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[Received May 2, 1961]

# The Preparation and Properties of Some Nitrogen-Containing Derivatives of Petroselinic Acid<sup>1</sup>

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## Abstract

Petroselinonitrile was prepared by distilling the ammonolysis products of petroselinic acid over phosphorus pentoxide, and also from parsley seed oil without first isolating the petroselinic acid. A high-boiling antioxidant was employed during the reaction to control polymerization. The reaction by-products were segregated from the pure petroselinonitrile by urea complexing. Petroselinamide was obtained from petroselinic acid by the acidolysis of urea. Although it was not possible to reduce the petroselinonitrile by catalytic hydrogenation without affecting the ethylenic linkage or without producing a mixture of the primary, secondary, and tertiary amines, petroselinonitrile was converted to primary petroselinylamine in good yields by reduction with metallic sodium and alcohol in toluene. The hydrochloride and the acetyl derivative of the pure primary amine have also been prepared.

## Introduction

THE NITROGEN-CONTAINING derivatives of the high molecular weight fatty acids continue to hold interest and importance among aliphatic derivatives owing to the wide range of their physical and chemical properties which characterize the various representatives of this class. Aside from being useful chemical intermediates, their surface active and biological properties have made them a subject of commercial interest and many scientific investigations.

Much literature has been published on the preparation of the various amides, nitriles, and amines of the long chain fatty acids, and especially of stearic and oleic acids. During our investigation of the chemistry of petroselinic acid (*cis*-6-octadecenoic acid) isolated from parsley seed oil (1), it became of interest to prepare some of its nitrogen derivatives and determine their properties and potential industrial utility. Although the preparation of petroselinamide and its subsequent reduction to the petroselinylamine with lithium aluminum hydride has already been published (2), the preparation and characterization of petroselinonitrile has not been reported. The purpose of this paper is to describe the chemical modification of petroselinic acid at the carboxyl group with the view of preparing and characterizing some of its nitrogen-containing derivatives.

## Experimental

**Materials.** The parsley seed oil was obtained by extraction of the flaked seed with hexane. When the

solvent was removed, the dark green oil had an I.V. of 100.5 and a saponification number of 172.9. The fatty acid composition of parsley seed oil is approximately: 76% petroselinic, 15% oleic, 6% linoleic, and 3% saturated acids.

Pure petroselinic acid used in this experiment (mp 29.5-30.1C) was obtained from the oil by low temperature fractional crystallization of the mixed fatty acids (1). Ozonolysis of this acid and chromatography of the degradation products yielded adipic acid as a sole dibasic acid, indicating that no other unsaturated acids were present as impurities.

**Preparation of Petroselinonitrile from Petroselinic Acid.** A 500 ml three-necked round bottom flask was equipped with a thermometer, a gas-dispersion tube with a fritted cylinder, and 75 cm long water condenser through which steam was circulated throughout the reaction. The flask was charged with 130 g of pure petroselinic acid and 1 g of Ionol antioxidant,<sup>3</sup> and the mixture was heated to 150C. The temperature was maintained at 150C for three hr and then raised to and maintained at 250C for an additional 17 hr while a fast stream of anhydrous ammonia gas was passing through. The rate of the ammonia stream was such that the water formed during the reaction was continually swept out. The removal of water was facilitated by the steam-heated condenser which also melted the solid petroselinamide (mp 73C) being swept up with the hot ammonia allowing it to drip back into the reaction flask. The reaction mixture, which was first allowed to cool to room temperature, was then distilled over 6.5 g of phosphorus pentoxide at reduced pressure (120-140 mm) with anhydrous ammonia sweeping through it at a slow rate. The first fraction distilling at 69-188C was composed mostly of short chain pyrolysis products and was discarded. The major part of the second fraction (101.3 g, I.V. 94.5) which distilled at 188-242C was composed of *cis*-6-octadecenonitrile with some *trans*-6-octadecenonitrile (as shown by infrared analysis) and a small amount of saturated by-products. The entire second fraction was dissolved in 300 ml. of ether, washed with 100 ml. of 3% aqueous sodium hydroxide to remove the unreacted petroselinic acid and then with three 100 ml portions of water. The ethereal solution was dried over anhydrous sodium sulfate and on removal of the solvent there remained 100 g of crude petroselinonitrile. The product was then dissolved in 600 ml. of boiling methanol containing 100 g of urea. The urea complex which precipitated overnight at room temperature was filtered off and on decomposition with 3% aqueous hydrochloric acid yielded 12.4 g

