Preparation of Pure Petroselinic Acid

D. CHOBANOV, M. AGOVA, E. CHOOPAROVA and R. CHALUCKOVA,
Institute of Organic Chemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria

Abstract

Petroselinic acid of 99.5–100% purity has been isolated from coriander, fennel and anise oil by acid soap crystallizations at 4C, followed by urea segregations at room temperatures.

Introduction

THE ISOLATION OF PETROSELINIC acid by lithium or lead salt separation, followed by solvent crystallization or fractional distillation of the solid fatty acid methyl esters (1,2) is tedious. The urea fractionation alone, as applied for the purpose by Shenolikar and Subbaram (3), leads to a rather impure petroselinic acid. In order to simplify the isolation Fore et al. (4) used a single low temperature crystallization of the mixed fatty acids of parsley seed oil from 90% ethanol. After removal of palmitic acid as urea complex pure petroselinic acid has been obtained by final crystallization from petroleum ether. Recently (5) methyl petroselinate has been easily prepared from the same oil by low temperature solvent crystallization of the mixed methyl esters, followed by urea complex formation and fractional distillation. The crystallizations by these methods have been conducted in the range of −25 to −30C, the yields being up to 35% with respect to the acid initially present in the oil.

In order to avoid the low temperatures and to obtain pure petroselinic acid in considerably higher yields the acid soap crystallization technique was applied in combination with urea complexes. The former technique was successfully used for the preparation of oleic (6) and erucic acid (7). The procedure described below was applied for the isolation of petroselinic acid from Coriandrum sativum, Foeniculum vulgare and Pimpinella anisum cultivated in this country.

Experimental

The oils were extracted from ground seeds with petroleum ether (bp, 35–60C) using a Soxhlet type all-glass extractor. The samples of the mixed fatty acids were prepared by the usual saponification method with potassium hydroxide in ethanol. The nonsaponifiables were not removed. The yields and the individual composition of the fatty acids are reported elsewhere (8).

Acid Soap Crystallizations

A solution of 50 g of fatty acids in 250 ml of 95% methanol was prepared, containing half of the quantity of sodium hydroxide, required for neutralization. It was allowed to stand for 5 hr at 4C and the crystals formed were filtered off on a Buchner funnel. Four recrystallizations at 4C were then carried each time for 3 hr, dissolving the crystals in 100, 70, 70, and 60 ml of 95% methanol, respectively. A first crystal fraction of the acid soaps was thus obtained.

All the filtrates, except the first one, were combined. About 250 ml of the solvent was then distilled off and the residue was dissolved in 60 ml of 95% methanol. The clear solution was allowed to stand for 3 hr at 4C. The solid fraction was crystallized four times as above, each time for 2 hr, using 30, 20, 20, and 20 ml of 95% methanol, respectively. The solid fractions of the two sets of crystallizations were combined and the nonsaponifiable constituents were extracted in the usual manner. The soap solution was acidified with an excess of 5% hydrochloric acid and the upper layer was extracted with ether. The extract was washed and dried, and the solvent was removed. The pale yellow product was petroselinic acid, which was free of other unsaturated acids and contained 3 to 7% of palmitic acid.

Urea-Adduct Separation

Petroselinic acid was purified by removing palmitic acid as urea complex. The following procedure for 10 g was used with success for other quantities.

Raw petroselinic acid (10 g) and 3 g of urea were dissolved in 15 ml of methanol by heating. The clear solution was allowed to crystallize overnight at room temperature. The crystals were filtered off and washed with a cold saturated solution of urea in methanol. Most of the solvent of the filtrate and of the washing liquid was distilled off, the residue was taken up in water, acidified with dilute hydrochloric acid and extracted with ether. The extract was washed and dried, the solvent was removed, and the liberated fatty acids were treated once more in the same manner with 3.5 g of urea in 25 ml of methanol. After the second treatment petroselinic acid of 99.5–100% purity was obtained from the filtrate.

The acid was isolated by this procedure from coriander, fennel, and anise oil, containing 40.8, 45.7 and 29.6% of petroselinic acid, respectively. The yields of pure acid were 80.4, 61.2, and 65.3%, respectively, based on the petroselinic content of the oils. The differences in the yields are due to the composition of the oils, especially to that of the nonsaponifiable constituents.

Analysis

The pure petroselinic acid was oxidized with methaperiodate-permanganate after von Rudloff (9), as modified by Youngs (10). The scission products were analyzed by liquid-liquid chromatography (11). By this method the normal dicarboxylic acids C_3 to C_{10} can be quantitatively determined. Azelaic acid was not detected even in traces, so that oleic and linoleic acid were not present in the final petroselinic acid. The absence of palmitic acid was proved by reversed-phase columnar chromatography (8) of the same oxidation product.

The purified petroselinic acid showed mean iodine value (Wijs), 89.6 (theo. 89.9); mp = 29.5–30.1C; $n^{40/D} = 1.4528$.

Discussion

The acid soap fractionation was studied by quantitative fatty acid analysis of each filtrate. A reversed phase chromatographic method (8), developed for the purpose, was applied. The distribution of the individual fatty acids among the fractions corresponded to their solubilities. Linoleic acid remained in the filtrates to a greater extent than oleic acid. The amount of the latter decreased more slowly in the solid fractions. By this analysis a selectivity of combining the components as acid soap dimers was observed. During each crystallization a recombination of the dimers occurred. As a result petroselinic acid participated in a greater amount as least soluble dimers. On account of this recombination the yield of petroselinic acid considerably increased.

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