TABLE VIII

Calcium Stability of α-Sulfonated Esters, p.p.m. $CaCO_3$

| R | Palmitates<br>$C_{14}H_{29}CH(SO_3Na)CO_2R$ | Stearates<br>$C_{16}H_{33}CH(SO_3Na)CO_2R$ |
|---|---|---|
| $CH_3$ | >1800 | 800 |
| $C_2H_5$ | >1800 | 540 |
| n-$C_3H_7$ | >1800 | 460 |
| n-$C_4H_9$ | 590 | 620 |
| n-$C_5H_{11}$ | 920 | 1060 |
| n-$C_6H_{13}$ | 850 | 720 |
| $(CH_3)_2CH$ | ...... | >1800 |
| $C_2H_5CHCH_3$ | 1500 | ...... |

There was no simple relation between calcium stability and molecular weight. Values for the α-sulfonated stearates were generally lower. Esters of secondary alcohols had higher calcium stability than esters of corresponding primary alcohols.

*Metallic ion stability.* Metallic ion stability (5) was measured for six esters with the results shown in Table IX. The esters were least stable to the trivalent ion, $Al^{+++}$.

TABLE IX

Metallic Ion Stability of α-Sulfonated Esters [a]

| | Na Me αSP | Na Me αSS | Na Pr αSS | Na iso Pr αSS | Na Bu αSP | Na sec Bu αSP |
|---|---|---|---|---|---|---|
| Mg | 100 | 100 | 100 | 100 | 100 | 100 |
| Al | 14 | 12 | 14 | 10 | 9 | 11 |
| Ca | 93 | 71 | 13 | 38 | 14 | 33 |
| Fe | 100 | 100 | 100 | 100 | 100 | 100 |
| Ni | 100 | 100 | 100 | 100 | 100 | 100 |
| Cu | 100 | 100 | 100 | 100 | 100 | 100 |
| Zn | 100 | 100 | 100 | 100 | 99 | 38 |
| Ba | 37 | 27 | 26 | 27 | 23 | 26 |
| Pb | 70 | 54 | 43 | 48 | 43 | 60 |

[a] Metallic ion stability (5) = 10 × no. of ml. of 1% metal salt solution, tolerated by 10 ml. of 1% surface active agent.

## Summary

In a comparison of the solubility, detergency, and surface-active properties of the mono- and disodium salts of α-sulfonated lauric, myristic, palmitic, and stearic acids, it has been shown that the less soluble α-sulfopalmitates and α-sulfostearates, and sodium α-sulfomyristic acid as well, are the best detergents. The easily soluble disodium α-sulfolaurate resembles a simple electrolyte with little evidence of surface-active properties. Ammonium α-sulfopalmitic acid and triethanolammonium α-sulfopalmitic acid are more soluble surface-active agents and detergents than the sodium salts. Triethanolammonium α-sulfopalmitic acid is exceedingly soluble in water at room temperature.

The sodium salts of alkyl α-sulfopalmitates and α-sulfostearates are easily prepared from the isolated crude diacid. The esters of primary alcohols containing from one to six carbon atoms are readily soluble in water and quite stable to hydrolysis, especially in acid solution. Salts of α-sulfonated esters of secondary alcohols are stable both to acid and to alkaline hydrolysis. This behavior extends the range of possible application.

## Acknowledgment

We wish to acknowledge the assistance of Solis James in the preparation of salts of α-sulfonated acids and the measurement of solubility, and of Anna A. Stawitzke in detergency measurements. Microanalysis for nitrogen and sulfur were performed by Ruth B. Kelly.

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# Highly Unsaturated Fatty Acids. II. Fractionation by Urea Inclusion Compounds[1]

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THE phenomenon of the formation of crystalline urea inclusion compounds[4] with straight chain organic compounds was discovered by Bengen (2) in 1940. In the last three years the new technique has been the subject of several investigations. Schlenk (3), Zimmerschied *et al.* (4), and Schlenk and Holman (5, 6) confirmed Bengen's findings and extended his observations. The new reaction has offered many useful applications. Besides the main finding of Bengen that urea can be used to separate straight chain compounds from branched or cyclic compounds, numerous investigators have demonstrated that various straight chain compounds can be separated by this means. For example, the new technique has been applied for preparation of methyl oleate (6, 7, 8) and for the preparation of concentrates of linoleic and linolenic acids (9). Enrichment of the unsaturated fatty acids of soybean oil has been accomplished by this method (10). For detailed discussion of urea in-

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[4] The term "inclusion compounds," although somewhat clumsy, seems to be the most accurate generic term to describe the class of compounds to which urea and thiourea "complexes" and "adducts" belong (1).

clusion compounds, the reader is referred to a current review (1).

