sulfate. The solvent was removed under vacuum; 42.3 g. of fatty acids were obtained. Approximately 5 g. of the fatty acids were recrystallized from aqueous alcohol, yield 2.8 g., m.p. 30–34°, and then from petroleum ether (40–60°), m.p. 37–42°. The melting point of the acid did not increase upon repeated crystallization, neutral. equiv. 282.2, conjugated dienoic acids 99.5%. The mother liquor was concentrated, and upon cooling an acid, m.p. 33–34°, was obtained. From the ultraviolet spectrum the presence of conjugated double bonds was indicated; this acid may be the 9,11-octadecadienoic acid reported by Schmidt and Lehmann (4).

In order to isolate 8t,10t-octadecadienoic acid, 10 g. of the fatty acids were dissolved in 30 ml. of petroleum ether (40–60°) and irradiated for 2–3 hrs. with ultraviolet light in the presence of traces of iodine. The solution was cooled and filtered; 5.2 g. of crystals, m.p. 44–48°, were obtained. Upon recrystallization from petroleum ether (40–60°), 3.8 g. of crystals, m.p. 56–56.5°, were obtained. From the infrared spectrum data, the configuration of the double bonds of the acid was indicated as conjugated *trans,trans*-dienoic acid. The presence of conjugated double bonds was further confirmed by ultraviolet spectrum data.

Anal. calc. for $C_{18}H_{32}O_2$: carbon, 77.14%; hydrogen, 11.42%.
Found: carbon, 77.09%; hydrogen, 11.47%.

Oxidation of 8t,10t-Octadecadienoic Acid with Potassium Permanganate in Acetone. One g. of the pure 8t,10t-octadecadienoic acid, m.p. 56–56.5°, was dissolved in dry acetone (25 ml.) in a 100-ml. round-bottomed flask. Approximately 4 g. of the powdered potassium permanganate were added slowly to the contents of the flask, which was cooled whenever necessary during the addition of potassium permanganate. The material in the flask was refluxed on a steam bath for about 2 hrs. The acetone was removed, and cold water was added to the flask. The material was acidified with dilute sulfuric acid, and excess permanganate was decolorized by sodium bisulfite. The contents in the flask were warmed until an almost clear solution was obtained. Upon cooling, the material was extracted with ether, washed with saturated sodium chloride solution, and dried over anhydrous sodium sulfate. The solvent was removed under vacuum, and the residue was extracted with hot water. The water extract was treated with activated charcoal and filtered. Upon cooling, suberic acid crystallized out. It was recrystallized from a mixture of benzene and petroleum ether (40–60°), m.p. 139.5–140°, mixed melting-point with an authentic sample of suberic acid, 139.5–140.5°.

Hydrogenation of 8t,10t-Octadecadienoic Acid. Two-tenths g. of acid was dissolved in 10 ml. of ethyl acetate and hydrogenated in the presence of platinum catalyst. The catalyst was filtered off, and the solvent was removed under vacuum. The residue was recrystallized from ethyl acetate, m.p. 68–69°, mixed melting-point with an authentic sample of stearic acid, m.p. 68–69°.

Summary

Oleic acid was brominated with N-bromosuccinimide, followed by addition of free bromine to the double bond. Upon debromination of the brominated product with zinc in ethanol and fractionation of the resultant ethyl esters, the fractions containing 74–75% of conjugated dienoic acids were combined. The ethyl esters were hydrolyzed; upon irradiation by ultraviolet light of the fatty acids in petroleum ether (40–60°) in the presence of a trace of iodine, and upon cooling, 8t,10t-octadecadienoic acid, m.p. 56–56.5°, was obtained in 15–20% yield.

