The Preparation of Hydroxystearic Acids from Red Oil (Commercial Oleic Acid)

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Abstract

The hydroacetoxylation of red oil (commercial oleic acid) in acetic acid solution has been studied. The optimum hydroacetoxylation conditions were obtained under anhydrous conditions using sulphuric acid as a catalyst at:

1. a concentration of 1% (based on the wt of red oil),
2. at a reaction temp of 70C,
3. at a ratio of acetic acid: oleic acid of 3:1.

Some 70 hr were required under these conditions to obtain maximum (60–70%) addition to the double bond.

Some 50% (based on the wt of red oil) of pure hydroxystearic acids was isolated from this acetoxylation mixture by simultaneous deacetylation and esterification, followed by distillation, saponification, acidification, and crystallization of the acids from hexane.

For the isolation of a less pure (50–60%) hydroxystearic acid, the mixture following distillation was hydrogenated, saponified, and acidified. Suitable hydrogenation conditions were found to be 110–115C, at a pressure of 300 psi for 4 hr. Selectol C was the catalyst of choice used at a concentration of 0.2% (nickel based on the wt of fatty acids). An 85% wt yield of this product was obtained.

Introduction

Studies on the chemical utilization of inedible tallow in these laboratories led to an attempt to effect a simultaneous acetolysis and acetic acid addition.

Glycerine stearate/oleate + acetic acid ⟶ triacetin + stearic acid + acetoxy stearic acid.

The results were disappointing, and studies were then undertaken on the acetolysis (1) and the acetic acid addition separately. This work showed that the optimum conditions for the two reactions are so different as to be almost mutually exclusive.

The addition of acetic acid to double bonds

$$-CH=CH- + CH_3-COOH \longrightarrow -CH_2-CH(OCOCH_3)-$$

has been described for oleyl alcohol (2), dicyclopentadiene (3), and oleic acid (4), and generally requires a strong mineral acid catalyst. Formic acid, only ten times stronger than acetic acid in aqueous solution, is 10^4 stronger from the standpoint of its autoprotolysis const, and so does not require an added catalyst (3,4). These reactions are hetero additions, a hydrogen adding to one carbon atom and the acetoxy group to the other member of the double bond. From analogy to such reactions as "hydrobromination," the term "hydroacetoxylation" is proposed for this reaction.

TABLE I

The Effect of Perchloric Acid Catalyst Concentration on Hydroacetoxylation of Red Oil

Reaction conditions: acetic acid:red oil ratio—3:1 (w/w), temp—70C

Time (hr)	Perchloric acid concentration (w/w on red oil)									
	0.2%		0.5%		1.0%		2.0%		3.0%	
	I.V.	S.V.	I.V.	S.V.	I.V.	S.V.	I.V.	S.V.	I.V.	S.V.
87	54.4	252	34.5	271	24.6	285	23.9	284	24.1	283
112	......	......	......	......	22.6	285	22.8	284	23.9	281
159	37.6	267	27.8	281	22.6	285	23.9	284	23.8	280

The objective of our work was the preparation of 9/10 hydroxystearic acid. Since 12-hydroxystearic acid has an established use in high-temp lubricants, it was felt that 9/10 hydroxystearic acid might have similar properties.

Experimental Procedures and Data

The work was initiated by studying the effect on the rate of hydroacetoxylation of the concentration of the perchloric acid catalyst. The results are given in Table I.

The results show that 1.0% perchloric acid (based on the wt of red oil) is the optimum level at this temp.

The effects of time, and temp on the degree of hydroacetoxylation are shown in Figures 1 and 2. The addition to the double bond in oleic acid was measured by two means: the decrease in I.V. (see Fig. 1) and the increase in saponification value (see Fig. 2). The increase in saponification value is more reliable since it is a direct measure of the number of acetoxy groups added. Theoretically, the decrease in I.V. should give the same result, but there are side reactions which cause the disappearance of double bonds, without the addition of acetoxy groups. Figure 2 shows the saponification value becoming const, while Figure 1 shows a slow but steady decrease in I.V. with time.