From these examples of the use of urea inclusion compounds for the preparation of unsaturated fatty acids, it seemed to be a logical choice for the enrichment of the fatty acids with four and more double bonds from natural sources. Inclusion compounds of fatty acids or esters containing more than three double bonds have not been yet reported in the literature to the authors' knowledge. Schlenk and Holman (6) found that the yields of inclusion compounds of linoleic and linolenic acids were low, suggesting that the more highly unsaturated fatty acids may be even more difficult to bind as inclusion compounds.

Preliminary experiments in separation of the ethyl esters of fish oil acids indicated that segregation was possible but that the esters were poorly soluble in methanol saturated with urea. Constant stirring was therefore necessary during cooling to prevent the mass separation of the esters as a hypophase. On the other hand, free fatty acids from the same oils did not give this difficulty.

In addition to the segregation of acids and esters of fish oils, the technique was applied in the concentration of the methyl esters of highly unsaturated fatty acids from natural sources having a very low content of these acids. Hog adrenal lipid generously supplied as a petroleum ether extract by Upjohn and Company was used for this purpose.

## Experimental Procedure

Fish oils were saponified by refluxing with KOH-ethanol for 1.5 hrs. under nitrogen. After dilution with water, unsaponifiables were extracted with petroleum ether and ethyl ether. The acids were liberated by acidifying with diluted HCl (1:1) and extracted with petroleum ether. The solution was dried over anhydrous sodium sulfate, and the solvent was then removed under reduced pressure in a stream of oxygen-free nitrogen. The ethyl esters of cod liver oil fatty acids were prepared by refluxing the acids with absolute ethanol containing sulfuric acid equal to 3% of the weight of fatty acids. Methyl esters of hog adrenal fatty acids were prepared by acid interesterification of a petroleum ether extract of hog adrenal lipid.

Segregation of 200 g. of cod liver oil ethyl esters in 1,500 ml. methanol was performed by successive additions of urea. In step 1, 135 g. urea were used and, in each of steps 2 to 5, 150 g. urea were used. In each step the urea was brought into solution by stirring and heating, and the complex was allowed to form by slow cooling to room temperature with stirring. In step 6 an additional yield of inclusion compounds was obtained by cooling to 5°C. At each step the solid was filtered off and washed with about 200 ml. benzene, and esters recovered from the washings were added to the filtrate. The last filtrate comprised the final fraction.

The esters were recovered from each fraction, and the ester content of the solids and iodine values and relative hexaene acid contents of the esters were determined. Alkaline isomerization was performed in a part of this investigation by the method of Holman and Burr (11). The refined method of Herb *et al.* (12, 13) appeared during the course of this work and was used thereafter on new units of work.

The segregations of the fatty acids of cod liver oil (400 g.), shark liver oil (400 g.), pollack liver oil (400 g.), menhaden oil (290 g.), herring oil (386 g.), salmon oil (390 g.), and Myvarine industrial oil[5] (390 g.) were performed by a procedure similar to that outlined above. The number of fractions was increased to nine or ten, and the increments of urea added were 200 g. for step 1, 150 g. for step 2, and 100 g. for subsequent steps. The last solid fraction was obtained at 5°C.

Fractionation of the methyl esters of hog adrenal lipid was effected by two somewhat different ways, each involving three precipitations with urea. In one, from 100 g. methyl esters in 750 ml. methanol, two successive precipitations were obtained by adding two 150-g. portions of urea in the usual manner. A third fraction was obtained by dissolving 30 g. urea and cooling to 5°C.

In the second method, from 100 g. methyl esters in 1,700 ml. methanol, three solid fractions were obtained by steady addition of 150 g. urea in each step. For this purpose a 2-liter cylinder was used, inside which a stainless steel perforated cone fitted snugly at the top. The urea was added to this cone, and it was then pushed slightly below the surface of the methanol solution. The top of the cylinder was heated by steam, and the bottom was cooled by an ice water bath. By this arrangement the urea dissolved slowly and passed through the cone perforations, and the inclusion compound settled down to the bottom of the cylinder.

