

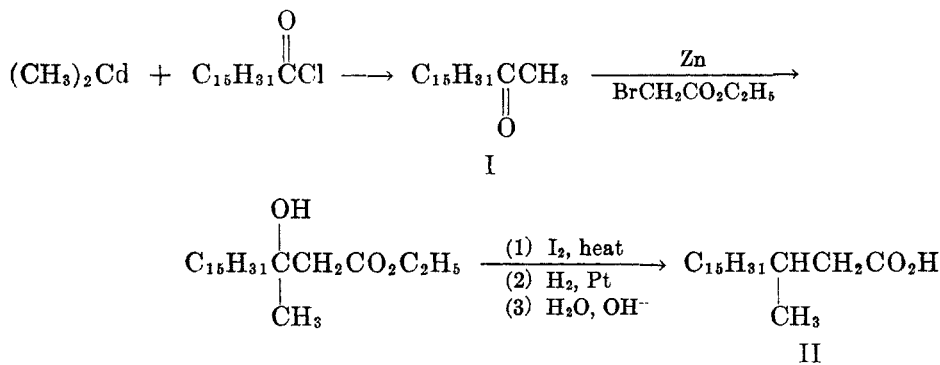
BRANCHED-CHAIN FATTY ACIDS. X. SYNTHESIS OF ACIDS WITH BRANCHING METHYL GROUPS NEAR THE CARBOXYL

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In order to make a study of the effect of neighboring branching groups on the rate of hydrolysis of amides, as reported in the next paper of this series, it was necessary to prepare several branched-chain acids with one or more methyl groups on carbons near the carboxyl. The preparation of α -methyl acids is easily accomplished by alkylation of diethyl methylmalonate, followed by hydrolysis and decarboxylation. The two acids prepared for the present work, 2-methyloctadecanoic acid and 2-methyldocosanoic acid, have been synthesized previously (1), and our constants were in good agreement with those previously reported.

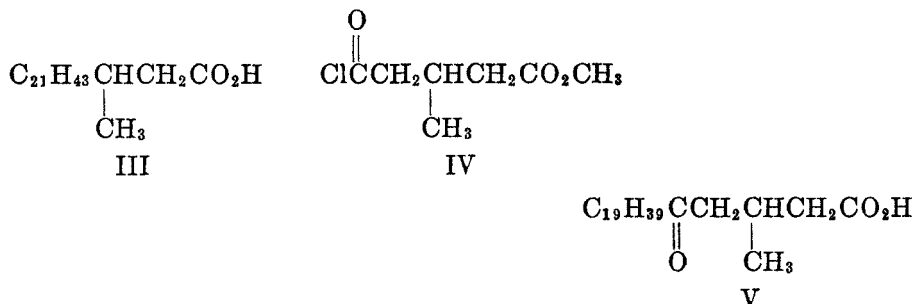
Two β -methyl acids, 3-methyloctadecanoic acid (II) and 3-methyltetracosanoic acid (III), were prepared. Both of these acids have also been prepared previously, but by less convenient or less satisfactory procedures. 3-Methyloctadecanoic acid (2) was prepared previously by alkylation of diethyl malonate with 2-bromoheptadecane, no precautions being taken to avoid formation of isomeric secondary bromides during conversion of 2-heptadecanol to its bromide. It has been pointed out in a previous paper (3) of this series that the use of secondary halides for synthesis of pure compounds is undesirable. The previous sample of 3-methyloctadecanoic acid was purified with great difficulty, and the best sample was reported as melting at 48.5–49°. The sample prepared in the present work, by methods utilizing no secondary halides, was purified with ease and melted at 50.8–51.3°. The sequence of reactions used was the following:



The yields at all steps were reasonably good.

