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 ¼ 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_{18}-cyclic alcohol monomers (containing 40% cyclic, 53% stearyl, and 7% palmityl) and saturated C_{20}-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_{18}- and C_{20}-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

R. L. Reichert conducted hydrogenations and Shulton, Inc. made valuable suggestions and evaluated the saturated cyclic alcohols in cosmetic formulations.

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Chemical Reactions Involved in the Deep Fat Frying of Foods. I. A Laboratory Apparatus for Frying Under Simulated Restaurant Conditions[1]

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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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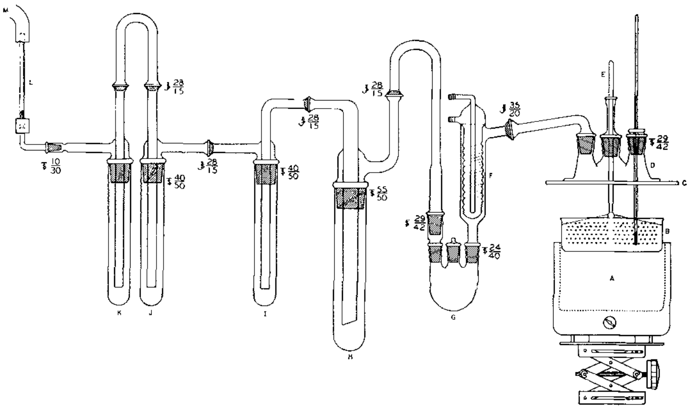

FIG. 1. Laboratory deep fat frying apparatus used for preliminary experiments.

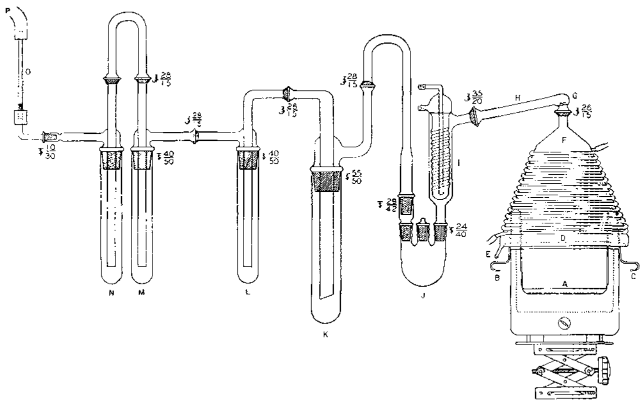

FIG. 2. Modified laboratory apparatus for deep fat frying under simulated restaurant conditions.

Experimental

Laboratory Deep Fat Frying Apparatus

The apparatus used in preliminary experiments for the quantitative collection of the volatile decomposition products under simulated restaurant conditions is shown in Figure 1. A Sunbeam household deep fat fryer (A), 8¼ in I.D. 9½ in O.D. containing 2300 ml of oil at 185C was used. The fryer was made to fit snugly a flat flange type resin reaction flask top (D), 5½ in. I.D. through an aluminum ring (C). The ring had an O.D. of 10½ in. and an I.D. of 6 in. A groove was engraved in the bottom side of the aluminum ring to fit the edge of the deep fat fryer. The center neck of (D) was fitted with a ground glass stirrer shaft (E) in a ground glass bearing (Kontes Glass Co. No. K-78100). The end of the stirrer shaft was attached to an aluminum basket (B) perforated with holes of ¼ in. diameter. The basket could therefore be lifted or lowered without leakage of gases.

For frying, the basket (B) was lifted out of the oil by the use of the shaft (E). The fryer was lowered with the aid of the laboratory jack. Ten moist cotton balls were then placed in the basket for frying. The cotton balls were previously washed thoroughly first with ethanol and then with redistilled hexane. Each of the cotton balls contained 75% of water and weighed 2 g. The laboratory jack was then used to raise the fryer to fit the resin reaction flask top snugly. A vacuum pump connected to the end of the flowmeter (M) was turned on to draw a current of air through the top of the fryer and then the train of traps at a rate of 7.2 l/min as indicated by the flowmeter (L). The basket was now dipped into the oil by lowering the shaft (D) and the cotton balls began to fry.

