and fractional distillation. A small amount of myristicin is collected in the forerun of the distillation; the C_{18}-fraction consists of pure methyl petroselinate.

In accordance with previously reported values (3), GLC analysis showed that the total lipid of coriander seed *(Coriandrum sativum)* contains about 50–55% petroselinic acid and only a small percentage of nonsaponifiable material. Therefore, it also constitutes a convenient source for the preparation of petroselinic acid.

Since the phenol ether, myristicin, overlaps in GLC analysis with methyl petroselinate and methyl oleate and has similar solubility properties, care must be exercised in the routine analysis and isolation of the "methyl esters" derived from seed oils. If the esters are prepared by methanolysis of the total oil without prior extraction of the nonsaponifiable material, certain peaks in the gas chromatogram may be interpreted erroneously as representing methyl esters of fatty acids.

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The Preparation of Lauryl Alcohol and 6-Hydroxycaproic Acid from Petroselinic Acid[1]

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Abstract

Lauryl alcohol and 6-hydroxycaproic acid have been prepared from the ozonolysis products from both petroselinic acid and its ethyl ester by reduction with sodium borohydride. Satisfactory conversion of the ozonolysis product from ethyl petroselinate to lauryl alcohol and ethyl 6-hydroxycaproate was also achieved by catalytic hydrogenation, but the hydrogenation product was contaminated with small amounts of diethyl adipate and ethyl laurate as indicated by gas liquid chromatography. A procedure has been devised using ion exchange resin for the conversion of sodium 6-hydroxycaproate to 6-hydroxycaproic acid without the concomitant formation of lactones or polyesters.

Introduction

SEEDS of the plant family *Umbelliferae* yield oils having a relatively high content of petroselinic acid and have potential for development of a new oilseed crop for industrial utilization.

Petroselinic (*cis*-6-octadecenoic) acid, because of the unusual location of its ethylenic bond, is a potential source of a number of difunctional 6-carbon, and monofunctional 12-carbon compounds which are not readily available from other domestic fatty acids. The application of certain types of reductive cleavage to the ozonolysis products of petroselinic acid should result in the formation of 6-hydroxycaproic acid and lauryl alcohol. 6-Hydroxycaproic acid has been synthesized by Stoll and Rouvé (1). It has also been obtained in admixture with its lactone by other workers (2,3). Lauryl alcohol is available by the reduction of laurate esters from coconut oil.

The reduction with sodium borohydride of the ozonolysis products from other unsaturated fatty acids, or their esters, to yield *omega*-hydroxy acids and alcohols has been reported recently by Sousa and Bluhm (4), Benton and Kiess (5), and Diaper and Mitchell (6). The latter authors also investigated the use of catalytic hydrogenation of ozonolysis products for the same purpose but obtained higher yields and purer products by the sodium borohydride reduction.

The present work describes the preparation of lauryl alcohol and 6-hydroxycaproic acid by reduction of the ozonolysis products of both petroselinic acid and its ethyl ester, and includes a comparative analysis of the products by conventional and gas liquid chromatography.

Experimental

Materials. Petroselinic acid (I.V., 88.0) was prepared by a previously described procedure (7). Ethyl petroselinate (I.V., 80.4) and the esters which were used as standards, excepting ethyl 6-hydroxycaproate, were obtained by esterification of the corresponding acids with ethanol using sulfuric acid as catalyst. Ethyl 6-hydroxycaproate was prepared by the reaction of *epsilon*-caprolactone with boiling, absolute ethanol in the presence of a catalytic quantity of sodium hydroxide, and 6-hydroxycaproic acid from *epsilon*-caprolactone by saponification followed by acidification with an ion exchange resin. All other chemicals were commercial products.

Ozonolysis Procedure. Petroselinic acid or ethyl petroselinate was dissolved in 5 ml of ethanol per g of sample and a mixture of ozone and oxygen was bubbled through the ice-salt bath cooled solution until the rapid uptake of ozone ceased as indicated by the release of iodine from aqueous potassium iodide by the exit gases. The ozonization time was approx 11 min per 0.01 mole of sample.

Reduction of Ozonolysis Products with Sodium Borohydride. A freshly ozonized solution of 56.8 g (0.02 mole) of petroselinic acid in absolute ethanol was added to a stirred, ice-salt bath cooled, slurry of 15.0 g of sodium borohydride in 80 ml of absolute ethanol at such a rate that a temp of 20–30C was maintained. Addition of the ozonolysis product required 1¼ hr, and stirring of the reaction mixture at the same temp was continued for an additional hr. The reaction mixture was then diluted with 380 ml of distilled water after which 350 ml of aqueous ethanol was removed by distillation.

