

# Preparation of Alcohols from Cyclic Fatty Acids<sup>1</sup>

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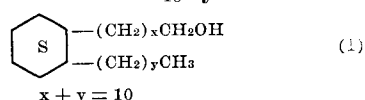
## Abstract

Saturated C<sub>18</sub>- and C<sub>20</sub>-cyclic alcohols have been prepared by catalytic hydrogenation of methyl esters from cyclized linseed monomeric acids, purified saturated C<sub>18</sub>-cyclic acids, ethylene adduct of conjugated soybean fatty acids, and ethylene adduct of conjugated octadecadienoic acids. The cyclic alcohols have also been prepared from free acids of crude cyclic linseed, cyclic linseed monomeric, and ethylene adduct of 9,11,*t,t*-octadecadienoic. Conversion of esters and acids was 88–99% by hydroxyl determination; by gas-liquid chromatographic analysis, almost quantitative. Hydrogenations were carried out with 10%, by weight, copper chromite catalyst, an initial hydrogen pressure of 2,100 psi, and a temperature of 280C for 3–5 hr.

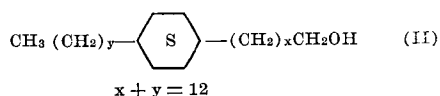
Preliminary evaluations indicate that saturated C<sub>18</sub>- and C<sub>20</sub>-cyclic alcohols have a potential use in cosmetic formulations.

AT THIS LABORATORY Friedrich and his co-workers (2,4,5) have shown that liquid saturated C<sub>18</sub>-cyclic monocarboxylic acids can be prepared from linseed oil, linolenic acid, and tung oil. They (3) also prepared C<sub>20</sub>-cyclic monocarboxylic acids by the reaction of ethylene with soybean and linoleic acids. Because these unique cyclic fatty acids have such low melting points, a survey of their derivatives for potential industrial use was initiated.

The hydrogenation of esters to alcohols in the presence of suitable catalyst is a well-known reaction (1). Saturated cyclic fatty alcohols were prepared by the copper chromite-catalyzed hydrogenation of C<sub>18</sub>- and C<sub>20</sub>-cyclic monocarboxylic acids or their methyl esters. The conversion of acids or esters to saturated cyclic fatty alcohols ranged from 88–99%, based on hydroxyl determination. The saturated C<sub>18</sub>-cyclic alcohols (I)



are vicinally disubstituted cyclohexanes. The saturated C<sub>20</sub>-cyclic alcohols (II) are 1,4 disubstituted



cyclohexanes. Preliminary evaluations of these saturated C<sub>18</sub>- and C<sub>20</sub>-cyclic alcohols indicated potential in cosmetic formulations.

## Experimental

**C<sub>18</sub>-Cyclic Acids.** C<sub>18</sub>-cyclic monocarboxylic acids were prepared by alkali cyclization of linseed oil in glycols (4,5). Crude cyclic acids were obtained by acidification and removal of solvent from the mixture; cyclic monomeric acids, by flash distillation of crude acids to remove dimeric and polymeric materials; and purified saturated cyclic acids, by complete hydrogenation of cyclic monomeric acids and removal of straight-chain acids by low-temperature crystallization from acetone.

**C<sub>20</sub>-Cyclic Acids.** C<sub>20</sub>-cyclic monocarboxylic acids were prepared by the addition of ethylene to 9,11,*t,t*-octadecadienoic acid, linoleic acid, and soybean fatty acids (3).

**C<sub>18</sub>- and C<sub>20</sub>-Cyclic Methyl Esters.** Methyl esters of the C<sub>18</sub>- and C<sub>20</sub>-cyclic monocarboxylic acids were made with absolute methanol and concentrated H<sub>2</sub>SO<sub>4</sub> catalyst or either a BF<sub>3</sub>-etherate or a HCL-2,2-dimethoxy-propane system.

