Studies in Interesterification. II. Acidolysis of Some Vegetable Oils with Lauric Acid[1]

M. M. CHAKRABARTY and K. TALAPATRA, Department of Applied Chemistry, Calcutta University, Calcutta 9, India

Abstract

Acidolysis reactions of cottonseed oil, peanut oil, mahua oil (*Madhuca latifolia*), and palm oil with lauric acid were investigated with special reference to the influence of catalysts and the relative proportions of oil and lauric acid on the extent and type of fatty acids displaced from an oil. Catalysts such as sulfuric acid, zinc oxide, calcium oxide, magnesium oxide, aluminum oxide, and mercuric sulfate were used. The reaction generally was carried out by heating oil and lauric acid at 150C ± 2 for 3 hr.

The reaction products were separated and then analyzed by UV spectrophotometry and GLC. Sulfuric acid was found to be the best catalyst with 1 part of oil and 1.2 parts of the displacing acid (lauric acid) for displacement of high-molecular-weight fatty acids from an oil by low-molecular-weight fatty acids. The nature of the displacement of fatty acids varied from oil to oil, depending on their compositions. It was further indicated that linoleic acid was displaced preferentially over oleic acid in an amount dependent on its initial content in an oil with a corresponding increase in saturated acids content. A broad similarity in displacement patterns, in general, was noted; the fatty acids above C_{18} were not displaced as in the case of peanut oil. The results demonstrate the feasibility of introducing lauric acid in the vegetable oils for the production of interesting oils with vastly different physical and chemical properties.

Introduction

AMONG THE INTERESTERIFICATION reactions of fats, acidolysis has been studied in somewhat lesser detail. The reaction involves the replacement of an acyl group of a triglyceride with an equivalent group derived from another fatty acid. Various conditions have been prescribed for the reaction, and it has been established that the uncatalyzed acidolysis reaction generally requires the use of higher temperatures (250–300C) compared with those catalyzed by various agents. Typical catalysts used are sulfuric acid, boron trifluoride, mercuric sulfate, oxides and soaps of aluminum, magnesium, tin, and zinc.

Properties of the original fats can be altered by the exchange of one or more of the acyl group of the fat by higher or lower molecular-weight fatty acids. In most of these processes the operator has limited control over the composition of the final product. As random interchange of the fatty acid radicals occurs, any specific acid will distribute itself indiscriminately between the esterified and free acid portions. However operational conditions have been devised for preferential incorporation of high-molecular-weight fatty acids. Many workers, notably Eckey (1), have succeeded in altering the composition of fats. Markley (2) and Swern (3) have recently reviewed the acidolysis reactions of fats.

In the present investigation the acidolysis reactions of a number of vegetable oils have been studied. The catalytic activity of a number of catalysts was first established by reacting cottonseed oil with lauric acid under different conditions. After the establishment of optimum conditions with respect to a particular catalyst, efforts were also directed toward the maximum exchange of lauric acid with the fatty acids of cottonseed oil in varying ratios of reactants. For comparison, studies were also made on uncatalyzed reactions under identical conditions for different lengths of time. By taking advantage of the two suitable catalysts, optimum concentration, and temperature, then peanut oil, mahua oil, and palm oil were acidolyzed. The reaction products (the glycerides as well as the unreacted fatty acid along with the displaced fatty acids) generally were analyzed with ultraviolet (UV) absorption spectrophotometry and gas-liquid chromatography (GLC) along with other usual methods after the separation of the glycerides from the displaced and unreacted fatty acids.

Experimental Procedures

The oils and lauric acid were obtained from known sources, and their purity and composition were determined by standard methods (4,5) and by GLC.

Refining and Bleaching

The oils were first refined by alkali treatment to an acid value of less than 0.1, then bleached with 2% fuller's earth and 0.5% active charcoal to negligible peroxide value and completely dried under vacuum.

