The whole product was purified by sublimation under reduced pressure, giving 1.8 g. (40%) of cyclohexylacetamide, m. p. 163–165°. Recrystallization from methanol raised the melting point to 169.5–170.3°, cor. (reported m. p. 171–172°[19]). An authentic sample of cyclohexylacetamide for comparison was prepared from cyclohexyl bromide by the malonic ester synthesis[20]; it melted at 169.6–170.1° cor., and the melting point of a mixture of the synthetic sample with the product of the Willgerodt reaction showed no depression. The amide was converted to the anilide, m. p. 130.7–131.5°. The mixed melting point of the anilides derived from the product of the Willgerodt reaction and the synthetic sample showed no depression.

Willgerodt Reaction with Ethyl Cyclohexyl Ketone.—Ethylcyclohexylcarbinol was prepared by the reaction of cyclohexylmagnesium bromide with propionaldehyde. The carbinol was oxidized to the corresponding ketone by means of chromium trioxide in water and acetic acid.

The Willgerodt reaction was carried out with 4.0 g. of ketone at 165 ± 5° for six hours; the quantities of the reagents and the composition of the ammonium polysulfide were the same as for the reaction with methyl cyclohexyl ketone. The crude amide was sublimed under reduced pressure; the sublimate weighed 1.20 g. (27%), m. p. 113–115°. One recrystallization from methanol gave colorless plates of β-cyclohexylpropionamide, m. p. 119–120° cor. (reported m. p., 120°[21]). An authentic sample of this amide, prepared from cyclohexylacetic acid by the Arndt–Eistert reaction, melted at 118–119° cor.,[22] and a mixture of the latter sample with the product from the Willgerodt reaction showed no depression of melting point. Both specimens of amide were converted into the corresponding anilides, m. p. 97–97.5°, and mixtures of the two anilides showed no depression of melting point.

Summary

The Willgerodt reaction has been found to occur with completely aliphatic compounds of the type $RCO(CH_2)_nH$ to yield amides of the type $R(CH_2)_nCONH_2$ without rearrangement of the carbon skeleton, in analogy with known reactions of aryl alkyl ketones. The reactions of nine aliphatic carbonyl compounds with ammonium polysulfide are described.

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[19] Gutt, *Ber.*, **40**, 2068 (1907).

[20] Hope and Perkin, *J. Chem. Soc.*, **95**, 1364 (1905).

[21] Zelinsky, *Ber.*, **41**, 2677 (1908).

[22] We are indebted to Miss Doris C. Koch for this preparation.

PHILADELPHIA, PA. RECEIVED JULY 5, 1945

[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY,[1] PHILADELPHIA 18, PA.]

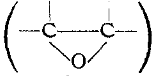
Hydroxylation of Monounsaturated Fatty Materials with Hydrogen Peroxide

BY DANIEL SWERN, GERALDINE N. BILLEN, THOMAS W. FINDLEY AND JOHN T. SCANLAN

The reaction of hydrogen peroxide with the lower fatty acids to form per-acids is reversible[2] and therefore it goes to completion if the per-acid is allowed to react as formed with an unsaturated compound. If the conditions favor rapid formation of the per-acid without causing decomposition, quantitative utilization of the active oxygen for such an oxidation is feasible, since the per-acid usually reacts very rapidly with unsaturated compounds. With most aliphatic acids, formation of the per-acid is a very slow reaction at moderate temperatures (40° or below) unless catalyzed.[3] For example, hydroxylation of oleic acid with a large excess of hydrogen peroxide in acetic acid solution requires a week at room temperature,[4] and during that extended period decomposition, probably of the hydrogen peroxide, results in considerable loss of active oxygen. Raising the temperature increases the rate of reaction considerably but aggravates the loss of active oxygen by increasing the rate of decomposition.[5]

Unlike the other aliphatic acids, however, formic acid reacts rapidly with hydrogen peroxide at moderate temperatures to give performic acid.[6] We have found that when oleic acid is mixed with hydrogen peroxide (25 to 30% aqueous solution) and formic acid at room temperature, an exothermic reaction begins almost immediately and is complete within two to four hours at 40°. Because of the short reaction time and the low temperature, little active oxygen is lost by decomposition, and the hydrogen peroxide is utilized in almost stoichiometric proportions.