3-Methyltetracosanoic acid was prepared from the acid chloride (IV) of methyl hydrogen β -methylglutarate, a very convenient starting material intro-

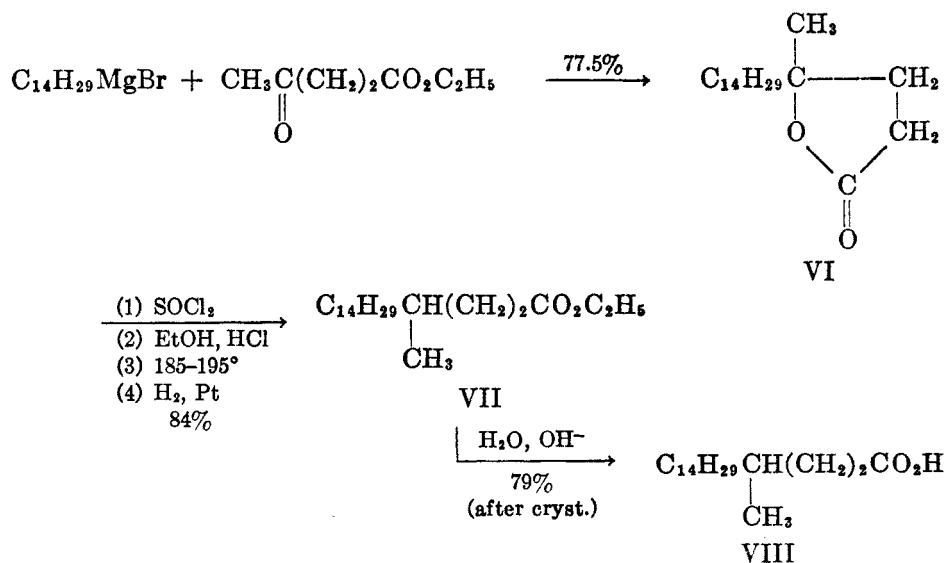
duced by Ställberg-Stenhagen (4) for preparation of either racemic or optically active branched-chain acids. This starting material was also used for the previous preparation (5) of 3-methyltetracosanoic acid, proceeding by way of a multistep process, involving acylation and alkylation of β -keto esters to 3-methyl-5-ketotetracosanoic acid (V).



In the present work, the ester of keto acid, V, was obtained in one step in 80% yield by reaction of the acid chloride, IV, with the cadmium reagent from *n*-nonadecyl bromide. Wolff-Kishner reduction of this keto ester yielded the desired branched-chain acid, III.

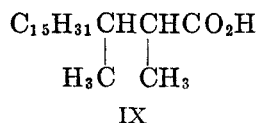
n-Pentacosanoic acid, needed for the investigation reported in the next paper, was prepared by a similar sequence of reactions, starting with the ester acid chloride of pimelic acid and the cadmium reagent from *n*-octadecyl bromide.

4-Methyloctadecanoic acid (VIII) was prepared by a method previously used (3, 6) for making 4-methyl acids or alcohols of lower molecular weight. The process was found equally effective with *n*-tetradecyl bromide as starting material, as indicated in the following equations.



The yields are comparable with those previously obtained. In the low-pressure hydrogenation to give ester, VII, the hydrogen absorption was equal to theory, within the limits of accuracy of the equipment used; nevertheless, after five crystallizations of acid VIII from acetone, the product (m.p. 51.2–51.6°; theoretical equivalent weight) gave a weakly positive Baeyer's test for unsaturation. Neither the melting point nor the unsaturation test could be altered by further crystallization. After rehydrogenation in glacial acetic acid (with no appreciable drop in pressure) and recrystallization, the acid melted at 52.6–52.8° and gave a negative test for unsaturation. Apparently, traces of unsaturated acid were carried along in solid solution or in mixed crystals.

2,3-Dimethyloctadecanoic acid (IX) was prepared from 2-heptadecanone and ethyl α -bromopropionate *via* the Reformatsky reaction, by a sequence of reactions similar to that outlined for preparation of acid, II.



