TABLE IV
Average Value of id/C of Different Soaps in Various Supporting Electrolytes

Soap	LiCl	id/C $MeHSO_4$	KCl
Copper palmitate	1.742	2.021	0.461
Copper myristate	1.012	1.335	0.445
Cobalt palmitate	1.847	.....	0.567
Cobalt myristate	1.657	.....	0.769

appears before zero voltage. The second wave is well defined. Reduction of cobalt soap takes place in only one step. The value of $E_{3/4}$–$E_{1/4}$ for copper wave ranges from −0.055 to −0.06 in KCl and LiCl indicating a reversible nature of the wave, whereas in $MeHSO_4$ the abnormally high value suggests an irreversible nature. An irreversible nature is shown for cobalt soaps in LiCl and KCl as the value is again high.

The metal concn in the soap (C) in m.moles/litre, diffusion current (id) in micro amp and id/C show in Tables II and III.

From Table III it is clear that the diffusion current is a linear function of the concn of metal in the soap, and also the value of id/C remains fairly constant. Hence, this method can be employed for the determination of the metal content in soaps. An average value of id/C in different supporting electrolytes shows in Table IV; the table also shows that the value of id/C is smaller in glycol medium. This may be due to high viscosity of glycol.

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Relative Reactivity Toward Hydrogenation of the Oleoyl Group in the 2- and 1,3-Positions of Triglycerides

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Abstract

Olive oil was hydrogenated to an iodine value (I.V.) of ca. 50 under widely differing operating conditions. Three types of catalyst were employed. Each catalyst was used at the lowest possible operating temp and at 170C. The hydrogenated samples were subjected to lipase hydrolysis to remove a portion of the acyl groups in the 1,3-positions, and the fractions obtained, as well as the unhydrolyzed samples, were analyzed for fatty acid composition and content of *trans* monoenes. From these data it was concluded that the position of the oleoyl group in the triglyceride molecule is not a factor in the rate of hydrogenation or isomerization.

Introduction

THE QUESTION as to whether or not unsaturated acyl groups in the 1,3-positions of triglycerides hydrogenate more readily than do similar groups in the 2-position is both of theoretical and practical interest. Should it be possible to even partially direct the addition of hydrogen, then hydrogenation would become an even more powerful tool in the preparation of special fats.

Bushell and Hilditch (4) investigated this aspect of hydrogenation in 1937 and concluded that the position of the oleoyl group in a triglyceride did not affect the rate of hydrogenation. Some of their starting materials were synthesized by methods now open to question, and their hydrogenated products were analyzed by fractional crystallization. Since then much better instruments and techniques for carrying out work of this type have become available. After the investigation to be reported here was completed, the authors learned that Mattson and Volpenhein (10) had made a similar investigation. The latter workers randomly rearranged the acyl groups in a soybean oil and then subjected the oil to a single hydrogenation. Samples were withdrawn as the hydrogenation progressed and were analyzed for saturated acids, *trans* acids, and poly-, di-, and monounsaturated acids. Mattson and Volpenhein concluded that the position of an unsaturated acyl group did not affect its rate of hydrogenation.

The present investigation differs from the two cited above. The behavior of the oleoyl group toward both hydrogenation and geometrical isomerization was investigated. Because hydrogenation conditions have a marked effect on the course of the reaction (3,5), they were varied widely with respect to type of catalyst and temp.

Experimental

Materials. A refined and bleached olive oil was used as starting material in the hydrogenations. The fatty acid composition of this oil is recorded in Table I.

Two nickel catalysts were employed. The G-53 product, a commercial catalyst (Chemetron Corp.), was of the supported type prepared by electrolytic precipitation and dry reduction. The Raney nickel catalyst was prepared essentially according to the method given by Adkins and Billica (1) for their W-5 catalyst, which possesses a very high activity. The ethanol under which the catalyst was stored was removed before the hydrogenation was carried out.

The palladium catalyst (Baker & Co., Inc.) was of the carbon-supported type and contained 10% palladium by wt.

