The a-Sulfonation of Pelargonic, Stearic, and Substituted Stearic Acids[1]

J. K. WEIL, A. J. STIRTON, R. G. BISTLINE JR., and WALDO C. AULT,
Eastern Regional Research Laboratory,[2] Philadelphia, Pennsylvania

Direct sulfonation of higher fatty acids with sulfur trioxide or chlorosulfonic acid, without use of solvent, is possible, but the product must then be isolated as the sodium salt. Use of a chlorinated solvent permits isolation of the α-sulfo acid. Sulfonation with dioxane sulfur trioxide in place of sulfur trioxide gave a nearly colorless α-sulfostearic acid.

Substituted stearic acids derived from oleic or elaidic acids (phenyl-, 9,10-dichloro-, and 9,10-dihydroxystearic acids) were α-sulfonated with dioxane sulfur trioxide. Solubility, detergent, and surface-active properties were examined and related to structure.

The surface-active properties of sodium α-sulfopelargonic acid are not very evident, but the octyl ester, with a much lower critical micelle concentration (0.08% compared to 1.00%), was found to be a very efficient wetting agent.

METHODS FOR THE α-SULFONATION of the higher saturated acids include the use of sulfur trioxide vapor (7), stabilized liquid sulfur trioxide (17), or chlorosulfonic acid (2,8,9). These methods have seldom been directly compared. Other methods of possible application to the higher saturated acids are the reaction of the fatty acid anhydride with either 100% sulfuric acid or pyrosulfuric acid, demonstrated with propionic acid anhydride (1), and the use of dioxane sulfur trioxide, shown to give α-sulfonation rather than ring sulfonation of certain ω-phenylalkanoic acids (16).

The present report is a comparison of laboratory methods for the α-sulfonation of pelargonic, stearic, and certain substituted stearic acids derived from oleic or elaidic acids (phenyl-, 9,10-dichloro-, and 9,10-dihydroxystearic acids). Surface-active and related properties of the sulfonated products were examined as part of a general program to relate structure with useful properties.

Sulfonating Agents and Methods for α-Sulfonation

Sulfur Trioxide. The direct sulfonation of saturated fatty acids, from lauric to behenic, with liquid sulfur trioxide, has been described in detail elsewhere (17). Nearly quantitative yields of the isolated α-sulfo acid are possible by the drop-by-drop addition of stabilized liquid sulfur trioxide in 1.5 to 1.7 molar ratio to the fatty acid dispersed or dissolved in chloroform, carbon tetrachloride, or tetrachloroethylene. The temperature is controlled so that it reaches 60–65°C. in the final stage. Somewhat lighter-colored products may be obtained by the use of sulfur trioxide vapor, distilled from liquid sulfur trioxide and mixed with nitrogen.

Direct sulfonation of higher fatty acids with sulfur trioxide is possible without the use of solvent. However the dark reaction mixture and difficulties in filtration require that the product be isolated as the sodium or potassium salt or an easily purified derivative rather than as the free α-sulfo acid $RCH(SO_3H)\text{-}CO_2H$.

Chlorosulfonic Acid. Chlorosulfonic acid may be used in about the same way as liquid sulfur trioxide.

Very little reaction of chlorosulfonic acid with stearic acid takes place below 50°C., and a final temperature of 70° is required for nearly quantitative sulfonation. In contrast, liquid sulfur trioxide accomplishes 30% sulfonation in 30 min. at room temperature, and reaction is completed as the temperature is increased to 60°. Because of the higher reaction temperature required there is no improvement in color by the use of chlorosulfonic acid.

As with sulfur trioxide, direct sulfonation without solvent is possible by the use of chlorosulfonic acid, but the product must be isolated as the salt or an easily purified derivative.

Dioxane Sulfur Trioxide. Reaction of dioxane sulfur trioxide rather than sulfur trioxide with palmitic or stearic acid, in carbon tetrachloride, was found to result in color improvement and the isolation of a white or cream-colored α-sulfo acid. Dioxane sulfur trioxide was selected to accomplish the α-sulfonation of 9,10-dichlorostearic, 9,10-dihydroxystearic, and phenylstearic acids so as to avoid decomposition and ring sulfonation. The products were isolated as sodium salts.

Other Methods. Dioxane sulfur trioxide and many other sulfur trioxide adducts are useful in the sulfation of oleyl alcohol without reaction at the double bond (19). However attempts to use sulfamic acid, pyridine sulfur trioxide, or a complex of urea with chlorosulfonic acid in the α-sulfonation of the higher fatty acids were unsuccessful.

