Monohydroxylation of Unsaturated Oils: I. Sulfation-Hydrolysis and Sultone-Formation

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Abstract

Hydroxy unsaturated glycerides were sought from safflower and linseed oils by partial sulfation with sulfuric acid, followed by hydrolysis of sulfate to hydroxy groups. Sulfation of oleic-rich oils or their fatty acids and subsequent hydrolysis (effected conveniently with acidified barium chloride) yielded hydroxy products corresponding to 50–70% of the monoene content. Sulfation of a mixture of methyl oleate and linoleate with 78% w/w of sulfuric acid was directed mainly at the oleate component. Safflower oil was partially sulfated without side reactions using 78% or 79% w/w of sulfuric acid, the hydrolyzed products showing hydroxyl value (HV) of about 35 for a loss of 13 units of iodine value (IV). Use of more concentrated sulfuric acid, and subsequent hydrolysis, led to sulfur-containing products which include sultones. Treatment of a *trans,trans,* but not of a *cis,trans* conjugated diene with sulfuric acid led to sultone formation. It is postulated that when linoleate is sulfated with strong acids, acid-isomerization to a *trans,trans* conjugated diene occurs, probably followed by 1,4-addition of –OH and –SO_3H and quick dehydration of these moieties to give a 1,4-sultone. Linseed oil was apparently sulfated without side reactions using 80% w/w sulfuric acid at 0–5 C and then hydrolyzed to a product of HV 77 and IV 159.

Introduction

Oils containing a high proportion of unsaturated monohydroxy acids, such as castor or dimorphotheca, undergo several industrially useful reactions. Treatment of unsaturated oils suitably with peracids yields products containing vicinal hydroxy groups. Steric factors limit the reactivity of these diols when used in ester-type or alkyd surface-coatings, or in sulfated surfactants (1). Hence in attempting to increase the reactivity of polyunsaturated oils such as safflower and linseed for such uses, the partial introduction of single hydroxyl groups at or near the double bonds seemed to be a good approach.

One successful route to this end was to epoxidize some of the double bonds of glycerides, followed by ring-opening of these epoxy to monohydroxy groups by hydrogenation over palladium on carbon. Saturation of the residual double bonds was prevented by the presence alongside of either silver nitrate or cupric nitrate which probably act as *pi*-complexing agents (2,3).

The present paper reports another approach to the same end based on the partial sulfation of double bonds, and hydrolysis of the resulting sulfate to hydroxy groups. Roe et al. (4) were able to obtain 9(10)hydroxystearic acids from oleic acid using molar volumes of 80% v/v sulfuric acid for sulfation and diluted acid for hydrolysis, but stated that the presence of linoleic acid lowered the yields. Numerous attempts have been made in the past (5,6) to sulfate vegetable and fish oils. The conclusions are often contradictory. However, the use of 80% v/v sulfuric acid at 90 C appears to be conducive to formation of mainly hydroxy products (5–7). Undesirable reactions in the sulfation would be the formation of hydroxy sulfonates, and the hydrolysis of glycerides to fatty acids from which further condensation, dehydration and polymerization side reactions could arise. A method for separate determination of the three acidic groups of sulfate, sulfonate and carboxyl by volumetric titration (8) was used with advantage in the work.

Materials and Experimental Procedures

Oils and Esters

Safflower, linseed, peanut and mustard oils were commercial refined products. Kusum oil (*Schleichera trijuga*) was a commercial product alkali-refined in the laboratory. Methyl oleate and linoleate were concentrates with iodine value (IV) 90 and 145 and were obtained by urea adduct isolation from suitable fatty acid mixtures. A *cis,trans* conjugated diene was obtained by partial hydrogenation of α-elaeostearic acid with hydrazine hydrate (9–11). The unreacted triene and the 11 *trans,* 13 *trans* conjugated diene were removed by maleic anhydride adduction in benzene (12) to leave the concentrate of *cis,trans* conjugated diene (by UV, 77% diene and 3% triene conjugation; IR bands at 983 and 948 cm^{-1}). *Trans, trans* conjugated diene was obtained by isomerization of a linoleic acid concentrate in alkaline glycol (13), crystallization at −50 C from acetone of the conjugated diene, and conversion to the *trans,trans* form (IR peak at 960 cm^{-1}) by isomerization in pentane solution using iodine (14) under UV irradiation.

Sulfation Procedure

The fatty material (10 g) was placed in a glass vessel and held at the required temperature by an external cooling bath. Sulfuric acid, usually of 80% strength v/v, was prepared by rough mixing of the acid and ice water, titration against alkali and suitable final adjustment with acid or water. The acid was added dropwise for 30 min to the vigorously-stirred fatty material, and stirred for 2 hr after completing addition. A part of the product was retained for analysis of acidic groups. The remainder was hydrolyzed to replace sulfate with hydroxyl by warming with a saturated aqueous solution of barium chloride acidified with 10% of conc. HCl.

