Thus, whilst the available chemical evidence does not definitely differentiate between structures I and III, the light absorption suggests that cyclooctatetraene oxide is cycloöcta-2,5,7-triene-1,4-oxide (III).

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Sodium Salts of Alkyl α-Sulfopalmitates and Stearates[1,2]

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Salts of sulfonated esters of the higher saturated fat acids have been shown to be surface active agents,[3,4] but their preparation in a state of purity has not been adequately described. The reaction of liquid sulfur trioxide with palmitic or stearic acid results in α-sulfonation,[5] and we have now prepared from the diacid ($R'CH(SO_3H)CO_2H$, method D) or the monosodium salt ($R'CH(SO_3Na)CO_2H$, method M) 24 esters of the general formula $R'CH(SO_3Na)CO_2R$, where R′ is $C_{14}H_{29}$ (palmitate series) or $C_{16}H_{33}$ (stearate series). In 22 cases R was a normal alkyl group of 1 to 18 carbon atoms. Two esters of secondary alcohols were included. Tables I and II give the melting points, methods of preparation, and elemental analyses.

The elemental analyses agreed with the theoretical values, the maximum deviation in the value for percentage of carbon being 0.47 and the average deviation 0.21.

The sodium salts of the α-sulfonated esters were white hygroscopic solids, readily soluble in water, the solubility decreasing with increase in molecular weight. They were unexpectedly resistant to hydrolysis, especially in acid solutions, presumably because the sulfonate group retards hydrolysis at the ester linkage through steric hindrance. Since saponification of the esters may be incomplete even after a four-hour reflux period with excess alcoholic potassium hydroxide, saponification equivalent values are not useful indications of purity.

The melting points of the methyl esters were considerably higher than those of the next four homologs. Beginning with the hexyl esters, the compounds became transparent solids at the temperatures noted in parentheses, before melting some 10 to 30° higher, usually with decomposition. Esters of secondary alcohols had higher melting points than esters of corresponding primary alcohols.

TABLE I, $C_{14}H_{29}CH(SO_3Na)CO_2R$

R	Melting point, °C.	Method	Elemental analyses found, %			
			C	H	S	Na
CH_3	180.9–182.8	D	54.41	8.63	8.62	6.20
C_2H_5	95.2–96.7	D	55.95	8.96	8.42	5.91
C_3H_7	63.3–65.1	M	56.74	9.13	8.01	5.66
C_4H_9	59.7–60.6	M	57.94	9.33	7.78	5.47
C_5H_{11}	60.8–61.6	M	58.46	9.50	7.63	5.29
C_6H_{13}	(177–179) 189–190	M	59.63	9.69	7.14	5.08
C_8H_{17}	(187–189) 202–203	D	61.10	10.06	6.85	4.78
$C_{10}H_{21}$	(191–193) 206–206.5 d.	D	62.22	10.21	6.32	4.59
$C_{12}H_{25}$	(157–158) 168–168.8	D	63.69	10.74	5.93	4.36
$C_{16}H_{33}$	(188–189) 219–221 d.	D	66.26	10.59	5.53	3.91
$C_{18}H_{37}$	(195–196) 217–219 d.	D	66.60	10.88	5.17	3.66
$CH_3CH_2CHCH_3$	113.5–114.2	D	58.13	9.55	7.75	5.56

TABLE II, $C_{16}H_{33}CH(SO_3Na)CO_2R$

R	Melting point, °C.	Method	Elemental analysis found, %			
			C	H	S	Na
CH_3	179.8–180.0	M	56.85	9.15	8.04	5.70
C_2H_5	97.4–99.2	D	57.58	9.35	7.93	5.55
C_3H_7	72.3–73.6	M	58.48	9.64	7.52	5.26
C_4H_9	66.5–67.6	M	59.64	10.01	7.28	5.30
C_5H_{11}	64.8–65.6	M	60.02	9.97	7.15	5.01
C_6H_{13}	(167–169) 186.2–187.4	M	61.20	9.61	7.07	4.89
C_8H_{17}	(170–172) 193–195 d.	D	62.68	10.09	6.85	4.53
$C_{10}H_{21}$	(191–193) 215–216 d.	D	63.53	10.34	6.24	4.24
$C_{12}H_{25}$	(194–196) 208–210 d.	D	64.74	10.72	5.85	4.17
$C_{16}H_{33}$	(193–194) 218–220 d.	D	67.10	10.90	5.23	3.76
$C_{18}H_{37}$	(209–210) 221–223 d.	D	67.58	11.03	5.07	3.66
$(CH_3)_2CH$	75.8–77.2	D	59.11	9.72	7.57	5.22