The outstandingly rapid rate of formation of performic acid is not due entirely to the high acidity of formic acid. Its rate of formation is three times that at which peracetic acid is produced from hydrogen peroxide and glacial acetic acid with sulfuric acid as catalyst.

Reasoning from the successful epoxidation of fatty materials with perbenzoic[7] and peracetic acids,[8] we expected that under the same mild conditions performic acid also would yield epoxy  compounds. Such was not the case, however; no epoxy compounds were present in the oxidation products even when the reaction was carried out at 25°. The products consisted almost exclusively of hydroxy-formoxy derivatives. There is little doubt that epoxy compounds are the initial products of the reaction and that further action of the strongly acidic formic acid results in the opening of the oxirane ring with addition of formic acid to yield the hydroxy-

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[1] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture.

[2] d'Ans and Frey, *Ber.*, **45**, 1845 (1912); d'Ans and Kneip, *ibid.*, **48**, 1136 (1915).

[3] Smit, *Rec. trav. chim.*, **49**, 675 (1930).

[4] (a) Hilditch, *J. Chem. Soc.*, 1828 (1926); (b) Hilditch and Lea, *ibid.*, 1576 (1928).

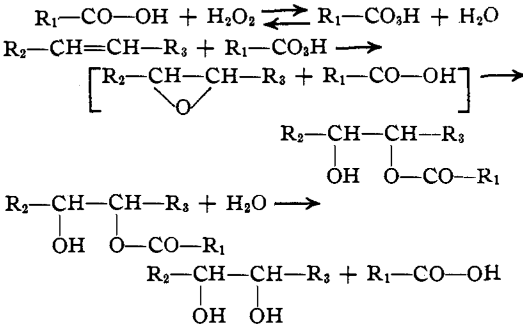
[5] Scanlan and Swern, THIS JOURNAL, **62**, 2305 (1940).

[6] Toennies and Homiller, *ibid.*, **64**, 3054 (1942).

[7] Swern, Findley and Scanlan, *ibid.*, **66**, 1925 (1944).

[8] Findley, Swern and Scanlan, *ibid.*, **67**, 412 (1945).

formoxy derivatives as shown below. That the acidity is the determining factor here is indicated by the fact that, when an acetic–peracetic acid solution containing 1% of sulfuric acid reacts with monounsaturated fatty materials, epoxy compounds are not obtained, whereas omission of the sulfuric acid results in good yields of epoxy derivatives.[8] The reactions involved are



$$R_1{-}CO{-}OH + H_2O_2 \rightleftarrows R_1{-}CO_3H + H_2O \qquad (1)$$

(2)

$$\underset{\substack{|\\OH}}{R_2{-}CH}{-}\underset{\substack{|\\O{-}CO{-}R_1}}{CH}{-}R_3 + H_2O \longrightarrow \underset{\substack{|\\OH}}{R_2{-}CH}{-}\underset{\substack{|\\OH}}{CH}{-}R_3 + R_1{-}CO{-}OH \qquad (3)$$

The performic acid reaction, which appears to be a general one for the hydroxylation of isolated ethylenic linkages, was applied to oleic, elaidic, and hendecenoic (undecylenic) acids and to oleyl alcohol, methyl ricinoleate, and red oil. In each case, with the exception of red oil (commercial oleic acid, which usually consists of 65 to 75% oleic acid and 25 to 35% saturated and polyunsaturated acids), quantitative yields of hydroxy-formoxy compounds were obtained, and these could be readily converted by alkaline saponification to the corresponding glycols in quantitative yields. The hydroxy-formoxy compounds developed an increasingly strong odor of formic acid on standing in closed containers, and during a period of several months exposure to the air the neutralization equivalent of hydroxyformoxystearic acid diminished from the correct theoretical value to almost that of dihydroxystearic acid. These facts suggest the possibility of obtaining the free glycols from the formate esters by hydrolysis with water alone.