<sup>1</sup> Presented at the AOCS meeting in New Orleans, Louisiana, May 7-9, 1962.

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<sup>3</sup> A Shell Chemical Corporation brand name for 2,6-di-*tert*-butyl-4-methyl phenol, bp 257-266C.

of material (I.V. 71.9) which contained mostly the *trans*-6-octadecenitrile and the saturated by-products. After the removal of the urea complex, the filtrate was treated with 800 ml of 3% aqueous hydrochloric acid and extracted with three 250 ml portions of chloroform. The combined chloroform extracts were washed with water until free of acid and then dried over anhydrous sodium sulfate. After evaporation of the solvent and drying in a rotary evaporator under high vacuum, the remaining gold-colored oily material weighed 87.6 g and contained only *cis*-6-octadecenitrile as shown by infrared analysis (73.3% yield).

Anal. Calcd. for  $C_{18}H_{33}N$ : C, 82.05; H, 12.62; N, 5.32; I.V., 96.3.

Found: C, 81.63; H, 12.48; N, 5.30; I.V., 96.5;  $d_4^{20}$ , 0.8375;  $n_D^{25}$ , 1.4553; bp 296–298C.

*Preparation of Petroselinonitrile from Parsley Seed Oil.* In the same apparatus employed in the preparation of petroselinonitrile from pure petroselinic acid, 351.8 g of parsley seed oil and 3.5 g of Ionol antioxidant were reacted with anhydrous ammonia for 24 hr at 250C. During this time 35.2 g of oily material distilled over and was discarded. The cooled reaction mixture was then distilled over 20.0 g of phosphorus pentoxide at reduced pressure (100–120 mm) with anhydrous ammonia sweeping through it at a slow rate. The first fraction (21.4 g) which distilled over at 65–158C was discarded. The second fraction (282.2 g) distilling at 160–248C was dissolved in 500 ml of petroleum ether, washed with 250 ml of 3% aqueous sodium hydroxide to remove the unreacted acid, and then with water until free of alkali. The petroleum ether solution was dried over anhydrous sodium sulfate and then decolorized by passing it through a column packed with a mixture of 200 g of active alumina and 200 g of active coconut charcoal. The column was then washed with fresh petroleum ether until the eluate was colorless. After the solvent was distilled off and the residue dried in a rotary evaporator under high vacuum there remained 226 g of a dark brown mixture of fatty nitriles (I.V., 98.5). The component fatty nitriles were separated by urea complexing as follows: A 151 g portion of the mixed fatty nitriles was dissolved in 2500 ml of boiling methanol containing 500 g of urea. The urea complex which precipitated overnight at 5C was filtered off, dried in a desiccator under high vacuum (488.1 g) decomposed with 600 ml of 3% aqueous hydrochloric acid and then extracted with three 200 ml portions of chloroform. The chloroform solution, after being washed with water until free of acid, was dried over anhydrous sodium sulfate, evaporated, and dried in a rotary evaporator under high vacuum, yielding 127.7 g of gold-colored product (I.V., 92.2) presumably composed of 6- and 9-octadecenitriles (*cis* and some *trans*) and the saturated nitriles. After the removal of the urea complex, the filtrate was concentrated to 1000 ml, treated with 1000 ml of 3% aqueous hydrochloric acid and extracted with chloroform. The chloroform solution yielded 22.1 g of a dark brown material having an I.V. of 132.4. The mixed fatty nitriles which had previously formed a urea complex were again dissolved in 800 ml of boiling methanol containing 130 g of urea and allowed to crystallize at room temperature overnight. The solid urea complex was filtered off and dried (86.5 g) and on decomposition yielded

