The malonic acids, heated above their melting points, yielded α-Δ^2-cyclopentene fatty acids, which are closely related to chaulmoogric acid and are, therefore, important in the study of the treatment of leprosy.

Culion, Philippine Islands

[Contribution from the Chemical Laboratory of the University of Illinois]

THE SYNTHESIS OF 9-, 10-, 11-, 12- AND 13-HYDROXYSTEARIC ACIDS

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Received November 12, 1926 Published February 5, 1927

The hydroxy derivatives of the higher fatty acids are of interest from many standpoints. Such compounds have been found in the waxes of certain conifers such as *Juniperus sabina, Juniperus communis, Picea excelsa, Pinus silvestris, Thuja occidentalis.*[2] They have been found in carnauba wax,[3] in certain resins long used medicinally as purgatives,[4] in cochineal,[5] in wool fat,[6] in brain tissue[7] and humus.[8] More recently they have been discovered in adipocere[9] and East Indian wax.[10] It is obvious that the hydroxy acids form an important class of naturally occurring compounds, concerning which very little is known.

Hydroxy acids are also formed readily by the addition of sulfuric acid to olefinic acids and subsequent hydrolysis of the products. When it is considered that several of the most important fatty acids are olefinic acids, such as oleic, erucic, linoleic, etc., it lends interest to the hydroxy derivatives formed from them. Although the hydroxy acids from the olefinic acids have been extensively studied by many investigators, the discrepancy in the results is surprising. This is the first of a series of researches to determine the structure of many of these hydroxy acids through synthesis by a method which can leave no doubt as to their constitution and purity.

This communication describes the preparation of 9-, 10-, 11-, 12- and

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[1] This communication is an abstract of a portion of a thesis submitted by C. G. Tomecko in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[2] (a) Kawalier, *J. prakt. Chem.*, **60**, 321 (1853); **64**, 16 (1855). (b) Boudier, *Compt. rend.*, **147**, 1313 (1908).

[3] Stürcke, *Ann.*, **223**, 313 (1884).

[4] (a) Kromer, *J. prakt. Chem.*, [2] **57**, 450 (1898). (b) Taverne, *Rec. trav. chim.*, **13**, 207 (1894). (c) Power and Rogerson, This Journal, **32**, 105 (1910); *J. Chem. Soc.*, **101**, 16 (1912).

[5] Liebermann and Bergami, *Ber.*, **20**, 964 (1887).

[6] Darmstaedter and Lifschütz, *Ber.*, **29**, 2893 (1896).

[7] Thierfelder, *Z. physiol. Chem.*, **43**, 26 (1904–1905).

[8] Schreiner and Shorey, This Journal, **32**, 1675 (1910).

[9] Ruttan and Marshall, *J. Biol. Chem.*, **29**, 323 (1917).

[10] Lipp and Kovács, *J. prakt. Chem.*, [2] **99**, 247 (1919).

13-hydroxystearic acids. The procedure used was that developed by Noller with Adams[11] in a research on the synthesis of dihydrochaulmoogric and dihydrohydnocarpic acids. It consisted in condensing aldehyde esters of the general formula $CHO—(CH_2)_x—CO_2CH_3$, where x is 7, 8, 9, 10 and 11 with the proper Grignard reagent, $CH_3—(CH_2)_y—MgBr$, where y is 8, 7, 6, 5, 4, respectively.

$$CH_3(CH_2)_yMgBr + CHO(CH_2)_xCO_2CH_3 \longrightarrow CH_3(CH_2)_yCHOH(CH_2)_xCO_2CH_3 \longrightarrow CH_3(CH_2)_yCHOH(CH_2)_xCO_2H$$

The aldehyde esters containing 9, 10 and 13 carbon atoms were made, respectively, by the ozonation of methyl oleate, methyl undecylenate and methyl erucate. The aldehyde esters with 11 and 12 carbon atoms were made from methyl dodecenoate and methyl tridecenoate, which were produced by the following series of reactions from ethyl undecenoate.

