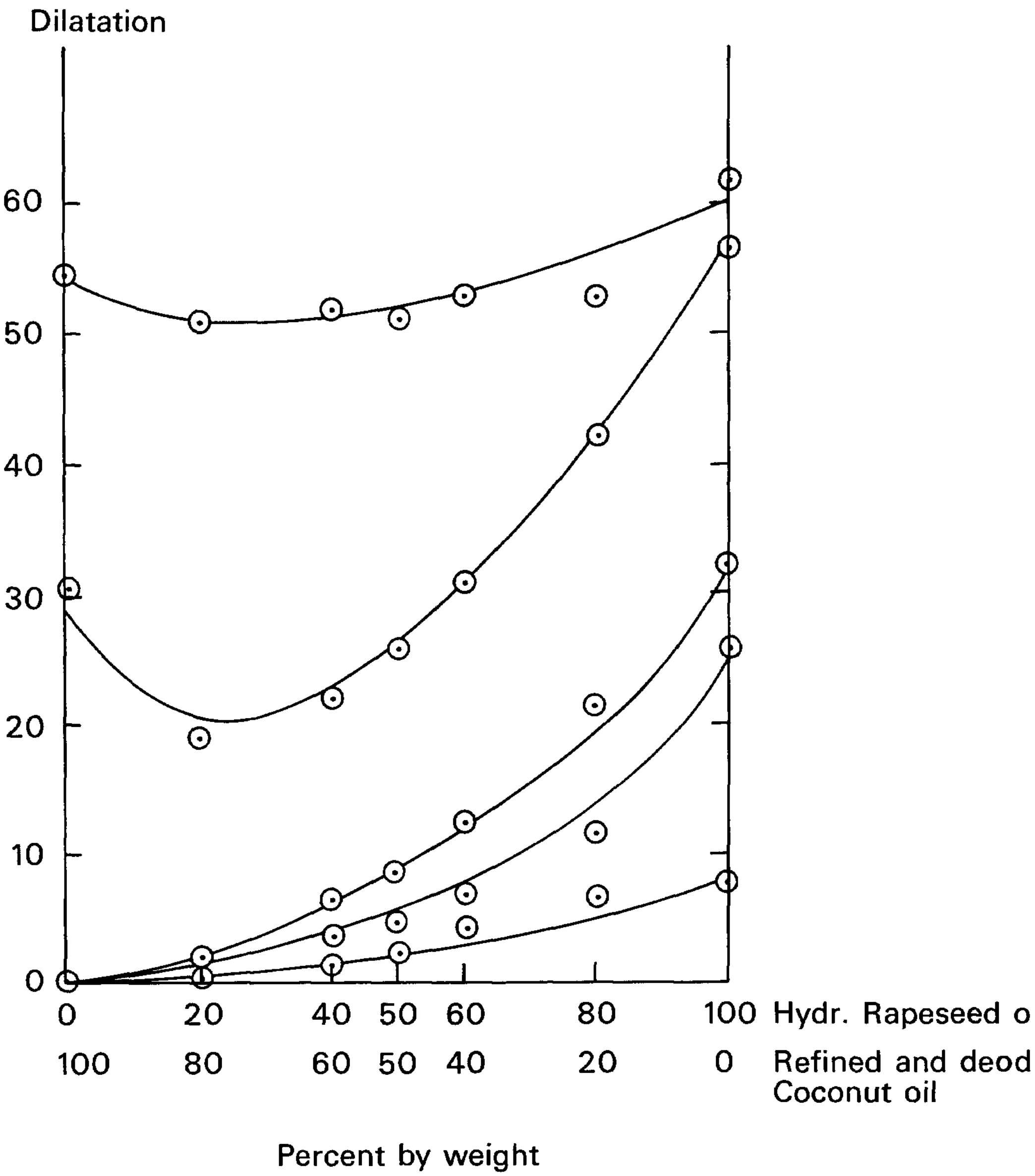
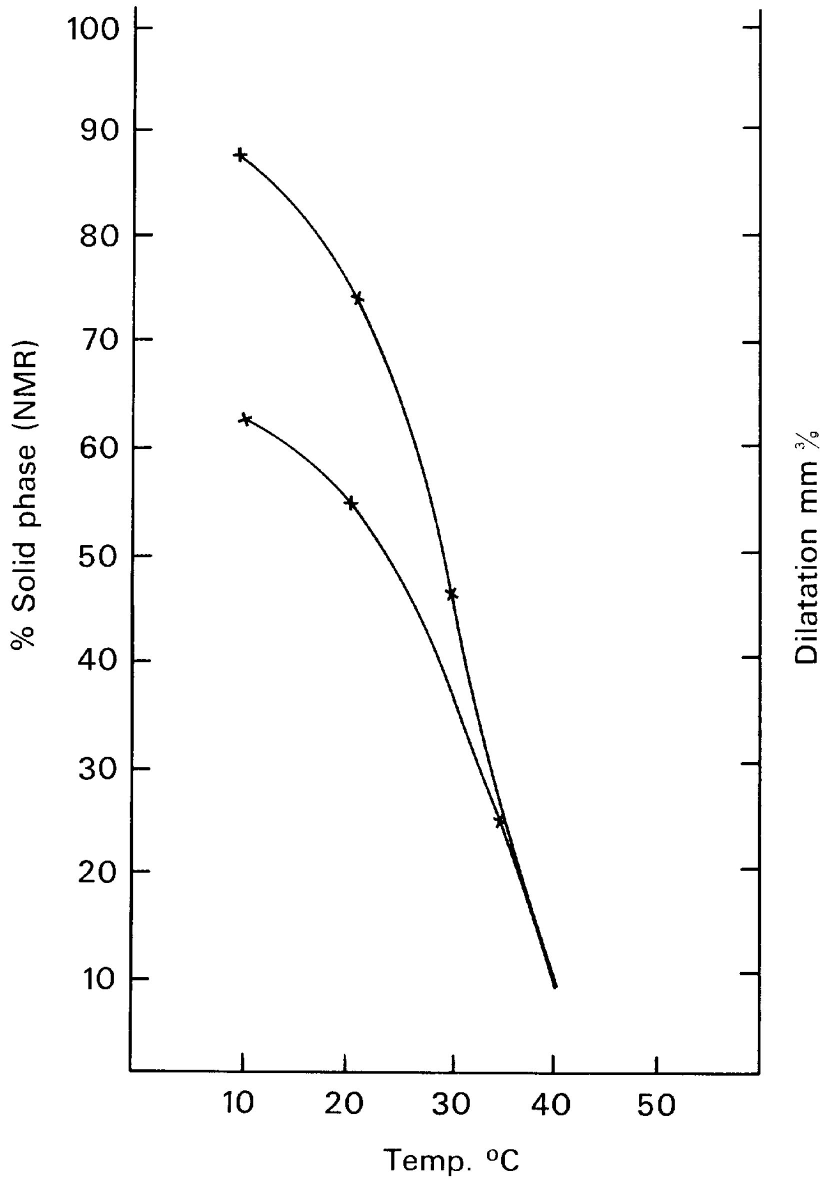