The yield in this Reformatsky reaction was very poor, however, even with a large excess of zinc and bromo ester, and the over-all yield of acid IX was only 9%, in contrast with the 45% over-all yield of acid II. For preparation of larger amounts of this acid, required for other work, different methods of synthesis are being investigated. The synthetic 2,3-dimethyloctadecanoic acid consists of a mixture of two racemic forms. One of these, m.p. 63.4–64.4°, was easily isolated by recrystallization of the synthetic mixture from acetone.

EXPERIMENTAL

Microanalyses by C. W. Koch and V. H. Tashinian. All melting points are corrected, all boiling points are uncorrected. All distillations, unless otherwise specified, were through a half-meter Podbielniak type column with heated jacket and partial reflux head.

2-Methyloctadecanoic acid was prepared essentially as described by Schneider and Spielman (1). Similar yields were obtained with hexadecyl bromide or hexadecyl iodide. After several crystallizations from acetone the constant m.p. 54.6–55.1° was reached (S. and S., 54.5°).

The *amide* was prepared by the method used for others described in this paper, as follows. A mixture of 10 g. of acid and 8 g. (2 mole equivs.) of thionyl chloride was heated under reflux until gas evolution had ceased (1–2 hours), then excess thionyl chloride was removed *in vacuo*. The residual acid chloride, dissolved in dry, purified dioxane, was added dropwise to a stirred solution of ice-cold concentrated aqueous ammonium hydroxide. The white, crystalline amide precipitated in nearly quantitative yield. After four crystallizations from methanol, *2-methyloctadecanamide* had the constant m.p. 105.3–105.7° (S. and S. 104.5°).

The *tribromoanilide* was prepared as previously described (7), except that the acid chloride was made with thionyl chloride; yield, after one crystallization from ethanol, 81%, m.p. 101–103°. After four more crystallizations, the constant m.p. 117.2–117.3° was reached.

Anal. Calc'd for $\text{C}_{25}\text{H}_{40}\text{Br}_3\text{NO}$: C, 49.21; H, 6.60.

Found: C, 49.56; H, 6.58.

2-Methyldocosanoic acid. The starting material for preparation of 1-bromoeicosane required for this synthesis was a commercial product (Neo-fat No. 17, Armour and Co.) described as a mixture of unsaturated C₂₂ acids. A 200-g. sample of this material was esterified with 270 ml. of absolute ethanol containing 13 ml. of concentrated sulfuric acid. After dilution of the reaction mixture with water and extraction, the esters were distilled from a Claisen flask to yield 101 g. of b.p. 150–220° (2 mm.). There was a large tarry distillation residue. The distillate was hydrogenated in the presence of 20 g. of copper chromite catalyst (8), at 250° and an initial cold pressure of 4000 lbs. per sq. in. (272 atmos.). Hydrogenation was complete in 90 minutes, and the pressure drop corresponded to consumption of 6.5 moles of hydrogen per mole of ester (calculated as C₂₂). The resultant mixture of solid alcohols was distilled from a Claisen flask, b.p. 158–210° (2 mm.), wt. 96.1 g. The alcohol mixture was treated with anhydrous hydrogen bromide by the usual method (9) and the bromides distilled through the column. The following fractions were obtained:

FRACTION NO.	PRESSURE, MM. Hg	B.P., °C.	WEIGHT G.
1	2.0	150–172	5.9
2	2.0	172–174	12.0
3	2.2	174–187	10.7
4	2.2	188–190	13.5
5	2.2	190–203	5.2
6	2.2	203–205	20.8
7	2.2	205–223	3.3
8	2.2	223–225	14.1
Residue	—	—	2.4

Since Fraction 6 is eicosyl bromide (*cf.* below), Fractions 2, 4, and 8 must be respectively hexadecyl, octadecyl, and docosyl bromides. Thus, Neo-fat No. 17 appears an excellent source of a variety of bromides, although not a high yield source of any one bromide.

Fraction 6 was redistilled and a center cut of 13.6 g. of crystalline eicosyl bromide used for preparation of 2-methyldocosanoic acid. After purification of the acid by distillation of its methyl ester and three crystallizations from acetone, the m.p. was 66.7–66.9° (S. and S. 67–67.5°); equiv. wt. 354.7 (Calc'd 354.6).