$$\text{(a) } CH_2{=}CH—(CH_2)_8—CO_2C_2H_5 \longrightarrow CH_2{=}CH—(CH_2)_8—CH_2OH \longrightarrow CH_2{=}CH—(CH_2)_8—CH_2Br$$

$$CH_2{=}CH—(CH_2)_8—CH_2CN \longrightarrow CH_2{=}CH—(CH_2)_8—CH_2CO_2CH_3 \longrightarrow CHO—(CH_2)_9—CO_2CH_3$$

$$\text{(b) } CH_2{=}CH—(CH_2)_8—CH_2—CH(CO_2C_2H_5)_2 \longrightarrow CH_2{=}CH—(CH_2)_8—CH_2—CH_2CO_2CH_3 \longrightarrow CHO—(CH_2)_{10}—CO_2CH_3$$

The pure methyl esters of the hydroxy acids were obtained without difficulty in yields of 25–35% of the calculated amounts in all cases except one, in which the yield was considerably lower. The corresponding hydroxy acids were obtained quantitatively by saponification. Although the hydroxy esters were purified before saponification, the hydroxy acids produced required several recrystallizations from acetone before giving a constant melting point, though the difference in the melting points of the crude and purified products was frequently not more than two or three degrees. This is a property, however, rather common among aliphatic acids.

With pure, closely related homologous acids available, the opportunity

TABLE I

MIXED MELTING POINTS OF VARIOUS ACIDS

Compn., %	-Hydroxystearic acid	M. p. of mixture, °C.	Solid p. of mixture, °C.	Compn., %	-Hydroxystearic acid	M. p. of mixture, °C.	Solid p. of mixture, °C.
30	9 (m. p., 74–75°)	74–76	73–68	10	10 (m. p., 81–82°)	...	...
70	10 (m. p., 81–82°)	...	...	90	12 (m. p., 78–79°)	75–76	70–68
70	9	...	...	30	10	...	...
30	10	67–72	64–61	70	12	73–74	67–64
30	12 (m. p., 78–79°)	...	...	50	10	...	...
70	13 (m. p., 77–77.5°)	70–71.2	62–59	50	12	69–70	60–58
70	12	...	...	70	10	...	...
30	13	71–73	64–61	30	12	72–73	65–63
				90	10	...	...
				10	12	76–78	74–71

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[11] Noller with Adams, THIS JOURNAL, **48,** 1080 (1926).

was taken to make a few experiments to determine how much effect on the melting point of one acid the impurity of another acid might have. Table I presents the melting points carried out quantitatively on pure acids. All melting points were taken by melting the acids before placing them in the capillary tubes, so that there would be no danger of traces of solvent being present.

It is obvious from these results that too much reliance cannot be placed upon the melting points as a criterion of purity. Practically all of the materials melted quite sharply, as sharply as is expected of most pure substances. The five mixtures of different proportions of 10- and 12-hydroxystearic acids showed only a few degrees' difference in the melting points. Since the various hydroxy acids have essentially the same solubility, it can be seen how difficult it is to be certain when the hydroxy acid is pure. Of peculiar interest is the melting point of the mixture of 30% of 9-hydroxy- and 70% of 10-hydroxystearic acids. The melting point is essentially the same as that of the pure 9-hydroxy acid and the mixture melts almost as sharply. This is significant on account of the results of many investigations described below in which attempts have been made to separate 10- and 9-hydroxystearic acids by crystallization.

The conclusion from these experiments is merely that any method for preparing such acids as these, which might give as by-products very closely related homologous acids, cannot be considered reliable, and no confidence should be placed in the results, unless extreme precautions be taken.

9-Hydroxystearic Acid.—Early work on adipocere led the investigators to conflicting results in regard to the acids present in the material. Although Ebert[12] recognized the presence of an hydroxy acid in this material as early as 1875, a more satisfactory chemical study of the acids was not made until 1918 by Ruttan and Marshall.[9] These authors isolated from the mixture two hydroxy acids, one melting at 84.5° and the other at 78.5°. They considered these to be the 10-hydroxystearic acid and 9-hydroxystearic acid, respectively, the former because it corresponded in properties to the previously reported 10-hydroxystearic acid; the latter because it was assumed that the hydroxy acids were probably formed from oleic acid and consequently the 9-hydroxy acid would be the only other possible product.