Acidolysis Reaction

The refined and bleached oil was taken in a round-bottomed flask, fitted with a long air-condenser with lauric acid in different proportions by weight (1:0.5, 1:0.8, 1:1, 1:1.2, 1:1.5, 1:2). The catalyst (of reagent quality) was added: concd. sulfuric acid (sp gr 1.84, 0.5% w/w or 1% w/w), zinc oxide (0.25% w/w or 0.4% w/w), calcium oxide (0.25% w/w), magnesium oxide (0.25% w/w), aluminum oxide (0.25% w/w), or mercuric sulfate (1% w/w). Then it was heated in an oil bath at 150C ± 2 for 3 hr. To observe the effect of absence of catalyst in the reaction mass, the mixture of oil and fatty acid was also heated for variable lengths of time without the addition of the above substances.

Recovery of Samples

The reaction mass was taken up after cooling in petroleum ether (bp 40–60C) and subjected to washing with water (when sulfuric acid was used) and/or filtration (when solid catalysts were used), followed by removal of water and solvent to recover the mixture of glycerides and free fatty acids. These were then subjected to extraction with 90–95% ethanol at the melting temperature of the oils a number of times

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[1] Part I. M. M. Chakrabarty, S. Das, and K. Talapatra, Fette, Seifen, Anstrichm. *68*, 310–313 (1966).

until the glycerides were lacking the free fatty acids, as shown by negligible acid value (4) and by monitoring by thin-layer chromatography (6). When no catalyst was used, ethanol extraction was applied directly to the reaction mass after cooling. The recovered glycerides and the free fatty acids were then separately analyzed.

The method of extraction was tested with a known mixture of cottonseed oil and lauric acid in order to find out the distribution of triglycerides and lauric acid in each other.

Analysis

The analytical characteristics, viz., saponification value, iodine value, refractive index, and slip point (SV, I.V., RI, SP) of the original oils, lauric acid, and the products separated after the reaction were determined by AOCS methods (4). Some of the acidolyzed products were separated on a thin layer of silica gel by using petroleum ether (bp 40–60C), diethyl ether, and acetic acid in the proportions of 70:30:2 (v/v) in order to detect any formation of mono- and/or diglyceride during acidolysis reactions (7). The fatty acid composition was determined in all the cases by the alkali isomerization UV spectrophotometric method, according to Hilditch (5), by using a Beckman quartz spectrophotometer, Model Du, with 1-cm cells. In a number of selected cases GLC was applied.

The apparatus was an analytical gas chromatograph (F&M, Model 700 R-12) with a dual flame ionization detector. Methyl esters were prepared according to the methods advocated by Riemenschneider et al. (8) or Hilditch (9). Pure nitrogen gas with a flow rate of 40 ml/min was used as the carrier gas. The columns (stainless steel 6 ft long by ¼ in. O.D. with a 2-ft by ¼-in. compensating column) were packed with 10% Lac 446 (F&M Scientific Corporation, Avondale, Pa.) on 60–80 mesh diatoport S and were operated at 180C. The percentage composition of the components (by weight) by GLC was obtained by measuring the area under each peak and calculating the ratio of these areas to the sum of the area under all of the component peaks.

Results and Discussion

A selection of the results is presented in Tables I to III.

Table I gives the analytical values of the original starting materials (cottonseed oil, peanut oil, mahua oil, palm oil, and lauric acid), and Table II those for the different reaction products obtained from cottonseed oil by using different catalysts and different ratios of reactants. Table II also gives the results without catalyst with varying reaction times. The results of other oils are shown in Table III.