Methods (10) for the α-sulfonation of amides, anhydrides, and esters of the higher fatty acids were explored to some extent. In our experience the reaction of these compounds with sulfur trioxide in the presence of a chlorinated solvent was accompanied by varying degrees of hydrolysis and resulted in products difficult to purify. When the method for the α-sulfonation of propionic acid anhydride with 100% sulfuric acid (1) was applied to stearic acid anhydride, no reaction occurred.

Sodium α-Sulfopelargonic Acid and the Octyl Ester

Pelargonic acid may be sulfonated with or without solvent, as shown in the following examples.

Sodium α-Sulfopelargonic Acid. Pelargonic acid was sulfonated with liquid sulfur trioxide, with carbon tetrachloride as the solvent, as described for the higher homologs (17), and isolated as the pure monosodium salt $C_7H_{15}CH(SO_3Na)CO_2H$, yield 60%. Analysis: calculated for $C_9H_{17}NaO_5S$, N.E. 260.3, 8.84% Na, 12.32% S; found, N.E. 260.3, 8.78% Na, 12.22% S.

α-Sulfonation Without Use of Solvent. Sulfur trioxide, 0.2 mole, was distilled from stabilized liquid sulfur trioxide, and the vapor mixed with nitrogen was carried across the surface of the stirred liquid acid (0.13 moles pelargonic acid) and drawn into solution by the vortex. Rate of distillation was con-

---

[1] Presented at the fall meeting, American Oil Chemists' Society, New York, N. Y., October 17–19, 1960.

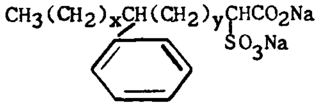
[2] Eastern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

trolled so that the reaction temperature did not exceed 75°C. at the final stage. After completion 100 ml. of water were added at room temperature, the stirred mixture was cooled to 5°, most of the unreacted pelargonic acid was removed by filtration, and the monosodium salt was precipitated with aqueous sodium chloride as a light gray solid, yield 47%. Analysis: found, N. E. 260.4, 8.68% Na. Sodium α-sulfopalmitic acid was obtained in a similar manner by leading the vapors of sulfur trioxide, mixed with nitrogen, over molten palmitic acid.

Sodium Octyl α-Sulfopelargonate. The pure monosodium salt was esterified by the method described for sodium alkyl α-sulfopalmitates and stearates (15). A stirred mixture of 25 g. of sodium α-sulfopelargonic acid, 200 ml. of octanol-1, 50 ml. of toluene, and 2 ml. of concentrated sulfuric acid was refluxed seven hours with azeotropic removal of water. Sodium octyl α-sulfopelargonate $C_7H_{15}CH(SO_3Na)CO_2C_8H_{17}$, yield 89%, did not melt below 250° and, like the higher homologs, was too resistant to alkaline hydrolysis for analysis by means of the saponification equivalent. Analysis: calculated for $C_{17}H_{33}NaO_5S$, 6.17% Na, 8.61% S; found 6.35% Na, 8.62% S.

Sodium Salts of Chain-Substituted α-Sulfostearic Acids

Disodium α-Sulfophenylstearate. A dioxane sulfur trioxide complex was prepared by the addition of 24.0 g. (0.30 mole) of stabilized liquid sulfur trioxide to a cold stirred solution of 33.5 g. (0.38 mole) of dioxane in 300 ml. of carbon tetrachloride. Phenylstearic acid (76.5 g., 0.212 mole), prepared from purified oleic acid (14), was added, and the reaction mixture was stirred and heated to 60°C. for 1 hr. Dilution of the sulfonation mixture with 95% ethanol, neutralization with 18 N NaOH, filtration, and recrystallization from water gave disodium α-sulfophenylstearate,



(where x + y = 14) in a yield of 57%. Analysis: calculated for $C_{24}H_{38}Na_2O_5S$, 9.49% Na, 6.62% S; found, 9.44% Na, 6.50% S. Structure was confirmed by the absence of an absorption peak at 225 mμ characteristic of ring-sulfonated products, such as the disodium p-sulfophenylstearate (13) used for comparison. α-Sulfonation rather than ring sulfonation was further shown by the identification of benzoic acid rather than p-sulfobenzoic acid as the product from alkaline permanganate oxidation.