20.6 g of mixed nitriles (I.V. 79.9) presumably the *cis*- and *trans*-9-octadecenitriles, the *trans*-6-octadecenitrile, and the saturated nitriles. The filtrate containing the product which did not form a urea complex was treated with 800 ml of 3% aqueous hydrochloric acid and extracted with chloroform. From the chloroform solution was isolated 105 g (60.8% yield assuming that the oil contained 13% unsaponifiables as derived from the saponification equivalent) of petroselinonitrile contaminated with a trace of the *trans* isomer as shown by infrared analysis (absorbance 0.05 at 20 g per liter concentration in chloroform).

Anal. Calcd. for  $C_{18}H_{33}N$ : C, 82.05; H, 12.62; N, 5.32; I.V., 96.3.

Found: C, 82.17; H, 12.70; N, 5.15; I.V., 96.3;  $n_D^{25}$ , 1.4582.

*Preparation of Petroselinamide.* A mixture of 94.1 g (0.3 mole) of pure petroselinic acid and 20.4 g (0.3 mole) of urea was stirred and slowly heated until a reaction started at 140–160C as evidenced by the vigorous evolution of gas. When the reaction subsided the temperature was raised and maintained at 200C for 8 hr. The cooled mixture was then dissolved in 200 ml of benzene and washed with 75 ml of 3% aqueous sodium hydroxide to remove the unreacted acid and then with water until free of alkali. The benzene solution was dried over anhydrous sodium sulfate and the solvent stripped off under vacuum employing nitrogen as a sweep-gas, yielding 85.1 g of solid petroselinamide (I.V., 85.8). The crude petroselinamide was twice recrystallized from two 300-ml portions of petroleum ether yielding 44.3 g of white crystalline petroselinamide (47.8% yield) having a melting point of 72–73C [lit. mp 74–75C (2)] and an I.V. of 90.2 (theoretical I.V., 90.2).

*Preparation of Petroselinylamine.* A solution of 80 g (0.3 mole) of pure petroselinonitrile in 100 ml of *n*-butyl alcohol and 500 ml of toluene was slowly added during a 30 min period to a mechanically stirred mixture of 30 g (1.3 moles) of melted sodium dispersed in 500 ml of toluene at 100C. Stirring was continued and the temperature maintained at 100C for an additional 30 min. Then the heating was stopped, 50 ml of *n*-butyl alcohol was added and stirring was continued, until the mixture cooled to room temperature. To the cooled mixture was cautiously added 500 ml of water and then 500 ml of 25% aqueous hydrochloric acid. Most of the toluene, butanol, and water were distilled off and the residue made alkaline with 200 ml of 25% aqueous sodium hydroxide. The mixture was then extracted with three 150 ml portions of ether, the combined ethereal extracts washed with water until free of alkali and dried over anhydrous sodium sulfate. After evaporating the solvent and drying the residue in a rotary evaporator under high vacuum, there was recovered 79.2 g of the petroselinylamine which had an I.V. of 94.2. Infrared analysis of a sample showed that there was no unreacted nitrile present. The entire portion of the crude petroselinylamine was crystallized from 200 ml of petroleum ether at –20C yielding 65.3 g of white crystals which melted at 17C [lit. mp 18–20C which rose after several weeks to 40–45C (2)].

Anal. Calcd. for  $C_{18}H_{37}N$ : I.V. 94.9.

Found: I.V., 94.7; bp, 286C;  $d_4^{20}$ , 0.8212;  $n_D^{25}$ , 1.4586.