Figure 1 shows that at 100–110C, equilibrium is established at a higher I.V. than at 60–80C. How-

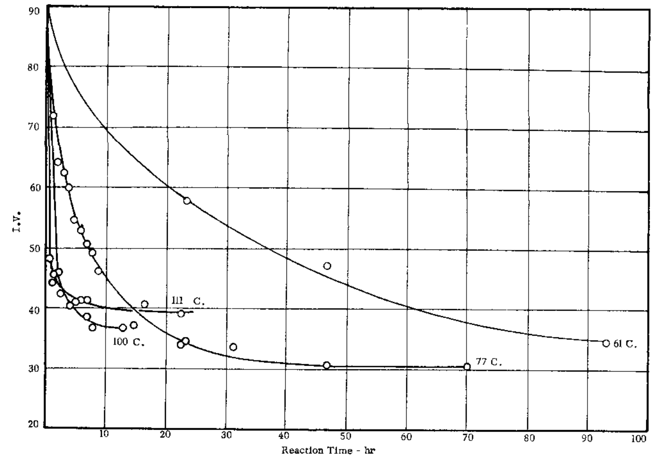

Fig. 1. The effect of temp on the rate of hydroacetoxylation of red oil in acetic acid (1:2 w/w) as followed by I.V. determination. Reaction conditions: catalyst-perchloric acid; catalyst concentration—1.0% (based on wt of red oil).

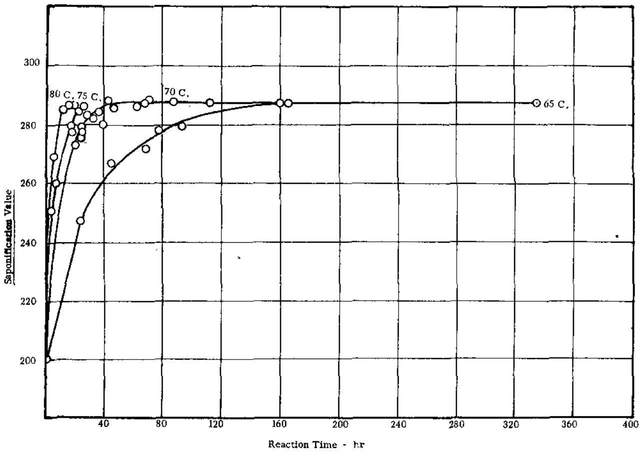

FIG. 2. The effect of temp on the rate of hydroacetoxylation of red oil in acetic acid (1:3 w/w) as followed by saponification value determination. Reaction conditions: catalyst-perchloric acid; catalyst concentration—1.0% (based on the wt of red oil).

ever, since there is less charring at the lower temp, 70C has been chosen as the optimum to give both a a good rate and adequate degree of hydroacetoxylation. A reaction time of 70 hr is required at this temp to reach a const saponification value.

The effect of varying the acetic acid to red oil ratio on the rate of hydroacetoxylation is shown in Figure 3. In these tests, the overall catalyst concentration, rather than the concentration based on the wt of red oil, was kept const. Despite this change in procedure, the rates differ sufficiently to indicate that a ratio in the range 2:1–3:1 is required. Since the addition was greater at a ratio of 3:1, it was the one chosen.

Under optimum conditions, addition to the double bond of the order of 60–70% is obtained. At this stage, the catalyst is neutralized and excess acetic acid is removed at a reduced pressure.

Recovery of Pure (99.5%) Hydroxy Acids

Alkaline hydrolysis of acetoxystearic acids yields hydroxystearic acids. Alkaline saponification is the only satisfactory method of hydrolysis for obtaining hydroxy acids, as Twitchell or high pressure splitting gives estolides which are dimers produced by esterification between two hydroxystearic molecules.

To obtain a product which contains more than 60–70% hydroxystearic acid, it is necessary to fractionate this crude mixture. Initially, this fractionation was effected by crystallizing the product from hexane; however, it was found impossible to obtain a product of consistently high purity. Therefore, it was found necessary to distill the mixture prior to the separation of the hydroxy acids. This procedure yielded a high-purity hydroxystearic acid consistently.