The *amide*, after one crystallization from methanol, reached the constant m.p. 109.4–109.8° (S. and S. 109–109.5°).

2-Heptadecanone (I). Pure palmitic acid was isolated from Armour's Neo-fat No. 1–56. A 500-g. lot was esterified with methanol and sulfuric acid, and the esters were distilled to yield 64% of methyl palmitate, b.p. 165–167° (4 mm.). There was also obtained a few per cent of methyl myristate and about 14% of methyl stearate. Palmityl chloride, prepared from the acid with thionyl chloride in 85% yield, was distilled rapidly from a Claisen flask, b.p. 165–170° (4 mm.).

A solution of dimethylcadmium in 250 ml. of benzene was prepared as has been previously described (10) from 10.3 g. (0.425 atom) of magnesium and excess methyl bromide. To the stirred solution, originally at room temperature, there was added during about two minutes a solution of 65.9 g. (0.24 mole) of palmityl chloride in 75 ml. of benzene. After spontaneous reflux had ceased, heating under reflux with stirring was continued for one hour, then the mixture was worked up as has been described for keto esters (11). Distillation in a Claisen flask yielded 37 g. (61%) of crystalline distillate. Systematic recrystallization from methanol gave a total yield of 33.5 g. (55%) of pure 2-heptadecanone, m.p. 44.5–46.3°. The best sample melted at 45.0–46.5° [literature, m.p. 48° (12), 46.2–46.7° (2)].

3-Methyloctadecanoic acid (II). In a three-necked flask fitted with efficient mechanical stirrer was placed 125 ml. of dry sulfur-free toluene and 13 g. (0.2 atom) of zinc foil which

had been cut in strips, sanded lightly, and made into loose rolls. The apparatus was dried thoroughly by distillation of 25 ml. of toluene, then the mixture in the flask was kept at boiling as there was added, during one hour, a solution of 50 g. (0.3 mole) of ethyl bromoacetate and 25.5 g. (0.1 mole) of 2-heptadecanone in 100 ml. of toluene. Although the zinc had dissolved soon after addition was complete, heating under reflux with stirring was continued for an additional hour. After the organometallic complex had been decomposed with ice and dilute sulfuric acid the aqueous layer was separated and extracted with benzene. The extracts were washed with water and saturated sodium chloride solution, and solvent was removed by distillation, last traces in a vacuum. The residue was heated at 190–200° with a few crystals of iodine for one hour. The unsaturated ester was rapidly distilled from a Claisen flask, b.p. 186–200° (4 mm.), weight 16.3 g. (50.5%).

Hydrogenation of the unsaturated ester at room temperature with 0.1 g. of platinum catalyst in 50 ml. of 95% ethanol was complete in about 6 minutes. Ethyl 3-methyloctadecanoate was obtained in quantitative yield, b.p. 186–188° (4 mm.). Saponification of 19.5 g. of the ester with 2 equivalents of 7% alcoholic potassium hydroxide gave a quantitative yield of crude acid, m.p. 48.6–49.8°. After one crystallization from acetone, there was obtained 15.8 g. of acid, and after two additional crystallizations, the m.p. was constant at 50.8–51.3°, equiv. wt., 298.5 (calc'd 298.5). The acid previously prepared (2) from a secondary halide was reported as melting at 48.5–49°.

The *amide*, after four crystallizations from methanol, melted at 93.6–94°.

Anal. Calc'd for $C_{19}H_{39}NO$: C, 76.71; H, 13.21.

Found: C, 76.59; H, 13.34.

The *tribromoanilide*, after three crystallizations from 95% ethanol, formed clusters of white needles, m.p. 110.2–110.6°.

Anal. Calc'd for $C_{25}H_{40}Br_3NO$: C, 49.21; H, 6.60.

