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The Keeping Quality of Elaïdinated Fats[*]

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DURING a long experience with elaïdinated fats (1) we always noticed that these fats showed a remarkably enhanced keeping quality as compared with ordinary or hydrogenated oils and fats. One of the causes of this behavior is obvious as elaïdinated oils contain considerably more solid glycerides (more in fact than most hydrogenated oils of an equal melting point), which means of course that their percentage of liquid unsaturated oil is less. In a solid fat the oxidation rate will largely depend on the amount of diffusion of the oxygen from the surface to the unsaturated (most liquid) components so one of the causes of better keeping quality (i.e. the larger percentage of solids) is purely *physical*. There may, however, as well be other causes of a *chemical* nature. We may suppose that:

1. Traces of Selenium originating from the elaïdination process may act as an antioxidation catalyst.
2. Known positive oxidation catalysts such as traces of metals like Fe, Al, Ni, etc. may have been eliminated in the course of the elaïdination with Se followed by the usual refining.
3. The elaïdo configuration of the unsaturated acids may prove to be more resistant towards oxidation than the oleic configuration (cis-trans isomerism).

The first supposition may be tested by comparing the rates of oxidation (by means of peroxide formation) of elaïdinated oils containing Se and the same oils after complete elimination of this element. The second supposition might be checked by comparing the velocity of peroxide formation of a selectively hydrogenated oil containing traces of metal and that of the same oil after treatment with selenium and elimination of this element. As selective hydrogenation also causes elaïdination to the equilibrium stage, the only difference between these two oils will be the presence of metal traces in the first. The third hypothesis may be tested by comparing the oxidation rates of an oil or fat before and after elaïdination, provided these fats do not contain traces of metals or selenium.

Now, some investigators (2) have shown that liquid oleic acid is considerably more readily oxidized than solid elaïdic acid. This, however, does not prove necessarily that the space configuration of these acid molecules is of any influence since it might merely be a consequence of the physical condition of both acids, as pointed out by us in the beginning of this article. To prove the influence of space configuration one must compare both the elaïdic and the oleic forms in the liquid condition.

Experimental

The following oils (for particulars see Table I) were used:

1. Soya bean oil.
2. Elaïdinated soya bean oil containing some Se.
3. Elaïdinated soya bean oil, deselenised.
4. Hydrogenated soya bean oil.
5. Elaïdinated hydrogenated soya bean oil containing some Se.
6. Elaïdinated hydrogenated soya bean oil, deselenized.
7. Palm oil.
8. Elaïdinated palm oil, deselenised.

TABLE I

Oil	p.p.m. Se	Setting point	Iodine value (Hanus)
1. Soya bean	0	......	126,5
2. Soya bean elaïdinated	1105	......	126.
3. No. 2 deselenised	0	......	126.
4. Hydrogenated soya bean	0	30,6	74,5
5. Hydrogenated soya bean, elaïdinated	470	30,6	74,5
6. No. 5 deselenised	1,5	30,6	74,5
7. Palm oil	0	24,8	52.
8. Palm oil elaïdinated deselenised	0	33,1	51,5

All oils were refined, elaïdinated with Se, and deselenised in the usual way. Immediately after deodorization they were subjected to oxidation by blowing dry air at room temperature through them, using an orifice 1 mm. in diam. at 80° C., and a rate of 500 cc. per minute. The peroxide formation was measured at intervals of time by estimating the Lea Index (1 gr. fat, 10 cc. $CHCl_3$, 15 glacial acid, under CO_2 1 cc. saturated KI solution; titration with 0,01 n thio sulphate solution after standing 5 minutes and dilution with 70 cc. water; soluble starch used as

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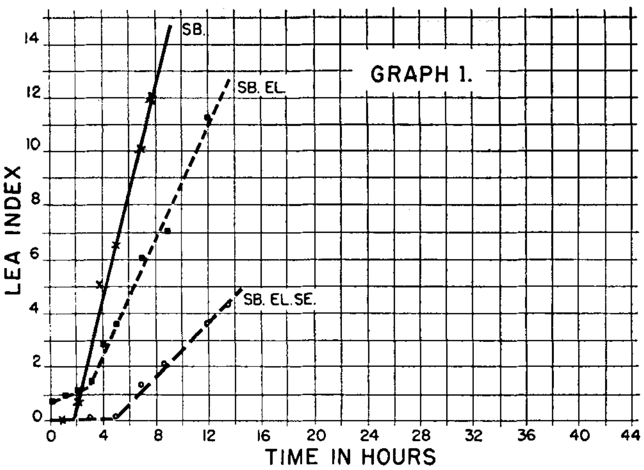
[*] Fourteenth scientific publication of the N. V. Ned. Research Centrale, the Hague, Holland.

