

## Isomeric Arylsteoric Acids

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The viscous oily arylsteoric acid from oleic acid and an aromatic compound, with aluminum chloride as the condensing agent, was found by gas-liquid chromatography of alkyl aryl ketone oxidation products to be a mixture of 12 position isomers with substitution at C-6-17 in the fatty acid chain. Distribution of isomers depends in part on the relative reactivity of the particular aromatic compound. Substitution predominates at the C-17 atom and at positions near the middle of the chain. Crystalline arylsteoric acids isolated in low yield from the viscous oil are the 17-aryl isomers. Phenylsteoric and ethoxyphenylsteoric acids formed with methanesulfonic acid as the condensing agent are also mixtures of 12 position isomers.

The Friedel-Crafts reaction of oleic acid with excess of aromatic hydrocarbon, with aluminum chloride as the condensing agent, gives an oily arylsteoric acid as the main product. In the case of benzene, *o*- and *p*-xylene, and *o*- and *p*-chlorotoluene it had been possible to isolate a crystalline arylsteoric acid from the main product by repeated crystallization from acetone at  $-20^{\circ}$ , in yields of 1-7% for the crystals compared to 37-75% for the oil.<sup>2</sup> The oily arylsteoric acid, in the

case of benzene, has been variously considered as primarily a mixture of the 9- and 10-phenyl isomers,<sup>3</sup> of, if double-bond migration (hydride ion transfer) is extensive, as a mixture of several isomers<sup>2</sup> or a mixture in which the 17-phenyl isomer predominates.<sup>4</sup>

By gas-liquid chromatographic separation of alkyl aryl ketone oxidation products we have found that the oily arylsteoric acid is a complex mixture of 12 position isomers, with the aromatic group attached at positions 6-17 on the C<sub>18</sub> fatty acid chain. The crystalline

(1) Eastern Regional Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

(2) A. J. Stirton, B. B. Schaeffer, A. A. Stawitzke, J. K. Weil, and W. C. Ault, *J. Am. Oil Chemists' Soc.*, **25**, 365 (1948).

(3) J. Harmon and C. S. Marvel, *J. Am. Chem. Soc.*, **54**, 2515 (1932).

(4) C. D. Nenitzescu and A. Glatz, *Bull. soc. chim. France*, 218 (1961).



## ISOMERIC ARYLSTEARIC ACIDS

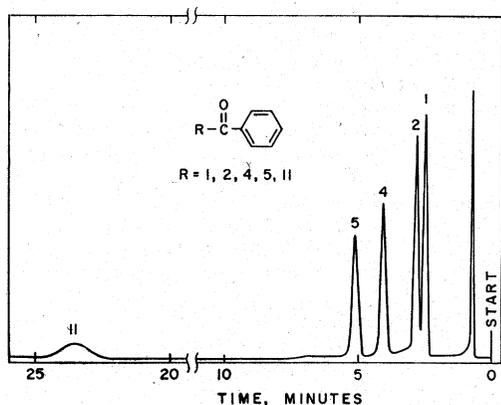


Figure 1.—Separation of reference compounds.

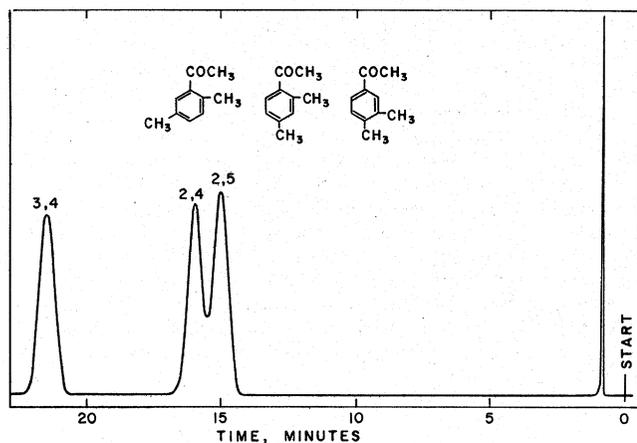


Figure 2.—Separation of reference compounds.