Estimation of Acid Groups (8)

A known weight of the material containing carboxyl, sulfate and sulfonate groups was titrated in a 1:1 solution of ether-95% ethanol with standard alkali to a phenolphthalein end point to give the total acid value. Acidification of the titrated solution with a known volume of 0.5 N HCl and back titration with a standard alkali to thymol blue produced acidity owing to carboxyl alone. Another sample was hydrolyzed with 0.5 N HCl at 60 C for 20 min, and a weighed quantity of the hydrolyzed material, now free of sulfate, was titrated against alkali to produce carboxyl plus sulfonate.

TABLE I

Sulfation-Hydrolysis of Safflower Oil

No.	Acid strength, % (w/w)	Oil: acid ratio (w/w)	Temp C	AV	HV	IV
1	75	5	27	8.6	23	121
2	78	10	0	8.6	36	113
3	78	5	0	8.4	33	114
4	78	5	27	8.9	35	114
5	79	5	0	10.4	36	110
6	79	10	0	32.7	47	110
7	80	5	0	10.5	31	111
8	82	5	0	18.8	47	110

Results and Discussion

Sulfation-Hydrolysis of Safflower Oil

Sulfation of safflower oil (IV 126) was carried out with graded strengths of sulfuric acid from 70–82% w/w at temperatures of 0 C or 27 C followed by hydrolysis of sulfate with acidified barium chloride. Some representative results are shown in Table I. The best sulfations are those in which the AV is low, and the hydroxyl value (HV) developed corresponds to the loss of IV. These occur with 78% and 79% sulfuric acid (Expt. 2 to 5), but proceed only to a limited degree to yield products of HV ca. 35. Higher HVs are shown for experiments 6 and 8 but result from glyceride hydrolysis.

To determine whether the limited sulfation of safflower oil occurs with the oleate or linoleate radical, methyl oleate, methyl linoleate and a 1:1 mixture were each sulfated with five parts of 78% w/w of sulfuric acid and the products were hydrolyzed and analyzed. Both in methyl oleate and the mixture, the ratio of the HV gain to the IV loss was about 2 against a theoretical value of 2.12, whereas in methyl linoleate it was 0.8. Thus the sulfation reaction occurred preferentially with oleate, while in linoleate sulfation, reactions which do not lead to hydroxyl formation occur. Increasing the sulfuric acid strength to 85% w/w only enhanced such side reactions in linoleate.

Sulfation-Hydrolysis of Oleic Rich Oils

Oils rich in oleic acid should give rise to products of high HV. Accordingly three oils were thus sulfated with 79% w/w of mineral acid at various temperatures. The mixed fatty acids from these oils were also sulfated. All these results are shown in Table II.

The three oils were peanut, kusum (*Schleichera trijuga*) and mustard (rape, *Brassica campestris*) which have oleic acid contents of 48%, 45% (also 18% eicosenoic) and 35% (also 7% eicosenoic) respectively. Hydroxyl values of 50–60 were achieved and the mixed acids had slightly higher values than the oils. About 60–70% of the monoenoic acids appeared to be hydroxylated on sulfation and hydrolysis of the mixed fatty acids. By comparison, pure oleic acid on similar treatment produced 80% of hydroxystearic acid. Crystallization of the products from hexane produced 35–40% (on the weight starting material) of hydroxy acids of HV 125, 100 and 147 and mp 77, 76, 79 C respectively from the three oils.

Sulfation-Hydrolysis of Linseed Oil

Use of various strengths of sulfuric acid between 78% and 85% w/w showed that treatment of linseed oil (IV 180) with 5 parts of 80% w/w sulfuric acid at 0 C for 2.5 hr gave the best product of AV 10.5, HV 77 and IV 139. The AV was low and the ratio of HV gain to IV loss was 1.9; when higher strengths of acid were used, this ratio was lowered. Thus reasonably satisfactory hydroxylation of linseed oil via sulfation was possible.

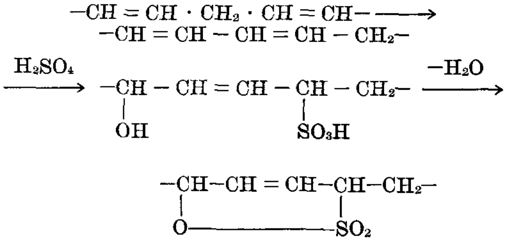
TABLE II

Sulfation-Hydrolysis of Oleic Rich Oils and Their Fatty Acids

Sulfation	Peanut		Kusum	Mustard	
Oils					
IV of starting material	92		68	103	
Conditions					
H_2SO_4, % (w/w)	79	85	79	70	79
Oil-acid ratio (w/w)	3	5	10	10	5
Temp. C	0	Ambient	Ambient	15–20	Ambient
Time, hr	2	2	2	2	2
Analysis of sulfated-hydrolyzed oils					
IV	54	35	38	61	58
HV	46	48	41	56	56
Total AV	15.4	21.3	10.4	12.8	19.4
Carboxyl AV	14.8	19.5	9.9	10.9	18.2
Mixed fatty acids					
IV of starting material	90		65	102	
Conditions					
Common to all, 79% H_2SO_4 (w/w), oil-acid 1:10, ambient temperature, 2 hr					
Analysis of sulfated-hydrolyzed products					
IV	60		30	58	
HV (as esters)	50		58	50	
HV gain/IV loss	1.7		1.4	1.3	
Hydroxy acids obtained by crystallization					
Yield, %	35		30	38	
HV	125		125	147	
mp C (two crystallizations)	77		76	79	