From the standpoint of effective and economical utilization of hydrogen peroxide, simplicity and ease of operation, and high yields of hydroxylated product, the hydrogen peroxide–formic acid process described below is the best one available at present for hydroxylation of long chain, monounsaturated aliphatic compounds. In a similar process, in which glacial acetic acid plus a small concentration of sulfuric acid is substituted for formic acid, a slightly larger proportion of the active oxygen is lost by decomposition because of the longer reaction time. The yields, however, are about the same in these two processes and one or the other should be satisfactory for the industrial production of hydroxylated fatty materials. Perhaps the reason hydrogen peroxide has not been used commercially for such reactions is that all published processes have required either large excesses of peroxide[4,6,8] or expensive auxiliary chemicals.[9] In the process described here only 1.025 moles of H_2O_2 are required for each mole of monounsaturated compound oxidized to the glycol. Hydrogen peroxide is expensive, but its relatively low molecular weight compensates for that disadvantage. For example, one pound of hydrogen peroxide will convert eight pounds of oleic acid to almost nine pounds of 9,10-dihydroxystearic acid. Furthermore, it leaves only water as a residue.

Experimental

Starting Materials.—Oleic acid, oleyl alcohol,[10] elaidic acid[11] and methyl ricinoleate[12] were purified by methods described elsewhere. The undecylenic acid was the Eastman Kodak Company white label grade. It was fractionally distilled before use, and the fraction boiling at 177–178° (23 mm.) was employed in the oxidations. The red oil (commercial oleic acid) was a light-colored grade and was used without further purification. The hydrogen peroxide was the commercial grade described as 100-volume (25 to 30%) hydrogen peroxide. Its exact peroxide content was determined[13] immediately before use in each case. In all of the following examples, 102.5% of the theoretical quantity of hydrogen peroxide was used. Unless otherwise stated the formic acid was the 98–100% grade.

Hydroxylation of Oleic Acid with Hydrogen Peroxide–Formic Acid.—To a well-stirred solution of 14.1 g. (0.05 mole) of 99.5% oleic acid in 42.3 ml. of formic acid at 25°, 6.90 g. of 25.3% hydrogen peroxide was added in one portion. The reaction became vigorously exothermic after a time lag of about five minutes.[14] The temperature was maintained at 40° with a cold water-bath at the beginning and with a warm water-bath toward the end of the reaction. The reaction mixture became homogeneous in about twenty minutes. One-gram samples were withdrawn at half-hour intervals for determination of the peroxide content of the solution.[13] After about two hours no further disappearance of peroxide was observed. Approximately the theoretical quantity of hydrogen peroxide was consumed. The products were isolated in one of three ways. In batches of this size, the formic acid was recovered by distillation under reduced pressure to yield hydroxy-formoxystearic acids as a residue, or the reaction mixture was poured into cold water, and the product was extracted with ether. Evaporation of the water-washed ether layer yielded hydroxy-formoxystearic acids as a nonvolatile residue. In larger scale operations (100 g. or more), the reaction mixture was poured into three or more volumes of water. The aqueous layer was discarded, and the oil was washed several times with water. By all three procedures, quantitative yields of hydroxy-formoxystearic acids were obtained as a low melting solid (iodine number, 2 to 4; neutralization equivalent: calcd., 345; found, 345 to 350). The hydroxy-formoxy compounds were heated for one hour at 100° with an excess of 3 *N* aqueous sodium hydroxide, and the pale-yellow soap solution was poured into an excess of hot 3 *N* hydrochloric acid with stirring. The oil which formed was allowed to solidify, and the aqueous layer was discarded. The white solid was remelted with hot water and stirred to remove any residual salts and soluble acids. The white solid obtained on cooling was air-dried. The yield was 15.6 g. (99%). The material at this point was fairly pure 9,10-dihydroxystearic acid, m. p., about 90 to 92°; neutralization equivalent, 315 to 320; iodine number, 2 to 4. A 5-gram portion was finely ground, washed three times by decantation with

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[9] Milas, Sussman and Mason, THIS JOURNAL, **61**, 1844 (1939).