**Saturated C<sub>18</sub>-cyclic Alcohol Monomers.** A 500-ml stainless-steel Magne-Dash autoclave was charged with 200 g of monomeric cyclized linseed methyl esters (containing 40% cyclic) and 20 g of copper chromite catalyst (10% by weight). After the autoclave was flushed and pressurized with hydrogen to 2,100 psi at room temperature, the charge was heated rapidly with stirring to 280C. During this period the hydrogen pressure was maintained between 1,475 and 2,100 psi until 280C was reached. After 2 hr at 280C the uptake of hydrogen was very small. Total reaction time at 280C was 3 hr. After cooling, contents of the autoclave were diluted with 200 ml acetone, and the catalyst was removed by filtering through a heated funnel. The acetone was removed by distillation, and the alcohols were flash distilled under nitrogen at 0.07–0.14 mm. Because the alcohol monomers tend to solidify at 35–40C, a steam-heated condenser was used. A distillate fraction (168.2 g), 98% conversion, bp 118–168C, and a residue (15.7 g) were obtained. This standard procedure (SP) was followed in the preparation of other cyclic fatty alcohols.

**Purified Saturated C<sub>18</sub>-Cyclic Alcohols.** These alcohols were prepared from the methyl esters of purified hydrogenated cyclic acids (190 g) by the SP procedure, except that it was unnecessary to add additional hydrogen during the reaction. Distillation of crude alcohols (155 g) gave 1.7 g, bp 103–129C/0.15 mm; 142.9 g, bp 129–152/0.15 mm; and 6.8 g residue. The main fraction showed 0 saponification equivalent and 69% conversion of ester to alcohol, based on hydroxyl determination. Because of the apparent low conversion, the alcohols were fractionally distilled in a vacuum-jacketed Vigreux column. The first fraction (18.5 g) distilled at 90–129C/0.07 mm, N<sub>D</sub><sup>20</sup> 1.4638, and contained 79% alcohols and 21% hydrocarbon by GLC analysis. The second fraction (64.9 g) distilled at 129–134C/0.07 mm, N<sub>D</sub><sup>20</sup> 1.4685, and contained 98.8% alcohols, based on hydroxyl determination. The third fraction (44.8 g) distilled at 134–138C/0.07 mm, N<sub>D</sub><sup>20</sup> 1.4694, and contained 98.8% alcohol based on hydroxyl determination.

Since GLC indicated that the second and third fractions were identical and free of hydrocarbon, they were combined, N<sub>D</sub><sup>20</sup> 1.4689.

**Crude Saturated C<sub>18</sub>-Cyclic Alcohols.** A 2-liter stainless-steel Magne-Drive autoclave was charged with 400 g of crude linseed cyclic acids (containing 37.4% cyclic and 9.5% polymer) and 40 g of copper chromite catalyst. After the autoclave was flushed and pressurized with hydrogen to 2,100 psi at room temperature, the charge was heated rapidly with stirring to 280C. Samples of the reaction mixture were taken at various intervals for analysis. The filtered sample showed an iodine value (I.V.) 14 and an acid value (A.V.) of less than 1 after 11 hr. The crude

<sup>1</sup> Presented AOCs meeting in Minneapolis, Minn., 1963.  
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TABLE I  
 Properties of Saturated Cyclic Alcohols

| Alcohols                               | Source                          | Cyclic, % | OH, % | I.V. | A.V. | M.P. C           | Viscosity, CP <sup>a</sup> 60C |
|--|---------------------------------|-----------|-------|------|------|------------------|--------------------------------|
| C <sub>18</sub> monomeric              | LSO                             | 40        | 6.14  | 0.7  | 0.45 | 42-53            | 11.7                           |
| C <sub>18</sub> purified               | LSO                             | 100       | 6.2   | 1.1  | 0.45 | -40 <sup>b</sup> | 18.7                           |
| C <sub>18</sub> crude <sup>c</sup>     | LSO                             | 37.5      | 5.9   | 0.5  | 0.65 | 38-46            | .....                          |
| C <sub>20</sub> monomeric              | SBO                             | 47.9      | 5.8   | 1.3  | 0.56 | 37-51            | 41.8                           |
| C <sub>20</sub> monomeric              | Linoleic acid                   | 80.2      | 5.4   | 1.0  | 0.47 | 23-25            | 18.7                           |
| C <sub>20</sub> monomeric <sup>c</sup> | 9,11,11,11-Octadecadienoic acid | 100       | 5.5   | 0.3  | 0.99 | 22-25            | 28.0                           |

<sup>a</sup> Determined with Hoake Rotovisco.