The hydrochloride salt of petroselinylamine was precipitated from 50 ml of anhydrous ether by satu-

rating the ethereal solution in which 15 g of the pure petroselinylamine was dissolved with anhydrous hydrogen chloride gas. On recrystallization from petroleum ether there was obtained 9.6 g of the pure petroselinylamine hydrochloride: mp, 115–116°C; percent HCl, 11.97 (theoretical, 11.99%). The acetyl derivative of petroselinylamine was prepared by heating 10.5 g of pure petroselinylamine with 100 ml of acetic anhydride for one hr on a steam bath. The excess acetic anhydride was decomposed by heating the solution with 100 ml of saturated aqueous sodium acetate (trihydrate) solution for another hr. The solution was then cooled to 0°C and the crude solid filtered off on a Büchner funnel which had been cooled previously to –20°C. The product was recrystallized from petroleum ether at –20°C and dried in a desiccator under high vacuum, yielding 8.6 g of white waxy N-acetyl petroselinylamine: mp, 29°C; I.V., 82 (theoretical I.V., 82).

### Discussion

The preparation of fatty acid nitriles by passing a fast stream of anhydrous ammonia through the melted fatty acid is a process that involves a dehydration of the ammonium salt to form the amide which in turn loses another molecule of water to form the nitrile. The condition may be expressed by the following equilibria:



It is evident that if conditions are employed providing for an efficient removal of the water which is formed during the dehydration step, the reaction is forced to the right. Thus an excess of ammonia passing through the reaction mixture at a fast rate would favor the neutralization of the fatty acid, and at the same time, serve as a sweep-gas for the removal of the water. The use of a dehydration catalyst such as phosphorus pentoxide would insure further that no water was present to allow the reaction to proceed in the reverse.

The long reaction period and the high temperature required for the ammonolysis of unsaturated fatty acids encourages polymerization at the olefinic linkage (3, 4), some isomerization of the *cis* double bond to the *trans* configuration, and cracking of the long chain (5), yielding a variety of by-products. During preliminary experiments in our laboratory with petroselinic acid, samples of the reaction mixture were obtained periodically throughout the entire course of the reaction and analyzed for their I.V. and the amount of unreacted acid. The progress of the ammonolysis was also followed by infrared analysis. By comparing the amount of absorbance per g of material of each sample at 4.5 (C≡N stretching), 6.05 (amide C=O absorption), 6.35 (primary amide NH<sub>2</sub>

deformation), and 10.35 microns (*trans* ethylenic CH deformation), the rate of formation of the nitrile, amide, and the *trans* isomer and then the disappearance of the amide could be determined. All spectra were obtained with a model 137 Perkin-Elmer Infracord Spectrophotometer at 100% transmission and with the slit over-ride set at 25 μ. The concentrations of the chloroform solutions were all very close to 20 g per liter and all were measured in a 1 mm rock salt cell against the pure solvent in the reference cell.

Table I illustrates the changes that take place during the course of the ammonolysis of petroselinic acid when no antioxidant is employed and may be compared with Table II where an antioxidant was used in the reaction. It is evident from the data that polymerization may be effectively controlled by the use

TABLE II  
Progress of Ammonolysis of Petroselinic Acid with Ionol Antioxidant

Reaction time (hr)	Temperature (°C)	I.V.	Infrared absorbance				% Unreacted acid
			4.50 μ	6.05 μ	6.35 μ	10.35 μ	
3	150	89.5	.....	>1.00	0.42	.....	32.87
6	250	89.6	0.08	>1.00	0.68	.....	11.05
10	250	89.9	0.12	>1.00	0.45	.....	7.04
14	250	90.0	0.14	0.90	0.27	0.09	3.23
17	250	90.8	0.16	0.70	0.22	0.09	2.21
20	250	91.0	0.17	0.60	0.19	0.09	1.14

of high-boiling antioxidants such as Ionol or pyrogallol. When temperatures are employed just high enough (235–250°C) to permit the conversion of the ammonium salt to the amide, the formation of short chain by-products by cracking of the long chain is reduced. The amide can then be converted into the nitrile by distilling it over a dehydration catalyst such as phosphorus pentoxide or active alumina. When an unsaturated fatty acid is allowed to react with ammonia in the presence of the dehydration catalyst over a long period of time, a greater amount of the *trans* isomer and other high-boiling polymeric by-products (6) are formed at a faster rate as shown in Table III in the case of petroselinic acid.