Dilatation
60
50
40
30
20
10
0
0 20 40 50 60 80 100 Hydr. Rapeseed o
100 80 60 50 40 20 0 Refined and deod
Coconut oil
Percent by weight

FIGURE V



NMR and dilatometric valves as functions of temperature

FIGURE VI

These problems led Holm and co-workers to the development of a practical method for analyzing the secondary oxidation products, which has later been adopted by the IUPAC under the name of the benzidine value. In addition to determining the peroxide value this method made it possible for oil and margarine factories to estimate the extent of oxidation in oils more precisely than before, and all the way from the seed through processing and production of the finished margarine.

OXYGEN UPTAKE OF RAPESEED OIL

The oxidative deterioration of rapeseed oil has also been studied from the most fundamental point of view, i.e. the oxygen uptake of the oil. Our aim has been to develop a simple and reliable method for measuring the amount of oxygen found in an oil or taken up during the various stages of processing in the factories. The determination of dissolved oxygen is carried out by a pH-meter with a special oxygen adapter. (Figure VII).

The oxidation mechanism of natural fats is complicated, especially because one must take into account the effects from natural or synthetic antioxidant systems. With a low oxygen content in the liquid phase and in a state of equilibrium between the gas phase and the liquid phase, it may be assumed that the autoxidation rate is proportional to the partial pressure of oxygen. (Figures VIII and IX).

FLAVOUR STABILITY

In the work of Moser et al. a specific flavour effect occurring in Cruciferae seed oil was established. The flavour characteristic and the oxidative stability of crambe seed, mustard seed, rapeseed and soybean oils were studied. The oils were produced in the laboratory and the flavour evaluations were performed by a test panel of 20 trained judges, and analyses of variance and F-tests were used to test the means on a 10-point scale. The description of the flavour of freshly deodorized oils was dominated by the term "buttery", with "nutty" or "beany" flavours present in minor amounts. After 4 days storage at 60°C the terms "rancid", "beany", "painty", "grassy" were given to oils when they did not contain citric acid. The presence of citric acid markedly protected the oils and there was no general difference between soybean oil and the samples of the Cruciferae seed oils. However, when samples with added citric acid were exposed to light for two hours, the soybean oil was given the same descriptive terms as the oil without citric acid, while the Cruciferae oils exhibited a significant drop in the flavour scores and developed a definite "rubbery" flavour which was often accompanied by a "garlic" or "onion-like" flavour, (Table II).

