ous hydroxy fatty esters isolated chromatographically. The diene content of the reduced hydroperoxides agrees well with values reported in the literature (1,5,16). The diene content of the chromatographed methyl dimorphecolate is higher than reported by Smith *et al.* (20) for their preparations but agrees well with the value reported by Chipault and Hawkins (6) for pure *trans-trans* conjugated methyl linoleate. The extinction coefficient of methyl 12-hydroxystearate at 2.8 μ is higher than that reported for ricinoleate and the absorption band is much sharper. Because of these two conditions no association of the hydroxyl groups is indicated. These results also confirm the purity of the hydroxy fatty esters obtained by LPC. This method has been a valuable adjunct to the study of various oxygen-containing fatty acid and esters and was used to characterize the hydroxy esters obtained from the hydrogenation of methyl linolenate hydroperoxides (9). This work offers a basis for the development of analytical methods to determine the hydroxy and other polar acid content of fatty glycerides and their derivatives.

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The Hydrogenation of Fatty Oils with Palladium Catalysts. VI. Hydrogenation for Margarine

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Abstract

Satisfactory margarine stocks have been made with a palladium on carbon catalyst in laboratory, pilot plant, and plant processing. The catalyst was shown to make a satisfactory product even when, on continued re-use, the ratio of oil to metal used reached 400,000 to 1.

TWO PREVIOUS ARTICLES (1a,1b) of this series dealt with the palladium catalyzed hydrogenation of various fatty oils for shortening stocks. The processing factors controlling the composition of the products were elucidated, and it was shown that with proper processing satisfactory products could be obtained both in the laboratory and in the pilot plant.

This article is concerned with the use of palladium catalysts in hydrogenation of various oils for margarine in laboratory, pilot plant, and plant processing. By proper choice of conditions and of catalysts margarine stocks with satisfactory plastic properties, having widely different compositions, were made. Satisfactory margarine stocks having both a high and a low *trans* isomer content were made in the pilot plant. Margarine stocks with a high *trans* isomer content could be obtained with continued re-use of the catalyst even when the weight ratio of oil to metal reached 400,000 to 1 (Table II).

Experimental

The oils used in the work were soybean oil, I.N. 130; a mixture of 70% soybean, 30% cottonseed oil, I.N. 124; and peanut oil, I.N. 93. Laboratory and pilot plant experiments were done in the 1 gal (1c) and 50 gal (1b) stainless steel reactors described earlier. Processing was controlled in both cases by determination of refractive index at 45C. Analyses of the products were made according to A.O.C.S. official methods (2). Ubbelohde's drop point was determined by the official German method (3) except that the time on ice was shortened to 2 hr. The *trans* content of the hydrogenated fats was estimated from the infrared absorption of a carbon disulfide solution according to the procedure recommended by the A.O.C.S. Spectroscopy Committee (4). The spectrophotometer was a Perkin-Elmer Model 21.

Results and Discussion

The plastic properties of margarine are set by its uses to within rather narrow limits, which in turn determine the permissible range of *trans* isomers, solid acids, etc. Dilatometry has become, since its first use for fats in 1931 (5), the chief analytical method for the determination of plastic properties of fats, especially margarine and shortening. Various modifications in procedure and in desirable dilatometric numbers have been made (6–11) reflecting the widely different standards for margarine stocks in various countries. But in general, numbers, as measured by the American method, in excess of 2 at 36C give a waxy margarine. Taste and aroma are improved as this number is lowered. The dilatometric number at 42C must be zero. Dilatometric points at 21.1C and at 26.7C characterize the softness of the product at room temperature, ease of shaping, and ability to retain shape without refrigeration.