The volatile decomposition products and steam thus produced were drawn by the current of air flowing through the apparatus into the water cooled condenser (F). The condensate was collected in flask (G). The more volatile decomposition products were then condensed in the train of traps (H through K) which were cooled with dry ice. The frying was carried out once every 30 min. After each 6 hr of frying, the oil was allowed to cool to room temperature and the collected volatile decomposition products were washed out with ethyl ether.

Modified Deep Fat Frying Apparatus

The apparatus for the quantitative collection of volatile decomposition products used in the present investigation is shown in Figure 2. It was an improved and modified version of the apparatus used for preliminary experiments. The aluminum frying basket (A) was held in position by clamping at (B) and (C). The top of the Sunbeam deep fat fryer was fitted with an Alembic type cone (F) made of stainless steel. The cone was 10 in. high and had a top diameter of 5 in.; bottom diameter, 11 in. It was cooled with running water through aluminum coils wrapped around the outside of the cone. A glass connector (H) with an Alembic shaped head (G) was used to join the cone to the condenser (I).

For frying, the deep fat fryer containing 2300 ml of corn oil maintained at 185C was lowered until the aluminum basket was out of the oil. Ten moist cotton balls, prepared in the same manner as those used in the preliminary experiments, were placed in the aluminum basket. A vacuum pump connected to the end of the flowmeter (P) was turned on to draw a current of air through the top of the fryer and then through the train of traps at a rate of 7.2 liter/min as indicated by the flowmeter (O). The fryer was then raised until the cotton balls were immersed in the oil and fried.

The volatile decomposition products and steam thus produced were drawn by the current of air flowing through the apparatus into the stainless steel cone and then the condenser and the train of traps (K through N). The condensate collected on the inside of the cone could not drip back into the fryer because it was trapped by the Alembic edge (D). Excessive amount of volatile decomposition products and steam condensed in the cone would flow out from the exit

TABLE I
Physical and Chemical Changes of Corn Oil During Deep Fat Frying and During Continuous Heating

	Oil used for frying (hr)							Oil continuously heated
	0	3	6	12	30	60	90	90 hr
Free fatty acid (% oleic acid)	0.12	0.13	0.13	0.17	0.30	0.88	1.37	0.32
Peroxide number (meq/kg)	1.34	1.53	1.63	2.75	1.92	2.41	2.94	2.20
Iodine value (Wijs)	128	128	127	126	126	123	124	122
Refractive index (40C)	1.4675	1.4675	1.4680	1.4681	1.4681	1.4681	1.4681	1.4681
Color (photometric)	2.86	3.26	3.92	4.58	5.26	8.04	8.56	12.47
Viscosity (centistokes) 37.7C	39.7	40.0	40.3	43.2	42.3	44.9	43.9	50.4
Foaming (ml)	None	None	None	None	None	None	None	200

(E) and could be collected with a suitable container. Those which were not condensed in the cone were collected in the flask (J) and traps (K through N). Those condensed in the head of the connector tube (H) also could not drip back into the fryer because of the Alembic head (G).

Ten moist cotton balls containing approximately 16 g of water were fried every 30 min. Thirteen frying operations were done each day in 6 hr. After each 12 hr of frying, 800 ml of fresh corn oil was added into the fryer to replenish the oil absorbed by the cotton balls. After each 6 hr of frying, the oil was allowed to cool to room temperature. The apparatus was disassembled and all the condensates were washed out with distilled water and ethyl ether.