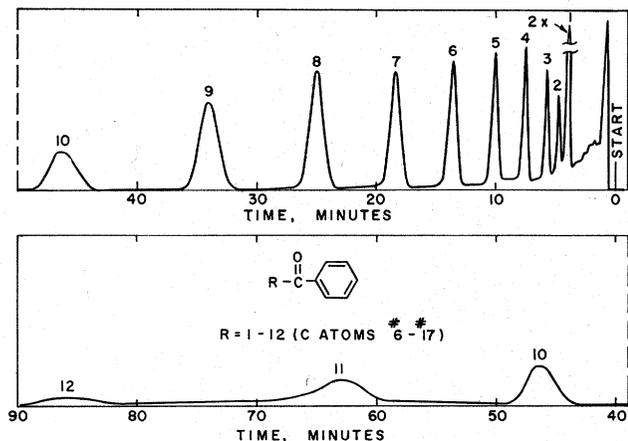


Figure 3.—Ketones from oily phenylstearic acid.

arylstearic acids from benzene, *o*- and *p*-xylene, and *o*- and *p*-chlorotoluene, m.p. 64.8–65.4°, 59.8–61.2°, 76.4–77.6°, 53.1–54.1°, 69.4–70.2°, respectively, were obtained from the oil by repeated crystallization from acetone at –20°. Oily phenylstearic and ethoxyphenylstearic acids were also prepared from oleic acid in a homogeneous reaction system with methanesulfonic acid as the condensing agent.<sup>7</sup>

**Alkyl Aryl Ketones.**—Acetophenone, propiophenone, valero-phenone, hexanophenone, laurophenone, 2,4-dimethylacetophenone, 2,5-dimethylacetophenone, and 3,4-dimethylacetophenone were commercial reagent chemicals. The 4-chloro-3-methylacetophenone and 2-chloro-5-methylacetophenone were prepared from acetic anhydride and *o*- and *p*-chlorotoluene, respectively, by the Friedel–Crafts reaction.<sup>8</sup>

**Chromic Acid Oxidation.**—Chromic acid, 15.3 g., was added in the course of 2 min. to a stirred solution of 10 g. of phenyl-

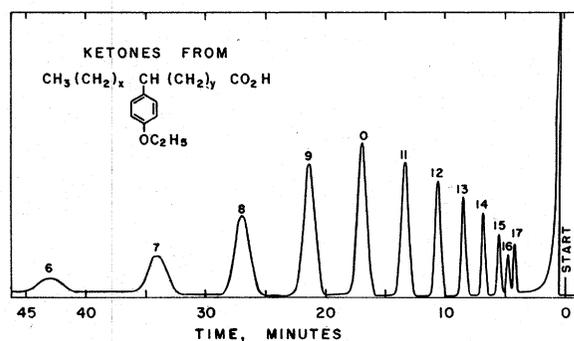


Figure 4.

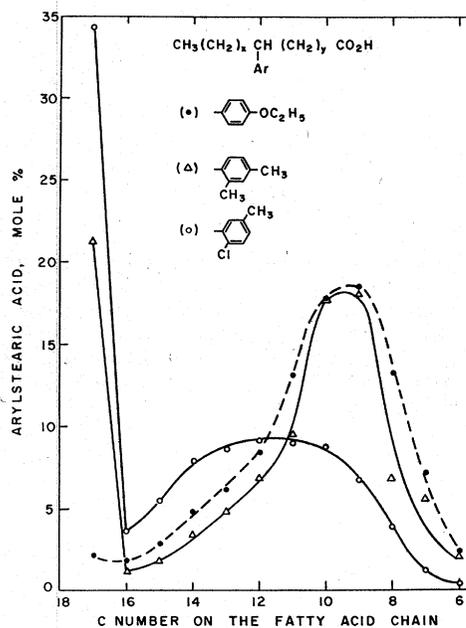


Figure 5.

stearic acid in 170 ml. of glacial acetic acid at 20°. The mixture was stirred for 2 hr., the temperature rising to 28°. Water and ethyl ether, 200 ml. each, were added, and the mixture was transferred to a 4-l. separatory funnel containing 2 l. of water and 200 ml. of ether. The aqueous layer was re-extracted twice with 300 ml. of ether and the combined ether extracts were washed free of water-soluble acids with a saturated sodium sulfate solution. The light green ether layer was neutralized with 6 *N* sodium hydroxide, until the ether layer was colorless and the aqueous layer green. The ether layer was separated, washed, concentrated to about 2 ml., dried with anhydrous sodium sulfate, and analyzed by gas-liquid chromatography.

**Chromatography.**—The chromatographic separations were carried out on a F and M Model 500 control panel with a F and M Model 720 dual column oven.<sup>9</sup> Gow-Mac W-2 filaments were used in the thermal conductivity cell and the d.c. power was supplied with a Gow-Mac Model 405-C:1.