REFERENCES

1. Smit, W. C., Rec. trav. chim., *49*, 539–551 (1930).
2. von Mikush, J. D., J. Am. Oil Chemists' Soc., *29*, 114–115 (1952).
3. Scheiber, J., German Pat. 513,540 (1930), Brit. Pat. 306,452 (1929).
4. Schmidt, H., and Lehmann, A., Helv. Chim. Acta, *33*, 1494–1502 (1950).
5. Grigor, J., MacInnes, D. M., McLean, J., and Hogg, A. J. P., J. Chem. Soc., 1069–1071 (1955).
6. Sparreboom, S., Koninkl. Ned. Akad. Wetenschapp., Proc. Ser. B, *59*, 472–479 (1956).
7. Ziegler, K., Späeth, A., Schaaf, E., Schumann, W., and Winkelmann, E., Ann., *551*, 80–119 (1942).
8. Rollett, A., Z. Physiol. Chem., *62*, 422–431 (1909).
9. Knight, H. B., Jordan, E. F. Jr., Roe, E. T., and Swern, Daniel, Biochemical Preparations, *2*, 100–104 (1952).

[Received June 26, 1959]

Octadecylsulfuric Acid. Properties of the Acid, Amine Salts, and Salts of Amino Acids[1]

E. W. MAURER, A. J. STIRTON, and J. K. WEIL, Eastern Regional Research Laboratory,[2] Philadelphia, Pennsylvania

IN A CONTINUATION of previous work on tallow alcohol sulfates (9) it became of interest to prepare and isolate long-chain alkylsulfuric acids, in particular, octadecylsulfuric acid. The purpose was to study the stability and properties of the free acid and to make use of the acid in the rapid screening of a variety of salts for detergent and surface-active properties.

Only a few references are known which concern the preparation and description of long-chain alkylsulfuric acids. Dodecylsulfuric acid was prepared by Ross and co-workers (7) as a flaky, hygroscopic, crystalline mass, by sulfation of dodecanol with chlorosulfonic acid by using liquid sulfur dioxide as the solvent. Dodecyl- and hexadecylsulfuric acids were prepared by Desnuelle and co-workers (3) by acidification and extraction of aqueous solutions of the sodium salts. By the use of conditions which minimize or exclude moisture we have found a direct method

[1] Presented at the spring meeting, American Oil Chemists' Society, New Orleans, La., April 20–22, 1959.
[2] Eastern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

for the preparation and isolation of dodecyl-, tetradecyl-, hexadecyl-, and octadecylsulfuric acids in a pure state.

Preparation of Alkylsulfuric Acids

Chlorosulfonic acid was the preferred reagent for the sulfation of the long-chain alcohol and isolation of the alkylsulfuric acid, according to the equation:

$$ROH + ClSO_3H \longrightarrow ROSO_3H + HCl, \text{ where R is } C_{12}H_{25},\ C_{14}H_{29},\ C_{16}H_{33}, \text{ or } C_{18}H_{37}$$

Chloroform was found to be the best solvent in preference to carbon tetrachloride or tetrachloroethylene. Solvent ratios ranged from 3–5 cc. chloroform/g. of alcohol with higher ratios for the higher homologs. The purified alcohols prepared from good commercial grades by vacuum distillation and low-temperature crystallization methods had the following constants: n-dodecanol, f.p. 24.1°, $n^{25/D}$ 1.4410; n-tetradecanol, m.p. 37.2–38.0°, $n^{60/D}$ 1.4318; n-hexadecanol, m.p. 49.3–49.6°, $n^{60/D}$ 1.4359; n-octadecanol, m.p. 58.1–58.6°, $n^{60/D}$ 1.4380.

Chlorosulfonic acid in 8% excess was added dropwise to a dispersion or solution of 0.2 mole of the long-chain alcohol in chloroform with rapid stirring. The mixture was gradually warmed to 25–30°, cooled to 0°, allowed to crystallize, and filtered at 0° under low humidity conditions. Because of greater solubility, dodecyl- and tetradecylsulfuric acids were crystallized at −20°, then filtered at 0°. Figure 1 illustrates the filtration process, outlined as follows.

a) A synthetic filter medium of polyethylene was used to insure rapid filtration. Filtration was slow when filter paper was used, apparently because parchment was formed in the presence of the sulfating agent.