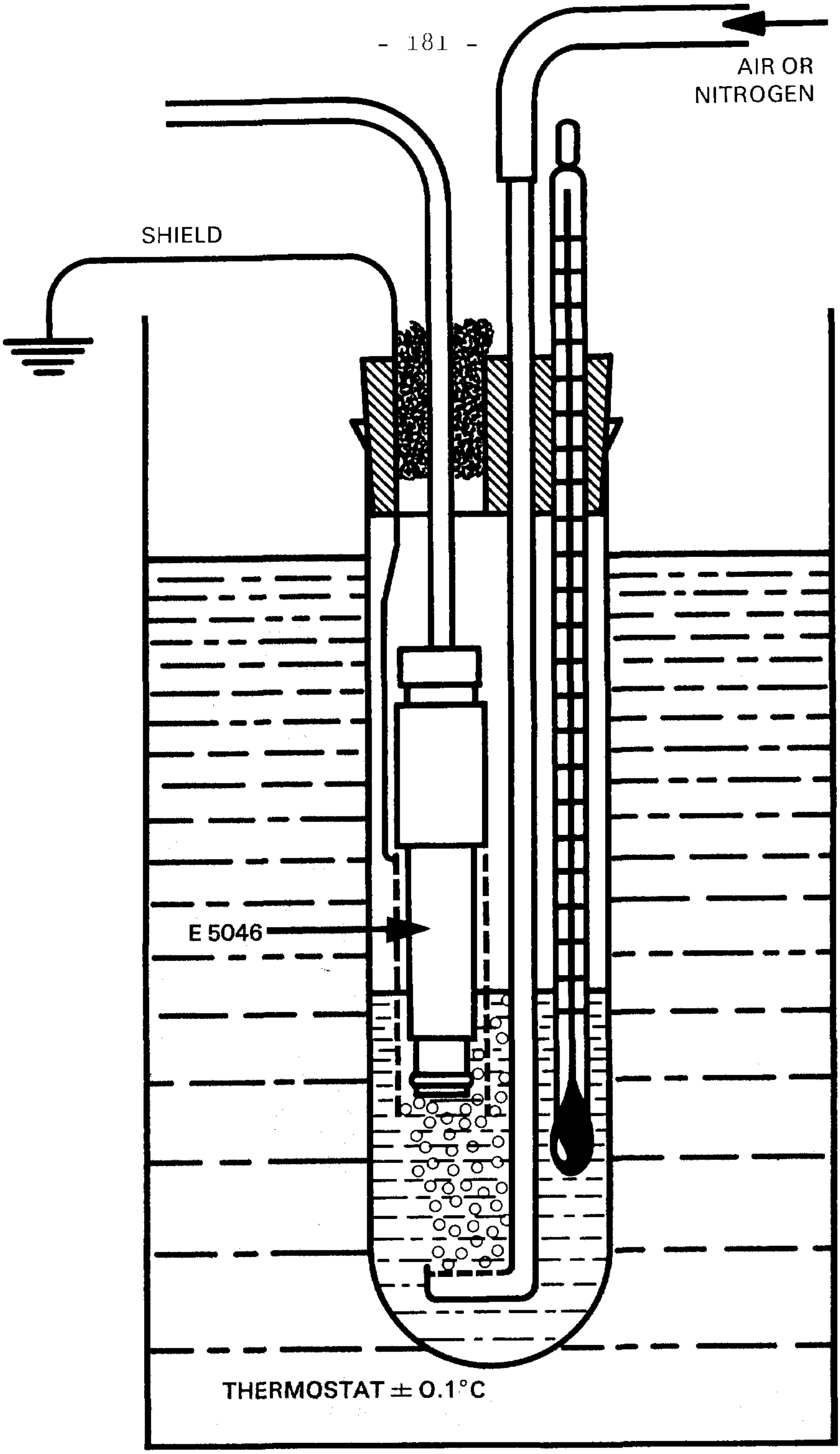
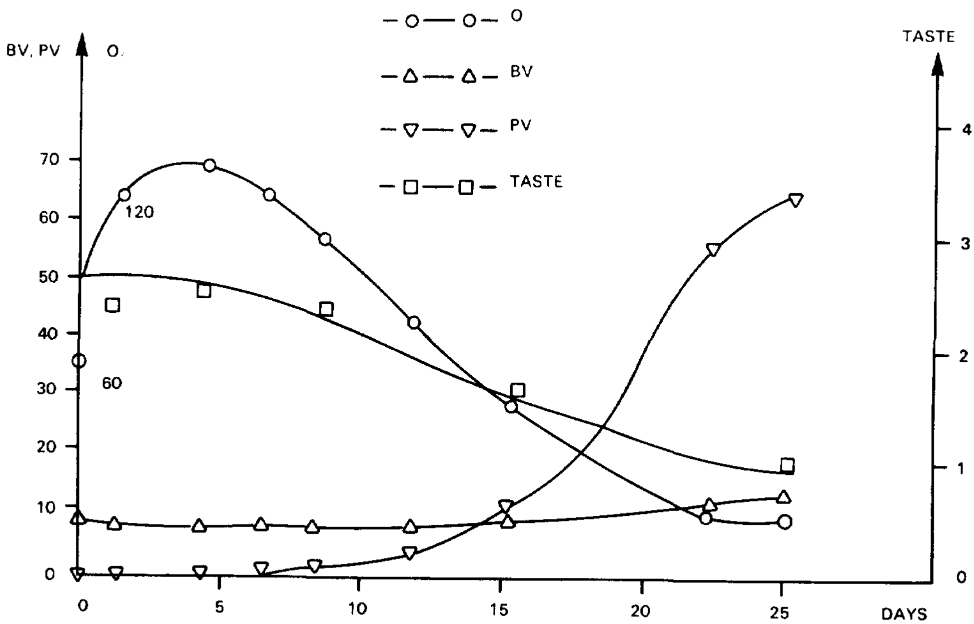