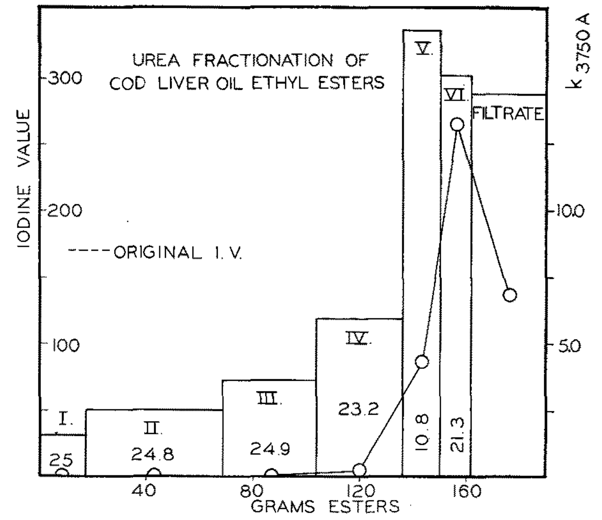

FIG. 1. Urea fractionation of cod liver oil ethyl esters. Widths of bars indicate weights of fractions, heights indicate iodine values. Circles indicate relative hexaene acid content as measured at 3750 Å after alkaline isomerization. Numbers within bars refer to ester content (%) of total precipitate.

## Results and Discussion

The results of the segregation of esters of cod liver oil are shown in Figure 1. The weight of esters in each fraction, their iodine values, and their extinction coefficients at 3,750 Å after isomerization with alkali are shown graphically. The ester contents of the solid inclusion compounds are shown for each fraction. It is obvious that the less unsaturated fatty

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[5] This is a mixture of shark liver oils obtained from Distillation Products Inc.

esters were bound in the initial fractions. The unsaturation of the ester fractions gradually increased although the hexaene acids appeared largely in the fifth and sixth fractions. It is interesting to note that the hexane content in fraction VI is greater than in the filtrate from this fraction, indicating that highly unsaturated esters can be bound as urea inclusion compounds. It should be pointed out that, in these fractions containing highly unsaturated esters, the ester content was rather low. Comparing fractions V and VI, the lowering of the temperature from room temperature to 5°C. yielded an additional fraction having a higher ester content. These observations point to the difficulty with which urea inclusion compounds of polyunsaturated esters are formed and suggest that reaction with urea is favored by lower temperatures.

The studies of fractionation of the several fish oil acid preparations showed a consistent pattern of segregation, different from that of the cod liver ethyl esters. An example is shown in Figure 2. It was found that the successive solid fractions showed increasing iodine values, all of which were lower than that of the final filtrate. The content of hexane acids did not increase significantly until the last one or two fractions were formed. The great bulk of the hexaene acids was found in the filtrate. In no solid fraction was the hexaene content comparable to that found in ester fractions V or VI. The findings suggest that the free polyunsaturated fatty acids form urea inclusion compounds with greater difficulty than do their esters. For practical purposes segregation of the hexaene acids can therefore be accomplished most easily by fractionation of the free acids, in which case nearly all will be found in the final filtrate. The iodine values of the final filtrates from all the fish oil acids segregated are listed in Table I. These results emphasize the usefulness of urea segregation for concentration of the very highly unsaturated acids derived from fish oils.

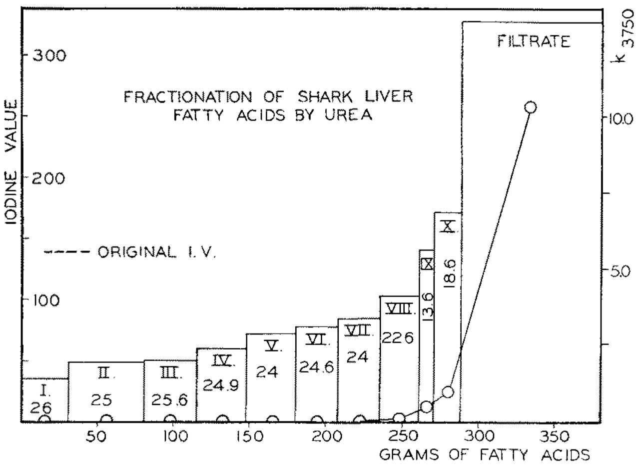

FIG. 2. Urea fractionation of shark liver oil fatty acids. Explanation of figure is the same as for Figure 1.