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[1] Presented at the AOCS Meeting, St. Louis, Mo., 1961.

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The product was extracted 3 times with 100-ml portions of petroleum ether, bp 35–60C. The petroleum ether solution was washed first with 50 ml of 2% aqueous sodium hydroxide and then with a 25-ml portion, followed by three 100-ml portions of distilled water. The solution was dried over sodium sulfate and filtered, after which the sample was heated on a steam cone under a stream of nitrogen gas until free of solvent. The residue was then treated with 35 ml of diethyl ether and filtered to remove a small amount of undissolved solid. After removal of the solvent as before, and filtration through a small bed of filter cel, 33.9 g (90.9% of the theoretical yield) of lauryl alcohol was obtained. Its mp, 22.8–23.6C, [lit., 23.8 (8)] refractive index, 1.4400 at 25.0C, and infrared spectrum were identical to those of an authentic sample of lauryl alcohol. It gave a phenylurethane (9) which melted at 75.2–76.2C [lit., 76C (10)] both alone and in admixture with phenylurethane prepared from known lauryl alcohol.

Anal. Calc. for $C_{12}H_{24}O$: OH, 9.12%. Found: OH, 9.00%.

The alkaline washing and the first water washing were combined and backwashed with 25 ml of petroleum ether and then united with the main aqueous phase. This was then acidified with 31 ml of concentrated hydrochloric acid and extracted 6 times with 300-ml portions of diethyl ether. After the diethyl ether solution had been dried over sodium sulfate and filtered it was concentrated to about 50 ml and filtered to remove a precipitate. After removal of the remainder of the ether, 15.4 g of a viscous liquid remained. An additional 11.4 g of a similar material was obtained when the aqueous phase was concentrated to 75 ml and extracted 3 times with 150-ml portions of diethyl ether. Infrared spectra of both samples revealed the presence of lactone or ester in addition to free carboxylic acid, and both burned with a green flame, indicating that other impurities, probably containing boron, were present. The combined samples, dissolved in 250 ml of ethanol were refluxed with 11.0 ml of 50% aqueous sodium hydroxide for 2.5 hr. Absolute ethanol, 200 ml, was added and the hot solution was filtered to remove precipitated solid. A total of 18.0 g of sodium 6-hydroxycaproate (58.4% of theory) was collected on stepwise crystallization of the filtrate at 25 and 5C followed by drying in a vacuum desiccator.

Anal. Calc. for $C_6H_{11}O_2Na$: C, 46.75; H, 7.19; Na, 14.92. Found: C, 46.54; H, 7.26; Na, 14.82.

The sodium content of the salt was unchanged on crystallization from 98% ethanol.

A chromatographic column (11 mm, i.d.) was packed with 24 ml of wet Duolite C-25[3], a weekly acidic ion exchange resin. The resin was acidified with 150 ml of 1 *N* hydrochloric acid and then washed with 1000 ml of distilled water.[4] The sodium 6-hydroxycaproate (1.89 g, 0.0123 mole) was dissolved in 5 ml of water, placed on the column, washed into the column with three 5-ml portions of water and then eluted with water until 150 ml of eluate had been collected. Titration of a 5.0 ml aliquot of the eluate, which required 3.94 ml of 0.1016 *N* sodium hydroxide, indicated that the 150 ml of eluate contained 0.0120 milliequivalents of acid. After removal of the water from the remaining 145 ml of eluate, there was obtained 1.52 g (96.8% of the theoretically possible yield of 6-hydroxycaproic acid from the sodium salt) of a hygroscopic, white solid, mp (sealed capillary), 41.8–43.1C [lit., 44C (1)]. The mp of the sample was not depressed by mixture with an authentic sample of 6-hydroxycaproic acid.

Anal. Calc. for $C_6H_{12}O_3$: neut. equiv., 132.2. Found: neut. equiv. 132.8.

The mp of the sample was virtually unchanged by crystallizations from chloroform, ethyl acetate, and methyl ethyl ketone.

In another experiment, an ozonolysis product from ethyl petroselinate (62.1 g, 0.20 mole) was reduced essentially as described for the ozonolysis product from petroselinic acid. The reaction mixture was then stirred and maintained at 30C or below while 410 ml of 1 *N* hydrochloric acid was added carefully. After it had been diluted with an additional 390 ml of distilled water, the reaction mixture was extracted 3 times with 1000-ml portions of diethyl ether. The ether extract was washed 3 times with 1000-ml portions of distilled water, dried over sodium sulfate and filtered. After most of the solvent had been removed by distillation, the sample was heated on a steam cone and stripped under vacuum with nitrogen gas until free of ether, leaving a residue of 59.2 g. An additional 3.5 g of material was obtained by reworking the various aqueous solutions, bringing the total crude yield to 62.7 g or 90.6% of the combined theoretically possible yields of lauryl alcohol and ethyl 6-hydroxycaproate.