A stainless steel coiled column 6 ft. × 0.25 in. o.d. packed with Diatoport W (60–80 mesh) coated with 10% Carbowax 20M gave the best separation with these homologous series of ketones.

The separations were carried out at temperatures ranging from 220° for phenylstearic acid oxidation products to 240° for the ketones from the arylstearic acids from the chlorotoluenes. All of the analyses were run isothermally since this gave the best log retention plots and the most accurate quantitative analysis with known reference mixtures.

**Reliability and Validity of Results.**—A known mixture of five acetophenone homologs, 20% each by weight, was separated as shown in Figure 1. A plot of log retention times against the

(9) Reference to specific manufactured items does not constitute recommendation by the U. S. Department of Agriculture over similar articles not mentioned.

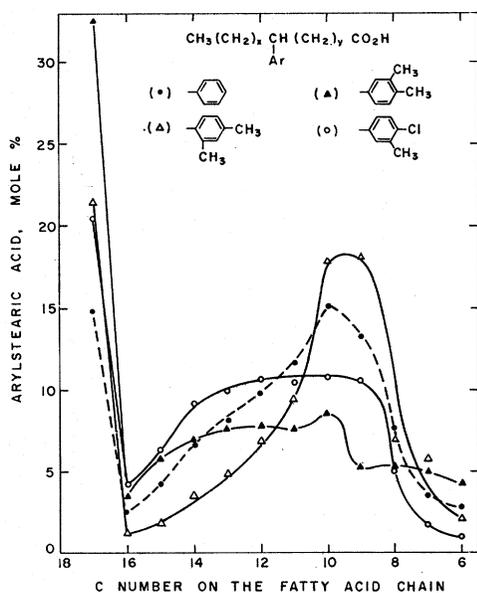


Figure 6.

number of carbon atoms gave a nearly straight line. Quantitative analysis of the mixture by gas-liquid chromatography gave the following results, % by weight: acetophenone, 18.2; propiophenone, 19.3; valerophenone, 21.0; hexanophenone, 22.2; laurophenone, 19.3. The chromatographic separation of a mixture of equal parts of three isomeric dimethylacetophenones is shown in Figure 2.

The separation of the alkyl aryl ketones obtained by chromic acid oxidation of oily arylstearic acids from benzene (aluminum chloride catalyst) and phenetole (methanesulfonic acid catalyst) is shown in Figures 3 and 4.

Distribution of isomeric arylstearic acids from benzene, *o*- and *m*-xylene, *o*- and *p*-chlorotoluene, and phenetole is shown in Table I and Figures 5 and 6. Oxidation and chromatographic separation experiments showed that the values of Table I for phenylstearic acid (aluminum chloride catalyst) could be closely duplicated with an average deviation of 0.24 mole %. As in the case of the reference acetophenone homologs, plots of the log retention time against numbers of carbon atoms gave a nearly straight line for each family of alkyl aryl ketones.

**Point of Substitution on the Benzene Ring.**—Chromic acid oxidation of a crystalline arylstearic acid isolated from the condensation of *p*-xylene with oleic acid<sup>2</sup> gave a dimethylacetophenone identical in retention time by gas-liquid chromatography with 2,5-dimethylacetophenone. The crystalline arylstearic acid is therefore 2',5'-dimethyl-17-phenyloctadecanoic acid.

Similarly the first member of the two series of alkyl aryl ketones from oily arylstearic acids from *o*- and *m*-xylene were found to have identical and superimposable retention time with 3,4-dimethylacetophenone and 2,4-dimethylacetophenone, respectively. The point of substitution of aliphatic carbon on the benzene ring is therefore as shown in Table I.

The chlorine atom of *o*- and *p*-chlorotoluene was found to direct the point of substitution of aliphatic carbon *para* and *ortho* to itself, respectively, as shown in Table I. This is true also in the Friedel-Crafts reaction of chlorotoluenes with acetic anhydride.<sup>8</sup> The first member of the series of alkyl aryl ketones from the oily arylstearic acid from *o*-chlorotoluene was found identical in retention time with 4-chloro-3-methylacetophenone.

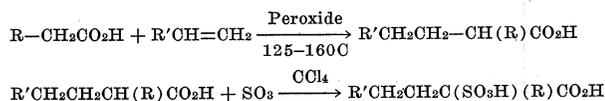
Oxidation of a crystalline arylstearic acid from *p*-chlorotoluene gave a ketone identical with 2-chloro-5-methylacetophenone in retention time and in the melting point of the oxime, 114–115°.