The results of the fractionation of hog adrenal methyl esters by the two ways previously described are presented graphically in Figure 3. The solid lines show results of the first method while the dotted lines show the results of the second, where formation of inclusion compounds took place from much more dilute methanol solution, and urea addition was gradual. The lower iodine values of the bound esters in the second experiment suggest that, under the conditions of low urea concentration and gradual addition of urea, segregation of fatty esters on the basis of unsaturation is more selective.

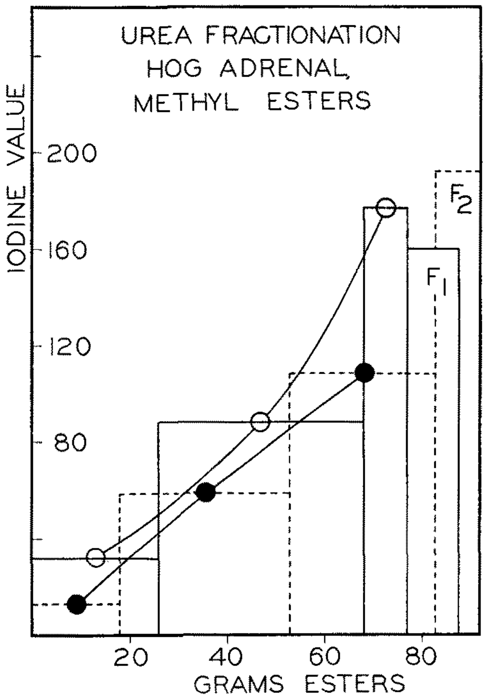

FIG. 3. Urea fractionation of hog adrenal methyl esters by two procedures. Solid lines and open circles refer to batchwise fractionation by first method. Dotted line bars and solid circles refer to gradual reaction with urea in more dilute solution. $F_1$ and $F_2$ refer to the respective final filtrates.

The striking differences in the tendencies of the highly unsaturated fatty acids and their corresponding esters to form urea inclusion compounds are difficult to explain. At first glance these appear to be due to one of three possible factors. The ethyl esters have longer chain lengths than the acids, and the lengthened chain could contribute to increased stability of their inclusion compounds. The relative position of the polar group along the chain might have an effect. Association of the acids to form dimers could also contribute to the difference between acids and esters in forming inclusion compounds.

To learn the effect of increased chain length by esterification upon the formation of inclusion compounds, a series of esters of cod liver oil fatty acids was prepared. The methyl, ethyl, n-propyl, and n-butyl esters were prepared by alkaline alcoholysis,

TABLE I

Segregation of Polyunsaturated Acids From Fish Oil Sources

| | Original fatty acids | Final filtrates |
|---|---|---|
| | *I.V.* | *I.V.* |
| Cod liver | 159.3 | 350.0 |
| Shark liver | 140.0 | 327.0 |
| Pollack liver | 155.5 | 322.0 |
| Herring | 148.0 | 294.0 |
| Salmon | 150.5 | 325.5 |
| Myvarine industrial | 122.0 | 312.5 |
| Menhaden | 167.0 | 356.0 |

using sodium (0.3-0.5% of the weight of the oil) as catalyst.

Systematic segregation of each of the ester preparations was then performed. The first fraction of inclusion compounds was obtained from 290 g. esters in 1,200 ml. methanol containing 200 g. urea. Seven subsequent fractions were obtained after adding seven 100-g. portions of urea and allowing the inclusion compounds to form overnight at room temperature. Fraction IX was prepared by cooling the filtrate from fraction No. VIII to —10°C. over night. Fraction No. X was obtained by adding 100 g. urea to the filtrate from Fraction No. IX and subsequent removal of solvent under reduced pressure without applying heat. The last fraction of inclusion compounds was filtered and washed with benzene, and the benzene washings were added to the filtrate.

Results of the fractionation showed a great similarity to those already obtained with the ethyl esters of cod liver oil fatty acids in that the last inclusion compounds were richer in their content of the highly unsaturated esters. An example of these results is presented in Figure 4 for the n-butyl esters of cod liver oil fatty acids. The segregation patterns of the various ester preparations did not show sufficient differences to indicate that increase in chain length has a significant effect on the tendency of the highly unsaturated esters to form urea inclusion compounds.