b) A layer of inert vinyl sheeting, such as Dow Saran Wrap, was loosely placed over the top of the Buchner funnel to separate the product from the rubber dam used to exclude moisture. Direct contact with rubber stains the product and deteriorates the rubber.

c) Filtration at 0° was accomplished in a refrigerated room to maintain low humidity conditions. Octadecylsulfuric acid has the highest melting point, is the least soluble, is the least hygroscopic, and may be filtered at room temperature, excluding moisture (Figure 1).

d) Solvent removal was completed in a vacuum desiccator in the refrigerated room at 0°. Change of the desiccant, $CaSO_4$, every two hours shortened the time by 50% and allowed complete solvent removal in 6–8 hrs.

Table I lists the analysis, melting point, yield, and purity. The alkylsulfuric acids are white crystalline solids, the hygroscopic nature of which increases with decreasing chain length. The relative purity of the acids shown by analysis and melting point was confirmed by conversion to the sodium alkyl sulfate and analysis for sodium. The yields obtained reflect the solubility of the acids under the particular conditions of solvent ratio and crystallization temperature.

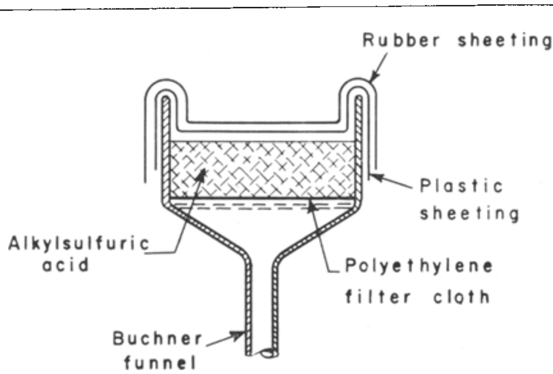

FIG. 1. Filtration technique for isolation of alkylsulfuric acids.

TABLE I
Alkylsulfuric Acids

Alkyl	Analysis			
	N.E.[a]		% S	
	Found	Calcd.	Found	Calcd.
Dodecyl	260	266	11.63	12.04
Tetradecyl	296	294	10.88	10.89
Hexadecyl	326	323	9.72	9.94
Octadecyl	354	351	9.14	9.15
	Melting point	Yield %	Purity[b] %	M. P. alcohol
Dodecyl	25–7°	65	97	24.1[c]
Tetradecyl	37–9°	75	98	37.2–38.0
Hexadecyl	40–2°	53	99+	49.3–49.6
Octadecyl	51–2°	65	99+	58.1–58.6

[a] Neutralization equivalent.
[b] Purity by conversion to the sodium alkyl sulfate and analysis for Na.
[c] Freezing point.

Stability on Storage

The four alkylsulfuric acids were stored in screw-cap bottles at 0° and were analyzed periodically. Dodecylsulfuric acid was the most difficult to prepare in a pure state and appeared to decompose or hydrolyze to the extent of about 15% in one week, judged by a decrease in the neutralization equivalent. The other three acids showed no significant change after storage for several months at 0°. Storage of octadecylsulfuric in a screw-cap bottle for one year at room temperature, with periodic analysis, showed an increase of 18 units in the neutralization equivalent corresponding to a moisture pick-up of 3–5%. This acquisition of water is not to be confused with hydrolysis.

Stability to Hydrolysis

Hydrolysis of a 0.05 molar solution of octadecylsulfuric acid in distilled water at 100° was 50% in less than half an hour, about equal to that for sodium octadecyl sulfate acidified with an equivalent amount of mineral acid. However at 60° (a frequently selected washing temperature) the degree of hydrolysis was only 10% after 3 hrs. and 16% after 7 hrs. These kinetic data do not fit conventional rate expressions, probably because micellization occurs with a decrease in the concentration of simple ions and molecules. Conductance and pH measurements, including measurements at both above and below the critical micelle concentration, indicate that octadecylsulfuric acid is about 50% ionized over a considerable concentration range. The c.m.c. by the dye titration method (2) is 0.0014%, or 0.0387 millimoles/l., about one-third of the value for sodium octadecyl sulfate.