<sup>b</sup> Pour point.

<sup>c</sup> Prepared from acids.

alcohols (370 g) were recovered as described for the SP but with 400 ml acetone. Apparently the recovered catalyst was deactivated, as evidenced by a change in the color of the catalyst from black to a copper red. To determine whether the residual unsaturation was present in the monomeric fraction or in the polymeric fraction, 112 g of the crude alcohols were flash distilled. The distillate fraction (108.5 g) had I.V. 6.5 and the residue fraction (2.4 g), I.V. 49.5. The hydrogenation of the crude alcohol mixture (360 g) was continued with 36 g of fresh copper chromite catalyst for 4 hr at 280C. Recovered crude cyclic alcohols (322.8 g) had I.V. 2.7 and A.V. 0.6. Distillation of crude cyclic alcohols (176 g) gave 7.5 g, bp 90-120C/0.15 mm; 155 g, bp 120-160C/0.15 mm; and 12.2 g residue. GLC analysis of the first fraction showed 36% saturated C<sub>18</sub>-cyclic alcohols, 40.6% stearyl alcohol, 14.3% palmityl alcohol, and 9.1% hydrocarbon. The main fraction contained 96% alcohols (based on hydroxyl determination) A.V. 0.65, I.V. 0.48, and by GLC 37.8% saturated C<sub>18</sub>-cyclic alcohols, 57.5% stearyl alcohol, and 4.7% palmityl alcohol.

**Saturated C<sub>20</sub>-Cyclic Soybean Alcohol Monomers.** The alcohols were prepared from the ethylene adduct of soybean methyl esters (450 g, 46.9% C<sub>20</sub>-cyclic adduct, 6.6% unreacted conjugated linoleate, 26% oleate, 5.4% stearate, and 15.1% palmitate) by the SP. For this preparation a 1-liter stainless-steel Magne-Dash autoclave was used. Distillation of crude alcohol monomers (414.3 g) gave 8 g, bp 90-131C/0.04 mm; 379 g, bp 131-180C/0.04-0.05 mm; and 32.3 g residue. Conversion of ester to alcohol was 96.5%.

**Saturated C<sub>20</sub>-Cyclic Alcohols.** The alcohols were prepared from the ethylene adduct of methyl linoleate (500 g, 83.6% C<sub>20</sub>-cyclic adduct, 6.8% unreacted conjugated linoleate, 3.2% stearate, 4.2% oleate, and 2.2% palmitate) by the SP. Distillation of crude alcohols (441.8 g) gave 1.8 g, bp 100-130C/0.1 mm; 389 g, bp 130-180C/0.1-0.2 mm; and 40.2 g residue. Conversion of ester to alcohol was 93%.

**Pure Saturated C<sub>20</sub>-Cyclic Alcohols.** The glass liner of a 300-ml Aminco high-pressure apparatus was charged with 6.3 g of ethylene adduct (100% cyclic) of 9,11-*t,t*-octadecadienoic acid and 0.65 g copper chromite catalyst. The autoclave was sealed, flushed, pressurized with hydrogen to 2,100 psi at room temperature, placed in a rocking device, and heated to 280C for 4.75 hr. After cooling, the autoclave contents were diluted with 20 ml acetone, and the catalyst was removed by filtration. Distillation of the recovered product (5 g) gave 0.4 g, bp 108-150C/0.07-0.1 mm, N<sub>D</sub><sup>20</sup> 1.4650; 3.4 g, bp 150-165C/0.1-0.2 mm, N<sub>D</sub><sup>20</sup> 1.4668; and 0.4 g residue. GLC analysis of the first fraction showed 92% saturated C<sub>20</sub>-cyclic alcohol, 3.4% stearyl alcohol, and 4.5% hydrocarbons. GLC analysis of the main fraction indicated saturated C<sub>20</sub>-cyclic alcohol containing undeterminable traces of stearyl alcohol and hydrocarbons. Conversion of acid to alcohol was 98.4%.