One or two of the numerous investigators[13,14] who have studied the action of sulfuric acid upon oleic acid and then hydrolysis of the product believe they obtained small amounts of the 9-hydroxystearic acid. This, however, has been by no means proved and most of the investigators maintain that they have obtained none at all.

The 9-hydroxystearic acid prepared in this research melted at 74–75°

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[12] Ebert, *Ber.*, **8**, 775 (1875).

[13] Ssabanejew, *J. Russ. Phys.-Chem. Soc.*, [1] **35**, 87 (1885); *Ber.*, **19**, 239 (1886).

[14] Geitel, *J. prakt. Chem.*, [2] **37**, 82 (1888).

with a solidification point only slightly lower. As a consequence it seems most probable that the acid of Ruttan and Marshall,[9] reported as the 9-hydroxy acid, consisted chiefly of the 10-hydroxy acid with a certain percentage of the 9-hydroxy acid present which lowered the melting point to that reported. In connection with Ruttan and Marshall's work it is important to consider the great difficulty of separating by crystallization two so closely related acids as the 9- and 10-hydroxystearic acids; moreover, the 9-hydroxy acid was obtained from the more soluble portion in the fractional crystallization and consequently could be separated in a pure form only with great difficulty.

10-Hydroxystearic Acid.—The action of concentrated sulfuric acid upon olive oil or oleic acid was studied by Fremy[15a] who, after hydrolysis, reported an acid melting at 54°. This same reaction has been studied by numerous investigators using slightly different conditions. Many different melting points for this hydroxy acid have been obtained, which are given in Table II.

TABLE II

REPORTED MELTING POINTS OF 10-HYDROXYSTEARIC ACID

Investigator	M. p., °C.
Fremy[15a]	54
Liechti and Suida[15b]	56–58
Saytzeff[15c]	83.5–85 (solid. at 68–63)
Ssabanejew[13]	79
Saytzeff, M., C. and A.[15d]	83–85 (solid. at 68–65)
Geitel[14]	81–81.5
David[15e]	80 (solid. at 68)
Tscherbakoff and Saytzeff[15f]	82–85
Shukoff and Schestakoff[15g]	83–85
Molinari and Soncini[15h]	37
Molinari and Barosi[15i]	41
Radcliffe and Gibson[15j]	85
Robinson and Robinson[15k]	83
Veselý and Majtl[15l]	81–82
This investigation	81–82 (solid. 78–77)

It is noticeable that the majority of the melting points vary from 80° to 85° and it is quite conceivable that the difference in the rate of determination of the melting point would cause a variation of one or two degrees in the reported values.

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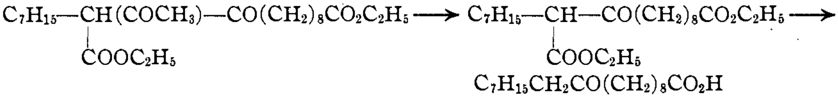
[15] (a) Fremy, *Ann.*, **19,** 298 (1836). (b) Liechti and Suida, *Ber.*, **16,** 2455 (1883). (c) Saytzeff, *J. prakt. Chem.*, [2] **33,** 310 (1886). (d) M., C. and A. Saytzeff, *ibid.*, [2] **35,** 369 (1887). (e) David, *Compt. rend.*, **124,** 467 (1897). (f) Tscherbakoff and Saytzeff, *J. prakt. Chem.*, [2] **57,** 31 (1898). (g) Shukoff and Schestakoff, *ibid.*, [2] **67,** 415 (1903). (h) Molinari and Soncini, *Ber.*, **39,** 2740 (1906). (i) Molinari and Barosi, *Ber.*, **41,** 2797 (1908). (j) Radcliffe and Gibson, *J. Soc. Dyers Colourists*, **39,** 4 (1923). (k) Robinson and Robinson, *J. Chem. Soc.*, **127,** 175 (1925). (l) Veselý and Majtl, *Bull. soc. chim.*, **39,** 235 (1926). (m) Ref. 13 and 14.

