Another explanation may be based on the difference in stability of various hydroperoxides. In addition to the effect of unsaturation on stability, much evidence has been presented to indicate that autoxidation of any single unsaturated fatty acid methyl ester yields more than one peroxide and that the stability of these peroxides varies widely (18–22). It is possible, therefore, that at the time the autoxidized methyl esters were reduced and analyzed, essentially all the unstable peroxides of linolenate had already decomposed leaving only the more stable peroxides which, indeed, proved to be stable even to the conditions of the carbonyl determination. On the other hand, the "unstable" oleate peroxides which are considerably more resistant to decomposition under normal conditions than the linolenate peroxides, remained virtually unchanged before analysis but were decomposed to carbonyl compounds during the determination. The linoleate peroxides occupy an intermediate position with regard to their stability and their decomposition during the carbonyl determination. In support of this explanation may be cited the low ratios of peroxide value to true carbonyl content (determined after reduction) for linolenate (2.7), compared to linoleate (5.9) and oleate (7.6).

In general, the results obtained with the four vegetable oils agree with those from the pure methyl esters. Olive oil, the unsaturated component of which is almost exclusively oleic acid, behaves as methyl oleate and shows a high conversion of peroxides to carbonyls during the carbonyl determination. The more unsaturated oils containing linoleic and linolenic acids show less peroxide interference. In this study, clear-cut differences between corn, safflower and linseed oils should not be expected because the rate of autoxidation of individual unsaturated fatty acid in mixtures is much different from that of the pure compounds and also because these oils had been oxidizing under uncontrolled conditions for different periods of time.

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Preparation of 2-Hydroxytridecanenitrile from Petroselinic Acid

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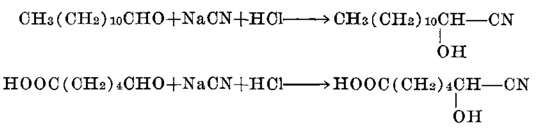
Abstract

The cyanohydrin of dodecanal has been isolated in 90% crude yield from reaction of hydrogen cyanide formed in situ with the mixed aldehydes resulting from reductive ozonization of petroselinic acid. Attempts to isolate the cyanohydrin of the other fragment, adipaldehydic acid, were unsuccessful.

Introduction

IN THE SEARCH for new oilseed crops in the New Crops program of the U.S. Department of Agriculture, one of the families of plants selected for study has been the *Umbelliferae* (carrots, fennel, parsley, etc.). The seed oils of these plants contain 30–75% petroselinic (*cis*-6-octadecenoic) acid, an isomer of oleic acid found with very few exceptions only in this family of plants. Any industrial utilization of the oils would depend primarily on the petroselinic acid or its derivatives. Consequently, the utilization research on these oils has been concentrated on the chemistry of petroselinic acid and various derivatives of the acid.

Reductive ozonization of petroselinic acid gives a mixture of dodecanal and adipaldehydic acid (1). This paper reports the reaction of such a mixture with hydrogen cyanide and work done to isolate the products of the reaction. The reactions of these aldehydes with sodium cyanide and hydrochloric acid (the latter reagents yielding hydrogen cyanide in situ) are as follows:



$$CH_3(CH_2)_{10}CHO + NaCN + HCl \longrightarrow CH_3(CH_2)_{10}\underset{\underset{OH}{|}}{CH}—CN$$

$$HOOC(CH_2)_4CHO + NaCN + HCl \longrightarrow HOOC(CH_2)_4\underset{\underset{OH}{|}}{CH}—CN$$

These cyanohydrins, which do not appear to have been reported in the literature, would be versatile intermediates for preparing many useful products. They could be hydrolyzed to alpha-hydroxy acids, for example, or reduced to alkyl-substituted ethanolamines (alkylolamines). Alpha-hydroxy acids have found utility in preparing resinous products (2), improved lubricating greases (3), and stabilizers for vinyl

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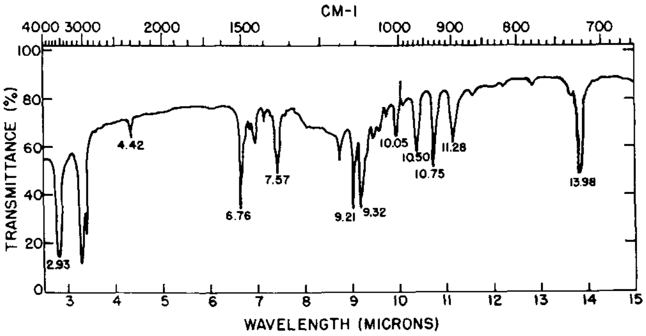

FIG. 1. Infrared spectrum of 2-hydroxytridecanenitrile.

halide resins (4). Alkylolamines have found many uses, such as in the preparation of various resin products (5–9), materials for treating paper, textiles, or leather (10,11), and in the production of emulsifiers and surface active materials (12,13).