## Discussion

The hydrogenation of esters or acids were conducted without a solvent at 280C. Based on weight of esters or acids, 10% Harshaw 1106 P copper chromite catalyst was used. The composition of the catalyst was 40% CuO, 47% Cr<sub>2</sub>O<sub>3</sub>, and 10% BaO. The reactions were not investigated at temperatures below 280C because of limitations on hydrogenation pressure. Under the conditions described, cyclohexadiene, cyclohexene, and straight-chain alkene linkages were hydrogenated simultaneously with the ester or acid group. When carried out with a small headspace, the hydrogenation of cyclic acids to alcohols deactivated the catalyst and required a longer reaction time. The deactivation of the catalyst is favored by the formation of water in the reaction mixture (1). The physical constants for the saturated cyclic alcohols are shown in Table I.

Hydrogenation of small samples of cyclic esters (not described) in the rocker-type autoclave required longer reaction times than those conducted in the Magne-Dash autoclave. Less efficient agitation in the rocker autoclave probably accounted for the longer reaction time.

For GLC analysis, samples of the saturated alcohols

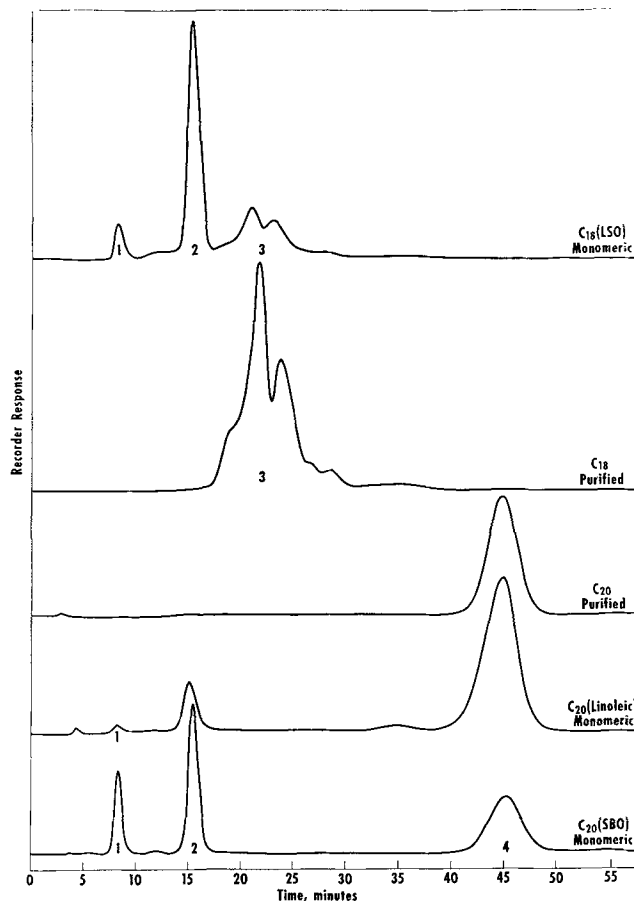


Fig. 1. Gas chromatograms of saturated cyclic alcohol acetates. Peaks: 1, palmityl; 2, stearyl; 3, C<sub>18</sub>-cyclic; 4, C<sub>20</sub>-cyclic.

were converted to acetate esters for increased resolution. The analyses were made using a Pye-Argon chromatograph, equipped with a radium-D detector. The 4 ft by  $\frac{1}{4}$  in. O.D. glass column was packed with 14% EGSS-X organosilicon polyester on Gas Chrom P. Good separation of the saturated cyclic alcohol acetates from straight-chain alcohol acetates was obtained at 175C and 35 cc per minute argon flow rate. GLC analysis showed the conversion of ester or acid to saturated alcohols to be almost quantitative with the formation of less than 2% hydrocarbons, which were easily separated by distillation. Gas chromatograms of saturated cyclic alcohol acetates are shown in Fig. 1.