# Branched Chain Fatty Acids and Sulfonated Derivatives

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## Abstract

Several 2-alkyl fatty acids containing 18–21 carbon atoms, were synthesized by tertiary butyl peroxide catalyzed addition of linear aliphatic carboxylic acids to normal terminal olefins. The products obtained in 35–70% yields were purified by fractional distillation. The acids were sulfonated with sulfur trioxide·dioxane adduct and isolated as the disodium salts in 60–80% yields.

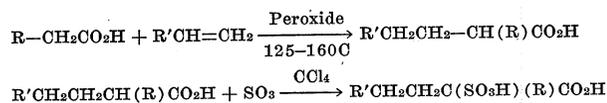


Surface active properties of the sodium salts of the 2-alkyl carboxylic acids and the corresponding sulfonated products were evaluated. Good wetting properties were observed for those sulfonated acids where the hydrophilic portion of the molecule was equidistant from the ends of the hydrocarbon chain.

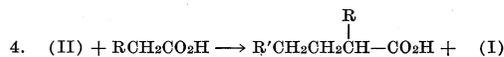
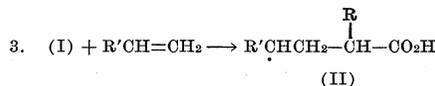
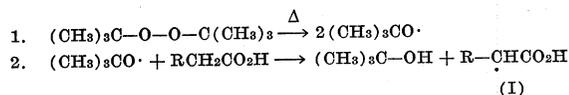
## Introduction

SALTS OF LINEAR CARBOXYLIC ACIDS (1), of 12–18 carbon atoms, and sulfonated derivatives exhibit increasing detergent power and decreasing solubility with increase in chain length. Useful surface active properties have been found when these materials are incorporated in detergent bars (2) and compositions (3). Previous studies have also shown that the sodium salts of  $\alpha$ -sulfonated linear aliphatic carboxylate esters (4,5),  $R-CH(SO_3Na)CO_2R'$  where R and R' are equivalent or nearly so, exhibit excellent wetting properties in both hard and soft water, stable foams and good calcium ion stability. Branching would therefore be expected to increase the solubility of carboxylic acid salts and derivatives while central location of the hydrophilic group should lead to enhanced wetting properties. These studies have now been extended to determine the surface active properties of sodium 2-alkyl carboxylates and their corresponding 2-sulfonated derivatives.

The general synthesis of these acids is conveniently expressed in the following equations where R and R' are linear alkyl groups.



Numerous investigations have shown that the addition of acids (6), esters (7,8), amides (9), and ketones (10, 11) to olefins occurs at the carbon atom alpha to the carbonyl group. These peroxide induced additions are believed to proceed via a free radical chain reaction involving a complex stepwise sequence.

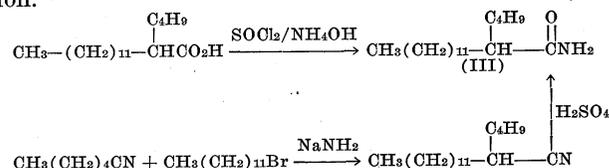


Chain initiation is represented by steps 1 and 2, while chain propagation occurs via steps 3 and 4. Chain termination can occur by dimerization of radicals I and II with themselves or each other. Telomerization involving successive additions of olefin molecules to radical II (actually a polymerization) is thought to be the most important side reaction observed in this process. High ratios of carboxylic acid to olefin minimize telomer formation.

Table I summarizes the physical properties and pertinent experimental data obtained in the synthesis of some 2-alkyl carboxylic acids. Purities of better than 95% are indicated by carbon, hydrogen analyses and neutral equivalents. The yields of alkylated acetic acids based on the quantity of olefins used range from 35–70% with the most highly branched product 2,2-dimethylhexadecanoic acid being obtained in the lowest yield. The ratio of nondistillable residue to product ranges from 0.30–0.40 with all of the acids except 2,2-dimethylhexadecanoic acid where this ratio equals 0.60. This effect of branching at the 2-carbon atom of the acid has been noted previously by Nikishin et al. (6,7) and attributed to steric hindrance.

Sulfonation of the 2-alkyl carboxylic acids proceeds smoothly with sulfur trioxide·dioxane adduct in carbon tetrachloride leading to product formation in 60–80% yields. Analyses of carbon, hydrogen, and sodium summarized in Table II indicate better than 95% purity in all samples. Some difficulties were encountered in determining sulfur by the oxygen flask combustion method were relatively high and low values were observed for these compounds. All of the sulfonated dialkyl acetic acids were isolated as the disodium salts in view of the ease of purification in this form. Attempts to sulfonate 2,2-dimethylhexadecanoic acid resulted in the formation of a complex mixture of products.