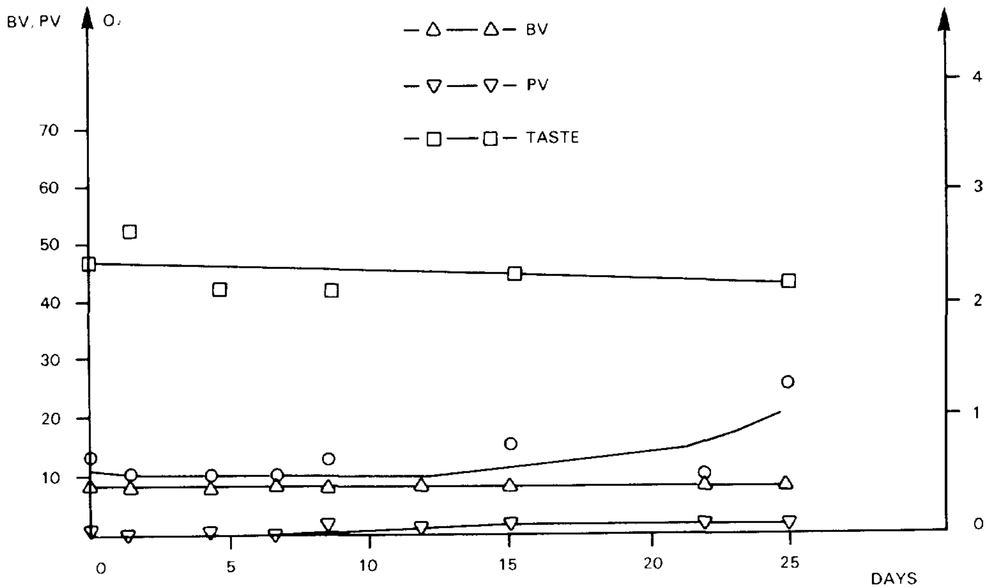