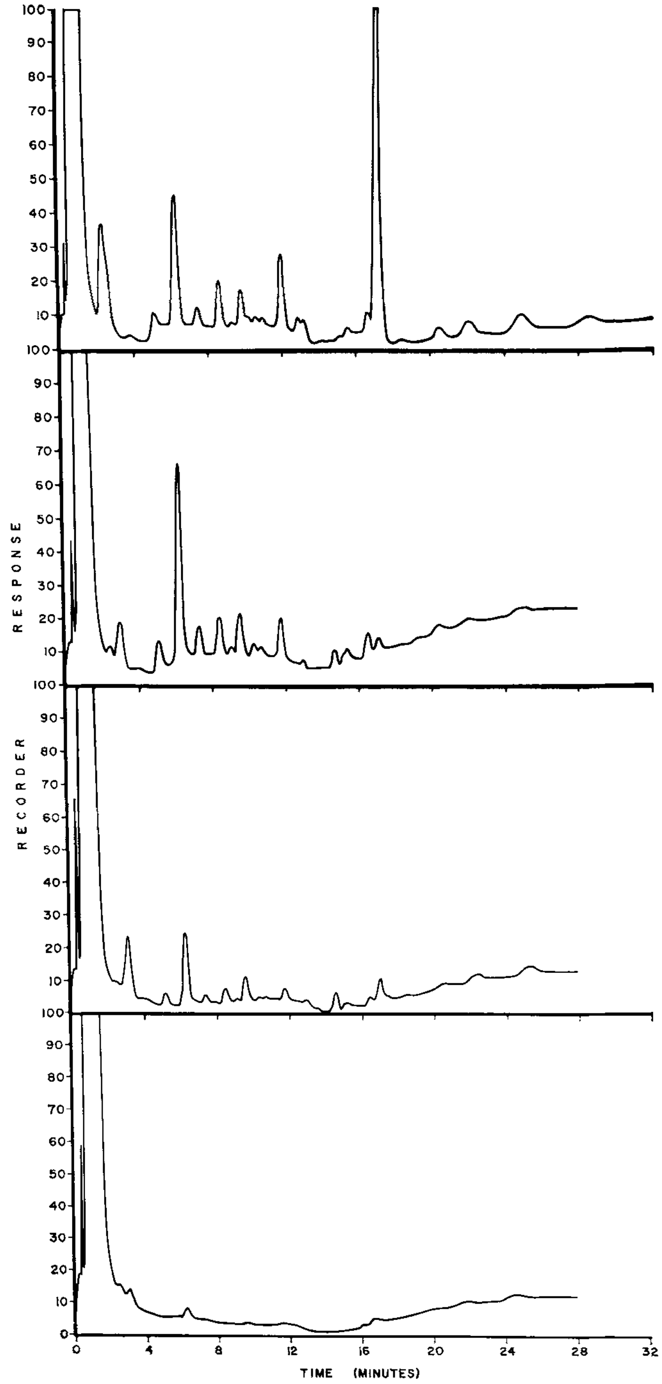

FIG. 3. Gas chromatogram of volatile acidic decomposition products collected during deep fat frying at 0–6 hr (bottom curve) 6–12 hr (lower center curve), 12–30 hr (upper center curve) and 60–90 hr (top curve).

Continuous Heating of Corn Oil

The modified deep fat frying apparatus was used. Corn oil, 2300 ml was placed in the Sunbeam deep fat frier and was continuously heated at 185C for 90 hr.

Extraction and Preliminary Fractionation of the Volatile Decomposition Products

The combined condensates and washings from the deep fat frying of cotton balls were extracted with ethyl ether and the extract concentrated according to the method of Chang (11). In order to remove the oil in the condensate due to entrainment during frying, the concentrated ether extract was then molecularly distilled in a bell-shaped flask with a flat bottom fitted with an Alembic distilling head. The distillations were done at 150C for 6 hr under a vacuum of 1–2 μ, while the sample was agitated with a magnetic stirrer.

The distillate was fractionated into acidic compounds and nonacidic compounds by extraction with 10% aqueous sodium carbonate solution.

Isolation of Volatile Decomposition Products Remaining in the Frying Oil

At the end of the experiment, the volatile decomposition products remaining in the corn oil were isolated by vacuum steam distillation. The distillate collected from distillation at 150C under 5 μ for 2 hr was extracted with ethyl ether and the ether extract treated in the same manner as described previously.