In this study we desired to establish the structure of the dealkyl acetic acids by synthesizing one of the acids or a derivative by a known and different reaction.



The amide III of 2-butyltetradecanoic acid was prepared by the standard thionyl chloride-ammonium hydroxide method to yield a white crystalline product mp 108C, % nitrogen 4.94, theory % nitrogen 4.95. Hexanenitrile was alkylated with dodecyl bromide using sodium amide (12) to form 2-butyltetradecanenitrile bp 126.5C at 0.25 mm;  $n_D^{20}$  1.4458. The nitrile, exhibiting a sharp band 4.39  $\mu$  and a purity better than 95% by gas-liquid chromatography was

<sup>1</sup> Presented at the AOCs Meeting, Chicago, Ill., October 1964.  
<sup>2</sup> E. Utiliz. Res. & Dev. Div., ARS, USDA.

TABLE I  
Experimental Data 2-Alkyl Carboxylic Acids<sup>a</sup>

| Acid                          | Formula  | MP <sup>c</sup><br>°C | BP <sup>c</sup><br>°C/mm | n <sub>D</sub> <sup>20°</sup> | Neut. equiv. |        | Analysis |       |       |        | Reactants |               | Reaction temp<br>°C | Yield per cent |        |
|-------------------------------|--|-----------------------|--------------------------|-------------------------------|--------------|--------|----------|-------|-------|--------|-----------|---------------|---------------------|----------------|--------|
|                               |  |                       |                          |                               | Found        | Theory | Found    | C     | H     | Theory | C         | H             |                     |                | Olefin |
| 2-Methylheicosanoic.....      | C <sub>18</sub> H <sub>37</sub> OH (CH <sub>3</sub> )CO <sub>2</sub> H             | 60-1                  | 172-4/0.2                | .....                         | 331          | 326    | 77.46    | 13.05 | 12.90 | 77.30  | 12.90     | Octadecene-1  | Propionic           | 140            | 57     |
| 2-Methyloctadecanoic.....     | C <sub>16</sub> H <sub>33</sub> CH(OH)CO <sub>2</sub> H                            | 54-5                  | 164-8/0.2                | .....                         | 305          | 298    | 76.58    | 12.72 | 12.75 | 76.50  | 12.75     | Hexadecene-1  | Propionic           | 138            | 56     |
| 2-Butyltetradecanoic.....     | C <sub>12</sub> H <sub>25</sub> CH(OH)CO <sub>2</sub> H                            | 26                    | 152-3/0.3                | 1.4500                        | 282          | 284    | 75.05    | 12.33 | 12.69 | 76.05  | 12.69     | Dodecene-1    | Hexanoic            | 160            | 63     |
| 2-Heptylundecanoic.....       | C <sub>7</sub> H <sub>15</sub>   | 18-9                  | 151/0.3                  | 1.4500                        | 283          | 284    | 75.94    | 12.43 | 12.69 | 76.05  | 12.69     | Nonene-1      | Nonanoic            | 160            | 60     |
| 2-Octyldecanoic.....          | (C <sub>8</sub> H <sub>17</sub> ) <sub>2</sub> CHCO <sub>2</sub> H                 | 33-4                  | 162-3/0.5                | 1.4445 <sup>b</sup>           | 287          | 284    | 75.89    | 12.64 | 12.69 | 76.05  | 12.69     | Octene-1      | Decanoic            | 160            | 68     |
| 2,2-Dimethylhexadecanoic..... | C <sub>14</sub> H <sub>29</sub> C(CH <sub>3</sub> ) <sub>2</sub> CO <sub>2</sub> H | 46.5-7.5              | 144-6/0.2                | .....                         | 287          | 284    | 76.17    | 12.59 | 12.69 | 76.05  | 12.69     | Tetradecene-1 | Isobutyric          | 145            | 36     |

<sup>a</sup> Properties of octadecanoic acids previously reported (11).  
<sup>b</sup> Determined at 35C.  
<sup>c</sup> All melting points and boiling points are uncorrected.  
<sup>d</sup> Reaction temperatures are indicated as the median of a 3-6° range.

hydrolyzed with sulfuric acid (12) to an amide mp 108-109C; % nitrogen 5.00, theory % nitrogen 4.95. A mixed melting point of this amide with the amide from 2-butyl tetradecanoic acid resulted in no melting point depression.