It seems improbable that sulfuric acid could be added to oleic acid in such a way as to obtain a pure 10-hydroxystearic acid entirely free from 9-hydroxystearic acid and consequently the variation in the reported melting points is probably due to amounts of impurity of the 9-hydroxy acid.

The structure of the 10-hydroxy acid was determined by Shukoff and Schestakoff,[15g] who oxidized it to the keto acid and then carried out a Beckmann rearrangement of the ketoxime. The products thus produced were pelargonic acid, ω-aminopelargonic acid, *n*-octylamine and sebacic acids. These results alone would tend to establish the fact that the original acid, although melting at the proper point, was really a mixture consisting chiefly of the 10-hydroxy acid with certain amounts of the 9-hydroxy acid.

Probably the most reliable work on the 10-hydroxy acid from oleic acid was that carried out recently by Veselý and Majtl,[15l] who carefully purified oleic acid before treating it with sulfuric acid according to the method of Fremy. They obtained an hydroxy acid melting at 81–82°, but offered as proof that traces of the 9-hydroxy acid were not present, only the fact that they obtained a constant melting point after repeated recrystallization.

A recent article describes the preparation of the 10-hydroxystearic acid by a method more complicated than that used in this research, but one which can leave no doubt that the hydroxy acid was free from any of its isomers. Robinson and Robinson[15k] reduced the corresponding keto-stearic acid. The keto acid was made by the condensation of *n*-heptyl-aceto-acetic ester with the half acid chloride-half ester of octane-α,α-dicarboxylic acid, followed first by a ketone splitting and then by an acid splitting. They report a melting point of 83°.



$$C_7H_{15}-\underset{\substack{|\\ COOC_2H_5}}{CH}(COCH_3)-CO(CH_2)_8CO_2C_2H_5 \longrightarrow C_7H_{15}-\underset{\substack{|\\ COOC_2H_5}}{CH}-CO(CH_2)_8CO_2C_2H_5 \longrightarrow C_7H_{15}CH_2CO(CH_2)_8CO_2H$$

11-Hydroxystearic Acid.—M., C. and A. Saytzeff[15d] report the preparation of iso-oleic acid in which the double bond is presumably in the 10,11 position in the chain. This acid, by treatment with sulfuric acid and hydrolysis, should lead to the 11-hydroxy acid, assuming as with the oleic acid that the position taken by the hydroxyl group is the one farther away from the carboxyl group. They report a melting point of 76–79° and a solidification point of 65–62°. Shukoff and Schestakoff[15g] attempted to prove the constitution of this product by oxidizing to the corresponding keto acid, by conversion to the oxime and then by a Beckmann rearrangement and hydrolysis. Only complex mixtures of products were obtained, indicating the probable impurity of the original hydroxy acid. Even if the hydroxy acid from oleic acid were pure, the dehydration would be likely to yield two olefinic acids and these latter upon addition of water could give three hydroxy acids. Little reliability can therefore be placed on the reported melting point.

Schreiner and Shorey[8] separated an hydroxy acid from humus which they believed to be the 11-hydroxystearic acid. There seems to be much question about this, however, and the probability is that their acid was the 2-hydroxystearic acid.

12-Hydroxystearic Acid.—The 12-hydroxystearic acid has been prepared by Kasansky[16a] from ricinoleic acid by acetylation, addition of hydrogen bromide to the double bond, replacement of the bromine by hydrogen and then by hydrolysis. He obtained a melting point of 81–82.5° with a solidification point of 78.5–78°. Grün and Woldenberg[16b] reduced catalytically methyl ricinoleate and then saponified the ester to the corresponding hydroxy acid which melted at 78°.