TABLE I

Laboratory Hydrogenations for Margarine Over Pd Catalyst

Ex.	Oil	Catalyst % Pd in oil	°C	Press. psig	Agit. rpm	Time min.	I.N.	Th. No.	% Linoleic acid	% Sat. acid	% Oleic acid	% *Trans* isomers	Wiley mp °C	Congeal Pt. °C	Solid Fat Index			
															21.1C	26.7C	36.0C	42.0C
1	s/b	1% Pd/C + Ag + Bi 0.00015%	185	45	620	190	81.5	73.2	9.8	15.8	74.4	50.0	36.6	25.6	18.5	13.0	2.0	0
2	”	1% Pd/C 0.0001%	185	40	620	45	82.5	72.0	12.6	16.8	70.6	49.0	36.8	25.2	16.4	12.2	2.1	0
3	s/b 70% c/s 30%	1% Pd/C + Ag + Bi 0.00015%	165	45	620	270	81.0	71.0	12.0	17.9	70.1	42.9	35.4	26.0	15.7	10.0	1.7	0
4	”	1% Pd/C 0.00015%	175	15	420a	90	86.0	72.9	15.8	16.1	68.1	48.0	36.0	25.0	14.3	9.0	1.0	0
	”	”	”	”	” b	105	84.0	71.9	14.5	17.2	68.3	51.0	36.5	26.0	18.0	12.3	1.5	0
5	”	5%Pd/C 0.0003%	165	8	290	130	84.3	72.0	14.8	17.0	68.2	54.3	35.5	25.7	16.0	11.7	2.3	0
6	”	1% Pd/C + Ag + Bi 0.0003%	175	15	420	280	84.4	72.8	13.9	16.0	70.1	49.0	34.3	25.4	16.5	9.4	0.7	0
7	”	5% Pd/C 0.0002%	175	15	420	130	85.2	72.5	15.3	16.5	68.2	48.0	37.5	25.7	14.6	10.6	2.0	0
8	s/b	5% Pd/C 0.00015%	175	40	800	190	82.6	70.0	15.2	19.4	65.4	45.8	43.8	28.0	21.0	18.8	7.9	4.4
9	Peanut	2% Pd/ 0.00025%	155	atm.	290	80	70.7	67.8	3.1	21.1	75.8	43.4	33.6	24.0	16.5	8.9	0.5	0

TABLE II

Pilot Plant Hydrogenations for Margarine

(A) High Trans Content

Ex.	Oil kg	Catalyst % Pd in Oil	°C	Press. psig	Agit. rpm	Time min.	I.N.	Th. No.	% Linoleic acid	% Sat. acid	% Oleic acid	% *Trans* isomers	Wiley mp °C.	Ubbelohde drop P. °C	Congeal Pt. °C	Solid Fat Index			
																21.1C	26.7C	36.0C	42.0C
1	s/b 42 c/s 18 60	5% Pd C 6.6 g, 0.00055%	150	15.0	140	200	85.6	73.0	15.2	15.9	68.9	57.0	33.3	32.4	24.8	16.5	10.7	0.9	0
2	” 50	Same reused from No. 1, 0.00075%	150	15.0	140	135	84.2	72.4	14.2	16.5	69.3	59.0	35.0	34.3	26.4	19.7	13.4	1.5	0
3	” 40	Same reused from No.2 + 1.6 g fresh, total 0.0009%	150	15.0	140	a* 115	83.2	71.9	13.6	17.0	69.4	60.0	35.5	34.8	27.0	20.2	14.5	1.8	0
						b 125	82.0	......	......	......	......	61.0	36.3	35.5	28.0	23.0	16.7	2.5	0
4	” 40	Same reused from No. 3 + 1.3 g fresh, total 0.001%	150	15.0	140	(a* (150	84.0	72.5	14.0	16.2	69.8	60.0	35.1	34.5	26.5	20.4	14.2	1.5	0
						(b 165	82.7	72.3	12.4	16.5	71.1	61.0	35.7	35.2	26.8	23.4	17.0	2.3	0
Average Nos. 1–4							84.2	......	14.2	16.4	61.3	59.0	34.7	34.0	26.2	19.2	13.2	1.4	0

* Numbers used for average.