### Experimental

#### Reagents

Tertiary butyl peroxide  $n_D^{20} = 1.3889$  was obtained from the Monomer-Polymer Corp., Philadelphia, Pa., and used as received. Reagent carbon tetrachloride was passed through a 12 in. silica gel column and stored over anhydrous sodium sulfate. Dioxane (Eastman yellow label) was distilled through a 24 in. vacuum jacketed column filled with protruded packing. The center cut was passed through a 12 in. column of silica gel and stored over anhydrous sodium sulfate. Sulfur trioxide (Sulfan-Allied Chemical Corp.) was freshly distilled immediately prior to use. The olefins (Humphrey-Wilkinson, petroleum derived) and aliphatic acids (Eastman Organic Chemicals) were distilled through a 24 in. column of protruded packing. Boiling points and refractive indices of the center cuts checked closely with the literature values.

**2-Alkyl Carboxylic Acids (6).** Carboxylic acid, olefin and t-butyl peroxide were used in the molar ratio of 10/1/0.25, respectively. To an appropriate sized four-neck round-bottom flask equipped with a condenser, stirrer, dropping funnel and thermometer was added two-thirds of the acid to be used. The remaining one-third of the acid was added to the olefin-peroxide mixture and placed in the dropping funnel. After heating the acid to the reaction temperature (125-160C), the acid-olefin-peroxide mixture was added dropwise over a 6-hr period with efficient stirring. After complete addition, the mixture was held at the reaction temperature for one hour to complete the reaction. Simple distillation at reduced pressure separated the mixture into crude fractions which were successively distilled through a 24-in. spinning band column.

**2-Sulfo-2-Alkyl Carboxylic Acids.** To a 500-ml round-bottom flask equipped with a bar magnet condenser and drying tube was added 240 ml of dry carbon tetrachloride and 0.17 mole dry dioxane. The stirred mixture was cooled to 15C and 0.15 mole of freshly distilled sulfur trioxide in 30 ml of carbon tetrachloride was added to form a white crystalline slurry. After stirring the sulfur trioxide-dioxane slurry for 10 min, 0.1 mole of pure dialkyl acetic acid in 30 ml of carbon tetrachloride was added. The

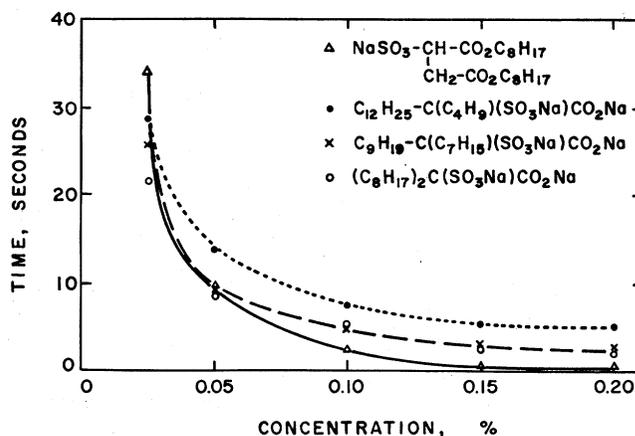


Fig. 1. Wetting ability versus concentration.

TABLE II  
Analysis of Disodium 2-Sulfo-2-Alkyl Carboxylates  
RR'C(CO<sub>2</sub>Na)SO<sub>2</sub>Na

| Compounds                                 | Substituents                   |                                 | Analysis |      |      |       |        |      |      |       |
|---|--------------------------------|---------------------------------|----------|------|------|-------|--------|------|------|-------|
|   |                                |                                 | Found    |      |      |       | Theory |      |      |       |
|   | R                              | R'                              | C        | H    | S    | Na    | C      | H    | S    | Na    |
| Disodium 2-sulfo-2-methyleicosanoate..... | CH <sub>3</sub>                | C <sub>18</sub> H <sub>37</sub> | 55.74    | 9.22 | 6.53 | 9.89  | 56.00  | 8.90 | 7.12 | 10.02 |
| 2-methyloctadecanoate.....                | CH <sub>3</sub>                | C <sub>16</sub> H <sub>33</sub> | 54.07    | 8.65 | 7.26 | 10.63 | 54.03  | 8.53 | 7.58 | 10.90 |
| 2-butyltetradecanoate.....                | C <sub>4</sub> H <sub>9</sub>  | C <sub>12</sub> H <sub>25</sub> | 53.40    | 8.40 | 8.30 | 11.28 | 52.94  | 8.33 | 7.84 | 11.27 |
| 2-heptylundecanoate.....                  | C <sub>7</sub> H <sub>15</sub> | C <sub>9</sub> H <sub>19</sub>  | 52.68    | 8.28 | 7.57 | 11.40 | 52.94  | 8.33 | 7.84 | 11.27 |
| 2-octyldecanoate.....                     | C <sub>8</sub> H <sub>15</sub> | C <sub>8</sub> H <sub>17</sub>  | 52.12    | 8.26 | 8.68 | 11.58 | 52.94  | 8.33 | 7.84 | 11.27 |