Thoms and Deckert[16c] obtained from a "hardened" castor oil an hydroxy acid which they reported as melting at 83°. Brochet[16d] also studied hydrogenated castor oil and reported the isolation of this same hydroxy acid with a melting point of 81°.

Since the 12-hydroxystearic acid thus obtained is optically active, the melting point of the synthetic product has little significance. The hydroxy acid prepared in this investigation melted at 78–79° and solidified 74–73°.

13-Hydroxystearic Acid.—The 13-hydroxystearic acid has never been described in the literature. It was readily prepared pure and melted at 77–77.5° with a solidification point of 73.5–72.5°.

Experimental Part

10,11-Undecenol-1.—This was prepared in 60% yields by the reduction of ethyl undecenoate according to the general procedure of Grün and Wirth.[17]

10,11-Undecenyl Bromide, $CH_2{=}CH{-}(CH_2)_8{-}CH_2Br$.—A solution of 57 g. of 10,11-undecenol-1 in 100 cc. of dry toluene was cooled to —5° and treated slowly with 33 g. of phosphorus tribromide dissolved in 100 cc. of dry toluene. After adding all of the phosphorus tribromide, the mixture was taken out of the ice-salt mixture and allowed to come to room temperature. Finally, it was heated on a steam-cone for two and one-half hours. The solution became colored and an orange deposit was formed. The clear solution was decanted and the toluene removed under diminished pressure. The residue was taken up with ether, washed with water and sodium hydroxide solution and finally dried over anhydrous calcium chloride. The ether was removed and the residue distilled under diminished pressure, the portion boiling between 102–104° at 4 mm. being collected. A higher-boiling fraction was obtained, probably a mixture of the two dibromides. The low fraction, after redistillation, boiled at 103° at 4 mm. n^{20}_{D}, 1.4638; d^{20}_{20}, 1.0295; yield, 38 g.

Anal. Subs., 0.3582: 15.66 cc. of 0.1 *N* $AgNO_3$. Calcd. for $C_{22}H_{21}Br$: Br, 34.28. Found: 33.86.

11,12-Dodecenitrile, $CH_2{=}CH{-}(CH_2)_8{-}CH_2CN$.—A mixture of 40 g. of potas-

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[16] (a) Kasansky, *J. prakt. Chem.*, [2] **62,** 363 (1900). (b) Grün and Woldenberg, THIS JOURNAL, **31,** 504 (1909). (c) Thoms and Deckert, *Ber. pharm. Ges.*, **34,** 23 (1921). (d) Brochet, *Bull. soc. chim.*, **35,** 630 (1923).

[17] Grün and Wirth, *Ber.*, **55,** 2208 (1922).

sium cyanide in a saturated aqueous solution and 100 cc. of ethyl alcohol was treated with 75 g. of undecenyl bromide and refluxed for 24 hours. The oily layer was separated, washed with water and dried over fused calcium chloride. A yield of 51 g. of dried nitrile was obtained; b. p., 117–119°, at 4 mm.; n^{20}_{D}, 1.4462; d^{20}_{20}, 0.8405.

Anal. Subs., 0.3504: 19.74 cc. of 0.1 *N* HCl. Calcd. for $C_{12}H_{21}N$: N, 7.82. Found: 7.80.

11,12-Dodecenoic Acid, $CH_2{=}CH{-}(CH_2)_9{-}CO_2H$.—A mixture of 51 g. of dodecenitrile was refluxed for 30 hours with a solution of 60 g. of potassium hydroxide in 150 cc. of ethyl alcohol. After distilling off all of the alcohol, the residue was diluted with water and acidified with hydrochloric acid. The oily layer was separated and the aqueous layer extracted twice with ether. After washing and drying, the ether was distilled and the residue fractionated under diminished pressure. The portion boiling at 143–144°, at 3 mm., weighed 48 g.; n^{20}_{D}, 1.4510; d^{20}_{20}, 0.9030.