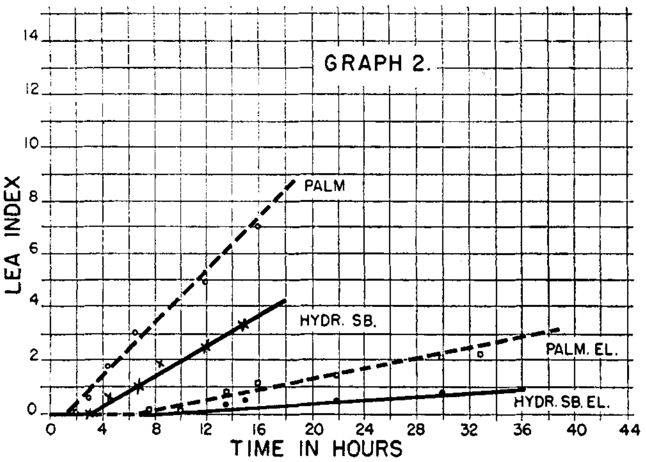
indicator; results expressed as cc. 0,002 n thio sulfate per gr.).

Table II shows the values obtained which have been plotted against time in Graphs 1 and 2.

Results, Discussion, and Conclusions

From Table II and Graphs 1 and 2 we can calculate the different induction times in minutes and the speed of oxidation expressed as increase of the Lea number per hour after it has begun. Table III shows the results obtained.





From these figures we may draw the following conclusions:

1. The presence of selenium considerably retards oxidation; this is shown clearly by the lengthened induction period and the reduction in the oxidation velocity of oils 2 and 5 as compared with the numbers 3 and 6.

TABLE III

No. of oil	Induction period in minutes	Velocity of oxidation $\frac{dL}{dt}$
Soya bean 1	100	2,33
Soya bean 2 (El. Se)	270	0,47
Soya bean 3 (El.)	180	0,85
Hydrog. S. B. 4	210	0,29
Hydrog. S. B. 5 (El. Se)	>2700	0,00
Hydrog. S. B. 6 (El.)	690	0,03
Palm oil 7	100	0,49
Palm oil 8 (El.)	500	0,09

El. Se = elaïdinated containing Se; El. = elaïdinated and deselenised.

2. The presence of only minute traces of metal present in a commercial edible oil such as hydrogenated soya bean oil causes a shortening of induction time and a greater rate of peroxide formation (compare No. 4 with No. 6).

3. The elaïdo configuration itself of the unsaturated components results in a longer induction period and a diminished rate of peroxide formation (compare Nos. 3 and 8 with Nos. 1 and 7).

4. The elaïdination or treatment of the oils with selenium yields products of much improved keeping quality (which is confirmed by organoleptic investigation) even if this treatment does not produce more solid components (the elaïdinated soya bean oil remains liquid at room temperature) or does not even raise the setting point (as is the case with the sample of elaïdinated hydrogenated soya bean oil).

5. In practice, at room temperature, the keeping qualities of the elaïdinated or selenium treated oils (also after deselenising them) will be still better owing to the physical condition of the treated oils as they will contain more solid components.

TABLE II

Peroxide Formation (Lea Index cc. 0,002 n/gr.)
40 gr. freshly steamed oils 500 cc. dry air/min.
80° C. orifice, diam. 1 mm.

Time in hours	Soya bean oil			Hydrogenated soya bean oil			Palm oil	
	Not elaïdinated No. 1	Elaïdinated 1105 p.p.m. Se No. 2	Elaïdinated 0,0 p.p.m. Se No. 3	Not elaïdinated No. 4	Elaïdinated 470 p.p.m. Se No. 5	Elaïdinated 1,5 p.p.m. Se No. 6	Not elaïdinated No. 7	Elaïdinated 0,0 p.p.m. Se No. 8
0	0,0	0,0	0,75	0,0	0,0	0,0	0,0	0,0
1	0,0	—	1,0	—	—	—	—	—
2	0,65	—	1,15	0,0	0,0	0,0	0,0	0,0
3	—	0,0	1,5	0,0	0,0	—	0,6	—
4	5,0	—	2,85	0,0	0,0	0,0	—	—
4½	—	—	—	0,6	—	—	1,75	0,0
5	6,5	0,0	3,65	—	0,0	—	—	—
6¾	10,0	1,25	—	—	—	—	—	0,1
7	—	—	6,1	1,0	—	0,0	3,0	—
7¾	12,0	—	—	—	—	—	—	—
8½		2,0	—	1,85	0,0	—	—	
9		—	7,1	1,6	—	—	—	—
10		—	—	—	—	0,0	—	0,15
12		3,6	11,3	2,5	—	—	4,9	
13½		4,3				0,25	—	0,85
15				3,3	0,0	0,35	—	
16							7,0	1,1
18								
22						0,40		1,35
25					0,0			3,50
30					0,0	0,60		2,0
33					0,0			2,1
45					0,0			

Summary

The causes of the considerably better keeping quality of elaïdinated oils and fats have been investigated through the rate of peroxide formation. They are physical as well as chemical in nature. The more solid composition of elaïdinated fats is the physical cause.