mixture was stirred at room temp for 15 min, 45C for 45 min, and 60C for an additional hour. The final light amber mixture was filtered to remove insolubles and evaporated under vacuum (0.2 mm/1 hr) to remove volatiles. The residue was dissolved in 250 ml of absolute ethanol and neutralized with a slight excess of 6 N sodium hydroxide. The precipitate formed was filtered and recrystallized two or three times from ethanol-water mixtures.

### Discussion

Pertinent surface active properties of the sodium salts of the 2-alkyl carboxylic acids and 2-sulfonated derivatives are summarized in Table III. The compounds are arranged in the order of increasing size of the 2-alkyl group with the properties of sodium octadecanoate and disodium 2-sulfooctadecanoate (disodium  $\alpha$ -sulfofearate) being included for purposes of comparison.

For both mono- and disodium salts, the Krafft point decreases as size of the 2-alkyl group increases. This is a reflection of the degree of molecular symmetry. Within a given series of isomeric compounds, the Krafft point decreases reaching a minimum for the most unsymmetrical molecule and then increases as the symmetry of the molecule approaches a maximum (compare compounds 1, 4, 5 and 6 or the corresponding disodium salts). The Krafft point for the most symmetrically branched molecules, however, is considerably below that of the linear molecule. Early workers in the field found that the Krafft point of soaps of linear carboxylic acids were roughly comparable to the melting points of the corresponding free

acids. This is not true for the soaps of the branched chain acids (compare data in Table III with Table I).

In most cases the critical micelle concentration (cmc) of the monosodium soaps could not be measured because clear micellar solutions were not obtained in the presence of pinacyanol chloride. For the disodium salts the homologs disodium 2-sulfo-2-methyloctadecanoate and disodium 2-sulfo-2-methyleicosanoate show an expected decrease to one-fourth of the value (0.97 compared to 0.24) for an increase in chain length by two carbon atoms (18). The good wetting agents, the last 3 compounds of Table III, are characterized by high cmc and high interfacial tension.

As previously mentioned excellent wetting properties are observed for compounds (4,5) of the type R-CH(SO<sub>3</sub>Na)CO<sub>2</sub>R' where the hydrophilic moiety is centrally located. The data in Table III indicate good wetting properties for disodium 2-sulfo-2-alkyl-carboxylates in distilled water but with rather poor calcium stability where values are available. These compounds apparently react readily with calcium ion forming insoluble salts. It is expected that esterification of the carboxylate group will result in improved wetting properties and good calcium ion stability. The good wetting ability of the 2-sulfonated derivatives is clearly shown in a plot of wetting time versus concentration (Figure 1) relative to Aerosol-OT.

As is frequently observed, good wetting properties are not necessarily accompanied by good detergency. With the exception of sodium 2-methyleicosanoate, detergency in distilled water is fair at best while for previously mentioned reasons this property is poor in

TABLE III  
Surface Active Properties\*  
Sodium Salts of 2-Alkyl Carboxylic Acids and 2-Sulfonated Derivatives