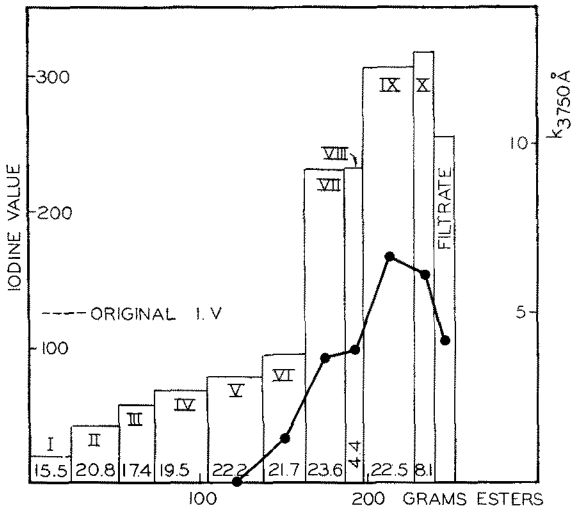

FIG. 4. Urea fractionation of cod liver oil-butyl esters. Explanation of figure is the same as for Figure 1.

It thus appears that the carboxyl group is the important factor in reducing the tendency of the highly unsaturated acids to form the inclusion compounds.

To verify these general observations, a few more experiments with pure substances were planned. If masking the carboxyl group by esterification is the major factor contributing to the difference in tendency to bind with urea, one should expect the n-alkyl esters of a pure unsaturated fatty acid to give a larger yield of inclusion compounds than the parent acid under standard conditions. If the greater tendency of the esters to form inclusion compounds is caused by the mere lengthening of the carbon chain, increasing the chain length of the esters should also give comparable increases in the yields of inclusion compounds.

Linoleic and linolenic acids obtained from the Hormel Foundation were used in these experiments. The various esters were prepared by esterifying the acids with the corresponding alcohols using sulfuric acid catalyst. A series of saturated fatty acids and their methyl and ethyl esters were also used in these experiments for comparison with linoleic and linolenic acids and their esters. The inclusion compounds were prepared by adding 30 ml. of a warm saturated solution of urea in methanol to 1.0 g. of acid or ester and cooling to room temperature with occasional shaking. The yields are presented in Table II.

TABLE II

Yields of Urea Complexes of Pure Acids and Their n-Alkyl Esters

| Substance | Temperature | $\frac{\text{g. complex}^{a}}{\text{g. substance}}$ |
|---|---|---|
| Linoleic acid | 25° | 1.45 |
| Methyl linoleate | | 2.44 |
| Ethyl linoleate | | 2.55 |
| n-Propyl linoleate | | 2.74 |
| n-Butyl linoleate | | 2.98 |
| Linolenic acid | 21° | 1.72 |
| Methyl linolenate | | 2.84 |
| Ethyl linolenate | | 2.93 |
| Palmitic acid | 25° | 3.98 |
| Methyl palmitate | | 4.05 |
| Ethyl palmitate | | 3.90 |
| Myristic acid | 30° | 2.49 |
| Methyl myristate | | 3.71 |
| Ethyl myristate | | 2.91 |
| Lauric acid | | 1.63 |
| Ethyl laurate | | 2.65 |
| Capric acid | | 0.65 |
| Ethyl caprate | | 2.14 |
| Caprylic acid | | 0.00 |
| Ethyl caprylate | | 1.21 |
| Ethyl caprate | 26° | 2.09 |
| Hexyl caproate | | 1.46 |

[a] Inclusion compounds contain approximately 25% of the included substance.

These data again show that unsaturated acids have less tendency to form urea inclusion compounds than do their esters and that the differences in tendency for various esters to react with urea are minor compared with the difference between acid and esters. In the case of linoleates where the series is complete, successive lengthening of the carbon chain by one carbon atom increased the yield of inclusion compound by small increments as might be expected. But it is clear that the major increase in yield of urea inclusion compounds consequent to esterification is not due to mere lengthening of the chain.