Definite relatively low melting points have seldom been reported for alkali metal salts of organic acids. Analogous compounds of low molecular weight, potassium ethyl sulfoacetate and potassium ethyl

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(1) This paper was presented at the Fall Meeting of the American Chemical Society, Chicago, Ill., September 7–11, 1953.

(2) The palmitate esters, for example, may also be named as 2-sulfohexadecanoic acid, 1-alkyl ester, 2-sodium salt or alkyl 2-sulfohexadecanoate, 2-sodium salt.

(3) F. Guenther, J. Conrad and K. Saftien, U. S. Patent 2,043,476 (June 9, 1936).

(4) A. J. Stirton, J. K. Weil, Anna A. Stawitzke and S. James, *J. Am. Oil Chemists Soc.*, **29**, 198 (1952).

(5) J. K. Weil, L. P. Witnauer and A. J. Stirton, THIS JOURNAL, **75**, 2526 (1953).

α-sulfopropionate, melt at 183 and 214°, respectively.[6]

The yields of the α-sulfonated esters ranged from 28 to 76%, the lower yields usually being due to the solubility of the esters in the alcoholic solutions from which they were purified by crystallization. The isolation of the diacid and the two methods of preparation are described in the Experimental part. Method D was generally preferred, and the diacid was its own esterification catalyst. Method M was most successful in the esterification of primary alcohols of 3 to 6 carbon atoms, of boiling points 98 to 155°.

Experimental

α-Sulfopalmitic Acid.—Stabilized liquid sulfur trioxide (0.613 mole) was added dropwise to a stirred slurry of 0.418 mole of palmitic acid in 500 ml. of tetrachloroethylene in the course of an hour; the temperature rose from 20 to 35°. The mixture was stirred at 60–65° for an hour, cooled overnight at 5°, and filtered. The residue was washed with cold chloroform and dried at room temperature under reduced pressure. The somewhat impure diacid, obtained in 82% yield (neut. equiv. 173.0) could be used directly in esterification.

Further purification by five crystallizations from chloroform at 0°, and drying for five hours at 75° at less than 1-mm. pressure gave a white, hygroscopic solid, m.p. 90.1–91.1°. Small amounts of water may lower the melting point from this value by as much as 20°. Potentiometric titration in 95% ethanol gave points of inflection at *p*H values of 4.5 and 8.8, as shown in Fig. 1.

Anal. Calcd. for $C_{16}H_{32}O_5S$: S, 9.53; neut. equiv., 168.2. Found: S, 9.33; neut. equiv., 170.8.

