tained compared with figures obtained by the official method. The agreement was satisfactory. Several minor suggestions were made, all of which were passed on to the Fisher Scientific Co.

Miscellaneous

The Committee has been requested to study some procedure by which to better evaluate fats for soap production with respect to color. This problem is being considered but we have no data to present now.

The following people have collaborated with the Committee in some part of this program: R. T. Milner, G. W. Agee, J. J. Ganucheau and B. W. Beadle.

E. W. Blank
E. W. Colt
F. G. Dollear
J. L. Laing
J. Fitelson
C. P. Long
J. E. Maroney
L. B. Parsons
H. A. Schuette
S. O. Sorensen
L. M. Tolman
F. C. Woekel
V. C. Mehlenbacher, *chairman*

Report of the Committee On Uniform Methods and Cooperative Work

Fall Convention—1944

Only two committee reports were submitted for consideration of the Committee on Uniform Methods and Cooperative Work at this Fall Meeting in Chicago, Oct. 25-27.

Soap Analysis Committee:

The Soap Analysis Committee report as submitted by M. L. Sheely, chairman, contained two recommendations. These were as follows:

1. That the complete set of methods for soaps containing synthetic detergents be adopted as tentative. The committee described these methods in their report.
2. That a new procedure for the determination of potassium hydroxide and potassium carbonate in potash paste soaps also be adopted as tentative.

These recommendations were considered by the Committee on Uniform Methods and Cooperative Work and have their approval. Upon motion by the chairman of the latter committee, and a proper second from the floor, these recommendations were adopted.

The Committee on Analysis of Commercial Fats and Oils:

This committee has done considerable work and has made the following recommendations with reference to changes in the Thiocyanogen method:

1. Increase the reagent from an excess of 100-150% to 150-200%.
2. Increase the potassium iodide from 1.00 gram to 1.66 grams.

With reference to the Fat Analysis Committee color standards they recommended that the table of interpretation, which has been published previously in Oil and Soap, be incorporated as part of the method.

All of the above recommendations were considered by the Committee on Uniform Methods and Cooperative Work and have their approval. Upon motion by the chairman of the latter committee, with a proper second from the chair, these recommendations were unanimously adopted.

J. T. R. Andrews
J. J. Ganucheau
C. P. Long
E. B. Freyer
T. C. Law
H. P. Trevithick
J. J. Vollertsen, Chairman

Solidification Point Curves of Binary Acid Mixtures

IV. Triacontanoic to Tetratriacontanoic Acids[1]

H. A. SCHUETTE, D. A. ROTH,[2] and R. M. CHRISTENSON [3]
University of Wisconsin, Madison, Wis.

IN earlier communications (6) from this laboratory on the subject of the analytical chemistry of the fatty acids there have been presented solidification-point diagrams for binary mixtures of consecutive pairs of so-called "even" acids from *n*-decanoic to *n*-triacontanoic and a discussion of the qualitative and quantitative aspects of these diagrams when viewed as analytical tools. With this communication we extend the list to the C_{34} acid, thus enlarging the scope of application of the resulting phase diagrams of binary mixtures to lac wax, cotton wax, and beeswax. The latter probably contains all of the even *n*-fatty acids from C_{24} to C_{34} (2), but a quantitative analysis of even so common a product has not yet been carried out.

The use of solidification-point diagrams in the analysis of fatty acid mixtures is dependent upon the fractional distillation of their methyl or ethyl esters into binary mixtures. Although the problem does not usually arise in the analysis of the glyceride oils, a successful separation of the acids commonly associated with many of the waxes must still be mastered; that it will come through improved distillation techniques is quite probable if our own experiences with Chinese insect wax (6d) may be deemed prophetic of success.

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[1] This investigation was supported in part by a grant from the Wisconsin Alumni Research Foundation, whose aid is gratefully acknowledged.

[2] Now Ensign, USNR. His doctoral dissertation, 1944, formed the basis for this communication.

[3] Present address: Pittsburgh Plate Glass Company, Milwaukee, Wis.

The *n*-fatty acids used in this study were of necessity prepared synthetically. Departing from our former practice of laboriously lengthening the chain by the step-wise addition of two carbon atoms, the process was shortened, but not successfully so in our first attempts, by increasing the number added at a time. The most direct method of affecting the formation of a carbon-to-carbon bond in a case of this type was suggested by the possibility of bringing about a reaction between a straight chain hydrocarbon with a terminal acetylenic group and a bifunctional straight chain compound containing a carboxyl, or a potential carboxyl, group at one end and a halogen atom at the other, viz:

$$RC \equiv CNa + X\,(CH_2)_n\,COOR \longrightarrow RC \equiv C\,(CH_2)_n\,COOR$$

This reaction, if successful, would be of value in the synthesis of unsaturated as well as saturated acids since methods are available for the reduction of acetylenic to ethylenic bonds. Although the possibility of the use of such a reaction was strengthened by the synthesis of behenolic acid by Bhattacharya *et al.* (1), difficulties subsequently encountered in the preparation of the necessary acetylene derivatives and even small amounts of the appropriate derivative of the high molecular weight acid led us to abandon this phase of the study for more promising methods.