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TABLE I

Hydrogenation Data and Analyses of Hydrogenated Samples Before and After Lipase Hydrolysis

Run No.	Hydrogenation conditions[a]	I.V. of oil	Hydrolysis of oil, %	Fraction analyzed	*Trans*,[b] %	Fatty acid composition, wt %[c]					$\frac{S^d}{S+O} \times 10^2$	*Trans*-Monoene x 10^2
						P	Po	O	S	L		
1	0.2% Ni (G-53), 110C	50.6	40.4	Unhydrolyzed oil	18.5	7.0	0.5	66.8	25.7	0.0	26.0	27.5
				1,3-Fatty acids	14.7	8.9	0.9	63.3	26.9	0.0	25.4	22.9
				Residual glycerides	18.7	4.5	0.7	70.9	23.9	0.0	24.0	26.1
2	0.2% Ni (G-53), 170C	50.5	19.3	Unhydrolyzed oil	38.1	8.8	0.5	61.9	28.9	0.0	30.1	61.0
				1,3-Fatty acids	28.3	18.6	0.5	50.4	30.0	0.0	32.8	55.6
				Residual glycerides	38.2	8.4	0.6	61.8	29.1	0.0	30.9	61.2
3	3.6% Ni (Raney), 85–95C	48.6	36.9	Unhydrolyzed oil	6.8	9.8	0.6	55.9	32.5	1.2	35.2	12.0
				1,3-Fatty acids	3.8	14.8	1.2	53.2	30.8	0.0	32.3	7.0
				Residual glycerides	6.4	8.1	0.6	53.4	35.6	2.3	39.0	11.8
4	3.6% Ni (Raney), 170C	50.3	20.7	Unhydrolyzed oil	34.0	9.9	0.7	61.2	28.2	0.0	29.8	55.0
				1,3-Fatty acids	26.2	16.3	0.5	57.8	25.4	0.0	25.7	44.9
				Residual glycerides	33.0	7.7	0.7	65.5	26.1	0.0	27.3	49.8
5	0.008% Pd, 30C[e]	51.0	28.0	Unhydrolyzed oil	31.1	10.0	0.6	62.7	26.7	0.0	28.1	49.1
				1,3-Fatty acids	26.0	16.5	0.0	56.7	26.8	0.0	27.4	45.9
				Residual glycerides	30.3	6.4	0.3	64.9	28.1	0.0	29.1	46.5
6	0.008% Pd, 60C	51.9	32.8	Unhydrolyzed oil	39.9	9.1	0.5	64.3	26.1	0.0	27.1	61.6
				1,3-Fatty acids	30.7	18.2	0.0	53.0	28.8	0.0	30.8	57.9
				Residual glycerides	40.4	7.0	0.6	65.8	26.6	0.0	27.6	60.9
7	0.008% Pd, 170C	50.6	27.7	Unhydrolyzed oil	40.3	10.4	0.5	60.3	28.8	0.0	30.6	66.4
				1,3-Fatty acids	30.0	19.2	0.0	51.3	29.5	0.0	32.0	58.5
				Residual glycerides	40.2	8.2	0.7	61.6	29.3	0.0	31.1	64.5
Original olive oil		82.8	15.4	Unhydrolyzed oil	0.0	9.5	1.0	81.7	2.2	5.3	.....	.....
				1,3-Fatty acids	0.0	16.2	0.7	74.2	5.4	3.2	.....	.....
				Residual glycerides	0.0	6.4	0.6	85.2	1.5	5.9	.....	.....

[a] All hydrogenations conducted at atmospheric pressure and same rate of hydrogen dispersion.
[b] Determined on methyl esters and calculated as methyl elaidate.
[c] Calculated on a methyl ester basis. P, palmitate; Po; palmitoleate; O, oleate; S, stearate, and L, linoleate.
[d] Corrected for original content of stearate.
[e] Carried out in hexane solution, 1:1 by wt.

The three types of catalysts which were employed where chosen because they have been found to differ greatly in their activity (5,6). Palladium catalysts are the most active available. The level of 0.008% which was employed was deemed just sufficient to produce an acceptable hydrogenation rate when used with the other operating conditions. At a lower level the rate of hydrogenation would have been decreased greatly, while use of a higher level would have produced only a slight increase in rate.