Anal. Subs., 0.2756: CO_2, 0.7275; H_2O, 0.2780. Calcd. for $C_{12}H_{22}O_2$: C, 72.67; H, 11.19. Found: C, 72.02; H, 11.29.

Mol. wt. Subs., 0.8437: 41.62 cc. of 0.1 *N* NaOH. Calcd. for $C_{12}H_{22}O_2$: mol. wt., 198.2. Found: 202.6.

Methyl 11,12-Dodecenoate, $CH_2{=}CH{-}(CH_2)_9{-}CO_2CH_3$.—A mixture of 76 g. of dodecenoic acid was refluxed for 12 hours with 2 cc. of concd. sulfuric acid and 160 cc. of methyl alcohol. The main part of the alcohol was then distilled and the residue diluted with water. The oily layer was separated, washed with sodium carbonate solution and finally dried over fused calcium chloride; b. p., 121–123°, at 3 mm.; n^{20}_{D}, 1.4414; d^{20}_{20}, 0.8805.

Anal. Subs., 0.1669: CO_2, 0.4486; H_2O, 0.1703. Calcd. for $C_{13}H_{24}O_2$: C, 73.56; H, 11.40. Found: C, 73.32; H, 11.42.

Methyl 10-Aldehydo-decanoate, $CHO{-}(CH_2)_9{-}CO_2CH_3$.—This ester was ozonized in the same way as the other unsaturated esters.[11] The resulting product was fractionated and a yield of 21 g. (35%) of aldehyde ester was obtained; n^{20}_{D}, 1.4430; d^{20}_{20}, 0.9594.

Anal. Subs., 0.1245: CO_2, 0.3060; H_2O, 0.1147. Calcd. for $C_{12}H_{22}O_3$: C, 67.24; H, 10.35. Found: C, 67.03; H, 10.30.

Semicarbazone of Methyl 10-Aldehydo-decanoate.—The semicarbazone was prepared by shaking an equal weight of the aldehydo ester and semicarbazide sulfate with twice the weight of sodium acetate in dil. alcohol. The semicarbazone was recrystallized thrice from absolute methyl alcohol; m. p., 114–115°.

Anal. Subs., 0.4050: N_2, 58.40 cc. (30°, 741.3 mm.). Calcd. for $C_{13}H_{25}O_3N_3$: N, 15.49. Found: 15.17.

10,11-Undecenylmalonic Ester, $CH_2{=}CH{-}(CH_2)_8{-}CH(CO_2C_2H_5)_2$.—To sodium malonic ester from 50 cc. of absolute ethyl alcohol, 4.6 g. of metallic sodium and 32 g. of malonic ester, 47 g. of undecenyl bromide was added and the solution refluxed until neutral; yield, 41 g., or 65%; b. p., 154°, at 2 mm.; n^{20}_{D}, 1.4450; d^{20}_{20}, 0.9411.

Anal. Subs., 0.1956: CO_2, 0.4952; H_2O, 0.1826. Calcd. for $C_{18}H_{32}O_4$; C, 69.18; H, 10.33. Found: C, 69.04; H, 10.43.

10,11-Undecenylmalonic Acid, $CH_2{=}CH{-}(CH_2)_8{-}CH(CO_2H)_2$.—The undecenylmalonic ester was saponified by being boiled with alcoholic potassium hydroxide. The alcohol was evaporated and the aqueous solution was acidified. The solid acid was taken up with ether and finally recrystallized from benzene. It melted constant at 112–113°.

Anal. Subs., 0.1495: CO_2, 0.3604; H_2O, 0.1256. Calcd. for $C_{13}H_{32}O_4$: C, 65.59; H, 9.44. Found: C, 65.70; H, 9.40.

Mol. wt. Subs., 0.1964: 15.45 cc. of 0.1 *N* NaOH. Calcd. for $C_{18}H_{32}O_4$: mol. wt., 312. Found: 309.

12,13-Tridecenoic Acid, $CH_2{=}CH{-}(CH_2)_{10}{-}CO_2H$.—Upon heating undecenylmalonic acid at 150° until the evolution of carbon dioxide ceased and then distilling under diminished pressure, tridecenoic acid was obtained; b. p., 192°, at 20 mm.; 162°, at 3 mm.; m. p., 38–39°.

