Structure and Surfactance

Sulfate Salts of Ricinoleo and Its Acetoxy Glycerides

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THE MONO-, di-, and triglycerides of ricinoleic acid present an interesting series, each containing three hydroxyl groups, of which only the monoglyceride has one primary hydroxyl group. Further structural variety can be achieved by blocking the hydroxyl groups in the fatty moiety—e.g., by acetylation. This article presents data on the surfactant properties of the sulfate salts of tri-, di-, and monoricinoleoglycerides; of mono- and diacetoxy oleoglycerides; and of two ricinoleoglyceride mixtures prepared by glycerolysis. Figure 1 pictures the compounds studied. No previous study of this nature has appeared to our knowledge.

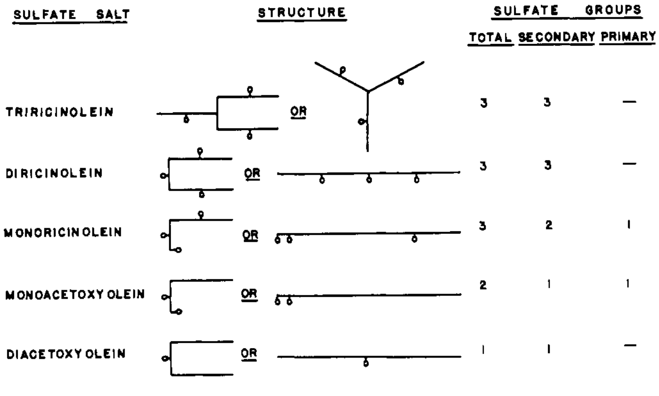

Figure 1. Structure of the products tested

EXPERIMENTAL

Base materials for sulfation were prepared as described below. Calculated or literature characteristics are given in parentheses after the experimental values which were determined by standard methods; for 1-monoglyceride contents, the method of Pohle and Mehlenbacher (5) was used.

Triricinolein. Castor oil was extracted successively with 2.5, 1.5, and 0.5 parts of commercial hexane freed of aromatics by shaking with concentrated sulfuric acid (8), to yield 60% of a residual triricinolein concentrate.

Ricinoleic acid for further synthesis was obtained (8) from triricinolein mixed fatty acids from which dihydroxystearic acid was removed by self-precipitation overnight. A first adduction with urea carried down 19% of a mixture of ricinoleic and nonhydroxy fatty acids, and a second adduction gave 50% of ricinoleic acid of high purity [saponification equivalent 297.2 (298), acetyl value 165.2 (165.0), iodine value 86.0 (85.2), $n^{25}\mathrm{D}$ 1.4705], leaving in solution the remaining 31% of fatty acids.

Diricinolein. Ricinoleic acid was sulfated to block the hydroxyl group, using a 0.25*M* excess of chlorosulfonic acid in the presence of 3 parts of chloroform at room temperature for 5 hours, followed by extraction with light petroleum of unsulfated ricinoleic acid. The sulfated product [% S 8.16 (8.5)] was converted by refluxing in chloroform solution with thionyl chloride to the acid chloride [% S 7.1 (8.1), % Cl 8.9 (8.94)]. One mole of glycerol-1-monochlorohydrin (Eastman Kodak) was mixed with 1 mole of pyridine, and kept ice cold in a stoppered flask. Two moles of the acid chloride in 3 parts of chloroform were added gradually in portions, and the mixture was allowed to stand for 72 hours (2). The ether solution of the product was washed successively with ice-cold 0.5*N* sulfuric acid, and the intermediate was isolated. Dechlorination was achieved by refluxing on a water bath for 1 hour with 200 ml. of 85% ethyl alcohol and an equal amount of solid silver nitrite for 1 hour. After filtration, the diglyceride product was taken in ether, decolorized with charcoal, and isolated. Desulfation was effected by boiling for 2 hours with 1.0*N* sulfuric acid, and free fatty acids were removed by alkali-washing to give the required diricinolein.

Monoricinolein. Isopropylideneglycerol (2,2-dimethyl-1,3-dioxolane-4-methanol) was prepared (4) by condensing glycerol with 6 volumes of acetone containing 1% hydrochloric acid in the presence of 0.4 part of anhydrous sodium sulfate, stirring for 4 hours at room temperature, and allowing to stand for 20 hours. A large excess of finely powered lead carbonate was added in installments to remove hydrogen chloride, the precipitate was filtered, and the filtrate was dried over anhydrous sodium sulfate and freed of acetone on a water bath. Purification by vacuum distillation (80° C. at 4 mm.) gave isopropylideneglycerol ($n^{35}\mathrm{D}$ 1.4295).