Saturated C<sub>18</sub>-cyclic alcohol monomers (containing 40% cyclic, 53% stearyl, and 7% palmityl) and saturated C<sub>20</sub>-cyclic alcohol monomers (containing 50.7% cyclic, 36.8% stearyl, and 12.5% palmityl) were evaluated in cosmetic formulations. In several different emulsion systems—hand creams, hand and body lotions, and an antiperspirant compound—saturated cyclic alcohol monomers imparted a better feel and esthetic appearance than could be obtained with either cetyl or stearyl alcohol. In deodorant antiperspirant formulations containing aluminum salts, the saturated

cyclic alcohols had much greater emolliency and reduced the tackiness inherent with the use of aluminum salts. When present in an aerosol medium, the hydrogenated cyclic alcohols had good lubricating properties for the valves. When incorporated in cosmetic formulations, little difference between C<sub>18</sub>- and C<sub>20</sub>-cyclic alcohols was noticed. In almost every product where saturated cyclic alcohols were used, the viscosity of the solution was reduced and the normal "body" of the finished formula was less than when cetyl and stearyl alcohols were used. These disadvantages were overcome by increasing the amount of saturated cyclic alcohol used between 50% and 100%. Hand and body lotions prepared with saturated cyclic alcohols were stable at 45C.

#### ACKNOWLEDGMENT

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## Chemical Reactions Involved in the Deep Fat Frying of Foods. I. A Laboratory Apparatus for Frying Under Simulated Restaurant Conditions<sup>1</sup>

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### Abstract

A laboratory apparatus has been designed which can be used to quantitatively collect the volatile decomposition products produced during deep fat frying under simulated restaurant conditions. In order to study the chemical reactions of frying fat without any inter-reaction with the food fried, moist cotton balls were fried in corn oil.

The oil used for frying was shown to differ considerably from oil which was continuously heated. The latter had a darker color and higher viscosity. It foamed significantly while the oil used for frying did not. Furthermore, the continuously heated oil had a much lower free fatty acid content than did the oil used for frying under simulated restaurant conditions.

The volatile decomposition products collected during frying of cotton balls in corn oil were separated into acidic and nonacidic compounds. Each group exhibited a definite gas chromatographic pattern after only a short period of frying. Part of the degradation products, particularly those of higher boiling points, were found to remain in the frying oil.

### Introduction

THE NUTRITIVE VALUE of frying fats has been a controversial issue. Results of investigations from laboratories using commercial frying fats indicate that they have no deleterious effect in human nutrition (1-3). On the other hand laboratory treated fats have generally resulted in gross symptoms of nutritional disorders (4-7). However, the conditions under which the fats were treated for these experiments were quite different from those used in commercial deep fat frying or in restaurants.

The chemical reactions which take place during deep fat frying are far from completely understood. Perkins and Kummerow (8) heated corn oil at 200C for 48 hr while aerating it with a stream of oxygen. The polymerized oil was saponified and the fatty acids fractionated by forming urea adduct followed by molecular distillation. Some physical and chemical constants of the fatty acid fraction were determined. The volatile decomposition products formed by bubbling air through synthetic triglycerides were analysed by Endres et al. by GLC retention times (9). Recently, Ota et al. collected the volatile decomposition products by blowing air through preheated soybean oil at 250C. They also characterized the gas chromatographic fractions by retention times (10).

The present paper describes an apparatus used for chemical characterization of the volatile and nonvolatile decomposition products produced during deep fat frying under simulated commercial conditions.

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