Dotriacontanoic acid was obtained by coupling docosyl zinc iodide with ω-carbethoxynonoyl chloride (5) or the half-ester half-acid chloride of sebacic acid. The resulting ester was converted to the corresponding *n*-saturated acid by reducing the keto group to hydroxyl, replacing the latter with iodine and then reducing the iodo acid with zinc dust in glacial acetic acid.

Tetratriacontanoic acid was prepared in 74% yield from dotriacontanoic acid by the classic malonic ester synthesis using the sequence of reactions and applying all the precautionary measures previously described (6d) to insure purity and yield of intermediates and product. Benzene was found to be the most satisfactory solvent for the recrystallization of these long-chain acids. It is necessary, however, to cool the solution slowly in order to obtain a crystalline product.

TABLE 1

Transition Point Data

Acid	Solidification Point		Resolidification Point[1] Reported[2]
	Observed	Reported[2]	
	°C.	°C.	°C.
Triacontanoic	93.10	......	93.2
Dotriacontanoic	95.42	......	95.5
Tetratricontanoic	97.75	98.0	97.8

[1] The resolidification point is that temperature at which the *partly* molten specimen in the capillary tube commences to resolidify when the temperature is lowered very slowly. It is a close approximation of the true solidification point.

[2] Frances, F., and Piper, S. H., J. Am. Chem. Soc. *61*, 577 (1939).

The solidification points (Table 1) of the acids which form the basis for this communication were found to be in agreement with what are deemed to be the best published values. Some 11 mixtures of two pairs of adjacent acids were made (Table 2), and diagrams were constructed (Figure 1) from the pertinent solidification-point composition data as before (6a).

TABLE 2

Solidification Points of Binary Acid Mixtures

Triacontanoic-Dotriacontanoic Acids		Dotriacontanoic-Tetratriacontanoic Acids	
Composition C_{30} Acid	Solidification Point	Composition C_{32} Acid	Solidification Point
mol. %	*°C.(corr.)*	*mol. %*	*°C.(corr.)*
0.00	95.40	0.00	97.75
9.07	93.98	10.12	96.20
21.46	91.88	25.40	93.98
35.95	90.02	34.48	92.71
42.94	89.46	43.06	92.15
50.64	89.22	51.77	91.84
59.68	89.02	60.45	91.71
68.26	88.78	65.26	91.41
72.20	88.67	70.41	91.35
76.26	88.69	75.87	91.45
80.21	88.86	84.36	91.88
84.12	89.30	92.09	93.57
92.17	91.11	100.00	95.40
100.00	93.10	....	....

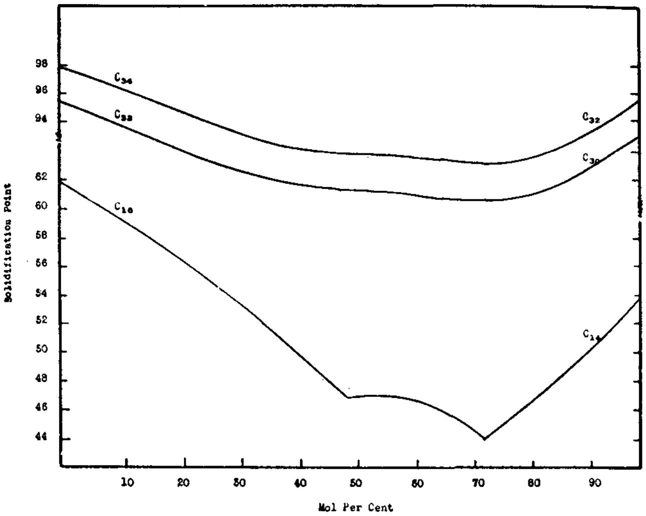

FIG. 1. Solidification point diagrams of binary mixtures of triacontanoic, dotriacontanoic and tetratriacontanoic acids.

Synthesis of Dotriacontanoic Acid

Ethyl Erucate. Rapeseed oil (600 g.) was heated for 24 hours with 1800 cc. of 95% ethanol containing 5% by weight of sulfuric acid. After removal of about one-half of the alcohol by distillation and its subsequent replacement by benzene, the whole was washed with water and re-extracted. The combined benzene extracts were washed with water and sodium bicarbonate solution (5%), dried with calcium chloride, and filtered. The crude esters, after removal of solvent, were distilled through a modified Widmer column. After a liberal forerun 252 g. of ethyl erucate were collected at 196-202° at 0.5 mm. Analysis revealed a saponification equivalent of 365.8; $C_{24}H_{46}O_2$ requires 366.5.

The method of preparation described above is far superior to the traditional hydrolysis-crystallization procedure (4).

ω-Carbethoxynonoyl Chloride. Ethyl hydrogen sebacate (75 g.), prepared by the interaction of the acid and its diethyl ester (7), and thionyl chloride (45 g.) were heated at 35° for four hours. After removal of the volatile products with aspirator vacuum at 100°, the ω-carbethoxynonoyl chloride was distilled through a modified Widmer column, a yield of 74% (b.p. 129-132° at 1 mm.) being obtained.