FIGURE VII



THE OXIDATION OF AN OIL STORED WITH AIR CONTACT

Figure VIII



THE OXIDATION OF AN OIL STORED WITHOUT AIR CONTACT

Figure IX

TABLE II

THE EFFECT OF CITRIC ACID ON CRUCIFERAE OILS EXPOSED TO LIGHT FOR 2 HOURS

Oil	Without Citric Acid		With Citric Acid	
	Score	Description	Score	Description
Crambe Seed	7.2	Buttery, beany	5.7	Rubbery, grassy, buttery.
Mustard Seed	4.6	Rancid, buttery, grassy.	2.1	Rubbery, rancid, grassy.
Rapeseed	6.9	Buttery, grassy	4.8	Rubbery, buttery
Soybean	6.1	Grassy, buttery, rancid.	6.5	Grassy, buttery, rancid.

Moser, H.A. et al., JAOCS, 42, 811 (1965).

The authors assume that this effect may be due to isothiocyanate compounds introduced into the oils from the meal during extraction and not completely removed by deodorization. Whatever the cause, the compounds in question must exhibit specific photochemical reactions in the presence of citric acid. In any case, it is a remarkable and specific effect caused by minor components in the Cruciferae seed oils which, as stated by the authors, "projects a new problem for study". Moser et al., also report results on industrially produced Swedish and Canadian rapeseed oils obtained in alkali refined and bleached form and deodorized in the laboratory. These results are shown in Table III in order to indicate the extrapolation of the results with the laboratory produced samples to products obtained from large scale operation with the processing practice prevailing before 1965.

The positive effect of citric acid on the flavour stability when the oils were kept in darkness is demonstrated in all three samples as well as the deleterious effect on the rapeseed oil produced in Sweden when exposed to the standardized illumination for two hours. The Canadian oil, however, did exhibit a higher flavour score with citric acid than without, being the only exception to the off-flavour inducing effect of citric acid in the presence of light. The authors remark, however, that the characteristic "rubbery" flavour was found in all samples but evidently less pronounced in the Canadian oil.

