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[Received April 7, 1960]

Preparation of Petroselinic Acid

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Petroselinic acid of a grade which is suitable for most laboratory applications has been prepared by a single crystallization of the mixed fatty acids of parsley seed oil from 90% ethanol. A product of higher purity has been prepared from this acid by application of urea segregation techniques for the removal of saturated materials. No evidence of the presence of unsaturated fatty acids other than petroselinic acid was found in either of these samples when their ozonolysis products were examined chromatographically. On the basis of iodine values, assuming the absence of other unsaturated materials, the purities of the two preparations are 96.0 and 99.4%.

IN CONNECTION WITH RESEARCH now in progress in this laboratory on the chemistry of petroselinic (*cis*-6-octadecenoic) acid, it was necessary to prepare moderate quantities of this material. The methods generally used for the preparation of petroselinic acid are tedious, employing lithium or lead salt separations in conjunction with solvent crystallization of the free acids or fractional distillation of their methyl esters (1,2,3). Recently a different approach has been applied to the problem by Shenolikar and Subbaram (4), who used urea segregation for the isolation of petroselinic acid. Although the procedure utilized 5 crystallizations of the urea complexes, their final product was rather impure as judged from its iodine value (84.1).

One of the chief difficulties in the isolation of pure petroselinic acid is effecting its separation from its isomer oleic acid. Solubility data for oleic and petroselinic acids presented by Kolb and Brown (5) suggested the possibility of separating these acids by a direct crystallization procedure.

Parsley seed oil was selected as the source of petroselinic acid because its component acids have been reported to contain a high percentage (70–76%) of petroselinic acid (1,2). The oil employed was found to contain approximately 25% of unsaponifiable material. Since it was first thought that the presence of such a large amount of unsaponifiables would unduly complicate the isolation of petroselinic acid, the initial experiments were conducted using fatty acids which had been freed of unsaponifiable material. In exploratory experiments, a number of solvents and various temperatures were employed in attempting to separate petroselinic acid from the other component acids. It was found that a satisfactory product could be obtained by a single crystallization either from ethanol or petroleum ether (b.p. 60–70°C.) at a temperature of −25°C. Further work showed that a comparable product could be obtained under the same conditions from fatty acids which still contained the unsaponifiable material. This product upon ozonolysis and examination of its degradation products showed no evidence of the presence of oleic or linoleic acid, and on the basis of its iodine value was considered to be approximately 96% pure. An acid of this purity is suitable as a starting material for many types of chemical modification.

It was found that an acid of higher purity could be prepared from the above-described product by application of urea segregation techniques for the removal of saturated materials. The petroselinic acid prepared in this manner had a melting point corresponding to that reported in the literature (6) and a purity of 99.4% based on iodine value determination. It contained no *trans*-isomers and, like its precursor, appeared to be free of other unsaturated acids.

Experimental

Parsley Seed Oil. Parsley seed which had been ground in a Bauer mill was extracted with petroleum ether (b.p. 35–60°C.) using a Soxhlet type extractor. In a typical preparation, 1,000.0 g. of the seed yielded 189.3 g. of a dark green oil having an iodine value of 115.7, a saponification number of 135.3 and containing 24.8% of unsaponifiable material. The mixed fatty acids, which had been freed of unsaponifiable material, had the following composition as determined by A.O.C.S. Method Cd 7-58 (7): monounsaturated acids, 84.6%; linoleic acid, 10.6%; and saturated acids, 4.6%. Ozonolysis of 500 mg. (approximately 1.8 millimoles) of the mixed fatty acids by the procedure described below yielded 0.27 millimole of azelaic and 1.27 millimoles of adipic acid. It is evident from the foregoing that this sample of parsley seed oil is similar in its fatty acid composition to those examined by other workers (1,2).

Ozonolysis Procedure. A half gram of the acid, accurately weighed, was dissolved in 35 ml. of methanol and ozonized at 0°C. The methanol was removed in a rotary dryer under reduced pressure, at room temperature or lower. To the residue were added 5.0 ml. of 90% fomic acid and 2.5 ml. of 30% hydrogen peroxide. The flask was fitted with a condenser and immersed in a glycerine bath. The temperature was raised slowly until reaction started at 80–90°C.

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as evidenced by the evolution of gas, and the temperature was kept near this point until reaction was completed (30–45 minutes). The temperature was then raised and the solution was actively refluxed for another 30–45 minutes. The mixed acids were then dried in a rotary drier under 3 mm. pressure at 60–80°C. The mixed acids were dissolved in 2.5 ml. of *tert*-amyl alcohol and diluted to 25.0 ml. with chloroform. An aliquot of this solution was chromatographed by a modification (8) of the procedure of Higuchi *et al.* (9). When this procedure was applied to an authentic sample of petroselinic acid, recoveries of adipic acid ranged from 75 to 82%.