Gas Chromatography

The nonacidic volatile decomposition products were fractionated with a Beckman GC-2A gas chromatograph with an 8 ft column (¼ in. diameter) packed with 15% Ucon Polar on 80/100 Mesh Chromosorb W. The temperature was nonlinearly programmed from 50–200C in 40 min with a Beckman Thermotrac.

The acidic volatile decomposition products in ethyl ether solution were directly converted into their methyl esters by the use of diazomethane (12). The esters were fractionated with a Wilkens A-90-P gas chromatograph with a 6 ft column (¼ in. diameter) packed with 20% stabilized DEGS on 70/80 mesh Anakrom with temperature nonlinearly programmed from 60–200C in 18 min.

Analytical Methods

Free Fatty Acids, Photometric Color, Iodine Value, and Peroxide Number were determined according to the Official Methods of the American Oil Chemists' Society. Colors were measured with 1 cm rectangular cells instead of 2.18 cm diameter cylindrical cuvettes Viscosity was determined at 37.7C with a Cannon-Fenske Viscometer (No. 200, Cannon Instrument Co.). Foaming was determined in a 250 ml high form graduated Griffin Beaker containing 160 ml of oil at 185C. Six square inches of Whatman No. 1 filter paper were moistened wih 0.7 g of distilled water. The papers were strung on a Nichrome wire and inserted to the 50 ml mark in the center of the beaker. The highest volume to which the oil foamed was noted.

Results and Discussion

Apparatus for Laboratory Deep Fat Frying

The apparatus shown in Figure 1 could be used for deep fat frying in the laboratory. To avoid any interreaction of the frying oil and the food fried, inert moist cotton balls were used for the frying. However, after some preliminary experiments, it was observed that considerable amount of volatile decomposition products of higher boiling point and some entrained oil were condensed on the resin reaction flask top. Since these condensates occasionally dripped back into the frying oil, they might undergo further decomposition to produce additional volatile decomposition products as artifacts. Furthermore, the resin reaction flask top was at an elevated temperature during the experiments. The condensate spread on the top as a film undoubtedly underwent further decomposition to produce volatile products which might not be the same as those produced from the oil during frying. Although this apparatus was abandoned after the exploratory experiments, it is described to avoid repetition by other researchers.

The modified apparatus shown in Figure 2 was found satisfactory for the quantitative collection of the volatile decomposition products produced during deep fat frying under simulated restaurant conditions.

Comparison of Frying Oil and Continuously Heated Oil

The appearance of the oil which was used for frying cotton balls in corn oil at 185C for 90 hr was quite different from the oil continuously heated for the same length of time at the same temperature. Some of the physical and chemical changes of corn oil when used for deep fat frying under simulated restaurant conditions are shown in Table I. These changes are also compared with those of corn oil which was continuously heated without frying and without replenishment with fresh oil every 12 hr.

The continuously heated oil 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 the oil used for frying. Since free fatty acids remaining in the heated oil may further participate in chemical reactions, the chemical structures of the final decomposition products might also be different in oils heated continuously and in oils used for frying. Recently, Kritchevsky (13) reported that rabbits fed with cholesterol suspended in corn oil had higher atheromata when free fatty acid content was increased to 0.5%. The present data, therefore, seem to indicate a possibility that the frying oil may have effects upon the metabolic pattern of lipids which are different from those of the continuously heated oil.

Volatile Decomposition Products Remaining in the Oil

When corn oil was continuously heated, there was a significant amount of volatile decomposition products remaining in the oil. They could be isolated from the oil by vacuum steam distillation. According to gas chromatographic analyses, these compounds, both acidic and nonacidic, were not qualitatively different from those which were evaporated during the heating period. When the oil was used for frying, there was still a significant amount of volatile decomposition products, both acidic and nonacidic, remaining in the oil. However, they consisted predominantly of compounds with higher boiling points. It is therefore concluded that the effect of the volatile decomposition products upon human nutrition should be studied because these compounds, at least those with higher boiling points, will partially remain in the frying oil and are thus consumed with the fried foods.