A 10.42 g sample of this material was refluxed for 2 hr with 54 ml of 0.559 *N* ethanolic sodium hydroxide. The saponification mixture was diluted with 100 ml of distilled water and extracted 3 times with 50-ml portions of diethyl ether. The ether solution was washed 3 times with 50-ml portions of water, dried over sodium sulfate and filtered. The residue remaining after removal of the ether at room temp under a stream of nitrogen gas, 5.92 g, corresponds to an overall yield of 95.6% of the lauryl alcohol theoretically obtainable. The sample had the following const: mp, 23.1–23.9C; $n_D^{25.0}$, 1.4403. Its infrared spectrum was identical to that of an authentic sample of lauryl alcohol, and it gave phenylurethane, mp and mixed mp with the phenylurethane derived from known lauryl alcohol, 75.2–76.2C.

Crude sodium 6-hydroxycaproate, 4.26 g, was recovered from the aqueous phase by drying, first on a steam cone under a stream of nitrogen gas and then under high vacuum in a desiccator over phosphorus pentoxide.

A 1.54-g aliquot of the sodium 6-hydroxycaproate was converted, without further purification, to 6-hydroxycaproic acid, 1.21 g, by the ion exchange procedure described above. The 6-hydroxycaproic acid thus obtained from ethyl petroselinate in an overall yield of 76.5% of theory, melted (sealed capillary) at 41.3–43.2C and had a neutral equivalent of 133.2. The mp of the sample was not depressed by mixture with an authentic sample of 6-hydroxycaproic acid.

Reduction of Ozonolysis Products by Catalytic Hydrogenation. For reduction of the ozonolysis products of ethyl petroselinate by catalytic hydrogenation, a variety of catalysts—platinum oxide with and without ferric chloride, ferrous chloride, stannous chloride, or ferrous sulfate as promoters; palladium-on-carbon in the presence of pyridine; palladium-

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[3] It is not the policy of the Dept. of Agriculture to recommend the products of one company over those of others engaged in the same business.

[4] After conversion of the resin to the acid state with hydrochloric acid it was necessary to wash it exhaustively with water. When the resin was washed only until the wash water was neutral the products had lower mp and higher neutral equivalents than those reported here.

on-calcium carbonate; copper chromite, and Raney nickel, were investigated at temp from 25 to 180C and pressures from 40 to 1500 psi. Of these catalysts, only platinum oxide and Raney nickel gave satisfactory conversion to the desired products, and even in the presence of a promoter frequent additions of fresh catalyst were necessary when platinum oxide was the catalyst employed. An example of a hydrogenation with Raney nickel catalyst is given below.

A freshly ozonized solution of 9.3 g (0.03 mole) of ethyl petroselinate in 72 ml of 95% ethanol, to which 0.007 g of hydroquinone had been added, was hydrogenated with Raney nickel catalyst (11) at a pressure of 36 to 40 psi for 19 hr. The hydrogen absorption after this time was 76% of theory and no additional hydrogen was absorbed when, after addition of a fresh portion of catalyst, the hydrogenation vessel was heated to 170–180C for 1 hr. After the catalyst had been removed by filtration, the solution was diluted with water and the product, 9.72 g, was recovered by ethyl ether extraction in the usual manner. The yield of crude product corresponded to 93.5% of that theoretically obtainable if lauryl alcohol and ethyl 6-hydroxycaproate were the only products.