Hydrogenation Apparatus and Procedure. Equipment and procedure were similar to those described previously (5,7). Briefly, the hydrogenations were carried out at atmospheric pressure in a small, all-glass apparatus. Hydrogen was circulated through the sample continuously by a small pump.

Methods of Analysis. To remove acyl groups from the 1- and 3-positions of the glycerides, the hydrogenated samples were subjected to lipase hydrolysis essentially according to the method of Mattson and Beck (8). However, the lipase hydrolyses were carried out at 48–50C, and the reaction was stopped after 15–25 min. The free fatty acids and glycerides extracted from the hydrolyzed mixtures after acidification were dissolved in ethanol and titrated to the phenolphthalein end point with a dilute solution of sodium hydroxide, and the glycerides were extracted. Then the soaps were acidified, and the resulting fatty acids extracted.

Portions of the hydrogenated samples before lipase hydrolysis and portions of the free fatty acids and residual glycerides obtained on hydrolysis were treated to obtain methyl esters. The boron trifluoride-methanol method was used to prepare the methyl esters of the free fatty acids; a modified sodium methylate catalyzed interesterification was used for the unhydrolyzed oil and the residual glycerides after hydrolysis. These methyl esters were analyzed by GLC, using a column (0.125 in. outside diam x 15 ft long) which was packed with diatomaceous earth coated with 10% diethylene glycol succinate polyester as the stationary phase. The chromatograph was equipped with an ionization type detector having tritium as the radiation source. A column temp of 180C and a flow rate of 30 ml argon/min were employed.

Content of *trans* isomers in the samples was determined by the AOCS procedure, Cd 14-61 (2).

Results and Discussion

Temp has a marked effect on the relative rates at which the different steps of the hydrogenation reaction proceed. In the runs represented in Table I, the lower temp used with each catalyst approached the lowest temp at which the hydrogenation could be completed in 8 hr. The temp of 170C is, of course, in the range employed commercially.

One can conclude on the basis of the data recorded in Table I that in none of the hydrogenations was there a significant difference in the degree of hydrogenation of the oleoyl groups in the 1,3- and 2-positions. This conclusion is based on the fatty acid compositions found for the hydrogenated but unhydrolyzed samples and for the fractions of these samples obtained on lipase hydrolysis. But the extent of similarity of these values is not readily apparent because of the presence of ca. 12% saturated acids in the olive oil. These acids occur mostly in the 1,3-positions of the triglycerides (9). A more accurate indication of the effect of hydrogenation on the oleoyl group in the 1,3- and 2-positions is obtained by calculating the ratio of stearic acid formed to the sum of stearic acid formed plus "oleic" acid found, $S/(S + O)$. Considering the accuracy of the methods employed and the manner in which the values were combined, this ratio is quite constant for each run.

The ratio of *trans* monoene to total monoene (last column in Table I) also is relatively constant for each run. The differences in each run are regarded as being within experimental error. However, this ratio varies from ca. 7–66% among the several runs. Because all samples were hydrogenated to ca. the same I.V., the relative influence of the different steps involved in the hydrogenation mechanism must have changed appreciably among the runs. The conclusion can be reached that during the hydrogenation of triglycerides the oleoyl groups in the 1,3-positions undergo geometrical isomerization to the same extent as do the oleoyl groups in the 2-position, regardless of the operating conditions employed. It is indicated that the oleoyl groups in "monosaturated-diolein," isomerize as readily as do the oleoyl groups

in "triolein." Olive oil is generally considered to contain about one-third of the former and two-thirds of the latter.

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Gas-Liquid Chromatography of Polar Fatty Derivatives[1, 2]

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Abstract

The direct separation of fatty amides is achieved using a polyamide, Versamid 900, as the partitioning agent on a support which need not be previously impregnated with strong alkali or acid, procedures usually followed in the GLC separation of highly polar materials. The combination of a neutral support and polar substrate permits the separation of unsubstituted and substituted long chain fatty amides with as many as 24 carbon atoms with good resolution, in a reasonable time, and with good peak symmetry. The observed area responses agree with the wt percentages of standard amide mixtures, indicating that no loss of amides occurs on the column under the conditions employed.