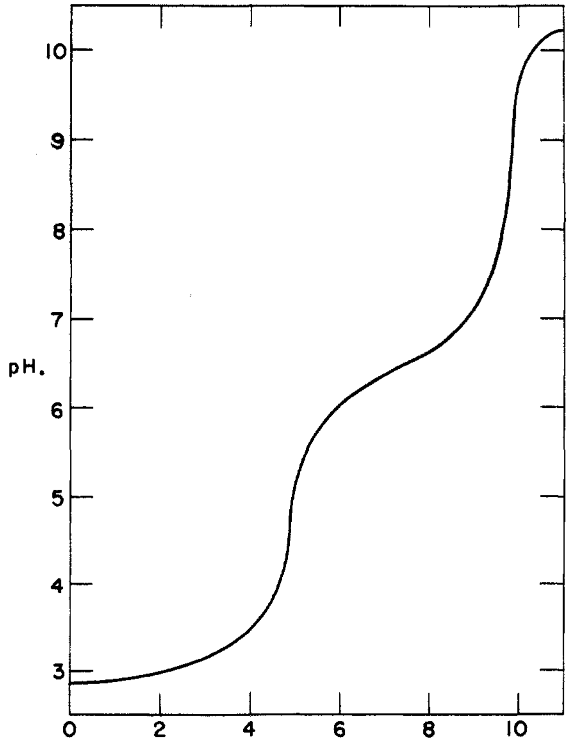

Fig. 1.—Potentiometric titration of α-sulfopalmitic acid in 95% ethanol.

Sodium Methyl α-Sulfopalmitate. Method D.—A solution of the diacid (0.142 mole) in 250 ml. of methanol was heated at the reflux temperature for 14 hours, and 12.3 g. of sodium acetate was added, with stirring, to give a clear solution, which was cooled to −25° and filtered. The residue was washed with cold methanol and dried in a vacuum oven, to give the crude ester as a light-brown solid. The yield was 93%. Purification by decolorizing with carbon and crystallizing twice from ethanol at −20° gave a white, hygroscopic solid. The yield was 35%.

Sodium Dodecyl α-Sulfopalmitate. Method D.—A solution of 0.062 mole of the diacid and 0.108 mole of dodecanol-1 in 200 ml. of toluene was heated and stirred at the reflux temperature for four hours, with the azeotropic removal of water. The solution was then neutralized with solid sodium carbonate, decolorized with carbon, filtered, cooled to −25° and filtered. The residue was a light cream-colored solid; the yield was 58%.

Sodium Amyl α-Sulfostearate. Method M.—A mixture containing 0.138 mole of the monosodium salt, 200 g. of pentanol-1 and 2 g. of concentrated sulfuric acid was heated and stirred for six hours at the reflux temperature, with azeotropic removal of water. The resulting clear solution was neutralized with solid sodium carbonate, decolorized with carbon, and filtered. The crude ester crystallized from the filtrate at −27°, was recrystallized from 50% ethanol and dried in a vacuum oven, giving the purified ester as a white hygroscopic solid; the yield was 76%.

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[6] R. Andreasch, *Monatsh.*, **46**, 639 (1925).

[7] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

Ultraviolet Absorption Spectra of Some Pyridine Derivatives

BY MICHAEL YAMIN AND RAYMOND M. FUOSS

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In a recent paper,[1] a series of quaternary derivatives of 1,2-di-(γ-pyridyl)-ethane and -ethylene were described. The parent bases form mixed crystals and are therefore difficult to separate by

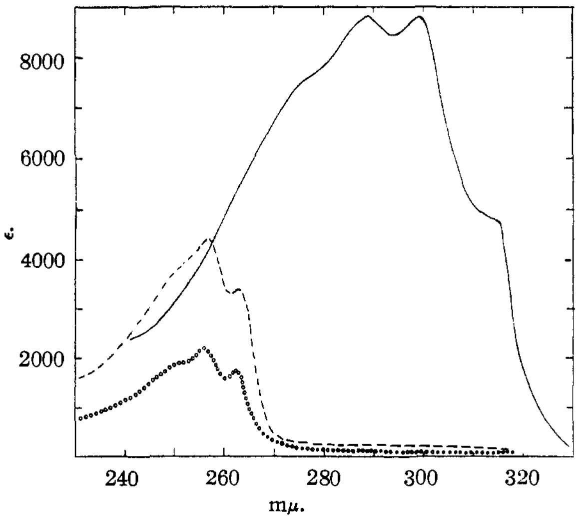

Fig. 1.—Absorption spectra of 1,2-di-(γ-pyridyl)-ethylene (solid curve); 1,2-di-(γ-pyridyl)-ethane (dashed curve) and picoline (dotted curve) in 95% ethanol.

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[1] B. D. Bergmann, F. E. Crane, Jr., and R. M. Fuoss, THIS JOURNAL, **74**, 5979 (1952).