TABLE III  
Progress of Ammonolysis of Petroselinic Acid with Ionol Antioxidant and 3% Activated Alumina

Reaction time (hr)	Temperature (°C)	I.V.	Infrared absorbance				% Unreacted acid
			4.50 μ	6.05 μ	6.35 μ	10.35 μ	
3	150	88.7	.....	>1.00	0.95	.....	10.69
6	250	87.4	0.14	>1.00	0.43	0.12	5.47
10	250	83.5	0.17	0.72	0.25	0.14	1.31
14	250	80.5	0.19	0.10	.....	0.19	1.09
17	250	75.6	0.20	0.07	.....	0.21	0.82
20	250	73.0	0.19	.....	.....	0.23	0.66

It is known that petroselinic acid can be segregated from various saturated and unsaturated fatty acids by fractional urea complex crystallization (7,8). It appeared likely that this procedure could be utilized in the separation of the by-products of the ammonolysis reaction from the pure petroselinonitrile. Thus by varying the temperature of crystallization and the ratio of urea and methanol to the amount of the mixture of fatty nitriles, it was possible to remove the saturated and most of the *trans* unsaturated products from the pure petroselinonitrile in the form of solid urea complexes.

The formation of the *trans* isomer and the tendency of the unsaturated products toward polymerization

TABLE I  
Progress of Ammonolysis of Petroselinic Acid with no Antioxidant

Reaction time (hr)	Temperature (°C)	I.V.	Infrared absorbance				% Unreacted acid
			4.50 μ	6.05 μ	6.35 μ	10.35 μ	
3	150	87.6	.....	>1.00	0.49	.....	33.22
6	200	87.4	.....	>1.00	0.70	.....	29.52
10	200	90.1	0.10	0.38	0.12	0.09	25.86
14	260	83.7	0.15	0.24	0.07	0.10	15.69
18	260	78.2	0.17	0.22	.....	0.13	5.47
22	260	71.3	0.17	0.22	.....	0.18	2.31
26	260	53.5	0.16	0.21	.....	0.20	1.52
30	260	43.5	0.15	0.19	.....	0.20	1.03

at the double bond indicated that the reaction conditions employed during the preparation of petroselinonitrile influenced somewhat the activity of the ethylenic linkage. This introduced the possibility that other positional isomers could also be formed. However, ozonolysis of a sample of the petroselinonitrile and chromatography of the degradation products yielded adipic acid as the only dibasic acid indicating that no other unsaturated nitriles were present as impurities and that the reaction conditions employed during the preparation of the nitrile did not cause any migration of the double bond.

As a rule amides derived from fatty acids are comparatively neutral wax-like solids which can serve as the starting point in the synthesis of nitriles, amines and other chemical derivatives. Although fatty acid amides can be produced in better yields by the reaction of ammonia with the fatty acid, we have prepared a sample of petroselinamide by the acidolysis of urea (9) method in order to obtain a pure sample for infrared studies which enabled us to follow better the progress of the ammonolysis reaction during the preparation of petroselinonitrile.

It was determined from the infrared curves of the pure compounds that the petroselinonitrile has an absorbance of  $4.5 \mu$  of 0.20 at a 20 g per liter concentration and none at 6.05 or  $6.35 \mu$ . The pure petroselinamide exhibited absorbances at 2.87 (primary amide free NH stretching), 2.99 (primary amide bonded NH stretching), 6.05 and  $6.35 \mu$  in the amount of 0.24, 0.25, >1.00 (0.20 per g), and 0.56, respectively at a 10 g per liter concentration and none at  $4.5 \mu$ .