TABLE III

THE EFFECT OF CITRIC ACID ON THE KEEPING QUALITY OF SWEDISH AND CANADIAN RAPESEED OIL

Treatment	SWEDISH				CANADIAN	
	Continuous Screw-Pressed		Extracted		Extracted	
	Without Citric Acid	With Citric Acid	Without Citric Acid	With Citric Acid	Without Citric Acid	With Citric Acid
Initial Flavour	7.8	8.4	8.0	8.1	7.7	7.4
4 Days at 60°C	4.2	7.0	4.9	6.9	4.5	6.1
2 Hours' Light Exposure	6.8	4.8	5.8	2.9	4.0	5.4
AOM-Value[x)]	20.0	9.0	15.1	4.6	22.4	21.4

x) Peroxide values after 8 hours under AOM conditions.

Moser, H.A. et al., JAOCS, 42, 811 (1965).

In conclusion, the flavour and flavour stability of properly processed, protected and stabilized rapeseed oil is completely satisfactory for an oil to be used in today's food industry. There are several reports showing that rapeseed oil is superior to e.g., soybean oil and sunflower seed oil. There are also reports in which rapeseed oil was found to be inferior to soybean oil, e.g., in the presence of citric acid and light. This only stresses the well-known point that many factors influence the flavour of vegetable oils and fats, some of which are general for all and some of which are specific for a certain oil.

SPECIFIC EDIBLE USES

SALAD AND COOKING OILS

Without doubt the rapid expansion of rapeseed oil utilization has been brought about or has been promoted by the careful evaluation of the use of rapeseed oil in foods especially in Canada. It may be concluded that carefully processed Cruciferae seed oils will compare favourably with other commercial oils in both, hot and cold applications.

From the results of the study by Riiner it can be concluded, that Cruciferae oils having erucic acid contents above 40-45 percent, may give rise to breakage of emulsions of salad dressings and mayonnaise when kept under refrigeration, and that crystallization is the cause. There is, however, a report in the patent literature of a specific application of hydrogenated rapeseed oil in the manufacture of food dressings where the oil phase in fact contains crystalline phases. Solid fats (2-8 percent) are melted with liquid oil (92-98 percent), mixed with the aqueous phase, and chilled. The solid fat portion, having an iodine value $\leq$12, consists of a blend of a so-called β-tending fat and hydrogenated rapeseed oil in proportions ranging from 1:4 to 4:1. The expression β-tending refers to the polymorphic form that is attained after tempering.

MARGARINE

A major use of rapeseed oil in Europe and Canada has been in margarine. Depending on specific prerequisites varying from country to country, a great interchangeability between rapeseed oils in hydrogenated or non-hydrogenated form and other oils, e.g., soybean oil, has been achieved from a food technological point of view. Specific pilot-plant work on margarine containing rapeseed oils has been reported by Zalewski and Kummerow and the application of transesterifications was reported by these authors and others.

A specific use of highly hydrogenated rapeseed oil, i.e., with iodine values below 30, and preferentially below 10, in retarding the oiling-out of margarine, is also claimed by Seiden. Small quantities of hydrogenated rapeseed oil (0.2-2.5 percent) in the formulation are reported to reduce the oiling-out tendency considerably, without too much adverse influence on the eating quality.

Reports on flavour evaluations of margarines are scarce in the literature. In a Canadian evaluation rapeseed oil margarines were compared favourably with soybean oil margarines.

SHORTENINGS OR COMPOUND COOKING FATS

The definition of different types of edible fat products is not completely clear. The word shortening was originally used in the American literature for fats employed in baking, making the bread shorter in texture. It has since then been transferred to fat products in general consisting of about 100 percent fats and oils, used not only in baking but also in domestic and institutional cooking, as well as in the rapidly increasing and diversified uses in the food industry. In the United Kingdom the expression compound cooking fat covers at least a part of the connotations of the American counterpart. Confusion between generic names is avoided when uses and properties are defined more precisely.

Moreover, in this case most of the literature reports emanate from Canada, and only in some specific cases, such as in puff pastries, are deviations being established in performance compared to shortenings from other types of fats.

Tremazi et al. compared the temperature ranges within which hydrogenated rapeseed oils and cottonseed oil could be expected to be plastic. It was stated that at comparable iodine values hydrogenated rapeseed oil shows a broader range of plasticity than hydrogenated cottonseed oil. This effect is further intensified by adding highly hydrogenated rapeseed oil as a plasticizer to fat blends intended to be used as shortening.