Comparison of Products Obtained by Sodium Borohydride Reduction and Catalytic Hydrogenation. The products obtained from ozonized ethyl petroselinate by both sodium borohydride reduction and catalytic hydrogenation employing Raney nickel catalyst were fractionated by chromatographic adsorption on aluminum oxide columns. The fractionations were carried out in the following manner: "Baker Analyzed"[3] aluminum oxide, 100.0 g, was slurried with 200 ml of petroleum ether, bp 30–60C, and poured into a 22-mm i.d. column. After the excess petroleum ether had been drawn off, the column was washed first with 200 ml of diethyl ether and then with 400 ml of petroleum ether in 50-ml portions. The sample, 0.1 g, accurately weighed, was added to the column in 1 ml of petroleum ether and eluted with successive 200-ml portions of petroleum ether; 9:1, 4:1, and 1:1 petroleum ether:diethyl ether; and diethyl ether. The eluate was collected in 20-ml fractions, the solvent was allowed to evaporate at room temp and the fractions were weighed. Thus the product from the sodium borohydride reduction was separated into 3 fractions and the product from the catalytic hydrogenation into 4 fractions. On the basis of the infrared spectra of and recovery data on the fractions and consideration of the contaminants which might be expected in the reaction products, either through presence in the original ethyl petroselinate or as reaction by-products, it was tentatively concluded that while ethyl 6-hydroxycaproate and lauryl alcohol were the principal components of both products, the sodium borohydride reduction product contained a small amount of the ethyl ester of a long chain fatty acid, probably ethyl palmitate, while in addition to this ester, the hydrogenation product contained small amounts of ethyl laurate and diethyl adipate.

TABLE I

Analyses of Crude Products from Reduction of Ozonized Ethyl Petroselinate

Component	Adsorption chromatography		
	Peak eluant volume	$NaBH_4$ reduction product	Catalytic hydrogenation product
	ml	%	%
Lauryl alcohol	480 ± 20	55.3	48.8
Ethyl hydroxycaproate	770 ± 70	41.7	40.7
Ethyl palmitate Ethyl laurate	145 ± 25	3.1	9.6
Diethyl adipate	310	0	0.9
Lauryl alcohol	......	......	......

Component	Gas liquid chromatography		
	Retention time	$NaBH_4$ reduction product	Catalytic hydrogenation product
	min	%	%
Ethyl hydroxycaproate	7.8	55.5	45.0
Ethyl palmitate	17.9	42.3	42.9
Ethyl laurate	21.0	1.3	1.2
Diethyl adipate	5.2	0	6.4
Lauryl aldehyde	11.2	0	4.1
Lauryl aldehyde	3.8	0.9	0.4

In order to further elucidate their compositions, the two products were analyzed by means of gas liquid chromatography. These analyses were carried out with a Barber-Colman Model 20 Gas Liquid Chromatograph[3] which was equipped with a tritiated titanium foil ionization detector and a 15 ft x ⅛ in copper column packed with 10% diethyleneglycol succinate polyester coated on 80–100 mesh diatomaceous earth aggregate. The operating conditions, identical for all analyses, were: column temp, 165C; detector temp, 210C, hydrogen flow rate through column, 50 ml/min; scavenge gas flow, 2 ml/min; sample split flow, 300 ml/min; chart speed, ⅓ in/min; sample size, 0.2 μl. The percentage of each component in a mixture was calculated from the peak by triangulation and, except in the case of lauryl aldehyde, a correction factor was applied to the result. These correction factors, determined experimentally using a synthetic mixture of known composition, were: ethyl laurate, 1.15; lauryl alcohol, 0.72; diethyl adipate, 1.41; ethyl 6-hydroxycaproate, 1.73; and ethyl palmitate, 1.10. The peak corresponding in retention time to lauryl aldehyde which appeared in the chromatograms of both the products and the known mixture may be an artifact as lauryl aldehyde was not included in the mixture.

Analyses by the two methods described above of the products obtained by sodium borohydride reduction and Raney nickel catalyzed hydrogenation of ozonized ethyl petroselinate, together with the peak eluant volumes and retention times of their components, are reported in Table I.

Discussion

The reduction of the ozonolysis product of petroselinic acid with sodium borohydride proceeds smoothly to give a good yield of lauryl alcohol but a poorer yield of 6-hydroxycaproic acid. Use of the ethyl ester instead of the free acid results in improved yields of both products, the increase being more marked in the case of 6-hydroxycaproic acid, possibly owing to the fact that ethyl 6-hydroxycaproate is less water soluble than 6-hydroxycaproic acid.

Of the hydrogenation catalysts investigated, only two, platinum oxide and an active Raney nickel gave satisfactory conversions of the ozonolysis product from ethyl petroselinate to lauryl alcohol and ethyl 6-hydroxycaproate. Of these, Raney nickel is to be preferred as frequent additions of fresh platinum oxide catalyst are necessary if the desired degree of hydrogenation is to be obtained. Comparison of the best product obtained by catalytic hydrogenation with that from sodium borohydride reduction indicates that comparable yields of ethyl 6-hydroxycaproate are obtained by the two methods but that sodium borohydride reduction results in somewhat better yields of lauryl alcohol. In addition, catalytic hydrogenation resulted in the production of small amounts of ethyl laurate and diethyl adipate as by-products. Gas liquid chromatographic analyses indicate that both of these products contain small amounts, less than 1%, of lauryl aldehyde though no aldehyde was detected by infrared examination of the lauryl alcohol isolated from the sodium borohydride reduction product. The aldehyde may have been formed by oxidation of lauryl alcohol either during storage or gas liquid chromatographic analysis, but the possibility that it resulted from incomplete reduction of the ozonolysis product cannot be excluded.