To a mixture of 1.1 moles of isopropylideneglycerol and 1.1 moles of pyridine cooled to 0° C. in a stoppered flask was added gradually 1.0 mole of the acid chloride of sulfated ricinoleic acid, and after 30 min. at 0° C. the product was allowed to stand at room temperature for 72 hours. The mixture was taken in ether and washed thoroughly with ice-cold 0.5*N* sulfuric acid several times. The intermediate was isolated ($n^{25}\mathrm{D}$ 1.4615) and hydrolyzed in ether solution with 6 volumes of concentrated hydrochloric acid added slowly while cooling in a cold-water bath. After 30 minutes the ether solution was washed free from mineral acid, and the product was freed from ether. The material was desulfated as described earlier, freed from free fatty acids by washing with 2% sodium bicarbonate solution, and isolated (% 1-monoglyceride 92.3).

Monoacetoxyolein. Ricinoleic acid was refluxed with its own weight of acetic anhydride for 2 hours, the product boiled with water for 30 minutes and repeatedly washed until free of acid. Final purification by vacuum distillation gave 12-acetoxyoleic acid [acid value 163.5 (165.0), I.V. 79.0 (74.6), $n^{35}\mathrm{D}$ 1.4530]. The corresponding acid chloride [% Cl 9.8 (9.84), $n^{35}\mathrm{D}$ 1.4530] was prepared using thionyl chloride, and on condensing this with isopropylideneglycerol as described earlier, monoacetoxyolein was obtained (% 1-monoglyceride 91.9).

Diacetoxyolein. Coupling of glycerol-1-monochlorohydrin with 12-acetoxyoleyl chloride as described earlier gave an intermediate product ($n^{25}\mathrm{D}$ = 1.4627) which on dechlorination with ethyl alcohol and silver nitrite yielded diacetoxyolein.

Ricinolein Mixtures. Several preparations of mono-, di-, and triricinolein mixtures were made by heating either triricinolein or ricinoleic acid with appropriate amounts of glycerol using 0.1% sodium hydroxide as catalyst in a

3-necked flask under stirring with a glycerol seal. Choice of triricinolein or ricinoleic acid as starting material, variations of temperature from 200° to 240° C., and of time of reaction from 3 to 5 hours had little effect on the composition of the final mixture, which was calculated from experimental values for 1-monoglyceride content (5) and from acetyl value. Particular care was taken to remove all glycerol, whose presence would vitiate the calculations, by washing the products in chloroform solution repeatedly with water. Experimental determination (5) by the modified periodic method indicated glycerol contents of less than 0.1%. Two mixtures of mono-, di-, and triricinolein selected for further surfactant studies analyzed as follows:

	Weight %		
	Tri-	Di-	Mono-
Ricinolein mixture I	10.3	48.7	41.0
Ricinolein mixture II	29.6	43.2	27.2

The analytical characteristics of the seven base materials are shown in Table I.

Table I. Raw Materials for Sulfation

	Iodine Value		Acetyl Value		n^{25}_D
	Exptl.	Calcd.	Exptl.	Calcd.	Exptl.
Triricinolein	82.6	81.7	157.2	159.2	1.4779
Diricinolein	76.9	77.9	203.2	216.3	1.4741
Monoricinolein	67.2	68.2	322.1	338.0	1.4728
Diacetoxyolein	70.4	69.0	72.4	76.2	1.4669
Ricinolein mixture I	71.8	...	264.3	...	1.4746
Ricinolein mixture II	77.6	...	243.6	...	1.4757

Sulfation and Neutralization. The seven products were sulfated in 3 parts of chloroform solution using a 0.25M excess of chlorosulfonic acid added dropwise over 1 hour with subsequent stirring for 5 hours. The sulfated products were analyzed for iodine value, acid value, and per cent sulfur trioxide (6) with the results shown in Table II. The sulfated products were neutralized dropwise to the exact value. Aqueous solutions of the products (0.5 to 0.05%) were prepared for testing.