Nature of the Nonsulfation Reactions With Safflower Oil

Safflower oil was sulfated at 0 C with 86% w/w sulfuric acid at a 1:3 w/w ratio and was hydrolyzed to a product of IV 70, HV 56, AV 28 (mostly carboxyl). The product also had 3.2% S, which corresponds to the presence of about 30% of fatty material carrying one sulfur atom. The product after hydrolysis showed distinct new peaks in the IR at 1170, 1360 and 920 cm^{-1} not present before hydrolysis. These are different from IR peaks for sulfate (1235, 1064 cm^{-1}), sulfonate (1050, 1180 cm^{-1}) or vinyl sulfonate. Bellamy (15) attributed absorption at 1155 and 1360 cm^{-1} to compounds of the type $C - \underset{O\quad O}{\underset{/\ \backslash}{S}} - R$; a sultone is of this class. A pure tridecan-1,2-sultone (Henkel and Co., Dusseldorf, West Germany) showed strong peaks at similar wavelengths (920, 1155 doublet, 1180 and 1340 cm^{-1}). A sultone could be formed by dehydration of a hydroxy sulfonate produced by addition of the elements of sulfuric acid to a diene system. Mustafa (16) has pointed out that 1,4- (or δ-) sultones are formed considerably more easily, and are more stable than 1,5-sultones. This would call for induced conjugation of the pentadiene system of linoleate to a conjugated diene system prior to formation of the sultone, perhaps via the hydroxy sulfonate:



$$-CH=CH\cdot CH_2\cdot CH=CH- \longrightarrow -CH=CH-CH=CH-CH_2- \xrightarrow{H_2SO_4} -\underset{OH}{\underset{|}{CH}}-CH=CH-\underset{SO_3H}{\underset{|}{CH}}-CH_2- \xrightarrow{-H_2O} -\underset{O}{\underset{|}{CH}}-CH=CH-\underset{SO_2}{\underset{|}{CH}}-CH_2-$$

Boiling a sultone with potassium hydroxide breaks the ring (17) and should regenerate the conjugated diene system.

An attempt was made to obtain a sultone concentrate by partitioning the mixed acids of the sulfated and hydrolyzed safflower oil (obtained by cold saponification and acidification) between 80% methanol and hexane (18). Analysis for sulfur showed that the sulfur-containing compound passed into both fractions, and this was confirmed by the strong IR absorptions exhibited at 1170 and 1360 $\mathrm{cm^{-1}}$ by both fractions.

Accordingly the total sulfated and hydrolyzed oil was boiled with 2 N aqueous potash solution (17) for 2 hr, the soap acidified and the fatty acids isolated. The aqueous layer contained all the original sulfur when estimated as barium sulfate. The fatty acids showed HV 18, AV 169, % S Nil, and strong diene conjugation at 232 mμ.

Next the sulfation of conjugated dienes themselves were examined. A *cis,trans* conjugated diene, the form most likely to arise from linoleate by double bond shift, was obtained for sulfation as described in the experimental portion. This material on treatment with 86% w/w sulfuric acid gave a sulfonate (IR 780 $\mathrm{cm^{-1}}$) and not a sultone (absence of IR peaks at about 1360, 1170 or 920 $\mathrm{cm^{-1}}$).

A *trans,trans* conjugated diene was next prepared as described earlier. Treatment of this with concentrated sulfuric acid (which was used to exaggerate any effect) and working up yielded a 1,4-sultone (IR 920, 1160 $\mathrm{cm^{-1}}$) (19). The identity was strengthened by refluxing the sultone with ammonium carbonate to yield the sulfonamide (20) (IR 1165 and 1360 $\mathrm{cm^{-1}}$). Thus the *trans,trans* conjugated form is favorably disposed to sultone formation on treatment with sulfuric acid. A *cis,cis* conjugated diene would be sterically less disposed for entry of bulky sulfur-containing groups.

One reason for poor hydroxylation of linoleate in the sulfation-hydrolysis route may thus lie in its susceptibility to mineral acid isomerization. Such shifts in the presence of strong sulfuric acid as a result of a carbonium ion formation are well documented (21–23). The formation of a conjugated diene system (perhaps *trans,trans* in configuration) appears to be immediately followed by the 1,4-addition of the elements of sulfuric acid and dehydration of the resulting hydroxysulfonate to a neutral sultone owing to the mineral acid present. Other reactions may also occur.

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