Traces of selenium have been proved to behave as a strong antioxidation agent. The elimination of traces of metals in the course of the process of elaïdination with Se also has a very favorable influence.

The elaïdo configuration of the unsaturated acids, however, has been shown to be the principal factor in retarding oxidation.

Acknowledgment

We are indebted to the Elaïdination Syndicate, 23 Bazarstraat, The Hague, Holland, for kind permission to publish these experiments.

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The Application of the Polybromide Yield in the Estimation of Methyl Arachidonate in Methyl Ester Mixtures

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IN a report from this laboratory in 1928 (1) it was noted that when a specimen of methyl arachidonate (methyl 5,8,11,14-eicosatetrenoate), prepared from liver lipids, was brominated in cold ether, only a small fraction of the predicted amount of insoluble polybromides resulted. The polybromide number, i.e., the per cent yield of polybromides, of the ester in question was 77.6 instead of the predicted theoretical value, 301. A similar observation with respect to esters of the highly unsaturated fatty acids of fish oils had been made by Brown and Beal in 1923 (2). On the basis of this behavior generally of acids and esters of this type and of this specific finding for methyl arachidonate it was proposed that the methyl arachidonate (MA) content of methyl ester mixtures could be calculated from the following equation:

$$\text{MA per cent} = \frac{\text{PN} \times 100}{77.6}$$ where PN is the polybromide number of the ester mixture in question. The following year one of us (J.B.B.) discussed this method of estimation further (3) and suggested a possible application of the method to linolenic acid (and its methyl ester). As improvements were made later in the method of preparation of MA and as purer specimens become available for study, the yield of polybromides was found to be somewhat higher. Thus Ault and Brown (4) reported a PN of 86.5 for a specimen of the ester which was prepared by debromination. Shinowara and Brown prepared specimens of MA by a combination of crystallization and distillation procedures, thus avoiding the possibility of isomerization during bromination and debromination. Although the purity of the products as calculated from their iodine numbers did not exceed 95%, the average PN of their preparations, calculated to 100% purity, was 90.7. Mowry, Brode, and Brown (6) reported a PN of 92.7 for their best product prepared by physical methods. In the meanwhile Smedley-Maclean and Nunn (7) had brominated arachidonic acid in 2% solution in several solvents, their results, expressed as PN's being the following: in 50-60° boiling petroleum ether, 256; in ether, 86-90; in carbon tetrachloride, 89; and in benzene, 100. They noted that about half of the polybromides insoluble in benzene and two-thirds of the bromides insoluble in petroleum ether were soluble in ethyl ether.

In 1930 A. K. Silberman (8) in this laboratory found the solubility of methyl octabromoarachidate in ether to be 0.0127 g./100 cc. of solution at 2-3°. The corresponding ethyl and butyl esters were about 10 times as soluble. Stoneburner (9) in this laboratory in 1940 found a somewhat higher solubility for the methyl ester in ether, namely 0.0409 g./100 cc. He brominated amounts of MA ranging from 2.119 g. to 0.0704 g. and obtained PN's (with five ether washings of product) of 98.3 to 49.7, respectively. However, when he attempted to correct these values (PN's) for dissolved bromides in the wash ether, anomalous values, namely PN's of 98.9 to 153.7, resulted. Thus in this laboratory we have realized for several years that the use of an empirical equation for the estimation of MA, or of other polyethenoic acids, based on polybromide (hexabromide or tetrabromide) numbers will result in considerable error in ester or acid mixtures of low contents of the ester or acids in question. In such mixtures the solubility error is excessive and solubility corrections are apparently not constant, probably because we are dealing with complex mixtures of isomeric polybromides.

Cramer (10) in this laboratory in 1942 attempted to correct for these errors in a large series of ester mixtures from human body fats by interpolation from a curve, the data for which were obtained by brominating 20, 30, 50, and 70 mg. of MA and determining the polybromide yields by essentially the method we have described below. The resulting yields of bromides were 8.9, 15.3, 28.7, and 43.5 mg., respectively, corresponding to polybromide numbers of 44, 51, 56, and 62. In his original work Cramer felt that the arachidonate content of an ester mixture could be found by interpolation from a curve in which he plotted arachidonate percentages against polybromide numbers based on the examples cited above.

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[1] Supported in part from funds granted by the Ohio State University Research Foundation to the University for aid in fundamental research.

[2] Supported by funds granted to the University by Wyeth inc., Philadelphia, Pa.