TEST METHODS AND RESULTS

Details of the test procedures used for determination

Table II. Analysis of Sulfated Products

	Iodine Value		Acid Value		% SO_3	
Sulfate From	Exptl.	Calcd.	Exptl.	Calcd.	Exptl.	Calcd.
Triricinolein	57.8	64.9	134.0	130.4	19.1	18.6
Diricinolein	55.9	56.9	169.7	188.7	24.2	26.9
Monoricinolein	49.7	41.5	242.7	274.9	34.6	39.2
Monoacetoxyolein	46.0	44.2	177.4	195.6	25.3	27.9
Diacetoxyolein	47.9	62.1	65.9	68.7	9.4	9.8
Ricinolein mixture I	44.9	...	181.7	...	25.9	...
Ricinolein mixture II	47.4	...	166.9	...	23.8	...

Table III. Surfactant Test Results

				Pour Foam Test of 0.2% Solution				Detersive Efficiency		
Sulfate Soap of	Calcium Tolerance Ca Ions, P.P.M.	Dispersing Power, Absorbance	Surface Tension 0.2% Solution, Dynes/Cm.	Initial ht., mm.	Subsidence after 5 min., %	Emulsification time, for Separation of 10 Ml., Sec.	Wetting Test, Concn. to Give Sinking Time of 25 Sec., %	1st wash ΔR	2nd wash ΔR	Average ΔR
TR	203.4	60	54.2	53	83	305	0.1121	1.0	2.5	1.75
DR	204.9	110	52.2	73	64	315	0.0832	1.4	3.0	2.20
MR	268.5	143	50.6	84	61	352	0.0772	5.0	10.7	7.85
MAO	274.5	182	49.8	124	50	286	0.1496	6.1	12.4	9.25
DAO	Turbid	Turbid	57.7	16	69	248 Oil separation	Very poor	0.7	1.1	0.90
RM I	217.7	235	52.8	76	62	338	0.0799	4.1	8.7	6.40
RM II	210.2	190	53.4	77	52	312	0.0916	2.7	7.0	4.85
LA	345.3	235	35.5	146	7.5	261	0.1251	6.4	12.9	10.2

Table IV. Surfactant Properties of Products Compared to Lauryl Sulfate Taken as 100

				Foaming Power				
Sulfate Salt of	Calcium Tolerance	Dispersing Power	Surface Tension Lowering	Initial height	Persistence	Emulsifying Power	Wetting Ability	Detersive Efficiency
TR	59	25	48	37	13	117	112	18
DR	60	47	54	50	31	121	150	23
MR	78	61	58	57	42	135	162	81
MAO	80	78	60	85	54	110	84	96
DAO	...	Turbid	39	11	33	...	Negligible	9
RM I	63	59	52	52	31	130	157	66
RM II	61	50	50	53	52	120	137	50

of calcium tolerance (by Hart's method), dispersing power (by the carbon black suspension procedure only, not by the Fisher-Dott method), wetting power (Draves-Clarkson), emulsifying power (using liquid paraffin), surface tension (Du Nuoy), detersive efficiency (double-wash technique using Oildag as soil) and foaming properties at room temperature (Ross-Miles) were all described in the earlier article in this series (*7*). The absolute values for these various surfactant tests are shown in Table III. To make comparisons easier, all values were calculated as a percentage of the corresponding value shown by sodium lauryl sulfate taken as 100. These comparative values are shown in Table IV.

DISCUSSION OF RESULTS

The following code is used in discussing the results:

Sodium Salt of Sulfated	Code	Sodium Salt of Sulfated	Code
Triricinolein	TR	Diacetoxyolein	DAO
Diricinolein	DR	Ricinolein mixture I	RM I
Monoricinolein	MR	Ricinolein mixture II	RM II
Monoacetoxyolein	MAO	Lauryl alcohol	LA

DAO with only one sulfate group in a 39-carbon chain was a product of very low solubility. Most properties therefore either could not be determined, such as calcium tolerance, dispersibility (turbid solution) and emulsifying power (instant separation of phases), or had no significance, such as wetting power, detergency (only slightly more than that of pure water), lowering of surface tension, and foaming properties.

Considering now the other products tested, certain surfactant properties were uniformly of a low order. Thus compared to lauryl sulfate the calcium tolerance of the present series was only some 60 to 70%, the dispersibility from 25 to 80%, the lowering of surface tension of a 0.2% solution about 50 to 60%, the foam height about half, and the foam sustenance only a tenth. In these properties, there was a distinct gradation, the products improving in the order TR, DR, MR, and MAO. In fact, the best of the products, MAO, had about 80% of the corresponding ability exhibited by lauryl sulfate, except for foam stability which was very low. The slight but distinct superiority of the sulfates of the two monoglyceride products, MAO and MR, can be attributed to the terminal or primary sulfate group which is carried by only these two products among those tested.