[10] Swern, Knight and Findley, *Oil and Soap*, **21**, 133 (1944).

[11] Bertram, *Chem. Weekblad*, **33**, 3 (1936).

[12] Kass and Radlove, THIS JOURNAL, **64**, 2253 (1942).

[13] Wheeler, *Oil and Soap*, **9**, 89 (1932).

[14] *Caution:* excessive overheating of large batches may result in explosions.

Skellysolve B (b. p. 63 to 70°), and filtered yielding 4.7 g. (93%) of 9,10-dihydroxystearic acid (m. p., 92°; iodine number, <1). Another 5-gram portion was crystallized from 95% ethyl alcohol (5 ml./g.) at 0 to 5°, giving 4.0 g. (79% yield) of pure 9,10-dihydroxystearic acid (m. p., 94°). Identical results were obtained when 90% formic acid was substituted for the 98% grade, although the reaction mixture never became homogeneous.

Hydroxylation of Elaidic Acid with Hydrogen Peroxide–Formic Acid.—To a well-stirred mixture of 26.7 g. (0.0915 mole) of 96.8% elaidic acid and 80.1 ml. of formic acid maintained at 40° 12.5 g. of 25.5% hydrogen peroxide was added dropwise. The subsequent procedure was the same as that described under the hydroxylation of oleic acid except that the crude 9,10-dihydroxystearic acid was washed with hot water without melting. The yield of crude 9,10-dihydroxystearic acid was 29 g. (97%). This material was fairly pure; m. p., 126–128°; neutralization equivalent, 315 to 320; iodine number 2 to 3. When 10 g. of this material was washed with Skellysolve B, 9.7 g. of 9,10-dihydroxystearic acid (m. p., 128–129°; iodine number, <1) was obtained. Crystallization of 10 g. of the crude product from 95% ethyl alcohol at 2° yielded 8 g. of pure 9,10-dihydroxystearic acid, m. p., 130–130.5°.

Hydroxylation of Red Oil (Commercial Oleic Acid) with Hydrogen Peroxide–Formic Acid.—To a well-stirred solution of 99.5 g. (0.354 mole of double bond) of commercial oleic acid (iodine number, 90.4; oleic acid, 67.8%; linoleic acid, 16.2%; saturated acids, 16.0%) dissolved in 300 ml. of formic acid (98 to 100%) at 25°, 48.8 g. of 25.3% hydrogen peroxide was added dropwise over a period of about fifteen to thirty minutes. The subsequent procedure was the same as that described under the hydroxylation of oleic acid. The reaction time was three hours. The crude 9,10-dihydroxystearic acid was a hard yellow cake that weighed 107 g. (m. p., 71–77°; neutralization equivalent, 315 to 320; iodine number, about 6). When 50 g. of this material was washed with Skellysolve B, it yielded 42 g. of somewhat impure 9,10-dihydroxystearic acid as a pale-yellow, waxy solid, m. p., 81.5–85.5°. Crystallization of 50 g. of the crude product from 95% ethyl alcohol (2 ml./g.) at 0 to 5° yielded 21 g. of fairly pure 9,10-dihydroxystearic acid, m. p., 92–94° (60% yield, based on the oleic acid content of the starting material).