TABLE III

Pilot Plant Hydrogenations for Margarine

(B) Low *Trans* Content

Ex.	Oil kg	Catalyst % Pd in oil	°C	Press. psig	Agit. rpm	Time min.	I.N.	Th. No.	% Linoleic acid	% Sat. acid	% Oleic acid	% *Trans* Isomers	Wiley mp °C	Congeal Pt. °C	Solid Fat Index			
															21.1 C	26.7C	36.0 C	42.0 C
1	Peanut 60	1% Pd/C 36 g, 0.0006%	65	18–20	420	280*	73.2	64.0	11.0	26.0	63.0	22.6	36.3	24.0	12.4	7.7	2.0	0
2	Peanut 50	Same reused from No. 1 + 10 g fresh, total = 0.0008%	90	10	420	a) 140	73.3	64.8	10.1	25.1	64.8	27.0	35.0	24.5	13.2	8.0	2.0	0
						b) 200	69.8	63.9	6.9	25.9	67.2	29.6	37.0	26.0	17.6	13.0	3.3	0
						c)** 230	68.5	63.8	5.4	26.9	67.7	30.8	40.5	27.0	19.7	16.0	4.6	+0.2
3	s/b 35 c/s 15 50 (total)	1% Pd/C + Ag + Bi 90 g, 0.0018%	90	10	420	a) 95	82.0	70.5	13.8	18.7	67.5	31.5	33.2	24.0	13.1	7.1	1.2	0
						b) 105	80.1	70.0	12.1	19.1	68.8	32.8	34.8	25.7	15.2	9.7	1.7	0
					Average..............................		75.7	......	10.8	23.3	63.3	28.7	35.3	24.8	14.3	9.1	2.0	0

* Began at lower temperature, 50C and lower pressure, 10 psig.
** Not used for average.

TABLE IV
Market Margarines

Ex.	I.N.	Th. No.	% Linoleic acid	% Sat. acid	% Oleic acid	% *Trans* Isomers	Wiley mp °C	Congeal Pt.°C	Ubbelohde Drop P°C	Solid Fat Index			
										21.1C	26.7C	36.0C	42.0C
1	80.7	71.1	11.5	17.7	70.8	40.2	36.8	25.5	35.1	16.0	11.1	2.0	0
2	79.1	71.7	8.7	16.9	74.4	50.1	34.0	25.2	33.5	20.1	12.1	0.3	0
3	80.3	72.0	9.8	16.6	73.6	44.9	36.4	25.8	35.5	17.5	11.8	2.2	0
4	86.0	72.2	16.7	16.9	66.4	42.9	35.5	26.0	34.7	17.6	12.9	1.5	0
5	81.5	68.0	16.3	21.8	61.9	32.0	35.0	24.8	33.4	15.0	10.0	1.0	0
6	79.0	69.4	11.5	19.7	68.8	35.0	36.4	25.7	34.0	16.2	11.9	1.7	0
7	90.4	73.3	20.8	16.0	63.2	50.2	34.3	24.5	32.3	15.7	10.0	0.5	0
Avg.	82.4	......	13.6	17.9	68.4	42.2	35.5	25.4	34.1	17.2	11.3	1.3	0

TABLE V
Plant Hydrogenation for Margarine

Process time min.	Butyro index 45C	Iodine number	Wiley mp °C	Congeal point °C	*Trans* %	Solid Fat Index			
						21.1C	26.7C	36C	42C
210	50.5	84	36.0	25.4	58.0	18.6	13.6	2.5	0
225	50.0	82	37.2	26.8	59.0	21.8	16.6	3.8	0.3

Laboratory Experiments. Table I shows the processing conditions for, and analyses of, products obtained by laboratory hydrogenation of various oils. These products varied from satisfactory to unsatisfactory, depending on the catalyst and processing conditions used. As expected from earlier work (1a), 1% palladium on carbon was more selective than 5% palladium. Additional selectivity was obtained by modification of the 1% palladium on carbon by addition of silver and bismuth (1c,12). When the less selective 5% palladium catalyst was used, a more satisfactory product was obtained by going to more selective processing conditions, i.e., lowering the pressure and the degree of agitation. In general, changes in the catalyst, catalyst concentration, and processing conditions influenced the selectivity and *trans* isomer formation in the same direction as was discussed in previous work (1a).

Pilot Plant Experiments. The amount of catalyst used in the laboratory experiments was so very small that it was impossible to make any reliable estimate of how many times the catalyst could be re-used and still have a suitable activity and selectivity. In pilot plant experiments the amount of catalyst used was larger and a good estimate of this figure could be obtained. The results of these experiments are shown in Table II.