Sodium α-Sulfophenylstearic Acid. The disodium salt was converted to the monosodium salt by solution in hot aqueous ethanol, acidification with excess hydrochloric acid, filtration of the crystallized product, and extraction with boiling acetone. Analysis: calculated for $C_{24}H_{39}NaO_5S$, N. E. 462.6, 4.97% Na, 6.93% S; found, N. E. 463.4, 5.08% Na, 7.04% S.

Disodium 9,10-Dichloro-α-Sulfostearate.[3] Additive low-temperature chlorination of elaidic acid gave a chloroform solution of 0.13 mole of the 9,10-dichlorostearic acid, which, without isolation of the dichloro acid, was added to a previously-prepared slurry of 0.26 mole of the dioxane sulfur trioxide complex in carbon tetrachloride. The sulfonation mixture was heated 30 min. at 60°C., diluted with an equal volume of 95% ethanol and neutralized with 18 N sodium hydroxide. The precipitate was crystallized from aqueous alcohol, decolorized with carbon, and crystallized from water to give disodium 9,10-dichloro-α-sulfostearate, $CH_3(CH_2)_7CHClCHCl(CH_2)_6CH(SO_3Na)CO_2Na$, as a white solid, yield 57%. Analysis: calculated for $C_{18}H_{32}Cl_2Na_2O_5S$, 14.85% Cl, 9.63% Na, 6.72% S; found, 15.13% Cl, 9.48% Na, 6.73% S.

Sodium 9,10-Dichloro-α-Sulfostearic Acid. Stabilized liquid sulfur trioxide was distilled, and the vapor mixed with nitrogen was passed into a carbon tetrachloride solution of 9,10-dichlorostearic acid (from elaidic acid). The general procedure was similar to that with liquid sulfur trioxide. The sulfonation product was first isolated as a brown disodium salt, yield 35% after two crystallizations from aqueous ethanol. A further crystallization of the disodium salt, conversion to the monosodium salt with excess hydrochloric acid, decolorization with carbon, and crystallization from 95% ethanol gave a nearly white product in a yield of 14%. Analysis: calculated for $C_{18}H_{33}Cl_2NaO_5S$, N. E. 455.4, 15.57% Cl, 5.05%Na, 7.04% S; found N. E. 461.6, 16.05% Cl, 5.17% Na, 7.21% S. Because of the number of purification steps and low yield of the final product, the monosodium salt, like the disodium salt, is best prepared by means of dioxane sulfur trioxide.

The mono- and disodium salts of α-sulfonated 9,10-dichlorostearic acid (from oleic acid) were prepared, but in a less pure state, and are not listed in Table I.

Disodium 9,10-Dihydroxy-α-Sulfostearate. The general procedure was the same with either the high- or the low-melting form of 9,10-dihydroxystearic acid. A mixture of 0.04 mole of the dihydroxy acid and 0.20 mole of the dioxane sulfur trioxide complex in 100 ml. of chloroform was heated to 60° for 1 hr., 100 ml. of water were added, chloroform was distilled, and the aqueous solution was refluxed 4 hrs. to hydrolyze secondary alcohol sulfates. The solution was cooled to 0°, insoluble unsulfonated dihydroxy acid was removed, the filtrate was neutralized and extracted with butanol. Evaporation of the butanol extract gave the disodium 9,10-dihydroxy-α-sulfostearate, $CH_3(CH_2)_7CHOHCHOH(CH_2)_6CH(SO_3Na)CO_2Na$, as a nearly white product in a yield of about 66%. Analysis: calculated for $C_{18}H_{34}Na_2O_7S$, 10.44% Na, 7.28% S; found, 10.11% Na, 10.09%Na, 7.33% S, 7.00% S, for the low- and high-melting forms, respectively. Isolation of the monosodium salt was difficult because of ester or estolide formation when the alcoholic solution of the disodium salt was acidified with excess hydrochloric acid.

Surface-Active and Related Properties

The solubility, surface tension, wetting, detergent and foaming properties, resistance to hard water, and critical micelle concentration (c.m.c.) of the several α-sulfofatty acid derivatives are compared in Table I.

Krafft Point and Solubility. Comparative aqueous solubility was conveniently expressed by the Krafft point, the temperature at which a 1% turbid dispersion became a clear solution on gradual heating (4). Since the solubility of disodium α-sulfomyristate and disodium α-sulfopalmitate is 1% at 10° and 50°, re-

---

[3] May be named as 2-sulfo-9,10-dichlorooctadecanoic acid, 1,2-di-sodium salt.