Hydroxylation of Oleyl Alcohol with Hydrogen Peroxide–Formic Acid.—As described under the hydroxylation of oleic acid, 13.4 g. (0.0491 mole) of 98% oleyl alcohol dissolved in 40.2 ml. of formic acid at 25° was oxidized with 6.65 g. of 25.7% hydrogen peroxide. The temperature was maintained at 40° throughout by cooling or warming as required. The total reaction time was two and one-half hours. The hydroxy-formoxy compounds, obtained in nearly quantitative yield (iodine number, about 6; saponification equivalent, 181; calculated saponification equivalent for mono-hydroxy-diformoxyoctadecane, 179) as a colorless, viscous oil, were refluxed with excess 0.2 *N* alcoholic potassium hydroxide for forty-five minutes, and the solution was poured into hot water with stirring. The aqueous layer was discarded, and the oil was washed with hot water (75°) until the washings were neutral. The white solid obtained was air-dried. The yield was 15 g. (quantitative); m. p., 68.5–70.5°. From 7.5 g., after washing with Skellysolve B, 5 g. of somewhat impure dihydroxyoctadecanol, m. p., 71–73°, was obtained (iodine number, <1). The remaining 7.5 g. was crystallized from ethyl acetate (7 ml./g.) at 1° to yield 3.6 g. of dihydroxyoctadecanol, m. p., 73–74°.

Anal. Calcd. for $C_{18}H_{38}O_3$: C, 71.4; H, 12.7; OH, 16.9. Found: C, 71.3; H, 12.6; OH,[15] 17.1.

The anomalous melting point of 73–74°, about 10° below the value reported in the literature for 9,10-dihydroxyoctadecanol-1[7,16] probably indicates that the product is a mixture of isomeric triols. The starting materials apparently contained other octadecanols besides oleyl alcohol.

Hydroxylation of Methyl Ricinoleate with Hydrogen Peroxide–Formic Acid.—As described under the hydroxylation of oleic acid, 15.6 g. of 98.4% methyl ricinoleate (0.0508 mole of double bond) dissolved in 47 ml. of formic acid at 25° was oxidized with 6.95 g. of 25.44% hydrogen peroxide. The temperature was maintained at 40° throughout by cooling or warming as required. The total reaction time was three hours. The reaction solution was poured into cold water, and the product was extracted with ether. The ether solution was washed with water until neutral, dried over anhydrous calcium sulfate, and filtered Evaporation of the ether gave a quantitative yield of a mixture of hydroxy-formoxy compounds (iodine number, 1 to 2; saponification equivalent, about 136; calcd. for methyl monohydroxy-diformoxystearate; saponification equivalent, 135). Saponification with aqueous 3 *N* sodium hydroxide, followed by acidification and washing with hot water, yielded 16.5 g. (96%) of the mixed 9,10,12-trihydroxystearic acids, m. p., 82–89°; neutralization equivalent: calcd. for 9,10,12-trihydroxystearic acid, 332.5; found, 331. A recently published method describes a procedure for separating these isomers.[12]

Hydroxylation of 10,11-Hendecenoic Acid (Undecylenic Acid) with Hydrogen Peroxide–Formic Acid.—As described under the hydroxylation of oleic acid, 19.5 g. (0.1023 mole) of 96.8% undecylenic acid dissolved in 58.5 ml. of formic acid at 25° was oxidized with 13.9 g. of 25.6% hydrogen peroxide. The temperature was maintained at 40° throughout by cooling or warming as required. The total reaction time was four hours. The reaction solution was poured into cold water, and the product was extracted from the water solution with several successive portions of ether. The combined ether solutions were washed with small portions of water until neutral, dried over anhydrous calcium sulfate, and filtered. Evaporation of the ether gave an almost quantitative yield of hydroxy-formoxyhendecanoic acids, a pale-yellow oil (iodine number, 6; neutralization equivalent, 255; saponification equivalent 121; calcd. for hydroxy formoxyhendecanoic acid: neutralization equivalent, 246; saponification equivalent, 123). This was saponified with an excess of *N* sodium hydroxide for one hour at 100°, and the soap solution was cooled to 20°. It was then poured with stirring into an excess of *N* hydrochloric acid maintained at 20° by the addition of ice. It was necessary to conduct the acidification at a low temperature to prevent the dihydroxyhendecanoic acid from polymerizing. Since this product is fairly soluble in water, the volumes of solution used should be kept at a minimum. The acidified mixture was cooled to 0°, and the precipitate of crude 10,11-dihydroxyhendecanoic acid was filtered off. It was a hard, white solid which weighed 15 g. (neutralization equivalent: calcd., 218; found, 221). It was dissolved in the minimum quantity of 95% ethyl alcohol at room temperature, diluted to turbidity with water, and redissolved by gentle heating (not above 40°). When this solution was cooled to −10° it yielded 10 g. (44%) of pure 10,11-dihydroxyhendecanoic acid, m. p., 84–85° (lit. 85–86°)[17]; neutralization equivalent: found, 216.