The catalyst was 5% palladium on carbon powder. The first experiment used 6.6 g of catalyst plus 25 g of carbon powder. The second experiment used the catalyst from the first, and the third and fourth, catalyst from the preceding experiment plus 1.6 g and 1.3 g, respectively, of fresh catalyst. The total is 190,000 g of oil hydrogenated with 9.5 g of catalyst or 0.475 g of palladium.

The conditions of these experiments contrast with those used for making shortening stock with the same catalyst. The margarine stocks were obtained by use of a higher temperature, lower pressure, lower speed of agitation, and without operation of the circulation pump or spray nozzles (1b).

In Table III are given the processing conditions and analyses of materials made to meet the requirements that the *trans* content be low. The products had a *trans* isomer content below, and a saturated acid content slightly above, that of seven American market margarines (Table IV). These products were obtained under less selective conditions than those in Table II, i.e., at a lower temperature and a higher speed of agitation, but the catalyst, 1% palladium on carbon, was more selective.

Peanut oil (Experiment 1) gave the lowest amount of *trans* isomers but the plastic properties were not especially good. With increased temperature and decreased pressure (Experiment 2) peanut oil gave a product with better plastic properties and with a higher *trans* content. These products would make suitable blending stocks. The best selectivity and plastic properties were obtained with a mixture of soybean and cottonseed oils using a more selective catalyst (Experiment 3).

Seven American market margarines were analyzed to provide a basis for comparison with margarine stocks made by palladium catalysts. These results, shown in Table IV, are in general comparable to previously published data (14,15). Of these margarines, only No. 7 showed very large amounts of linoleic acid and with a relatively high *trans* isomer content. Perhaps this margarine was made according to a recent patent (13) from corn oil only.

In Figure 1 three dilatometric curves are given for a) the average of margarine oils with high *trans* content; b) average of market margarines; c) average of margarine oils with low trans content. In general, experiments with palladium established the possibility of obtaining margarine stocks of wide variety, depending on conditions and on the catalyst used. Products with satisfactory plastic properties can be obtained with *trans* isomer contents varying from 32% to 60%. [Whale oil selectively hydrogenated by palladium for margarine stock also contains about 60% *trans* isomers (1d,16).]

Plant Processing. Table V shows the properties of a product obtained from the hydrogenation of 15,500 lb of soybean oil. I.N. 128, with 5% palladium on carbon catalyst. The reduction used 775 g of catalyst corresponding to 0.00055% of palladium based on oil. The temperature was 220–230F; pressure 62–65 psig; agitation, low; time of processing, 210–225 min. Three

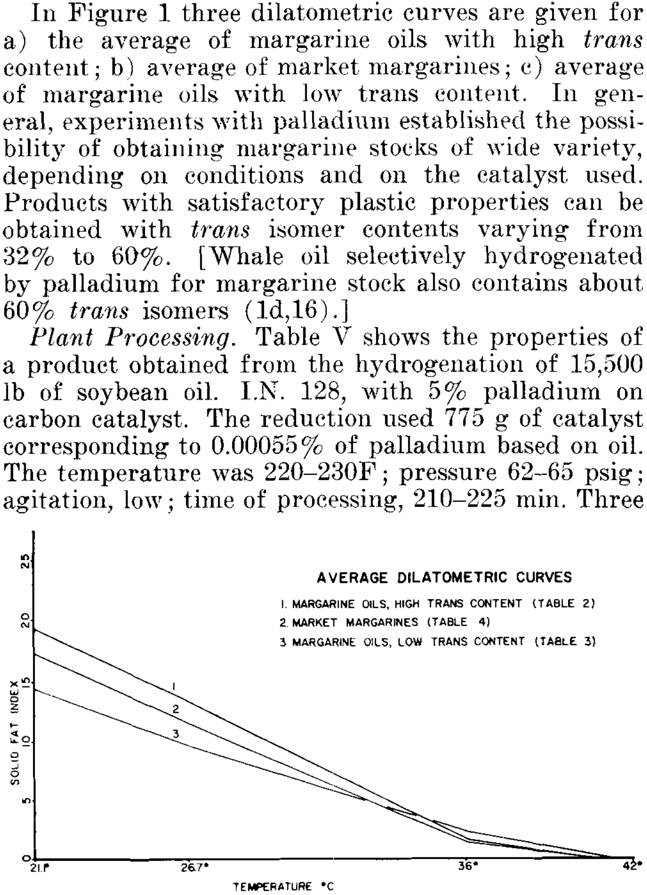

FIG. 1.

thousand g of carbon powder were added to the oil before processing.