Preparation of Petroselinic Acid. In a typical preparation, parsley seed oil (150.0 g.) was saponified by stirring for ½ hour with refluxing alcoholic potassium hydroxide (45 g. of 87% potassium hydroxide dissolved in 38 ml. of distilled water and 375 ml. of ethanol). The saponification mixture was allowed to cool and then was transferred to a separatory funnel and acidified with 66 ml. of concentrated hydrochloric acid in 750 ml. of water. The liberated fatty acids were separated from the aqueous phase, dissolved without further treatment, in 1,500 ml. of 90% ethanol, bleached with 15.0 g. of carbon black and crystallized at −25°C. for 16–20 hours. The white crystals were separated from the mother liquor by filtration, washed with 150 ml. of cold (−25°C.) 90% ethanol, and dried under high vacuum. The petroselinic acid thus obtained (53.2 g.) had a melting point of 28.0–29.8°C. When this acid was subjected to ozonolysis, adipic acid (yield 80%) was the only dibasic acid present in the fission products.

Anal.: Neut. equiv., 284.8; iodine value, 86.6.

A 50.0 g. sample of the crystal fraction was dissolved in 300 ml. of boiling methanol containing 50.0 g. of urea. The urea complex which precipitated during 16–20 hours at 25 ± 2°C. was removed by filtration, and the filtrate was crystallized at −25°C. for 4 hours. The crystal fraction, which had been separated from the mother liquor by filtration, was treated with 50 ml. of 2% hydrochloric acid and extracted with petroleum ether (b.p. 35–60°C.), using a total of 400 ml. of petroleum ether for this and the following operations. The petroleum ether solution was swirled with sodium sulfate, decanted and crystallized at −25°C. for 16–20 hours. The pure white crystals were first separated by filtration then dried under high vacuum in a desiccator containing sodium hydroxide. The purified petroselinic acid (36.6 g.) melted at 29.5–30.1°C. Ozonolysis of this acid yielded 85% of adipic acid, the only dibasic acid present.

Anal. Calcd. for $C_{18}H_{34}O_2$: Neut. equiv., 282.5; iodine value, 89.9. Found: Neut. equiv., 283.2; iodine value, 89.4.

Acknowledgment

The authors are indebted to Vidabelle O. Cirino, Dorothy C. Heinzelman, Marian C. Willis, and Zigrida M. Zarins for certain of the analyses.

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[Received June 6, 1960]

ABSTRACTS . . . . R. A. REINERS, Editor

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• Fats and Oils

RESPONSE OF THE β-RAY IONIZATION DETECTOR TO UNESTERIFIED LOWER FATTY ACIDS IN GAS-LIQUID CHROMATOGRAPHY. C. J. Böttcher, G. F. G. Clemens, and C. M. Van Gent (Dept. Phy. Chem., Univ. of Leiden, The Netherlands). *J. Chromatography* **3**, 582–4 (1960). Gas-liquid chromatography of C_4–C_{10} unesterified fatty acids with a *beta*-ray ionization detector indicated that the relative peak areas per unit was increased with increasing molecular weight up to 150. There was a tendency to reach a constant value for the higher molecular weights.

RHEOLOGY OF COCOA BUTTER. I. EFFECT OF CONTAINED FAT CRYSTALS ON FLOW PROPERTIES. C. Sterling and J. J. Wuhrmann (Dept. of Food Sci. and Tech., Univ. of California, Davis, Calif.). *Food Research* **25**, 460–3 (1960). Purified cocoa butter is characterized by a slight structural viscosity, even in the absence of suspended particles. As fat crystals form in the cocoa butter, the structural viscosity effect is enhanced. Submicroscopic aggregation of fat molecules during standing of the cocoa butter is evident by the augmentation of the viscous "coefficient." This effect is apparent before the formation of microscopically visible fat crystals.

SOME OBSERVATIONS ON THE REACTIONS OF STERCULIC ACID. R. F. Fawcett and J. C. Smith (The Dyson Perrins Lab., Oxford Univ.). *Chem. & Ind.* **1960**, 871–2. On adding a 1% solution of bromine in chloroform to a 1% solution of sterculic acid, stirred at 0°, exactly one equivalent of bromine was taken up. The resulting (liquid) dibromide shows absorption bands, one of which is characteristic of $-\underset{|}{C}Br-\underset{|}{C}Br-$. Esterification (with diazomethane) followed by heating under reflux in acetone with sodium iodide rapidly gave methyl sterculate diiodide. It was hoped that these iodine atoms would easily be eliminated with regeneration of the cyclopropene system, but no products with absorption at 1007 $cm.^{-1}$ or 1869 $cm.^{-1}$ were detected.

LABELING FATTY ACIDS BY EXPOSURE TO TRITIUM GAS. II. METHYL OLEATE AND LINOLEATE. E. Jones, L. Mason, H. Dutton, and R. Nystrom (Northern Regional Research Laboratory and Radiocarbon Laboratory, University of Illinois, Urbana, Illinois). *J. Organic Chem.* **25**, 1413–1417 (1960). Unsaturated fatty acid esters react at room temperature on exposure to gaseous tritium by addition of tritium to a double bond and with little or no substitution of tritium for hydrogen. Evidence for addition to olefinic bonds, rather than substitution for hydrogen, has been obtained from gas-liquid and liquid-partition chromatography of both the tritiated fatty acids and the tritiated products after mild oxidative cleavage. Tritiated fatty acid esters appear on chromatograms at positions of the next less-saturated member of the isologous series. The position of addition of the tritium is deduced from the radioactivity of the monobasic and dibasic acids produced by oxidation.