Salts of Octadecylsulfuric Acid

The usual method for the preparation of salts is by neutralization of the sulfation mixture with the selected base. Salts of amines and amino acids however can be obtained in much better yield and purity in less time from the isolated octadecylsulfuric acid, which is conveniently soluble in water, alcohol, or chlorinated solvents.

The general procedure was to form the salt in solution, using about 10% excess of the amine or amino acid and to crystallize from the solution at 0°. Carbon tetrachloride was a suitable solvent for the preparation of the triethylammonium (m.p. 70–72.5°) and the triethanolammonium salt (m.p. 86–86.8°). The salt with tris(hydroxymethyl)aminomethane (m.p. 124–7°) and the glycine salt were prepared in 95% ethanol. Salts with *DL*-leucine and *L*-methionine were prepared by adding the solid amino acid to a solution of octadecylsulfuric acid in absolute ethanol. In the case of the last four salts of Table II, excess of the amine and amino acid was removed by filtration at room temperature prior to crystallization. Melting points of the amino acid salts were indefinite.

TABLE II
Salts of Octadecylsulfuric Acid

Salt of amine or amino acid	Yield %	Analysis			
		% N		% S	
		Found	Calcd.	Found	Calcd.
Triethylamine	66	2.98	3.10	6.90	7.09
Triethanolamine	73	2.78	2.80	6.56	6.42
THAM[a]	50	2.94	2.97	6.72	6.79
Glycine	80	3.33	3.29	7.01	7.53
DL-Leucine	51	3.14	2.91	6.78	6.66
L-Methionine	65	2.78	2.80	12.97	12.83

[a] Tris(hydroxymethyl)aminomethane $(HOCH_2)_3CNH_2$.

Table II lists the yield and analysis for six salts, all of which are white crystalline solids more soluble than sodium octadecyl sulfate in water. Triethanolammonium octadecyl sulfate, in particular, has a solubility of about 10% at room temperature.

Surface-Active Properties

Table III lists the interfacial tension, emulsion stability, foam height, wetting time, and detergency values for octadecylsulfuric acid and salts with amines and amino acids. Values for sodium octadecyl sulfate are included for comparison.

Surface and Interfacial Tension. The duNoüy tensiometer was used. Surface tension ranged from 36.1 for the leucine salt to 41.6 for octadecylsulfuric acid; the value for sodium octadecyl sulfate was 40.6 dynes/cm. Interfacial tension was measured against refined mineral oil. Salts of the amino acids had the lowest values.

Emulsion Stability. Emulsions were prepared from light petrolatum and an aqueous solution of the surface-active agent (1, 9). The time in seconds required for partial separation was a measure of emulsion stability. Octadecylsulfuric acid and the salts with glycine and *DL*-leucine appear to be very good emulsifying agents.

Foam Height and Wetting Time. Foam height was measured by the Ross-Miles pour test (6) at 60°. The range 180–210 seconds showed comparatively little difference in foaming properties for the eight compounds. Wetting properties were measured by a standard binding tape method (8). At 60° octadecylsulfuric acid was the best wetting agent. Wetting time for the various salts ranged only from 18–26 seconds.

TABLE III
Surface-Active Properties. 0.1% Solution in Distilled Water

Compound	Interfacial tension 25°	Emulsion stability (1) 25°	Foam[a] height (6) 60°	Wetting time (8) 60°	Detergency[a] 60°
	dynes/cm.	*seconds*	*mm.*	*seconds*	ΔR
Octadecylsulfuric acid	10.4	1190	195	11	40.2
Triethylamine salt	7.0	690	190	21	13.8
Triethanolammonium salt	7.0	730	190	20	19.0
THAM[b] salt	9.1	730	205	23	29.7
Glycine salt	6.5	1050	210	19	39.7
DL-Leucine salt	4.3	1170	180	26	9.9
L-Methionine salt	5.9	840	200	20	13.4
Sodium octadecyl sulfate	14.2[c]	760[d]	210	18	41.3

[a] Salts were formed directly in aqueous solution.
[b] Tris(hydroxymethyl)aminomethane $(HOCH_2)_3CNH_2$.
[c] Not in complete solution at 25°.
[d] Measured at 50° because of limited solubility.