Volatile Decomposition Products Collected During Various Intervals of Frying

The methyl esters of the volatile acidic decomposition products collected during 0–6, 6–12, 12–30, 30–60, and 60–90 hr of frying were gas-chromatographed under identical conditions (Fig. 3). The quantity of volatile acids produced during the first 6 hr of frying was small and the number of peaks few. After 12 hr of frying, the number of peaks increased to 23. When the concentration of the gas chromatographic sample was increased, a total of 27 peaks could be counted. Further frying to 30 and even 90 hr did not increase the number of peaks. However, in the early stage of frying, acids of lower boiling points were more predominant. They were probably produced by breakdown of carbon chains. In the later stage, when the free fatty acid content was increased, acids of higher boiling points were more predominant. They were probably produced by hydrolysis of triglycerides. Gas chromatograms therefore show that during the initial stage of frying more acidic volatile decomposition products are produced by chain breaking through autoxidation. But during the later stage of frying, more acidic decomposition products are produced by hydrolysis of the ester linkages of triglycerides.

The volatile nonacidic decomposition products collected during 0–3, 3–6, 6–12, 12–30, 30–60, and 60–90 hr were also gas-chromatographed under identical conditions (Fig. 4). The number of peaks increased from 6 hr of frying to 30 hr of frying. All the peaks observed in 6 and 12 hr of frying were also observed in 30 hr of frying. No new peaks were observed in the volatile decomposition products when the oil was further used for 60 and 90 hr. This seems to indicate that the decomposition pattern of the frying oil remained essentially the same after the oil was used for frying for 30 hr when the oil could be considered as good and reuseable by commercial standards, until the oil was used for 90 hr when the oil would be considered as bad enough to be discarded.

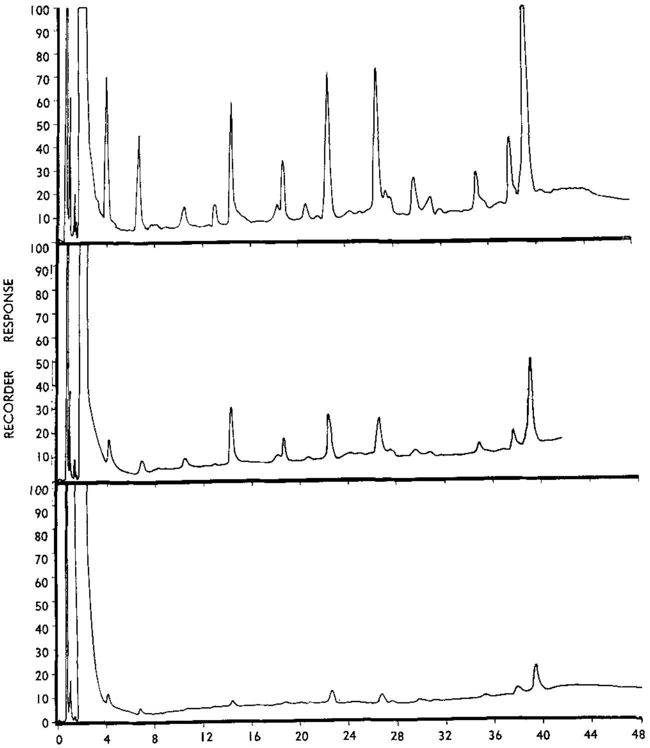

Fig. 4. Gas chromatogram of volatile nonacidic decomposition products collected during frying at 3–6 hr (bottom curve), 6–12 hr (center curve), and 12–30 hr (top curve).