Anal. Subs., 0.2124: CO_2, 0.5710; H_2O, 0.2160. Calcd. for $C_{13}H_{24}O_2$: C, 73.54; H, 11.41. Found: C, 73.31; H, 11.40.

Mol. wt. Subs., 0.5313: 25.23 cc. of 0.1 *N* NaOH. Calcd. for $C_{13}H_{24}O_2$: mol. wt., 212. Found: 210.5.

Methyl 12,13-Tridecenoate, $CH_2{=}CH{-}(CH_2)_{10}{-}CO_2CH_3$.—Tridecenoic was esterified similarly to dodecenoic acid. It boiled at 133°, at 3 mm.; n^{20}_{D}, 1.4438; d^{20}_{20}, 0.8819.

Anal. Subs., 0.2251: CO_2, 0.6114; H_2O, 0.2316. Calcd. for $C_{14}H_{26}O_2$: C, 74.28; H, 11.58. Found: C, 74.07; H, 11.51.

Methyl 11-Aldehydo-undecanoate, $CHO{-}(CH_2)_{10}{-}CO_2CH_3$.—By ozonation of 70 g. of methyl tridecenoate, a yield of 44 g. (63%) of aldehyde ester was obtained; b. p., 154°, at 5 mm.; m. p., 16°; n^{20}_{D}, 1.4458; d^{20}_{20}, 0.9504.

Anal. Subs., 0.2051: CO_2, 0.5116; H_2O, 0.1948. Calcd. for $C_{13}H_{24}O_3$: C, 68.37; H, 10.60. Found: C, 68.02; H, 10.63.

Condensation of Aldehyde Esters with Grignard Reagents.—The procedure was the same as that employed in previous work with the aldehyde esters,[11] equimolecular proportions of aldehyde ester and Grignard reagent determined by titration being used. The products after purification from methyl alcohol were saponified by heating with alcoholic potassium hydroxide, distilling off all of the alcohol, taking up in water and acidifying. They were purified from pure acetone. The following equations represent the reactions carried out.

$$CH_3{-}(CH_2)_8{-}MgBr + OCH{-}(CH_2)_7{-}CO_2CH_3 \longrightarrow CH_3{-}(CH_2)_8{-}CHOH{-}(CH_2)_7{-}CO_2CH_3$$
$$CH_3{-}(CH_2)_7{-}MgBr + OCH{-}(CH_2)_8{-}CO_2CH_3 \longrightarrow CH_3{-}(CH_2)_7{-}CHOH{-}(CH_2)_8{-}CO_2CH_3$$
$$CH_3{-}(CH_2)_6{-}MgBr + OCH{-}(CH_2)_9{-}CO_2CH_3 \longrightarrow CH_3{-}(CH_2)_6{-}CHOH{-}(CH_2)_9{-}CO_2CH_3$$
$$CH_3{-}(CH_2)_5{-}MgBr + OCH{-}(CH_2)_{10}{-}CO_2CH_3 \longrightarrow CH_3{-}(CH_2)_5{-}CHOH{-}(CH_2)_{10}{-}CO_2CH_3$$
$$CH_3{-}(CH_2)_4{-}MgBr + OCH{-}(CH_2)_{11}{-}CO_2CH_3 \longrightarrow CH_3{-}(CH_2)_4{-}CHOH{-}(CH_2)_{11}{-}CO_2CH_3$$

***n*-Nonyl Alcohol.**—This was prepared by the reduction of pelargonic aldehyde according to the method used for reducing heptaldehyde to heptyl alcohol.[18] The product boiled at 205–207° and was obtained in 46–57% yields.