Found: C, 49.38; H, 6.55.

2,3-Dimethyloctadecanoic acid (IX) was prepared by the procedure described for acid, II, except that in the Reformatsky reaction there was used 0.1 mole of 2-heptadecanone, 0.25 atom of zinc, and 0.5 mole of ethyl α -bromopropionate. The ethyl 2,3-dimethyloctadecanoate fraction of only 5.7 g. contained some 2-heptadecanone, which was removed from the acid after saponification. This reaction is probably subject to improvement but was not further investigated, since enough of the product for present purposes had been obtained, and other methods appear more promising for larger scale production.

After one crystallization of the crude 2,3-dimethyloctadecanoic acid from acetone, there was obtained 2.4 g. of m.p. 55.2–60°. After two additional crystallizations, one racemic form was obtained, m.p. 63.0–64.0°.

Anal. Calc'd for $C_{20}H_{40}O_2$: equiv. wt., 312.5. Found: equiv. wt., 312.7.

The *amide*, prepared from the acid from mother liquors of the above crystallizations, was obtained in 92% yield, and after crystallization from methanol melted at 63–69° (sample a). After several additional crystallizations, a sample (b) melting at 90–92.8° was obtained. Analyses indicate that these samples differ only in stereoisomeric content.

Anal. Calc'd for $C_{20}H_{41}NO$: N, 4.52. Found: (sample a) N, 4.52; (sample b) N, 4.62.

n-Nonadecyl bromide. Ethyl *n*-nonadecanoate was prepared from *n*-octadecyl bromide according to the method of Ruhoff (13), except that the yield was improved by use of a simpler and more efficient esterification process. From 374.5 g. (1.12 moles) of commercial *n*-octadecyl bromide there was obtained a quantitative yield of crude *n*-nonadecanoic acid, which, after four crystallizations from benzene-acetone, melted at 67.3–67.8° [Francis and Piper (14), m.p. 68.65°]. *n-Nonadecanamide*, after four crystallizations from methanol, melted at 109.5–109.8°. Since this amide appears not to have been prepared previously, it was analyzed.

Anal. Calc'd for $C_{19}H_{39}NO$: N, 4.71. Found: N, 4.68.

The crude acid (1.12 moles) was heated under reflux for two hours with 1100 ml. (16.9 moles) of commercial absolute ethanol and 44 ml. of concentrated sulfuric acid. After dilution of the reaction mixture with 3.5 liters of water and addition of sufficient ether and benzene to dissolve the solid ester, a small amount of dark solid was removed from the two-

phase solution by suction filtration. The aqueous phase was extracted with two additional portions of benzene, then the extracts were washed with water and 5% sodium carbonate solution. About 5 g. of sodium nonadecanoate was filtered from the two-phase solution during the latter extraction. Distillation of the solvent from the extracts and distillation from a Claisen flask of the residue yielded 340 g. (93%) of white crystalline ethyl nonadecanoate, b.p. 193–199° (2 mm.). Literature (15), b.p. 166–168° (0.3 mm.).

The ester (112 g.) was hydrogenated in the presence of 15 g. of copper chromite catalyst (8) at 270° at an initial cold pressure of 2350 lbs. per sq. in (194 atmos.). Hydrogenation was complete in about 2 hours from the time shaker and heater were started. Catalyst was filtered from a solution of the product in 1 liter of benzene. Distillation from a Claisen flask yielded 93 g. (95%) of white crystalline *n*-nonadecanol, b.p. 204–217° (3 mm.), m.p. 59–61° [literature (15), m.p. 62–63°].

The bromide was prepared from 96.5 g. of the alcohol with anhydrous hydrogen bromide, following the usual procedure (9). Distillation through the column yielded 107 g. (90%) of white nonadecyl bromide, b.p. 184–186° (2.5 mm.), m.p. 37.0–38.5° [literature (16), m.p. 38–39°].