Hydroxylation of Oleic Acid with Hydrogen Peroxide–Acetic Acid–Sulfuric Acid.—As described under the hydroxylation of oleic acid with hydrogen peroxide and formic acid, 14.4 g. (0.050 mole) of 98.1% oleic acid was dissolved in 43.2 ml. of glacial acetic acid containing 1.1 g. of concentrated sulfuric acid, heated to 40°, and oxidized at that temperature with 6.75 g. of 25.8% hydrogen peroxide. The reactions in which acetic and sulfuric acids were substituted for formic acid were not very exothermic. The total reaction time was six hours. The hydroxy-acetoxystearic acids, isolated in quantitative yield, had an iodine number of about 6 to 9, as compared with an iodine number of 2 to 4 obtained for hydroxy-formoxystearic acids. The yield of 9,10-dihydroxystearic acid, after saponification, acidification, and crystallization, was slightly lower than the yield obtained when hydrogen peroxide and formic acid were employed to oxidize oleic acid.

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[15] Ogg, Porter and Willits, *Ind. Eng. Chem., Anal. Ed.*, **17**, 394 (1945).

[16] Collin and Hilditch, *J. Chem. Soc.*, 246 (1933).

[17] Hazura and Grüssuer, *Monatsh.*, **9**, 947 (1888).

Hydroxylation of Elaidic Acid with Hydrogen Peroxide–Acetic Acid–Sulfuric Acid.—A well-stirred solution consisting of 270 g. (0.898 mole) of 94% elaidic acid, 810 ml. of glacial acetic acid, and 20 g. of concentrated sulfuric acid was heated to 40° and oxidized at that temperature with 122.8 g. of 25.5% hydrogen peroxide added dropwise over a period of fifteen minutes. The reaction was only slightly exothermic. A granular precipitate began to form after about thirty minutes and continued to increase in bulk as the oxidation proceeded. The total reaction time was five hours. The reaction mixture was poured into hot water (95 to 100°) and stirred for several minutes at that temperature. A semi-solid, white upper layer was obtained. The mixture was cooled to room temperature; the aqueous layer, which contained a small quantity of glistening needles, was filtered by suction, and the filtrate was discarded. The main bulk of the product was remelted with water and stirred for a few minutes to remove additional acetic acid and the lower aqueous layer was discarded. No precipitate was deposited from the second aqueous layer. The product, a hard white solid, was air-dried. It weighed about 300 g. and consisted of 40% hydroxy-acetoxystearic acids, the remainder being mainly dihydroxystearic acid (iodine number, 6 to 7; acid number, 170; saponification number, 224). The product was heated at 100° for one hour with an excess of 2 *N* aqueous sodium hydroxide, and the soap solution was poured into excess hydrochloric acid with stirring. The granular precipitate which formed was filtered by suction. It weighed 280 g., and consisted of somewhat impure 9,10-dihydroxystearic acid, m. p., 122–125° (lit. 130°). Crystallization from 95% ethyl alcohol (7 ml./g.) at 0 to 5° yielded 220 g. of pure 9,10-dihydroxystearic acid as glistening plates, m. p., 130–131°. The yield was 78%.