TABLE I

Surface-active and related properties

α-Sulfofatty acid derivative	Krafft point,[a] 1%	Surface tension, 0.2%, dynes/cm.	Wetting time (12), 0.1%, seconds	Foam height (11), 60°, 0.25%, 300 p.p.m. mm.	Detergency 60° ΔR[b]		Calcium stability (20) p.p.m. $CaCO_3$	Critical micelle concentration,[c] %
					0.1% 80 p.p.m.	0.25% 300 p.p.m.		
Sodium-α-sulfopelargonic acid	clear at 0°	34.0	>600	5	4	3	>1800	1.00
Sodium octyl α-sulfopelargonate	16°	25.8	instantaneous	185	16	12	420	0.08
Sodium α-sulfostearic acid	95°+	.....[d]	....[d]	....[d]	33	27	....[d]	0.005[e]
Disodium α-sulfostearate	92°	.....[d]	...[d]	....[d]	35	37	...[d]	0.10[e]
Sodium α-sulfophenylstearic acid	clear at 0°	36.7	45	160	43	28	455	0.005
Disodium α-sulfophenylstearate	35°	39.8	48	210	43	41	350	0.056
Sodium 9,10-dichloro-α-sulfostearic acid[f]	46°	.....[d]	....[d]	215	33	23	....[d]	0.017
Disodium 9,10-dichloro-α-sulfostearate[f]	29°	34.7	29	230	20	28	340	0.15
Disodium 9,10-dihydroxy-α-sulfostearate(LM)[g]	clear at 0°	31.4	>600	170	3	10	115	0.59
Disodium 9,10-dihydroxy-α-sulfostearate (HM)[h]	clear at 0°	37.3	>600	200	5	8	>1800	0.38

[a] Temperature at which a 1% turbid dispersion became a clear solution on gradual heating (4).
[b] Launder-Ometer, 1 swatch of standard soiled cotton/100 ml./jar, 30 steel balls, 2 replicates; ΔR = increase in reflectance after washing.
[c] Pinacyanole chloride method (3).
[d] Not adequately soluble for the particular test conditions.
[e] c.m.c. from solubility measurements (18).
[f] From elaidic acid.

spectively (15), the effect of chain substitution in the salts of α-sulfostearic acid is to increase solubility and approach or exceed the solubility of the homolog of four less carbon atoms.

Tests for solubility in organic solvents showed that only sodium octyl α-sulfopelargonate is soluble, to the extent of about 5% at 25°, in benzene, butanol, chloroform, and petroleum ether.

Surface Tension. The surface tension of 0.2% solutions was measured by the duNoüy tensiometer at room temperature. Sodium octyl α-sulfopelargonate has the lowest surface tension.

Wetting Properties. The wetting properties of 0.1% solutions at room temperature were measured by the tape method (12), using a 1-g. hook and 40-g. anchor and are recorded in Table I. Sodium α-sulfopelargonic acid and the disodium 9,10-dihydroxy-α-sulfostearates had practically no wetting properties under these conditions. Sodium octyl α-sulfopelargonate, with the hydrophilic group in the middle of the chain, proved to be a very effective wetting agent, as is further shown by comparison with other surface-active agents in Table II. Both the tape method and the Draves test (5) with a standard cotton skein were used.

The superior wetting properties of sodium octyl α-sulfopelargonate will encourage our further investigation of α-sulfo esters to relate structure with useful properties.

Detergency. Detergency was measured as the increase in reflectance after washing G.D.C. No. 26 (6) standard soiled cotton in solutions of indicated concentration and water hardness in the Launder-Ometer at 60°. The best detergents in soft water (0.1%, 80 p.p.m.) were the mono- and disodium salts of α-sulfophenylstearic acid, the mono- and disodium salts of α-sulfostearic acid, and the monosodium salt of α-sulfo-9,10-dichlorostearic acid. In hard water (0.25%, 300 p.p.m.) detergency of the monosodium salts decreased, and the best detergents were disodium α-sulfophenylstearate and disodium α-sulfostearate.

Foaming Properties. Foam height was measured by the Ross-Miles test (11) on 0.25% solutions in hard water at 60°C. Except for sodium α-sulfopelargonic acid, all compounds easily soluble at 60° gave good stable foams.

Calcium Stability. The calcium stability (20) was measured on 0.5% solutions at 25°. Most of the more soluble compounds have adequate calcium stability, but there is a very surprising difference between the dihydroxy compounds made from the low- and high-melting forms of 9,10-dihydroxystearic acid. However both dihydroxy compounds gave about equally clear solutions at 0.25% concentration in hard water of 300 p.p.m. at 25°.