The Versamid column has proved useful in the analysis of other polar fatty derivatives. Conjugated dienoic and trienoic acids run as their methyl esters are retarded sufficiently on Versamid 900 so that they may be estimated in the presence of other fatty acids. Mixtures of compounds with varying polarity, such as mono-, di- and triacetin, and glycerol, may be separated easily. Hydroxy and normal fatty acid methyl esters give equally symmetrical peaks.

Introduction

THE DIRECT SEPARATION of long chain fatty amides by gas chromatography has received little attention. The usual practice has been to hydrolyze the amides to acids which may be readily separated using conventional techniques. Metcalfe (5) showed that phosphoric acid treated polyester columns could be used to analyze amides, but observed that nitrile formation took place on the column. Subsequently these workers (6) obtained good separations of fatty amides with alkaline treated columns that were previously employed for the analysis of fatty amines (4), but no quantitative data were provided.

The object of our work was to produce a column for amide separations which would require neither acid nor alkali pretreatment, avoiding loss of the amides because of reaction with the column substrate. The rule of similarity suggested that a polyamide would serve as a stationary phase, and subsequent work with Versamid 900 resulted in a column which would resolve fatty amides and allow a response for those impurities associated with amides, such as nitriles and esters. This substrate also proved useful for mixtures with components having a wide range of polarity and for conjugated acids, such as those found in dehydrated castor oil.

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[2] Technical Paper, No. 259, ADM Co.

Experimental

Column Preparation. Two combinations of partitioning agent, Versamid 900, and solid support were used, either 20% w/w on 60–80 mesh or 5% w/w on 100–120 mesh Gas Chrom P. The particular combination used in an experiment is described in the accompanying figures. *n*-Butanol-chloroform (1:1) was found to be an effective solvent for the polyamide. The column material was packed into 4–6 ft aluminum tubing 0.25 in. OD. To obtain max temp stability for temp programming, the column was heated at 350C with a flow of nitrogen for 12 hr. The conditioned column was ready for operation min after insertion into the gas chromatograph.

Instrumental Conditions. An F & M Model 500 gas chromatograph was used in the work, with the bridge operated at 200 ma, detector block maintained at 300C, and a flow rate as described later. The analyses may be conducted isothermally, but the use of temp programming facilitates the identification of low-boiling impurities and increases the resolution of the amides. Since the amides are extremely high boilers it is important to maintain a high temp in the inlet, 275–400C. Care should be taken to insure that the inlet is not contaminated with impurities which would cause dehydration of the amides to cor-

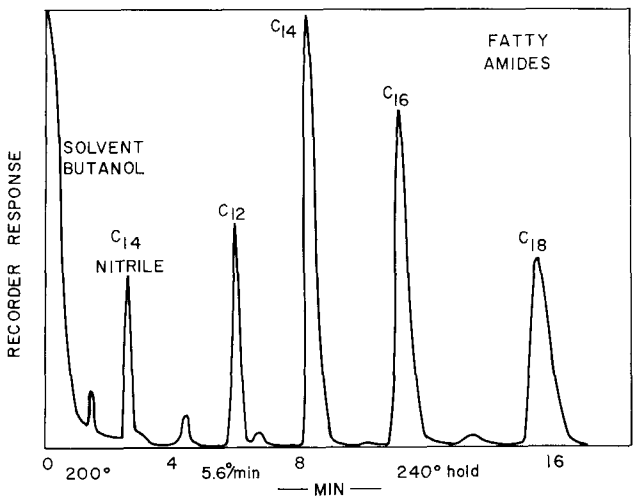

FIG. 1. Chromatogram of fatty amide from high cut coconut fraction, 5 ft column, 20% Versamid 900 on 60–80 mesh Gas Chrom P, temp programmed from 200C at 5.6°/min to hold at 240C, inlet 300C, detector 300C, flow rate 100 ml/min.