β-Methyl- γ -carbomethoxybutyryl chloride (IV). *β*-Methylglutaric acid was prepared by the method of Kent and McElvain (17), and converted to the anhydride, m.p. 46–47°, by the method of Ställberg-Stenhagen (4). The half ester was prepared by heating with methanol, according to the method (18) described for methyl hydrogen succinate, except that the product was distilled through the column to yield 17% of di-ester, b.p. 91.5–94° (5 mm.) and 71% of methyl hydrogen *β*-methylglutarate, b.p. 134–139° (4 mm.). The acid chloride (IV) was prepared with thionyl chloride (18) in 96.5% yield, b.p. 107–110° (16 mm.).

Methyl 3-methyl-5-ketotetracosanoate (ester of V). A cadmium reagent was prepared in 100 ml. of benzene, as previously described (10), from 2.4 g. (0.1 atom) of magnesium turnings and 34.7 g. (0.1 mole) of *n*-nonadecyl bromide. To this stirred mixture, at room temperature, was added in one portion a solution of 12 g. (0.067 mole) of ester acid chloride, IV, in 25 ml. of benzene. There was no appreciable evolution of heat. After the mixture had been stirred 75 minutes at room temperature it was heated under reflux for one hour. The viscous reaction mixture was treated with ice and sulfuric acid, then worked up as usual (10) for keto esters. On distillation from a Claisen flask, after a fore-run of 10 g., the crystalline keto ester was collected at 220–245° (ca. 0.5 mm.), wt. 22 g. (80%). From the fore-run was isolated 1.5 g. of octatriacontane (from coupling of the Grignard reagent), m.p. 80–81°.

For analysis, a sample of keto ester was crystallized four times from benzene, to give fine white crystals melting at 48.4–49.5°.

Anal. Calc'd for $C_{28}H_{50}O_3$: C, 76.04; H, 12.27.

Found: C, 76.55; H, 12.37.

3-Methyltetracosanoic acid (III). A 19.5 g. (0.048 mole) sample of distilled keto ester was reduced by the modified Wolff-Kishner procedure, as described by Huang-Minlon (19), except that the final heating period was for 5 hours at 210–215°. The cooled reaction mixture was diluted with water and acidified to give a quantitative yield of crude acid of m.p. 63–67°. This crude acid was esterified with 15 mole equivalents of commercial absolute alcohol in presence of sulfuric acid. About 1 g. of acid was removed as its salt, and the ester distilled through the column. After a fore-run of 2 g., the ethyl *3-methyltetracosanoate* was collected at 219–222° (1.4 mm.), wt. 15.6 g. (80%, over-all).

For analysis, a sample of distilled ester was crystallized three times from acetone, m.p. 43.3–44.9°.

Anal. Calc'd for $C_{27}H_{54}O_2$: C, 78.96; H, 13.25.

Found: C, 78.71; H, 13.23.

After saponification of the ester with alcoholic potassium hydroxide, the acid was crystallized twice from acetone, m.p. 68.0–69.1°. Ställberg-Stenhagen (5) reported m.p. 68.4–68.6° for the *dl*-isomer of III.

The *amide*, after two crystallizations from methanol, melted at 95–101°, resolidified only on cooling to 92°, re-melted at 99.5–101°. This behavior is essentially identical with that reported in (5).

Ethyl 7-ketopentacosanoate was prepared by a procedure essentially the same as described for the ester of V, starting with 0.1 mole of octadecyl bromide and 0.08 mole of the ester acid chloride of pimelic acid. The yield of keto ester, b.p. 230–260° (3 mm.), was 13 g. (39%), and a large fraction which appeared to be octadecane was obtained. This relatively low yield may have been due to an error, but yields in this range have been obtained on certain other cadmium reactions which have been checked several times. About 4 g. of hexatriacontane, m.p. 75–78° was isolated from this reaction, indicating at least 17% coupling of the Grignard reagent.

For analysis, a sample of the ester was crystallized three times from benzene, to give shiny plates melting at 66.0–66.9°.