TABLE II

The Effect of Time on the Simultaneous Methanolic Deacetylation and Esterification of the Acetoxy Acid Mixture

Reaction conditions:
Temp—reflux
MeOH: acetoxy acid ratio—1:1 (w/w)
Catalyst—sulphuric acid
Catalyst concentration—1% of MeOH (w/w)

Time hr	Saponification value	Acetylated saponification value
0	278	264
4	246	271
8	235	270
12	222	268
16	215	268
22	205	268
30	197	268
38	194	267

TABLE III

The Effect of Time and Alcohol Concentration on the Simultaneous Ethanolic Deacetylation and Esterification of the Acetoxy Acid Mixture

Reaction conditions:
Temp—reflux
Catalyst—sulphuric acid
Catalyst concentration—1% of EtOH (w/w)

Time (hr)	Ethanol: acetoxy acid ratio (w/w)			
	1:1		1.44:1	
	I.V.	S.V.	I.V.	S.V.
4.5	26.0	249	26.1	250
7.5	......	240	......	233
12.0	27.0	220	27.2	221
15.5	......	218	......	210
20.0	26.6	207	27.1	205
23.5	......	206	......	205
31.5	28.2	196	29.0	194
	1% additional catalyst added			
39.0	28.1	193	......	......

Since distillation was required, a reaction that could be used to advantage was simultaneous alcoholic deacetylation and esterification leading to the more volatile and stable methyl hydroxy esters.

$$\text{Acetoxystearic Acid} + \text{MeOH} \overset{H^+}{\rightleftharpoons} \text{Methyl 9/10 Hydroxystearate} + \text{Water} + \text{Methylacetate}$$

The effect of concentration and choice of primary alcohol on this reaction is summarized in Tables II and III.

The choice of alcohol would depend on whether methyl or ethyl acetate was desired as a by-product. Table III shows that for ethanolic deacetylation, a ratio of ethanol:acetoxy acids of 1:1 gives similar results to a 1.44:1 ratio. The latter is the same mole ratio as a methanol: acetoxy acid ratio of 1:1, (w/w). It should therefore be possible to perform a satisfactory methanolic deacetylation at a lower ratio than 1:1. Since the acetylated saponification value does not show any appreciable decrease during alcoholic deacetylation (the acetylated saponification value for the experiment reported in Table III remained const throughout also), the hydroxyl groups on the product are not destroyed.

The effect of the choice of acid catalyst involved is summarized in Table IV.

From these results, it appears that sulphuric acid is as good a catalyst as the more hazardous perchloric acid for this reaction, and 1% (based on the wt of alcohol) is sufficient to yield satisfactory results.

When the simultaneous alcoholic deacetylation and esterification was completed (after refluxing for 16 hr), the catalyst was neutralized, alcohol removed

TABLE IV

The Effect of Different Acid Catalysts on the Simultaneous Methanolic Deacetylation and Estrification of the Acetoxy Acid Mixture

Reaction conditions:
Temp—reflux
MeOH: acetoxy acid ratio—1:1 (w/w)
Catalyst concentration—1% of MeOH (w/w)

Time (hr)	Acid catalyst used	
	Sulphuric acid	Perchloric acid
0	S.V. — 258	S.V. — 258
1	......	250
2	......	247
3	234	......
4	......	241
5	224	......
8	211	226
24	190	202

TABLE V

The Effects of Variables on the Hydrogenation of the Acetoxy Acid Mixture
Acetoxy Acid Mixture (I.V. — 28.1)

(A)
Hydrogenation
Hydrogenated Acetoxy Acid Mixture

Method A-1
1. Alkaline sap.
2. Esterification
3. Distillation
4. Alkaline sap.
5. Acidification

Method A-2
1. Simultaneous alcoholic deacetylation and esterification
2. Distillation
3. Alkaline sap.
4. Acidification

(B)
Simultaneous Alcoholic Deacetylation and Esterification
Partially Deacetylated Ester Mixture

Method B-1
1. Hydrogenation
2. Distillation
3. Alkaline sap.
4. Acidification

Method B-2
1. Distillation
2. Hydrogenation
3. Alkaline sap.
4. Acidification

Method	Temp C	Pressure psi	Catalyst	Catalyst conc. (Ni based on wt of fatty acids)	Time (hr)	% Ester distillable	Analysis of hardened distilled ester	
							I.V.	% Hydroxy ester by OH value
A-1	150–160	300	Resistol C.	0.4	3	87.2	9.3	57.8
A-2	150–160	300	Resistol C.	0.4	3	85.1	10.6	46.0
B-1	110–115	300	Resistol C.	0.4	5	85.3	3.6	54.8
B-2	150–160	300	Selectol C.	0.2	3	84.1	3.2	49.0
B-2	100–105	300	Selectol C.	0.2	6	84.1	4.9	51.8
B-2	110–115	300	Selectol C.	0.2	4	84.1	4.5	54.8

at a reduced pressure, and the solution was washed neutral with warm water. Finally, the deacetylated esters were dried and distilled at a pressure of approx 1 mm of mercury.