Several interesting observations emerge from the results. It is seen that, of all the catalysts tried, sulfuric acid appears to be the best from the point of view of displacement of high-molecular-weight fatty acids by low-molecular-weight fatty acids, followed by zinc oxide and calcium oxide, which display more or less the same activity, followed by aluminum oxide and magnesium oxide. Mercuric sulfate appears to be the least active. It is also obvious that reactions without catalyst are slow and almost negligible although some reactions do take place. It also appears from the results of the study (Tables I and II) that there is an optimum ratio of the displacing acid to oil at a particular catalyst concentration. This opti-

TABLE I

Analysis of Original Oils and Lauric Acid

Oils/Acid	S V	I V	R I 40C	S P C	Fatty Acid Composition (wt %)														
					GLC									UV	GLC	Calcd. from UV and IV	GLC	By diff.	GLC
					C_8	C_{10}	C_{12}	$C_{14:0}$	$C_{16:0}$	$C_{18:0}$	$C_{20:0}$	$C_{22:0}$	$C_{24:0}$	$C_{18:2}$		$C_{18:1}$		S[a]	
Cottonseed oil	195.0	105.2	1.4651	<0				0.9	22.9	3.5				48.8	49.0	23.9	23.7	27.3	27.3
Peanut oil	190.1	94.5	1.4621	<0					9.0	4.6	2.9	2.1	1.4	26.8	26.2	52.9	53.8	20.3	20.0
Mahua oil	190.3	61.8	1.4602	26.0				0.2	23.5	21.6				15.1	15.4	39.9	39.3	45.0	45.3
Palm oil	199.1	53.9	1.4573	34.5				1.3	42.7	5.4				10.1	10.4	40.6	40.2	49.3	49.4
Lauric acid	281.9	0.0			0.6	7.2	89.5	2.7											100.0

[a] Total saturated.

TABLE II

Acidolysis of Cottonseed Oil with Lauric Acid

Reaction conditions	Products	S V	I V	R I 40C	S P C	Fatty Acid Composition (wt %) GLC						UV	GLC	Calcd. from UV and IV	GLC	By diff.	GLC
						C_8	C_{10}	C_{12}	$C_{14:0}$	$C_{16:0}$	$C_{18:0}$	$C_{18:2}$		$C_{18:1}$		S	
Oil : C_{12}: :1:1.2	AO[a]	219.8	73.8	1.4585	7.0	0.2	1.9	24.0	1.6	19.0	2.3	31.0	31.7	19.8	19.3	49.2	49.0
Cat. H_2SO_4–0.5%	RFA[b]	251.8	31.7	....	....	0.6	5.4	66.4	1.9	4.4	1.5	15.4	15.4	4.3	4.4	80.3	80.2
Oil : C_{12}: :1:1.5	AO	219.6	73.6	1.4585	7.0	0.1	1.9	24.1	1.7	19.0	2.2	32.0	31.8	19.2	19.2	48.8	49.0
Cat. H_2SO_4–0.5%	RFA	250.8	31.6	....	....	0.6	5.3	66.3	2.0	4.2	1.5	15.3	15.6	4.3	4.5	80.4	79.9
Oil : C_{12}: :1:1.2	AO	211.1	87.9	1.4602	4.0	0.2	1.0	13.0	1.5	20.6	3.1	38.9	38.9	21.4	21.7	39.7	39.4
Cat. ZnO–0.25%	RFA	265.6	16.2	....	....	0.6	6.5	77.8	2.1	2.3	0.5	8.0	8.1	1.9	2.1	90.1	89.8
Oil : C_{12}: :1:1.2	AO	211.9	87.2	1.4600	4.0	0.1	1.0	13.4	1.6	20.8	2.9	38.2	38.6	21.6	21.6	40.2	39.8
Cat. CaO–0.25%	RFA	265.9	15.4	....	....	0.6	6.3	77.8	2.2	2.2	0.9	7.5	7.9	2.0	2.1	90.5	90.0
Oil : C_{12}: :1:1.2	AO	209.4	88.5	1.4603	3.5	0.2	0.8	12.4	1.3	21.3	3.1	39.3	39.4	21.3	21.5	39.4	39.1
Cat. Al_2O_3–0.25%	RFA	267.9	14.5	....	....	0.6	6.7	78.3	2.6	2.0	0.6	7.0	7.1	2.0	2.1	91.0	90.8
Oil : C_{12}: :1:1.2	AO	208.7	89.1	1.4605	3.5	0.2	0.8	12.4	1.2	21.1	3.1	39.4	39.9	22.0	21.3	38.6	38.8
Cat. MgO–0.25%	RFA	269.0	13.4	....	....	0.6	6.5	78.6	2.5	2.4	0.6	6.4	6.6	2.0	2.2	91.6	91.2
Oil : C_{12}: :1:1.2	AO	204.1	94.3	1.4615	<3	0.2	0.5	8.7	1.2	21.6	3.3	42.0	42.4	22.0	22.1	36.0	35.5
Cat. $HgSO_4$–1%	RFA	272.1	10.6	....	....	0.5	6.7	82.0	2.4	1.4	0.2	5.2	5.3	1.3	1.5	93.5	93.2
Oil : C_{12}: :1:1.2	AO	203.7	95.1	1.4616	<0	0.2	0.4	8.2	1.4	21.7	3.4	42.5	42.7	22.1	22.0	35.4	35.3
3-hr heat	RFA	271.6	11.2	....	....	0.5	7.2	80.8	2.4	1.4	0.3	5.6	5.9	1.2	1.5	93.2	92.6
Oil : C_{12}: :1:1.2	AO	205.5	92.0	1.4611	<0	0.2	0.7	10.4	1.3	21.0	3.0	40.9	41.4	21.9	22.0	37.2	36.6
5½-hr heat	RFA	269.8	12.5	....	....	0.6	6.5	80.2	2.4	1.8	0.6	6.0	6.1	1.8	1.8	92.2	92.1