In the gas liquid chromatographic analyses, the response factors of lauryl alcohol, ethyl 6-hydroxycaproate, ethyl laurate, and diethyl adipate vary widely even though all of these materials are fatty derivatives. Large errors would be introduced by failure to consider response factors when analyzing mixtures of this type.

The conversion of the sodium salt of 6-hydroxycaproic acid to the free acid with mineral acid leads to the formation of esters in addition to the free hydroxy acid. However, it was found that utilization of a weakly acidic ion exchange resin for acidification of the salt results in little or no ester formation.

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Solubilities of Five Triglycerides in Aqueous Ethanol

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Abstract

The solubilities of trilaurin, trimyristin, tripalmitin, tristearin, and triolein in 90, 95.4, 98, and 100% ethanol between 40C and 90C were determined. The data were compared with data calculated by the ideal solution law.

Introduction

DATA on the solubilities of triglycerides in aqueous ethanol at moderate temps are rather limited although work has been reported by Loskit (1), Robinson, et al. (4), and McElry and King (2). Solubility of thirteen vegetable oils and lard in ethanol solutions was determined by Rao and Arnold (3).

In the current studies the solubilities of trilaurin, trimyristin, tripalmitin, tristearin, and triolein in four aqueous ethanol concentrations were determined using the method of Rao and Arnold (3). The ethanol concentrations were: 100, 98.0, 95.4, and 90.0%. The triglycerides were of 95% or greater purity obtained from Hormel Institute. They were prepared by transesterification of the corresponding pure methyl esters with triacetin. The purification consisted of partition between solvents and low temp fractional crystallization. The principal impurity is the corresponding diglyceride. Temperatures varied from 40 to 90C.

The solubility data for the triglycerides in 90.4% ethanol are shown in Figure 1 as the relation between mol fractions dissolved and the reciprocal of the absolute temp. The calculated values for ideal solutions are shown as broken lines for comparison with the experimental data. These values are based on the equation:

$$2.3 \log x_1 = \frac{\triangle H_1^F}{R}\left(\frac{1}{T_F} - \frac{1}{T}\right)$$

derived from the Clausius-Clapeyron equation, where X_1 = the mol fraction of the solute, $\triangle H_1^F$ = the heat of fusion of the solute, and T = temp in °K. The

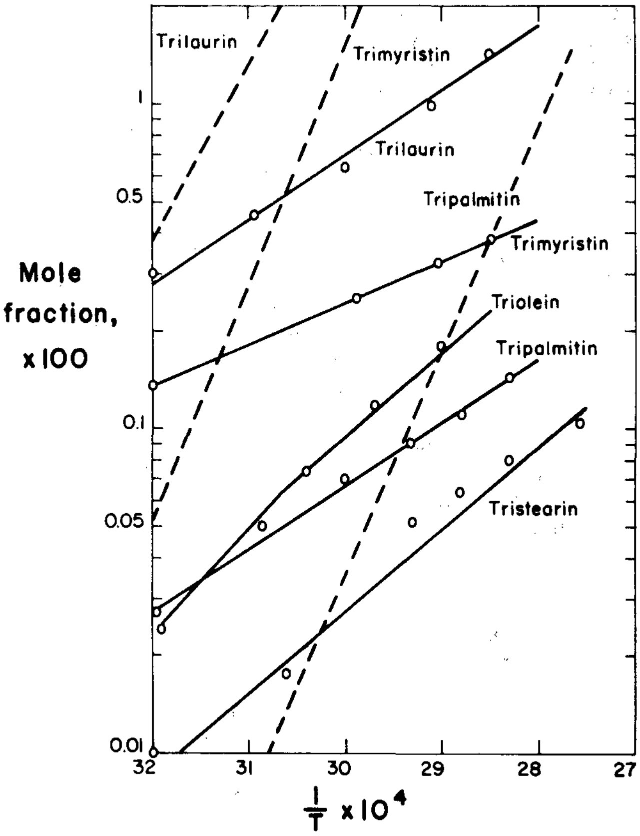

FIG. 1. Solubilities of triglycerides in 90.4% ethanol.
– – – ideal solution
T = degrees Kelvin