The Preparation and Properties of Some Petroselinylamine Derivatives[1]

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Abstract

Petroselinylamine (*cis*-6-octadecenylamine) has been prepared by an improved process in which petroselinic acid in xylene is subjected to ammonolysis and treated further to yield the primary amine without isolating the intermediate products. In addition, the petroselinylamine has been reacted with acrylonitrile, followed by reduction with metallic sodium and alcohol, to give N-substituted petroselinyl-1,3-trimethylenediamine adducts, and with ethylene oxide under pressure to yield the oxyethylated tertiary amine derivatives. The crude products in each case were mixtures of derivatives of various molecular weights. It was possible to isolate the N-petroselinyl-1,3-trimethylenediamine in its pure form from the crude mixture of hydrochloride salts by repeated recrystallizations from aqueous ethanol. The mixture of petroselinylamine-ethylene oxide derivatives could not be separated.

Introduction

THE VOLUMINOUS LITERATURE published in recent years on the preparation and properties of various nitrogen-containing derivatives from long-chain fatty acids of natural origin demonstrates the continually increasing interest in this field. The industrial production of high-molecular-weight amides has probably attracted more attention than any other type of long-chain aliphatic nitrogen compound because of their increasing importance as the most economical source of intermediate raw materials for the preparation of nitriles, amines, and other derivatives of fatty acids. During the past decade the actual and potential usefulness of the fatty amines and their derivatives has received wide recognition in the field of surface-active agents, corrosion inhibitors, plasticizers, resins, agricultural chemicals, and antimicrobial agents.

Because of its versatile character the amino group is capable of reacting as a proton acceptor, electron donor, or as a coordination group with a variety of functional groups belonging to other compounds. Although many unique and advantageous characteristics also have been attributed to the nature and configuration of the fatty alkyl chain alone, the amino substituent offers a suitable means of producing a multitude of derivatives with additional properties of industrial value. Among others, stearyl- and oleylamines already have been found useful as intermediates in the preparation of various oxyethylene and 3-aminopropyl derivatives and have been successfully employed in formulations: a) for the treatment of textile materials as antistatic, lubricating, fulling, and scouring agents (1); b) for polishing metals (2); c) as corrosion inhibitors for lubricating and fuel oils or gasoline (3–6); and d) for the treatment of water as antifoam and anticorrosion agents (7,8). It has been shown that petroselinic acid and some petroselinylamine derivatives possess antimicrobial properties which the oleyl and stearyl derivatives do not have (9,10).

During this study of the chemistry of petroselinic acid (*cis*-6-octadecenoic acid), which is a positional isomer of oleic acid (*cis*-9-octadecenoic acid) and a major fatty acid constituent of seed oils from plants belonging to the Umbelliferae family (11), it became of interest to prepare some of its nitrogen-containing derivatives and to determine their properties and potential industrial utility.

This paper describes a new method for the preparation of petroselinylamine from petroselinic acid, which offers higher yields of the final as well as the intermediate products, in a shorter time and with less effort than the previous procedure (12). It can be terminated at any appropriate time to obtain any of the intermediate products, or it can be extended to permit any number of subsequent reactions for further modification of the primary amine without isolating the intermediate products in their pure form. The cyanoethylation and oxyethylation of petroselinylamine are only examples to illustrate the suitability of this method for other purposes. The process could also be easily adopted for use with other fatty acids as starting materials or with different reagents to produce nitrogen-containing derivatives which are more complex and difficult to prepare by other means.

Experimental Section

Starting Materials

Petroselinic acid was prepared from parsley seed oil by the procedure of Fore et al. (13). The product obtained from the first crystallization of the mixed fatty acids in 90% ethanol at −20C, which melted at 28.0–29.5C and consisted of about 96% pure petroselinic acid, was used as a starting material in the present work.

Anhydrous ammonia, ethylene oxide, and practical-grade acrylonitrile of commercial origin were used without further purification.

Analytical Procedures

The elemental analyses of the hydrochloride salts of petroselinylamine and N-petroselinyl-1,3-trimethylenediamine were performed by the Midwest Microlab Inc., Indianapolis, Ind., and those of the petroselinylamine-ethylene oxide adduct, as well as its molecular weight, were determined by the Galbraith Laboratories Inc., Knoxville, Tenn.

The iodine values were determined by a modified Wijs method, designed for use with high-molecular-weight fatty nitrogen derivatives (14). Although the hydrogenation method gave iodine values for the hydrochloride salt of petroselinylamine-ethylene oxide adduct which closely agreed with those determined by the modified Wijs method, the hydrogen-iodine values for the compounds which contained primary amine groups were very inconsistent.

The amine values were determined potentiometrically by Methods No. Nb 1–62 and Nb 3–62, described in the "Official and Tentative Methods of the American

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The neutral equivalents were obtained by potentiometric titration.

Preparation of Petroselinylamine from Petroselinic Acid

A 3-necked, 500-ml round-bottom flask was equipped with a thermometer, a gas-dispersion tube with a fritted-glass cylinder, and a 40-ml Dean-Stark trap with a condenser, through which cold water was circulated throughout the reaction. The flask was charged with 200 g (0.68 mole) of petroselinic acid, 1 g of Ionol antioxidant (Shell Chemical Corporation brand name for 2,6-di-*tert*-butyl-4-methyl phenol, bp 257–266C), and 50 ml of xylene. A rapid stream of anhydrous ammonia was bubbled through the solution while its temperature was slowly increased from ambient to reflux over a period of about 1 hr. Heating was continued, and the solution was maintained at reflux for another 4 hr.