Detergency. Detergency was measured as the increase in reflectance $\triangle R$ after washing G.D.C. No. 26 (4) standard soiled cotton in the Terg-O-Tometer: 10 swatches/l., 20 min. 60°, 110 cycles/min. By analysis of variance a difference in $\triangle R$ of 1.8 was significant with 95% probability (5).

The salts used were prepared directly in aqueous solution by adding equivalent amounts of acid and base to hot distilled water. In addition to the compounds listed in Table III, detergency values were also obtained for salts of the following amines and amino acids: iminodiacetic acid (40.5), *DL*-alanine (34.3), ethanolamine (33.3), N-methylglucamine (32.4), diethanolamine (30.5), and isopropanolamine (17.0). Octadecylsulfuric acid and salts with iminodiacetic acid and glycine were about equal to sodium octadecyl sulfate in detergency. *DL*-Alanine, ethanolamine, N-methylglucamine, diethanolamine, and tris(hydroxymethyl)aminomethane salts were somewhat less effective, and the remaining salts were relatively poor detergents. Under these test conditions detergency decreased with an increasing degree of substitution at the nitrogen atom but increased with a greater content of hydrophilic hydroxyl or carboxylic acid groups.

Summary

Octadecanol, hexadecanol, tetradecanol, and dodecanol were sulfated with chlorosulfonic acid, and the corresponding alkylsulfuric acids were isolated in a pure state as white crystalline solids with definite melting points.

Octadecylsulfuric acid resembles sodium octadecyl sulfate in detergent and surface-active properties and in stability to hydrolysis at equal concentrations of hydrogen ion. It is more soluble in water than sodium octadecyl sulfate and readily soluble in organic solvents. The critical micelle concentration (0.0387 millimoles/l.) is only about one-third that of the sodium salt.

Isolation of octadecylsulfuric acid as a useful chemical intermediate made possible the preparation of a number of salts with amines and amino acids and their rapid screening for useful properties.

Acknowledgment

Microanalyses for nitrogen and sulfur were performed by Mrs. Ruth B. Kelly and Miss Laverne Scroggins.

REFERENCES

1. Briggs, T. R., J. Phys. Chem., *24*, 120–126 (1920); Martin, A. R., and Hermann, R. N., Trans. Faraday Soc., *37*, 25–29 (1941).
2. Corrin, M. L., Klevens, H. B., and Harkins, W. D., J. Chem. Phys., *14*, 480–486 (1946).
3. Desnuelle, P., Massoni, R., and Benoit-Micaelli, O., Bull. soc. chim., France *1953*, 595–599.
4. Draves, C. Z., and Sherburne, O. L., Am. Dyestuff Reptr., *39*, 771–772 (1950).
5. LeClerg, E. L., "Mean Separation by the Functional Analysis of Variance and Multiple Comparisons," U. S. Agricultural Research Service, ARS-20-3, 33 pp. (1957).
6. Ross, J., and Miles, G. D., Oil and Soap, *18*, 99–102 (1941).
7. Ross, J., Percy, J. H., Brandt, R. L., Gebhart, A. I., Mitchell, J. E., and Yolles, S., Ind. Eng. Chem., *34*, 924–926 (1942).
8. Shapiro, L., Am. Dyestuff Reptr., *39*, 38–45, 62 (1950).
9. Weil, J. K., Stirton, A. J., Bistline, R. G. Jr., and Maurer, E., W. J. Am. Oil Chemists' Soc., *36*, 241–244 (1959).

[Received June 29, 1959]