Anal. Calcd for $C_{27}H_{52}O_2$: C, 76.36; H, 12.34.

Found: C, 76.68; H, 12.12.

n-Pentacosanoic acid was obtained from the keto ester *via* Huang-Minlon reduction as described above. The acid was purified by distillation of the ester and three crystallizations from benzene-acetone, m.p. 82.6–83.2° [literature (14), m.p. 83.5°].

The *amide*, after three crystallizations from methyl ethyl ketone (Norit), consisted of fine, slightly tan crystals of m.p. 114.7–115.2°.

Anal. Calc'd for $C_{27}H_{53}NO$: N, 3.67. Found: N, 3.57.

γ -*Tetradecyl- γ -valerolactone* (VI) was prepared by the method (3, 6) described for lower molecular weight compounds. From 55.4 g. of *n*-tetradecyl bromide and 26 g. of ethyl levulinate there was obtained 41.5 g. (77.5%) of crystalline lactone, VI, b.p. 199–200° (4 mm.). For analysis, a sample was crystallized three times from methanol and once from acetone to yield fine white crystals, m.p. 45.5–46.7°.

Anal. Calc'd for $C_{19}H_{36}O_2$: C, 76.97; H, 12.24.

Found: C, 76.95; H, 11.97.

Ethyl 4-methyloctadecanoate (VII). Following a procedure slightly different from that (3) previously published, a solution of 17.8 g. of lactone, VI, and 21.3 g. (3 mole equivs.) of purified thionyl chloride in 20 ml. of dry benzene was heated under reflux for three hours. The cooled mixture was added dropwise during 15 minutes to 60 ml. of commercial absolute ethanol, and stirring was continued for an additional 15 minutes. After solvent had been completely removed, last traces in a vacuum, the residue was heated at 185–195° under the column until no more hydrogen chloride was evolved (2 hours). Distillation yielded 17.3 g. (89%) of ethyl 4-methyloctadecanoate, b.p. 163–164° (1 mm.).

The unsaturated ester (16.7 g.) was immediately hydrogenated at room temperature and low pressure with 0.25 g. of platinum catalyst in 60 ml. of 95% ethanol. Hydrogenation was complete in one hour, and distillation yielded 16.2 g. of saturated ester.

4-Methyloctadecanoic acid (VIII) was prepared by saponification of 15.2 g. of ester, VII. After one crystallization from acetone, there was obtained 9.6 g. of white crystals melting at 47.6–50.1°. After four more crystallizations, the m.p. remained constant at 51.2–51.6°. The acid prepared in another run reached the constant m.p. 52.2–52.4°. Both samples gave a weakly positive Baeyer's test for unsaturation. A 4.8 g. sample was rehydrogenated in 60 ml. of glacial acetic acid, with 50 mg. of platinum catalyst, for two hours. Dilution with water gave a quantitative recovery of crude acid, and after four crystallizations from acetone this sample melted at 52.6–52.8° and gave a negative Baeyer's test.

Anal. Calc'd for $C_{19}H_{38}O_2$: C, 76.45; H, 12.83; equiv. wt., 298.5.

Found: C, 76.39; H, 12.94; equiv. wt., 298.2.

The *amide*, after four crystallizations from methanol, melted at 79.7–80.2°.

Anal. Calc'd for $C_{19}H_{33}NO$: C, 76.71; H, 13.21.

Found: C, 76.83; H, 12.99.

The *tribromoanilide*, after five crystallizations from 95% ethanol, separated as nodules of small, white crystals, m.p. 95.3–99.3°. A sample placed in a bath at 97.2° melted at 97.2–97.6°.

Anal. Calc'd for $C_{26}H_{40}Br_2NO$: C, 49.21; H, 6.60.
Found: C, 49.12; H, 6.71.

SUMMARY

Several fatty acids with branching methyl groups near carboxyl have been prepared. Of this group, those which have not been previously reported are 4-methyloctadecanoic acid and 2,3-dimethyloctadecanoic acid.

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