Experimental

Ten grams of petroselinic acid, prepared from parsley seed oil by the procedure of Fore, Holmes and Bickford (14) was ozonized in methanol at 0C to the end-point as determined by the darkening of an acidified potassium iodide solution through which the exit gases were passed. Nitrogen was bubbled through the solution for a few minutes to remove dissolved ozone. Then 0.1 g of 10% palladium on charcoal was added to the ozonizing cylinder and hydrogen passed through the solution at room temperature until a negative test for peroxide was obtained with potassium iodide and acetic acid.

The catalyst was filtered out. The final volume of the methanol solution was 250 ml, to which 75 ml water was added. The solution was cooled to 10–20C and crystals of sodium cyanide added slowly until the solution became alkaline, then more sodium cyanide was added to a total of 3 equivalents of the petroselinic acid. Concentrated hydrochloric acid, diluted with an equal volume of water, was added dropwise with stirring to bring the pH of the solution to 5–6, while keeping the temperature between 10 and 20C. The methanol was evaporated off at 70C at 50 mm pressure and the residue taken up in 150 ml water plus 100 ml ethyl ether. Fifty percent sodium hydroxide solution was added slowly until the water phase remained alkaline after equilibrium of the two phases. The phases were then separated, and the water phase washed 4 times with 100 ml ether. All ether solutions were combined and washed with water to neutrality. The solution was dried with sodium sulfate and evaporated at 60C at 50 mm pressure to given 6.70 g (90% yield) of crude 2-hydroxytridecanenitrile. The infrared spectrum of this sample showed the presence of some dodecanal.

The crude material was dissolved in commercial hexane at room temperature (1:7) and set in refrigerator overnight at −10C. The yield was 4.49 g of crystals (60% of theoretical). These were recrystallized twice more from commercial hexane under the same conditions. The crystals were snow-white and had the following analysis: %C 73.15 (73.88), %H 11.68 (11.92), %N 6.58 (6.63), %OH 8.09 (8.05), mol wt 210 (211). The figures in parentheses are the calculated values. The melting point was 43.9C. The infrared spectrum, obtained in a KBr disc on a Perkin-Elmer Infrared Spectrophotometer Model 21, is shown in Figure 1. It shows the absence of any aldehyde by the lack of absorption at 5.75–5.81μ, the presence of free hydroxyl by an absorption peak at 2.93μ, and the presence of nitrile group by a low absorption peak at 4.42μ. The absorption of a nitrile group is suppressed by the presence of an oxygenated group attached to the same carbon atom as the nitrile group, as occurs in this compound (15).

6-Cyano-6-hydroxyhexanoic acid should be formed simultaneously with the formation of the 2-hydroxytridecanenitrile, but we were not able to isolate a material which could be shown to be this compound.

Discussion

The boiling points of dodecanal and methyl adipaldehydate or of dodecanal and adipaldehydic acid are so close as to make separation of the aldehydes by distillation unfeasible with ordinary laboratory equipment. Attempts were also made to isolate the aldehydes by reacting the mixed aldehydes with a saturated solution of sodium bisulfite in 40% methanol. The dodecanal formed an adduct which could be filtered out, but the adipaldehydic acid either did not form an adduct or remained in solution. The dodecanal adduct was dissolved in warm water, and treated with an aqueous solution of sodium cyanide (15). The crude tridecanenitrile was extracted with ethyl ether and recovered from the ether solution in yields comparable to those obtained from the reaction of the mixed aldehydes directly with sodium cyanide and hydrochloric acid. Since a great excess of sodium bisulfite was used in forming the adduct, this remained in solution, and greatly interfered with attempts to isolate the 6-cyano-6-hydroxyhexanoic acid since it released sulfurous acid when the solution was later acidified.

Higher yields of aldehydes can be obtained from the ozonides by chemical reduction with zinc and acetic acid, but since the 2-hydroxytridecanenitrile and the 6-cyano-6-hydroxyhexanoic acid were to be separated by partitioning the crude product between ethyl ether and an aqueous alkaline solution, the zinc precipitated as the hydroxide and caused much trouble with emulsions. For this reason, catalytic reduction of the ozonides with hydrogen was employed.

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