Critical Micelle Concentration and Summary of Properties. Critical micelle concentrations were determined by visual observation of the color change from blue to purple as the dye-surfactant solution, 10^{-5} molar with respect to pinacyanol chloride, was diluted with the dye solution of the same concentration (3). Sodium α-sulfopelargonic acid has the highest c.m.c. (1.00%) and, since wetting, foaming, and detergent properties were measured at much lower concentrations (0.1% and 0.25%), shows the least evidence of surface-active properties. The octyl ester however, with a much lower c.m.c. (0.08%), is a very effective wetting agent with fairly good foaming properties.

Compared to the sodium salts of α-sulfostearic acid, substitution of phenyl or two adjacent chloro-

TABLE II

Wetting Properties of Sodium Octyl α-Sulfopelargonate

Wetting time in seconds at 25°, concentrations in distilled water 0.01, 0.025, 0.05, and 0.10%, by (A) standard binding tape method (12), 1-g. hook, 40-g. anchor, and (B) standard cotton skein method (5), 3-g. hook, 40-g. anchor

Wetting Agent	0.01%		0.025%		0.05%		0.10%	
	A	B	A	B	A	B	A	B
Sodium octyl α-sulfopelargonate	75	>300	17.6	15.4	4.1	5.0	instantaneous	1.4
Sodium di(2-ethylhexyl) sulfo-succinate	190	>300	29.4	20.1	9.9	6.3	2.6	1.9
Sodium dodecyl sulfate	>300	>300	>300	>300	63.7	39.9	15.9	7.5
Sodium dodecylbenzenesulfonate (40% active ingredient)	>300	>300	200	>300	69.0	>300	27.7	27.2

or hydroxy-groups in the chain increased solubility. Phenylstearic acid is a mixture of several position isomers, and perhaps partly for this reason the salts of α-sulfophenylstearic acid show increased solubility. Substitution of the phenyl group in the hydrophobic chain did not effect much change in c.m.c. Disodium α-sulfophenylstearate has good detergent and foaming properties in hard water.

The substitution of two chlorine atoms increased both solubility and c.m.c. In Table I disodium 9,10-dichloro-α-sulfostearate has the best foaming properties.

Substitution of two hydrophilic hydroxyl groups in the hydrophobic chain markedly increased solubility and c.m.c. Wetting and detergent properties were poor, but foaming properties were moderately good although all three properties were measured at concentrations below the c.m.c.

Acknowledgment

Microanalyses for chlorine and sulfur were performed by Miss Laverne Scroggins.

REFERENCES

1. Backer, H. J., and Dubsky, J. V., Rec. trav. chim., *39*, 694–698 (1920).
2. Bert, L., Procofieff, M., and Blinoff, V., (Societe d'Innovations Chimiques), U. S. 2,420,968 (1949).
3. Corrin, M. L., Klevens, H. B., and Harkins, W. D., J. Chem. Phys., *14*, 480–486 (1946).
4. Démarcq, M., and Dervichian, D., Bull. soc. chim., *12*, 939–945 (1945).
5. Draves, C. Z., Am. Dyestuff Reptr., *28*, 425–428 (1939). See also A.A.T.C.C. Tech. Manual and Yearbook, 1957, pp. 154–155.
6. Draves, C. Z., and Sherburne, O. L., Am. Dyestuff Reptr., *39*, 771–772, (1950).
7. Günther, F., (1932), P.B. 30081, Office of Technical Services, U. S. Department of Commerce.
8. Günther, F., and Hetzer, J., (I.G.), U. S. 1,926,442 (1933).
9. Hemelian, W., Ann., *176*, 1–12 (1875).
10. Moyer, W. W., (Solvay Process Company), U. S. 2,195,186; 2,195,187; 2,195,188 (1940).
11. Ross, J., and Miles, G. D., Oil and Soap, *18*, 99–102 (1941).
12. Shapiro, L., Am. Dyestuff Reptr., *39*, 38–45, 62 (1950).
13. Stirton, A. J., Peterson, R. F., and Groggins, P. H., Ind. Eng. Chem., *32*, 1136–1137 (1940).
14. Stirton, A. J., Schaeffer, B. B., Stawitzke, Anna A., Weil, J. K., and Ault, W. C., J. Am. Oil Chemists' Soc., *25*, 365–368 (1948).
15. Stirton, A. J., Weil, J. K., and Bistline, R. G. Jr., J. Am. Oil Chemists' Soc., *31*, 13–16 (1954).
16. Truce, W. E., and Olson, C. E., J. Am. Chem. Soc., *75*, 1651–1653 (1953).
17. Weil, J. K., Bistline, R. G. Jr., and Stirton, A. J., "Organic Synthesis," *36*, 83–86, John Wiley and Sons Inc., New York, 1956.
18. Weil, J. K., and Stirton, A. J., J. Phys. Chem., *60*, 899–901 (1956).
19. Weil, J. K., Stirton, A. J., and Bistline, R. G. Jr., J. Am. Oil Chemists' Soc., *31*, 444–447 (1954).
20. Wilkes, B. G., and Wickert, J. N., Ind. Eng. Chem., *29*, 1234–1239 (1937).