The distillate was saponified with a 100% excess of sodium hydroxide (20% aqueous solution). After a 16-hr saponification with agitation at 70C, the material was acidified. The liquid fatty acids (70C) were well washed with hot water. The duration of these washes was kept to a min to reduce estolide formation.

The fatty acid mixture was dissolved in hexane. Sufficient hexane was then distilled from the solution to remove any moisture present. When the hexane to fatty acid ratio reached approx 1.1:1, distillation was discontinued, and the solution cooled with agitation initially to room temp and finally to a temp of 0C. Following filtration at 0C, the crystals were washed with hexane (0C).

The product obtained was hydroxystearic acid with the following const:

I.V.—4.0
Saponification value—190
Acid value—187
Acetylated saponification value—316
Hydroxyl value—177
Calculated percent hydroxy compound—99.5%

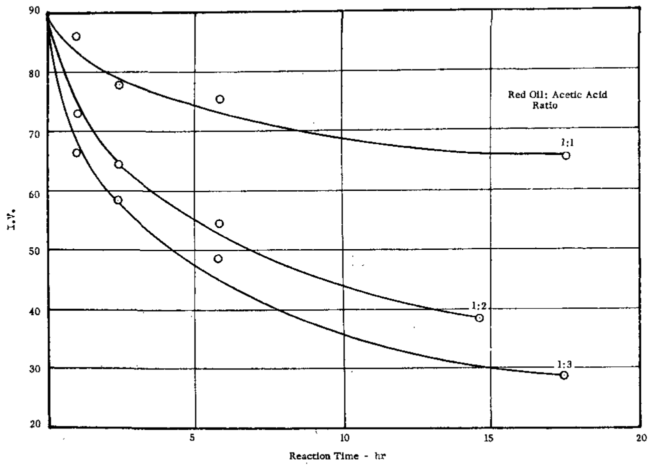

FIG. 3. The effect of acetic acid concentration on the rate of hydroacetoxylation of red oil. Reaction conditions: temp—77C; catalyst-perchloric acid; catalyst concentration—.33% (based on the total wt of the reaction mixture).

Since some estolides do form on acetoxylation and distillation, a further quantity of hydroxystearic acid of similar quality can be obtained by saponifying the distillation residues. The precise location of the hydroxyl groups was not investigated; it is known that reversible additions lead to double bond wandering, and the "red oil" was a ruminant fat oleic acid already containing "off-centre" double bonds, but the 9- and 10-hydroxystearic acids should still be the main products under these conditions of near minimal effective reaction time.

The total recovery of hydroxystearic acid was some 50% of the wt of red oil treated.

Recovery of 50–60% Pure Hydroxy Acids

For the manufacture of high temp lithium greases, it was felt that a mixture containing 50–60% hydroxy acid, and the remainder saturated acids, would be a satisfactory product. Consequently, the variables involved in the hydrogenation of acetoxystearic acid were investigated.

Four different routes (see Table V) for the conversion of the unreacted oleic acid to stearic acid were studied. The objective in these studies was to effect hydrogenation with a min loss of hydroxyl value of the hydroxy acids present. The analyses to determine the efficiencies of the four methods were performed on the esters rather than on the final acids to obviate inaccuracies due to estolide formation. Method A-1 yielded a product having the highest content of hydroxy esters (57.8%), but the economics of this route are questionable because it entails two alkaline saponifications. Methods B-1 and B-2 yielded products of identical hydroxyl contents (54.8%). However, Method B-2 is preferred as it requires only half the catalyst concentration (based on the wt of distilled ester). It is also obvious that at temp of 110–115C, destruction of the hydroxyl groups by hydrogenolysis is less than at temp of 150–160C. We suspect that the low hydroxyl value of the experiment at 100–105C is due to prolonged hydrogenation (6 hr).

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[Received February 12, 1962]