The synthesis of the higher aliphatic primary amines presents many problems. The most satisfactory method for the preparation of these amines is by reduction of the corresponding nitriles. The catalytic hydrogenation of nitriles is a reaction of considerable importance in organic synthesis and has been the subject of many investigations. However, by this means complex mixtures of primary, secondary, and tertiary amines are frequently obtained which are difficult to separate. A number of processes have been published for the hydrogenation of nitriles employing special techniques such as carrying out the hydrogenation at certain pressures and temperatures and in the presence of ammonia, moisture, alkali, and various solvents. By such modifications of the reaction conditions, the production of primary amines has been increased to as much as 60–70% but even this is not regarded as completely adequate. The most satisfactory procedure where a primary amine is produced in almost quantitative yield seems to be the hydrogenation of the corresponding nitrile in acetic anhydride over Raney nickel catalyst in the presence of a basic co-catalyst, followed by hydrolysis of the acetyl derivative with hydrochloric acid (10).

Further complications are encountered when the nitrile, as in our case, contains ethylenic bonds which are almost always attacked by hydrogen when the more active catalysts such as Raney nickel, platinum and palladium are used. When unsaturation is not to be eliminated the preferred catalysts are cobalt-molybdate and copper-chromium oxide (11). In our experiments with catalytic hydrogenation of petroselinonitrile it has been found that only the copper-chromite catalyst<sup>4</sup> reduced the nitrile under certain conditions without affecting the double bond but the yields of secondary and tertiary amines were rather

high. The cobalt-molybdate catalyst<sup>4</sup> has been found completely inactive under any laboratory conditions in the hydrogenation of petroselinonitrile. Only partial reduction of the nitrile group to the primary amine with a simultaneous conversion to the acetyl derivative was achieved by employing the copper-chromite catalyst in the presence of sodium hydroxide co-catalyst and acetic anhydride at 170–200°C and at pressure of 30 or 1000 pounds. Apparently under these conditions the catalyst becomes poisoned or the acetic anhydride reacts with the nitrile forming a triamide (12) so that the hydrogenation of petroselinonitrile does not proceed to completion.

Since satisfactory conditions for the catalytic hydrogenation of petroselinonitrile could not be established, the primary petroselinyamine was prepared in good yields by the reduction of petroselinonitrile with metallic sodium and alcohol in toluene (13). It was found that the free primary petroselinyamine is not stable in air at room temperature and on standing it readily evolves ammonia with the formation of the secondary amine as evidenced by the rise in its mp. However, when the freshly made primary petroselinyamine is converted into hydrochloride salt it can be stored unaltered for an indefinite length of time at room temperature.

The isolation of pure petroselinic acid from the various oils is a process requiring a number of operations, thus it can be of great commercial value that the petroselinamide and petroselinonitrile can be prepared directly from the oil in satisfactory yields. Since the nitrogen-containing derivatives of long chain fatty acids are versatile chemicals and a number of them have been utilized in industry, it is possible that the nitrogen-containing derivatives of petroselinic acid also have unique properties and may find uses in various fields such as surfactants, wetting and water-proofing agents, corrosion inhibitors, plasticizers, agricultural chemicals, and antimicrobial agents.

### Acknowledgments

The authors express their appreciation to Alva F. Cucullu and Ann L. Alford for the elemental analyses, and to Albert J. Crovotto of the Engineering and Development Laboratory for extraction of the oil from parsley seed. Our thanks go to The Harshaw Chemical Company which supplied us with the copper-chromite and cobalt-molybdate catalysts and to The Union Oil Company of California for their permission to use the cobalt-molybdate catalyst in our experiments.

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[Received March 12, 1962]

<sup>4</sup>The copper-chromite catalyst contained 51% of copper oxide and 47% of chromium sesquioxide and the cobalt-molybdate catalyst contained 9.32% molybdenum trioxide and 3% of cobalt oxide supported on gel alumina.