The butyro index for palladium processing gives a different correlation with I.N. than that obtained from nickel processing, due to the higher amount of *trans* isomers in the palladium product. Although much less selective conditions were used in the plant, i.e., higher pressure and lower temperature, these were offset by a much lower agitation, so that the product at 210 min was only slightly less selective than those obtained in pilot plant processing. Despite the slightly higher solid content of this product at 36C than is generally desirable for margarine stocks, it is not waxy, due probably to its *trans* isomers which have, of course, much lower melting points than the saturated glycerides present. The catalyst at the end of plant processing had lost about 15% of its initial activity, as determined by re-use in a laboratory hydrogenation of soybean oil.

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Estimating the Average Carbon Chain Length of Saturated Fatty Acid Esters by Infrared Spectroscopy[1, 2]

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Abstract

The average carbon chain length of saturated fatty acid esters can be determined by comparing absorption intensities in the 3.3 and 5.75 μ infrared regions. Data are presented for triglycerides, monoglycerides, and methyl esters. The method was used to follow the fractionation of hydrogenated milk fat from acetone, and the average values for fatty acid chain length were in good agreement with those obtained by gas chromatographic methyl ester analysis. The I.R. method is particularly applicable when only a few mg of sample is available and the material being fractionated contains both long and short chain saturated fatty acids.

Introduction

INFRARED ANALYSIS is extensively employed in lipid research, especially now that small, relatively inexpensive instruments are available and are becoming commonplace in research laboratories. A great amount of information is obtained quickly, only a few mg of material is needed, and the analysis is nondestructive.

An interpretation of I.R. data that has apparently been overlooked concerns the measurement of the average carbon chain length of certain saturated fatty acid esters by comparing the intensity of the C−H stretching vibrations of CH_2 and CH_3 groupings in the region of 3.3 μ with the C=O stretching of the COOR ester group in the region of 5.75 μ. Surprisingly, a literature search did not uncover any mention of this use of I.R. data. The intent of this report is to describe a method whereby an estimate can be made of the average carbon chain length of saturated triglycerides, methyl esters, and monoglycerides. To demonstrate the utility of the method data are presented for hydrogenated milk fat fractionated by low temperature crystallization from acetone.

Experimental Procedure

Infrared Analysis. A Perkin-Elmer Infracord Model 137 equipped with a 0.025 mm NaCl prism was used. A reference line was established on the chart by running a tracing in the 3.3 and 5.75 μ region with pure solvent in both the reference and sample cells. Then a solution of the test material was placed in the sample cell and the absorption traced at 3.0–3.5 μ and 5.5–6.0 μ. As many as 6 sample spectra can be traced on a single sheet of paper by repositioning the paper, clockwise, about the cylindrical drum after each test run. Only 3 or 4 min are needed for flushing and filling the cell, and for running the spectrum.

For determining the average carbon chain length of a fatty ester the absorbance units in the 3.3 μ region are divided by the absorbance units in the 5.75 μ region to establish the CH_2/COOR ratio. The value for this ratio is referred to a previously prepared plot of similar values for an homologous series of the esters to obtain the average chain length of the unknown sample.

Source and Purification of Esters. Triglycerides, 1-monoglycerides, and methyl esters were obtained from Distillation Products Industries, Rochester 3, New York. Purity of triglycerides and methyl esters were determined by I.R. spectroscopy and gas chromatographic methyl ester analysis. Contaminated samples were purified either by distillation or by crystallization from solvents. Gas chromatography revealed the monoglyceride samples to be at least 90% pure in regard to fatty acid content, but no attempt

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