Emulsifying power and wetting ability were of a high order in the present series and ran parallel. The sulfate of MR is outstanding, followed closely by those of DR and TR. All these products contain three hydrophilic groups, but only in MR is one of them primary. The sulfate of MAO, which again carries a terminal hydrophile, though bringing up the rear in regard to these properties, has good emulsifying and wetting ability. Wetting and emulsification are greatly reinforced when more than three, or even two, hydrophiles are present, and at a maximum when one of them is primary. This shows a strong parallel to the superior wetting ability of the disulfate arrived from ricinoleyl alcohol (*7*), which also carries a primary and a secondary hydrophile.

The influence of centrally or terminally situated hydrophiles is very well brought out in the detergent abilities. The products from MR and MAO, carrying primary sulfate groups, have washing abilities approaching that of lauryl sulfate. For all the other products, bearing only secondary hydrophiles, the detersive efficiency is only 10 to 20% of that of lauryl sulfate. This again is closely analogous to the series of compounds containing one or two hydrophiles in different positions studied earlier (*7*), in which the high detersive efficiency of the primary fatty alcohol sulfates was not affected either way by the presence of another sulfate in the chain. Another point deserves mention. The two adjacent hydroxyl groups in both the monoglyceride products MR and MAO are probably not fully sulfated because of steric hindrance, as is supported by the slightly low values in Table II for SO_3 content. They may therefore consist in part of very long-chain fatty alcohol sulfates with properties characteristic of the latter.

The two mixtures RM I and RM II show properties which closely reflect their contents of tri-, di-, and monoricinolein. In fact, the mean surfactant value, calculated on the percentage of each glyceride component present and the experimental values for the latter, are remarkably close to the respective experimental values. From a practical point of view, the actual composition of a ricinolein mixture is of little account in regard to either emulsification or wetting power of the sulfates, which will always be good. Only in regard to detersive ability will a high content of monoglyceride be desirable, since the sulfates of di- and triricinolein have poor washing ability.

Though many of the properties of the present compounds are undoubtedly a result of the corresponding hydrophile-lipophile balance (HLB) by the Atlas system (*1*), these qualities have in this discussion rather been related to the positions of the functional groups present.

The monoglyceride sulfates in general have had limited application in industry. In acid medium, in common with other anionic sulfate surfactants, the hydrophiles are hydrolyzed with loss of surfactant properties, and in alkaline medium, they split at the glyceride linkage to yield ordinary soaps. Hence their main use has been in household detergents, though to a limited extent since the housewife prefers a copious foam. The sulfates from ricinoleins however are likely to function even in alkaline medium, since hydrolysis at the glyceride linkage will give rise to soaps which also carry a central hydrophile; such products are known to be superior wetting agents (*3*).

ACKNOWLEDGMENT

The authors thank S. Husain Zaheer for his interest in this work, which was done during the tenure by V.V.R. Subrahmanyam of a Senior Research Fellowship of the Council of Scientific and Industrial Research, India.

LITERATURE CITED

(1) Atlas Powder Co., "General Characteristics of Atlas Surfactants," p. 3, 1960.
(2) Averill, H.P., Roche, J.N., King, C.G., *J. Am. Chem. Soc.* **51**, 866 (1929).
(3) Bohme, A., Th., Chem. Fabrik, Ger. Patent **597,957** (June 2, 1934).
(4) Fisher, E., Pfahler, E., *Ber.* **53**, 1606 (1920).
(5) Pohle, W.D., Mehlenbacher, V.C., *J. Am. Oil Chemists' Soc.* **27**, 54 (1950).
(6) Rosen, M.J., Goldsmith, H.A., "Systematic Analysis of Surface Active Agents," p. 203, Interscience, New York, 1960.
(7) Subrahmanyam, V.V.R., Achaya, K.T., J. CHEM. ENG. DATA **6**, 38 (1961).
(8) Subrahmanyam, V.V.R., Achaya, K.T., *J. Sci. Ind. Research (India)* **20D**, 45 (1961).

RECEIVED for review December 2, 1960. Accepted March 29, 1961.