The phenomenon is not limited to unsaturated acids and esters for with short chain saturated fatty acids and esters the same difference in yield of urea inclusion compounds is apparent. From Table II it will be seen that with the pairs of compounds having the same empirical formula, the ester gives a higher yield than the acid. Thus ethyl caprylate > capric acid, ethyl caprate > lauric acid, and ethyl laurate > myristic acid. It seems clear that the difference in yield of inclusion compounds between acids and their esters is largely due to the masking of the carboxyl group and that as the chain length increases, this difference disappears.

These observations suggest that the heat increment of an ester group is greater than that of an acid. However this is contrary to the data of Schlenk (3) and Redlich *et al.* (14), who found that the molar heat of formation of acids was greater than that of the corresponding esters.

A comparison of yields from ethyl *n*-caprate and *n*-hexyl-*n*-caproate, which differ only in the relative position of the ester group along the carbon chain, was made (Table II). Moving the polar group from near the end of the molecule to its center decreased the yield. The improved tendency of esters to yield inclusion compounds thus is not due to shifting the polar group of the acid away from the end of the molecule.

The presence of double bonds in the fatty acid molecules introduces steric irregularities in the fatty acid chain and consequent imbalance of the optimum intermolecular distances, diminishing the net attractive force stabilizing the inclusion compound. Shortening the carbon chain also reduces the energy of inclusion compound formation. With long chain saturated compounds the energy of formation of urea inclusion compounds is high and differences between acids and their esters are not apparent, but when the chain length is shortened or made irregular by the presence of double bonds, the total energy of formation is reduced to a point where differences between acid and ester are significant. It may be that the hydrogen bonding of two acids in an associated dimer reduces the total energy available for urea inclusion compound formation but that the potential ability of the carbonyl group to hydrogen bond with urea in the crystal lattice remains in the ester.

### Summary

1. Urea segregation has been found to be a useful tool in concentration of highly unsaturated acids and esters. Fatty acids and esters derived from fish oils and methyl esters of hog adrenal fatty acids have been fractionated, and the polyunsaturated acids have been enriched.

2. The tendency for fatty acids and esters to combine with urea decreases with increasing unsaturation. Combination is favored by lowered temperature. Polyunsaturated acids are concentrated in the final filtrate whereas esters of these acids appear in the final inclusion compound fractions. Fatty acid concentrates have been obtained with iodine values ranging from 294 to 356. Bound esters exhibited iodine values as high as 338.

3. The increased chain length brought about by esterification has a minor role in increasing the yield of inclusion compounds. Likewise, shifting of the terminal polar group in an acid toward the center of the molecule by esterification does not explain the higher yield of inclusion compound from esters.

4. The improved tendency of esterified acids to form urea inclusion compounds is probably due to blocking of association of acid groups. This effect is found in unsaturated acids and in short chain saturated acids. In long chain saturated acids and esters this effect is not noticed. Both give high yields of inclusion compounds because the effect of the carboxyl group is overshadowed by the high energy of formation contributed by the long carbon chain.

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# Comparative Detergency of Several Built Polyethenoxy Alkanoates

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NONIONIC detergents are generally composed of a hydrophobic radical such as a fatty or rosin acid (RCOOH) solubilized by a hydrophilic end group such as a polyethenoxy chain:

$$R\text{-}COO\text{-}(CH_2\text{-}CH_2\text{-}O)_x\text{-}H$$

In a previous article (1) the comparative detergency of polyethenoxy tallates was presented, and the optimum polyethenoxy or hydrophilic chain length for various tall oils rich in mixtures of fatty as well as rosin acids was determined. It seemed desirable to investigate the effect on detergency of the hydrophobic or alkanoate chain length in nonionic esters as well as the optimum ethenoxy chain length for each fatty acid. Therefore pelargonic, lauric, myristic, and stearic acids were condensed with various proportions of ethylene oxide, and the average molecular size of each sample was accurately determined by a saponification equivalent. Comparative detergency values in hard and soft water were determined on built compositions of each condensate, and the optimum combinations of hydrophobic to hydrophilic chain lengths were ascertained.

Since tall oils are known to contain secondary alcohols, such as various sterols in the non-saponifiable fraction along with the rosin and fatty acids, it became of interest to study the condensation of an alkanoic acid containing a secondary hydroxyl group and to ascertain the relative proportions of ether to ester formation as well as to determine the effect, if any, upon detergency. Since primary long chain alcohols have been successfully condensed (2) with ethylene