| Salt                                   | Krafft point <sup>b</sup><br>°C | Tension <sup>c</sup> |              | Critical micelle conc <sup>d</sup> 25C |          | Calcium ion <sup>e</sup> stability<br>ppm CaCO <sub>3</sub> | Wetting time <sup>f</sup> seconds |                           | Detergency terg-o-tometer <sup>g</sup> ΔR |                           | Foam height mm <sup>h</sup> |                           |
|--|---------------------------------|----------------------|--------------|--|----------|---|-----------------------------------|---------------------------|---|---------------------------|-----------------------------|---------------------------|
|  |                                 | Sur-face             | Inter-facial | Mmols/liter                            | Per cent |   | Dis-tilled water                  | 300 ppm CaCO <sub>3</sub> | Dis-tilled water                          | 300 ppm CaCO <sub>3</sub> | Dis-tilled water            | 300 ppm CaCO <sub>3</sub> |
|  |                                 | Dynes/cm             | Dynes/cm     |  |          |   |                                   |                           |   |                           |                             |                           |
| <b>Monosodium</b>                      |                                 |                      |              |  |          |   |                                   |                           |   |                           |                             |                           |
| 1) Octadecanoate.....                  | 67.5                            | .....                | .....        | 0.50 <sup>i</sup>                      | 0.015    | .....   | >300                              | >300                      | 35  | 29                        | 238                         | 65                        |
| 2) 2-Methyleicosanoate.....            | 56                              | 35.1                 | 26.3         | .....                                  | .....    | .....   | >300                              | >300                      | 30  | 11                        | 149                         | 0                         |
| 3) 2-Methyloctadecanoate.....          | 40.5                            | 26.1                 | 23.4         | 0.23                                   | 0.007    | .....   | >300                              | >300                      | 29  | 17                        | 217                         | 15/0                      |
| 4) 2-Butyltetradecanoate.....          | <1                              | 28.9                 | 13.4         | .....                                  | .....    | 74  | 48                                | >300                      | 21  | 5                         | 210/130                     | 10/0                      |
| 5) 2-Heptylundecanoate.....            | 12                              | 31.6                 | 14.5         | .....                                  | .....    | .....   | >300                              | >300                      | 20  | 6                         | 210/15                      | 115/8                     |
| 6) 2-Octyldecanoate.....               | 17                              | 31.6                 | 15.2         | .....                                  | .....    | .....   | 100                               | >300                      | 18  | 6                         | 230/45                      | 140/8                     |
| 7) 2,2-Dimethylhexadecanoate.....      | 39                              | 26.0                 | 10.2         | 0.50                                   | 0.015    | 258   | 86                                | >300                      | 25  | 11                        | 215                         | 100/25                    |
| <b>Disodium</b>                        |                                 |                      |              |  |          |   |                                   |                           |   |                           |                             |                           |
| 8) 2-Sulfo octadecanoate.....          | 92                              | .....                | .....        | 2.45 <sup>j</sup>                      | 0.10     | .....   | .....                             | .....                     | 20  | 26                        | .....                       | .....                     |
| 9) 2-Sulfo-2-methyleicosanoate.....    | 53                              | 41.4                 | 9.5          | 0.24                                   | 0.01     | .....   | >300                              | >300                      | 22  | 16                        | 193                         | 0                         |
| 10) 2-Sulfo-2-methyloctadecanoate..... | 43.5                            | 33.8                 | 6.0          | 0.97                                   | 0.04     | .....   | 49                                | >300                      | 22  | 17                        | 200                         | 45                        |
| 11) 2-Sulfo-2-butyltetradecanoate..... | 32.5                            | 36.7                 | 12.2         | 7.0                                    | 0.28     | 95  | 7.4                               | >300                      | 8   | 9                         | 85/5                        | 30/25                     |
| 12) 2-Sulfo-2-heptylundecanoate.....   | 55.5                            | 34.8                 | 13.5         | 9.1                                    | 0.37     | 36  | 4.8                               | 85                        | 8   | 9                         | 0                           | 160/30                    |
| 13) 2-Sulfo-2-octyldecanoate.....      | 67                              | 35.5                 | 15.7         | 14.1                                   | 0.57     | 31  | 5.0                               | >300                      | 8   | 8                         | 0                           | 95/25                     |

\* Some properties could not be determined because of the low solubility of some salts.

<sup>b</sup> The temperature at which a 1% dispersion becomes a clear solution on gradual heating.

<sup>c</sup> Determined at 0.1% concentration, 25C with a duNoüy tensiometer.

<sup>d</sup> Determined by pinacyanol method.

<sup>e</sup> Determined on 0.5% solutions (13).

<sup>f</sup> Determined on 0.1% solutions at 25C with a 5 g cotton skein and a 3 g hook (14).

<sup>g</sup> Measured by the increase in reflectance after washing G.D.C. #26 standard soiled cotton in 0.25% solution at 60C.

<sup>h</sup> Measured with 0.25% solutions by the Ross-Miles test at 60C (15). The ratios indicate foam height initially and after 5 minutes.

<sup>i</sup> Conductance method (16).

<sup>j</sup> Solubility method (17).

simulated hard water. Initial foam height for the 2-alkylcarboxylates in distilled water is good; however, where the alkyl groups are of comparable size rapid foam degeneration occurs in 5 min as indicated for monosodium salts (4-6). The remaining data suggest rather poor foaming properties for these salts in simulated hard water and for the sulfonated derivatives in both soft and hard water.

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