Epoxy Acid in Seed Oils of *Malvaceae* and Preparation of (+) *threo*-12,13-Dihydroxyoleic Acid[1,2]

C. Y. HOPKINS and MARY J. CHISHOLM, National Research Council (Canada), Ottawa, Canada

Seed oils of six species of *Malvaceae*, representing four genera, were found to contain *cis*-12,13-epoxyoleic acid in amounts estimated at 1.5–7% of the total fatty acids. Acetolysis of the oils gave the corresponding dihydroxyoleic acid, which was shown to be predominantly a *dextro*-rotatory form of *threo*-12,13-dihydroxyoleic acid. It was obtained optically pure, and its structure was confirmed by orthodox methods. The hydrogenation product, (+)-*threo*-12,13-dihydroxystearic acid, was also obtained optically pure and characterized. The best yield of dihydroxyoleic acid was obtained from the seed oil of *Malope trifida*.

Samples of oil from four other species of *Malvaceae* had a very low or negligible content of epoxy acid.

IT WAS SHOWN in earlier work that *cis*-12,13-epoxyoleic acid occurs in the glycerides of okra seed oil and kenaf seed oil in amounts up to 5% of the total fatty acids (1,2). The present work deals with the examination of other seed oils of the *Malvaceae* family and the detection of epoxy acid in some of them.

The oxirane oxygen content of each oil was determined and calculated as epoxyoleic acid. Oils having an apparent epoxyoleic acid content of more than 3% were acetylated, saponified, and partitioned by solvents to isolate the resulting *threo*-12,13-dihydroxyoleic acid. Isolation and identification of this acid confirmed the presence of *cis*-12,13-epoxyoleic acid in the oil and gave a further indication of the amount.

Attempts to convert the epoxy acid to monohydroxy acid by hydrogenating the entire oil and then to isolate the monohydroxy acid by solvent partition were not successful. It was not possible to obtain a pure hydroxy acid by this treatment, perhaps because of the formation of position isomers or because of the fact that the partition ratio for separating the acids is less favorable for mono- than for dihydroxy acids.

Dextro-rotatory Dihydroxyoleic Acid. Gunstone found that the oil of *Vernonia anthelmintica*, when treated by acetolysis, gave *levo*-rotatory *threo*-12,13-dihydroxyoleic acid (3). It is now shown that oils of the *Malvaceae* species, treated in the same way, give a *dextro*-rotatory form of the same acid. Preparation of pure (+)- and (−)-*threo*-12,13-dihydroxyoleic acids was reported recently in a preliminary communication from this laboratory (4). The (+) form was prepared from *Malope trifida* and the (−) form from *Vernonia colorata*. Their specific rotations were equal but of opposite sign. In both cases the natural epoxy acid is presumed to be optically active, but conversion to the dihydroxy acid is only partially stereospecific, resulting in a mixture of two enantiomers in which one predominates. The enantiomer present in excess was isolated by fractional crystallization. All of the *Malvaceae* oils which yielded *threo*-12,13-dihydroxyoleic acid in the present work gave the (+) isomer.

Hydrogenation of (+)-*threo*-12,13-dihydroxyoleic acid gave (+)-*threo*-12,13-dihydroxystearic acid. Since these two acids are new compounds, it was necessary to prove their structure; and this was done by analysis and by identification of the degradation products, as follows. The unsaturated acid, shown by analysis to be $C_{18}H_{34}O_4$, absorbed one mole of hydro-

---

[1] Presented in part at the annual meeting, American Oil Chemists' Society, New Orleans, La., April 20–22, 1959.

[2] Issued as N.R.C. 6042.