This effect is elaborated in the patent literature by adding small amounts of highly hydrogenated rapeseed oil as plasticizer to shortenings.

Besides being useful in providing an increased temperature range at which the products remain plastic, hydrogenated rapeseed oil is also reported to have favourable aerating properties in baking applications where this is desirable, e.g., in cake batter mixing operations where fat and sugar are first beaten. This effect was studied in detail by Linteris and Thompson in their work with fluid shortening development. For comparison some results obtained with 5 percent suspensions of a number of highly hydrogenated fats and oils in cottonseed oil and determined by a standard yellow layer cake performance tests are given in Table IV.

It may be seen that even without the addition of an emulsifier, which is common practice in aerating shortenings and margarines, the Cruciferae oils hydrogenated to low iodine values, produced fair batter and cake volumes. When an emulsifier was added, these 5 percent suspensions were completely satisfactory, in contrast to the other fats investigated. The authors further conclude, that fractions made from rapeseed and mustard seed oils and certain peanut oil fractions possess the properties desired for the production of a fluid shortening having aerating properties. The triglycerides indicated to be especially effective in this respect were of the behenoyldistearoyglyceride and behenoylstearoylpalmitoylglyceride types. Rapeseed oil hydrogenated, to an iodine value of one was, however, almost as effective as the triglyceride fractions used. It is interesting to note that no correlation was found between the polymorphic forms of the solid phases and their aeration properties in the systems investigated by Linteris and Thompson. It has been a rather common opinion that fats in the β'-form in general have a better creaming ability than with fats in the β-form. In the reported study this was not the case. When hydrogenated rapeseed oil was precipitated from liquid cottonseed oil at 21°C, the solid phases were in the β'-form and when precipitated at 29°C they were in the β-form. However, no difference in aeration properties was found.

TABLE IV

RESULTS OF YELLOW LAYER CAKE TEST WITH 5 PERCENT SUSPENSIONS OF HYDROGENATED FATS IN COTTONSEED OIL

		WITHOUT EMULSIFIER			WITH 1.2% MYVEROL 18:00 EMULSIFIER[x)]		
Type of Hydrogenated Fat	I.V.	Batter vol. cc/g	Cake vol. cc	Texture of Cake	Batter vol. cc/g	Cake vol. cc.	Texture of Cake
None	-	0.98	1,000	Hard	0.90	1,000	Hard
Soybean Oil	1	0.96	1,000	Med. Hard	0.96	1,060	Hard
Cottonseed Oil	1	0.94	1,080	"	1.03	1,155	Med. Hard
Palm Oil	2	1.05	1,080	"	0.93	1,155	"
Herring Oil	2	0.89	1,055	"	-	-	-
Lard	7	0.94	1,100	"	0.85	1,000	Med. Hard
Rapeseed Oil	1	1.01	1,045	Med. Soft	1.31	1,165	Soft
Mustardseed Oil	1	1.15	1,120	Soft	1.38	1,210	"
Plastic Shortening	-	1.23	1,210	Soft	1.23	1,210	"

x) Distilled saturated monoacylglyceride.

Linteris, L.L. and Thompson, S.W., JAOCS, 35, 28 (1958).

OTHER FOOD USES

Application of rapeseed oil after hydrogenation and fractional crystallization in solution has been reported for confectionary fats and for ice cream coating fats.

FUTURE USES

It can be concluded that Cruciferae seed oils may compete favourably with other vegetable oils and animal fats from the food technological point of view. The proportion among different oils depends in part on differences in quality, but also on other technological and economical factors, that have nothing to do with the quality of the oils themselves.

No doubt, plant breeding efforts will lead to new Cruciferae varieties with altered oil compositions. Considerable advances have already been made which will make the crop more competitive and meet the requirements of food manufacturers regarding functionality and shelf-life, thus offering a greater variation in the properties. Not to mention the nutritional aspects!