Hydroxylation of Red Oil (Commercial Oleic Acid) with Hydrogen Peroxide–Acetic Acid–Sulfuric Acid.—As described under the hydroxylation of red oil with hydrogen peroxide and formic acid, 100 g. (0.369 mole of double bond) of commercial oleic acid (iodine number, 93.7; oleic acid, 66.8; linoleic acid, 18.6; saturated acids, 14.6%) was dissolved at 25° in 300 ml. of glacial acetic acid containing 7.9 g. of concentrated sulfuric acid, and 51.2 g. of 25.1% hydrogen peroxide was added dropwise over a five-minute period. The temperature was maintained at 40° throughout by cooling or warming as required. The total reaction time was six hours. The yield of 9,10-dihydroxystearic acid, after saponification, acidification, and crystallization, was slightly lower than the yield obtained when hydrogen peroxide and formic acid were employed to oxidize red oil.

Summary

1. A new and rapid general reaction for the quantitative hydroxylation of long-chain, monounsaturated, aliphatic compounds has been described. The oxidizing agent, performic acid, is not isolated but is prepared and utilized *in situ*. This is accomplished by dissolving the unsaturated compound in formic acid and adding hydrogen peroxide. Because of the rapidity of the reaction and the mild conditions, only one mole of hydrogen peroxide is required for each mole of monounsaturated compound.

2. This reaction has been applied to pure oleic, elaidic, and hendecenoic (undecylenic) acids, oleyl alcohol, and methyl ricinoleate to give excellent yields of the corresponding hydroxy derivatives.

3. In addition, it has been shown that substantially identical results are obtained when acetic acid containing catalytic quantities of sulfuric acid is substituted for formic acid in the mixture with hydrogen peroxide. The oxidizing agent in this case is peracetic acid.

4. Either of the two hydroxylation methods described should be suitable for the industrial production of hydroxylated fatty acids and related compounds. Application of these reactions to red oil (commercial oleic acid) gave good yields of 9,10-dihydroxystearic acid, m. p., 92–94°

PHILADELPHIA, PENNSYLVANIA RECEIVED JUNE 25, 1945

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

Isolation of Constituents of Cane Juice and Blackstrap Molasses by Chromatographic Methods

BY W. W. BINKLEY,[1] MARY GRACE BLAIR[1] AND M. L. WOLFROM

In a previous communication[2] from this Laboratory, a chromatographic method for the separation of carbohydrate acetates was established. Application of this procedure has now been made to cane juice and to cane blackstrap molasses. The molasses was a typical Cuban blackstrap. The bulk of the fermentable sugars was removed from the molasses by fermentation with baker's yeast and the resultant solution was deionized by passage over ion exchange resins. The nature of the products fixed on the exchange resin columns is under further investigation. The non-fermented residue constituted 15.6%[3] of the original molasses, contained 10% of the original total sugar content (by reduction methods) and was a dark brown, hygroscopic solid with a bitter taste and a raisin-like odor. This product was acetylated with hot acetic anhydride and sodium acetate, a stringent acetylation procedure which no doubt led to the essential destruction of many of the sensitive substances contained in the mixture. The major portion of the fermentation glycerol was then removed as glycerol triacetate by distillation methods. The bulk of the residual acetylated material consisted of highly colored products which were strongly adsorbed by Magnesol, a behavior indicative of a polymeric struc-

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(1) Sugar Research Foundation Research Associate (W. W. B.) and Fellow (M. G. B.) of The Ohio State University Research Foundation.

(2) W. H. McNeely, W. W. Binkley and M. L. Wolfrom, THIS JOURNAL, **67**, 527 (1945).

(3) All percentages are on the basis of the original wet products