10-Ketodotriacontanoic Acid. A Grignard reagent was prepared from 21.8 g. docosyl iodide, obtained by the hydrogenolysis of ethyl erucate over copper-chromium oxide at 250° and 250 at. pressure, and subsequent interaction of the resulting alcohol with iodine in the presence of red phosphorus (6d), and 1.2 g. of fine magnesium turnings. The reaction was carried out in the conventional manner (3) except that the contents of the flask were stirred at room temperature with occasional heating to reflux temperature for 24 hours. Freshly fused zinc chloride (6.7 g.), dissolved in anhydrous ether, was added to the dark colored suspension of the Grignard reagent after which about one-half of the ether was distilled off while vigorous stirring was continued. The white suspended material which had formed was dissolved by the addition of 75 cc. of dry benzene after which ω-carbethoxynonoyl chloride (12.4 g. in 100 cc. of benzene) was added over a period of 40 minutes. The solution was vigorously stirred at reflux temperature for four hours. Hydrochloric acid solution (10%) was then cautiously added with stirring. The benzene layer was transferred to a two-liter separatory funnel with enough solvent (500 cc.) to keep the product in solution, then successively washed with warm water, sodium bicarbonate solution and water, dried with calcium chloride, and filtered before recovery of the benzene. To the residue, after saponification with an alcoholic solution of potassium hydroxide, barium chloride was added in order to precipitate the partially soluble potassium 10-ketodotriacontanoate. The contents of the flask were cooled to 10° and filtered. The barium soaps were dried at 110° under reduced pressure and then extracted with benzene in a Soxhlet extractor.

The barium soap was converted to the acid by suspending it in one liter of hot water to which, while stirring, enough hydrochloric acid solution was added to make the final concentration about 5%. The 10-ketodotriacontanoate acid, after recovery and drying, was esterified with ethanol containing sulphuric acid as catalyst. Its melting point, after recrystallization from ethanol, was found to be 74.4-74.8°. A yield of 35%, based on the docosyl iodide, was obtained.

10-Hydroxydotriacontanoic Acid. The keto ester (17.6 g.) and 50 cc. of anhydrous ethanol were heated with hydrogen for six hours at 150° and 100 at. pressure in the presence of Raney nickel. The resulting hydroxy ester (m.p. 81.8-82.5°), dissolved in one liter of boiling ethanol, was saponified by adding to it five grams of potassium hydroxide as a saturated solution and heating the mixture under reflux for six hours. The acid was liberated from the resulting soap—17.6 g. were obtained by agitating it for one hour in one liter of hydrochloric acid solution (5%). A yield of 16.6 g. of acid, melting at 120—-122°, was obtained.

10-Iododotriacontanoic Acid. The hydroxy acid (16.7 g.) iodine (5 g.) and red phosphorus (0.4 g.) were heated, with stirring, for 4.5 hours at 100° to 135°. The resulting iodo acid, which is very soluble in hydrocarbon solvents, was taken up in benzene and in this condition was washed first with water and then with sodium sulfite solution (5%). Finally it was dried over calcium chloride. On recovering the benzene by distillation, 19.8 g. of crude product (theoretical 20.4 g.) were obtained.

Dotriacontanoic Acid. The iodo acid was dissolved without further purification in 200 cc. of glacial acetic acid. The solution was heated to gentle reflux whereupon six grams of zinc dust were added in one-gram portions at 20-minute intervals. One-half liter of water was added to the warm filtrate in order to complete the precipitation of the acid which had already begun with a drop in temperature. On attempting to recrystallize the product from 500 cc. of acetic acid an insoluble layer formed because of the presence of water. Benzene (40 cc.) was then added and by boiling off a small amount of the mixed solvent enough water was removed to give a homogeneous solution. From the latter, upon being cooled, there was obtained a white solid which was subsequently recrystallized from benzene. Recrystallization from 500 cc. of benzene after boiling with charcoal and filter cell gave 13 g. of glistening plates of solidification point 95.42. This represents a yield of 76% from the keto ester.

Summary

n-Dotriacontanoic and *n*-tetratriacontanoic acids were synthesized for the purpose of preparing the solidification-point curves of binary acids in the series C_{30} to C_{34}. These curves are a continuation of the *n*-fatty acid series from C_{10} to C_{30} previously reported. Those presented in this communication indicate the tendency of the curves to assume a flattened form, with less pronounced breaks, as the homologous series of these compounds is ascended. The lower curves of the series have found application in the identification and estimation of the individual saturated fatty acids of glyceride oils. It is hoped that the long-chain acids which occur in waxes may be determined by a similar application of the higher curves.

Dotriacontanoic acid was obtained from the action of docosyl zinc iodide on the half-ester half-acid chloride of sebacic acid. The resulting keto ester was converted to the corresponding *n*-saturated acid by a modified procedure. This modified procedure involved reduction of the keto group to the hydroxy group, replacement of the hydroxy group with iodine and subsequent reduction of the iodo acid with zinc dust in glacial acetic acid.

Tetratriacontanoic acid was prepared from dotriacontanoic acid by a malonic-ester synthesis.

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