[a] Acidolyzed oil.

[b] Recovered fatty acid.

TABLE III

Acidolysis of Peanut, Mahua, and Palm Oil with Lauric Acid

Reaction conditions	Products	S V	I V	R I 40C	S P C	Fatty Acid Composition (wt %) GLC									UV	GLC	Calcd. from UV and IV	GLC	By diff.	GLC
						C_8	C_{10}	C_{12}	$C_{14:0}$	$C_{16:0}$	$C_{18:0}$	$C_{20:0}$	$C_{22:0}$	$C_{24:0}$	$C_{18:2}$		$C_{18:1}$		S	
Peanut oil:C_{12}: :1:1.2	AO[a]	217.2	73.0	1.4577	5.0		1.8	17.9	0.7	6.0	3.2	2.7	2.2	1.5	18.5	18.4	45.6	45.6	35.9	36.0
Cat. H_2SO_4–0.5%	RFA[b]	257.7	20.1	....	....	0.5	5.3	72.6	2.1	2.9	1.2				7.1	7.2	8.1	8.2	84.8	84.6
Peanut oil:C_{12}: :1:1.2	AO	211.6	77.1	1.4586	3.5										19.2		49.0		31.8	
Cat. ZnO–0.25%	RFA	264.0	14.4	....	....										5.9		4.1		90.0	
Mahua oil:C_{12}: :1:1.2	AO	217.2	45.8	1.4564	31.5		1.9	20.2	0.9	17.7	17.8				10.3	10.1	31.2	31.4	58.5	58.5
Cat. H_2SO_4–0.5%	RFA	260.2	15.8	....	....	0.6	6.4	68.6	2.3	5.1	4.0				4.5	4.7	8.5	8.3	87.0	87.0
Mahua oil:C_{12}: :1:1.2	AO	212.0	50.2	1.4570	30.0										10.5		35.8		53.7	
Cat. ZnO–0.25%	RFA	265.8	8.7	....	....										3.0		3.6		93.4	
Palm oil:C_{12}: :1:1.2	AO	220.7	38.2	1.4533	40.5		1.8	24.5	1.8	30.2	3.5				6.2	6.8	30.8	31.4	63.0	61.8
Cat. H_2SO_4–0.5%	RFA	259.6	12.9	....	....	0.7	5.6	64.8	2.2	12.9	1.7				3.0	3.2	8.2	8.9	88.8	87.9
Palm oil:C_{12}: :1:1.2	AO	213.4	42.9	1.4540	39.0										6.2		36.6		57.2	
Cat. ZnO–0.25%	RFA	266.9	7.5	....	....										2.7		2.9		94.4	

[a] Acidolyzed oil.