TABLE III

CONSTANTS OF METHYL HYDROXYSTEARATES

No.	Methyl hydroxy-stearate	Wt. of aldehyde ester, g.	Yield of pure hydroxy, g. (from CH_3OH)	B. p., °C., at ( ) mm.	M. p., °C.
I	9-hydroxy	30	17	212–216 (4)	45–46
II	10-hydroxy	45	25	213–217 (4)	53–54
III	11-hydroxy	16	10	204–206 (4)	49–50
IV	12-hydroxy	38	13	202–204 (4)	50–51
V	13-hydroxy	41	10	185–189 (2)	52–52.5

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[18] "Organic Syntheses" John Wiley & Sons, Inc., New York, vol. 6, **1926**, p. 52.

TABLE III (*Concluded*)

ANALYSES OF METHYL HYDROXYSTEARATES

Calcd. for $C_{19}H_{18}O_3$: C, 72.55; H, 12.18

No.	Subs., g.	CO_2, g.	H_2O, g.	C, %	H, %
I	0.0961	0.2545	0.1035	72.22	12.06
II	.1624	.4284	.1742	71.94	12.00
III	.1384	.3649	.1537	71.90	12.42
IV	.1151	.3084	.1265	72.33	12.29
V	.1080	.2828	.1205	72.04	12.28

ANALYSES OF HYDROXYSTEARIC ACIDS

Calcd. for $C_{19}H_{36}O_3$: C, 71.94; H, 12.08; mol. wt., 300.4

								Mol. wt. detn.		
-Stearic acid	M. p., °C.	Solid p., °C.	Subs., g.	CO_2, g.	H_2O, g.	C, %	H, %	Subs., g.	0.1 *N* NaOH, cc.	Mol. wt. found
9-Hydroxy	74–75	70–68	0.1891	0.4956	0.2018	71.49	11.94	0.3409	11.30	301.6
10-Hydroxy	81–82	78–77	.0894	.2346	.0947	71.56	11.85	.3099	10.29	301.2
11-Hydroxy	76–77	74–73	.1197	.3136	.1277	71.45	11.94	.5950	19.69	302.1
12-Hydroxy	78–79	73–72	.1256	.3304	.1336	71.74	11.91	.6474	21.39	302.1
13-Hydroxy	77–77.5	73–72	.0670	.1762	.0730	71.74	12.19	.5667	18.78	301.8

***n*-Nonyl Bromide.**—A mixture of 74 g. of *n*-nonyl alcohol, 240 g. of (42%) hydrobromic acid and 62 g. of concd. sulfuric acid was refluxed for 11 hours. The yield of product was 80%; b. p., 88°, at 4 mm.; n_D^{20}, 1.4533; d_{20}^{20}, 1.0183.

Summary

1. The 9-, 10-, 11- and 12-hydroxystearic acids have been previously prepared from unsaturated fatty acids or found in nature. 13-Hydroxystearic acid has never been prepared. The synthesis of these five acids and their esters has been accomplished by a procedure leaving no doubt as to their constitution and purity.

2. These acids were synthesized by condensing the proper alkyl magnesium bromide with the proper aldehyde ester, then by saponifying the product: $CH_3(CH_2)_xMgBr + OCH(CH_2)_yCO_2CH_3 \longrightarrow CH_3(CH_2)_x\text{-}CHOH(CH_2)_yCO_2CH_3 \longrightarrow CH_3(CH_2)_xCHOH(CH_2)_yCO_2H$.

URBANA, ILLINOIS

ETHERS OF DIACETONE ALCOHOL

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RECEIVED NOVEMBER 13, 1926 PUBLISHED FEBRUARY 5, 1927

In the preparation of mesityl oxide from diacetone alcohol by the action of small amounts of hydrochloric acid[1] the following phenomena were noted. If equal volumes of diacetone alcohol and of water containing a few percent. of hydrochloric acid are sealed in a glass tube and shaken, a homogeneous mixture results, since the alcohol mixes with water in any proportion. If the tube is then heated for an hour to 120°, mesityl oxide is formed by the splitting off of water from the alcohol, and since the former is only slightly soluble in water, the contents of the tube are

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[1] Hoffman, U. S. pat. 1,474,935 (1922).