ACKNOWLEDGMENTS

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Alkaline Cleavage of Hydroxy Unsaturated Fatty Acids. I. Ricinoleic Acid and Lesquerolic Acid

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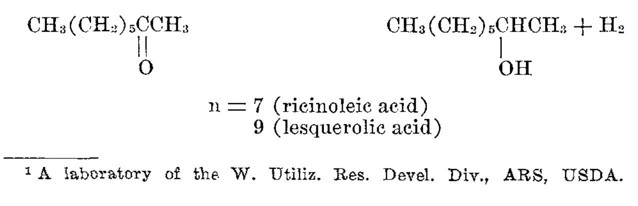
Abstract

The effects of temperature and media on the fusion of ricinoleic and lesquerolic acid derivatives with concentrated aqueous alkali were examined. Improved yields of ω-hydroxy acids were obtained by use of excess 2-octanol. The effect of excess 2-octanol is discussed in relation to a recently proposed reaction mechanism.

Introduction

HIGH TEMPERATURE (above 250C) alkaline fusion of derivatives of ricinoleic acid, 12-hydroxy-*cis*-9-octadecenoic acid, is a commercial method for manufacturing sebacic acid in high yield (1–9). Lower temperature (180–200C) alkaline fusion produces 10-hydroxydecanoic acid (1,5,9–12), but the yield is smaller than for sebacic acid. Analogous compounds are produced from lesquerolic acid, 14-hydroxy-*cis*-11-eicosenoic acid, which is the major fatty acid component of some *Lesquerella* seed oils (13,14). The high temperature alkaline fusion gives dodecanedioic acid (15). The low temperature reaction, which has not been reported previously, yields 12-hydroxydodecanoic acid. The following equations summarize the reactions:



$$CH_3(CH_2)_5\underset{\displaystyle OH}{\underset{|}{CH}}CH_2CH{=}CH(CH_2)_nCOOH$$

$$HOCH_2(CH_2)_{n+1}COOH + CH_3(CH_2)_5\underset{\displaystyle O}{\underset{||}{C}}CH_3$$

$$HOOCCH_2(CH_2)_nCOOH + CH_3(CH_2)_5\underset{\displaystyle OH}{\underset{|}{CH}}CH_3 + H_2$$

n = 7 (ricinoleic acid)
9 (lesquerolic acid)

In this investigation the effects of reaction media, reaction times, and temperatures on the alkaline cleavage of ricinolec acid and lesquerolic acid were examined. A procedure for enhancing yields of ω-hydroxy acids is discussed in relation to possible reaction mechanisms (1,5,16,17).

Experimental

Materials

Methyl Ricinoleate. This ester was prepared by alcoholysis of castor oil followed by fractional distillation of the mixed methyl esters under reduced pressure to give a product of > 98% purity (18).

Methyl Lesquerolate. Lesquerella fendleri oil (13, 19) was alcoholized with methanolic sodium methoxide, and methyl lesquerolate (~95% purity) was isolated by fractional distillation at 190–195C and 100–275 μ Hg.

2-Octanol. Eastman Kodak 66 (ketone-free) 2-octanol was used as obtained.

Analytical Techniques

Programmed-temperature gas-liquid chromatographic analyses were run on a model 720 F and M Gas Chromatograph. The column was a 3-ft, 0.25-in. stainless steel tube packed with 10% ECNSS-S (Applied Science Laboratories, Inc., State College, Penn.) on 100–120 mesh Gas Chrom P.

Procedures for Alkaline Fusion of Hydroxy Unsaturated Acids

A. Preparation of Sebacic Acid by High Temperature Alkaline Cleavage of Ricinoleic Acid. A one-liter nickel resin kettle and top were fitted with a sealed steel stirrer, heated dropping funnel, and a condenser for collection of volatile by-products. The reaction vessel was charged with 17.8 g of sodium hydroxide, 2.5 g of water, and 3.9 g of lead oxide as catalyst (8), and brought to 250 C with an electrically heated silicone oil bath. Methyl ricinoleate (78 g) was saponified with 20 g of sodium hydroxide in 12 ml of water. The soap was dissolved in 138 ml of hot water, and was

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