[b] Recovered fatty acid.

mum ratio happens to be 1 part of the oil and 1.2 parts of the displacing acid (lauric acid) for all catalysts since the extent of displacement remains almost the same even by increasing the relative proportions of lauric acid from 1.2 to 1.5 parts to 1 part of oil.

Examination of the analytical results on the recovered acid mixture shows that, at the optimum level of any catalyst, the proportion of fatty acids displaced remains practically the same. This is also corroborated by the results of analysis of the fatty acids of the corresponding glycerides. For example, it will be seen that, with sulfuric acid as catalyst, there is practically no change in fatty acid composition of either the resulting glyceride or the recovered mixed fatty acids when the ratio of cottonseed oil and lauric acid is 1:1.2 or 1.15 parts (w/w).

In each case, in the glyceride ca. 24% of lauric acid was introduced along with minor content (2.8%) of other saturated acids present originally in the lauric acid. At the same time the displacement of ca. 4% of palmitic acid, 1.2% stearic acid, 4.5% oleic acid, and 17% of linoleic acid from the oil itself by C_{12} also resulted. Comparison of the analytical characteristics of the original lauric acid and the displaced fatty acids shows that practically all the fatty acids displaced from the original oil have found their way into the recovered mixture of fatty acids. The same pattern is observed, although with varying constant displacements under comparable conditions, for the other catalysts.

It appears from the results that, in such reactions as could be expected, the increase of SV and decrease of IV and RI give a general idea of the effectiveness of the reaction. This is quite significant and also demonstrates that a product of constant composition is obtainable at equilibrium point. A prominent feature which can be noted is that proportionately more linoleic acid is displaced from the oil than oleic acid. Thus while the oleic-to-linoleic ratio in the original cottonseed oil is approximately 1:2, that in the product is approximately 1:1.5. Peanut, mahua, and palm oils also reveal that the more unsaturated linoleic acid is preferentially displaced by C_{12} although the content of oleic acid is higher than that of linoleic acid in all these cases.

Also the extent of displacement is more or less the same irrespective of the difference in fatty acid compositions. Further the proportionate increase in saturated acids in the acidolyzed oils by the introduction of lauric acid at optimum catalyst and conditions is practically the same (14–16%), being only slightly higher in case of peanut oil. Cottonseed oil however shows a still higher increase in the proportion of saturated acid content (ca. 22%) under identical conditions. Thus the net increase in saturated acids content is dependent on the amount of linoleic acid originally present in an oil. A characteristic feature noted in the case of the peanut oil product is that all the saturated acids above C_{18} are not displaced at all by the reaction whereas displacement occurs for saturated acids C_{18} and below. So far as saturated acids of C_{18} and below are concerned, palmitic acid appears to be proportionately more mobile.

The method employed for separation of the products of acidolysis into glyceride and fatty acid fractions is considered suitable because, with a known mixture of oil and lauric acid, the distribution of one in the other when extracted with 90–95% ethanol under identical conditions is found to be negligible. Thin-layer chromatography also supports the observation. It may be further stated that there is no formation of mono- or diglyceride during acidolysis reaction, as is evident by thin-layer chromatography.

Some of the important conclusions are given. 1) Introduction of lauric acid in oils to get a product of constant composition is possible under proper reaction conditions. These products as such, or after segregation into a number of oils by using already known methods, such as low temperature crystallization or liquid-liquid extraction, are capable of yielding interesting oils with good commercial possibilities. It can perhaps be interpolated from these experiments that the products of the reaction of mixed fatty acids of coconut and palm kernel oil or other low-molecular-weight single or mixed fatty acids offer endless scope for permutation and combination of fat products for diverse specifications and uses. 2) The use of displaced fatty acids after recovery also provides interesting possibilities as such or after re-esterification. 3) Although the full economy of the process remains to be worked out, it should not be difficult to devise plant operations for such reactions.

The study is being continued with other oils.

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