As more of the solvent distilled out, the reflux temperature of the reaction mixture gradually rose from 150 to 180C when the Dean-Stark trap was full. The water produced during dehydration of the ammonium salt and petroselinamide was swept out with the distilling xylene, collected, and periodically drained off from the trap. The amount of water served as an aid in estimating the extent of the reaction and in regulating the reflux temperature at which the dehydration process was most efficient. During the last hour of the reaction 10 g of P_2O_5 (representing 50–100% excess over the amount theoretically needed for the amide present at this point, as estimated by infrared spectroscopy) were carefully added to the reaction medium and its temperature was gradually increased to 230C in order to hasten the dehydration of petroselinamide and to ensure a more complete conversion to petroselinonitrile. The reaction mixture was allowed to cool to about 120C and was diluted with 400 ml of fresh hot xylene. The dehydrating agent was then filtered off and washed with the addition of 100 ml of hot xylene.

The cooled xylene solution of petroselinonitrile was mixed with 200 ml of *n*-butyl alcohol in a dropping funnel, then was slowly added over a period of 1 hr to a mechanically stirred mixture of 60 g (2.6 moles) of metallic sodium which was dispersed in 750 ml of xylene at 100C. Next 100 ml of *n*-butyl alcohol were added through the dropping funnel while stirring was continued and the temperature was maintained at 100C for another hour. Heating was then discontinued. The mixture was allowed to cool to room temperature, and 750 ml of water, followed by 750 ml of 25% aqueous hydrochloric acid, were cautiously added. Most of the xylene, butanol, and water were distilled off; the residue was made alkaline with 25% aqueous sodium hydroxide and extracted with xylene or ether, depending on the intended future use of the product.

At this stage the petroselinylamine can be obtained in 75–78% yields, based on petroselinic acid; the quantity isolated from the xylene extract was slightly higher than from the ether extract. If the petroselinylamine is not needed in its purest form or if it is to be subjected to further modification in the near future, the removal of such by-products as the excess butanol and its sodium salt can be effected sufficiently by washing of the cooled xylene solution with water.

Infrared analyses indicated that the crude product obtained from the reduction of petroselinonitrile was essentially the primary *cis*-6-octadecenylamine, containing only traces of the unreacted nitrile. The iodine and amine values were close to those calculated from theory. The petroselinylamine was stored at −20C in xylene at a concentration of 250 g/liter and remained sufficiently pure that it could be used for about one month. However infrared spectra and amine values disclosed that the primary amine was not stable under these conditions and that it was gradually transformed into its secondary and tertiary amine derivatives unless it was stored in the form of its hydrochloride salt. The following data for petroselinylamine standing at room temperature illustrate this transformation.

Time, weeks	Percentage of Total Amine Value		
	Primary	Secondary	Tertiary
0	100.0	......	......
1	65.5	27.0	7.5
2	52.5	38.5	9.0
3	44.0	46.0	10.0
4	37.5	52.0	10.5
8	32.5	56.5	11.0
26	30.0	58.5	11.5

The pure petroselinylamine was isolated from an ethereal solution as a solid hydrochloride salt. The ether extract from the above was first washed with water until free of alkali and dried over anhydrous sodium sulfate, then filtered and further dried over fresh pieces of finely cut sodium metal. The decanted anhydrous ethereal solution of petroselinylamine was next saturated with anhydrous hydrogen chloride gas until all petroselinylamine hydrochloride was precipitated and filtered out. The pure product, when completely dried under high vacuum, was a fine white crystalline solid, mp 115–116.5C, and was obtained in 44.1% yields, based on the starting amount of petroselinic acid.

Analytical. Calculated for $C_{18}H_{38}NCl$: C, 71.1; H, 12.6; N, 4.6; Cl, 11.7; IV, 83.5; NE, 303.9. Found: C, 70.9; H, 12.6; N, 4.6; Cl, 11.8; IV, 83.1; NE, 303.6.

Preparation of N-Petroselinyl-1,3-Trimethylenediamine

The same apparatus used in the preparation of petroselinylamine was now charged with 300 ml of the xylene solution that contained 75 g of petroselinylamine (0.28 mole), 45 g of acrylonitrile (0.85 mole), and 2 ml of a 50% aqueous sodium hydroxide solution. Nitrogen was slowly bubbled through the reaction mixture to provide a stirring for the ingredients and an air-free atmosphere surrounding it. The reaction temperature was maintained at 85–90C for 1 hr, then gradually increased, along with the rate of nitrogen sweeping through it, until the excess acrylonitrile and water were stripped off. The xylene solution was then cooled and filtered free of the small amount of solid which had formed during the reaction; fresh xylene was added to restore it to the original 300-ml volume.

The N-cyanoethylpetroselinylamine in xylene was reduced by the same procedure used for the reduction of petroselinonitrile, employing 37 g (1.6 moles) of sodium in 600 ml of xylene and a total of 150 ml of *n*-butyl alcohol. After acidification, most of the xylene, butanol, and water were distilled off; the residue was made alkaline with 25% aqueous sodium hydroxide and extracted with ether. The ethereal solution was dried over anhydrous sodium sulfate and filtered. The solvent was then evaporated, and the product heated over a steam bath and dried under high vacuum. The material thus obtained was a creamcolored, viscous liquid and weighed 94.8 g. This crude product had NE, 155.7; total AV, 360.3; primary AV, 197.5; secondary AV, 131.0; tertiary AV, 31.8.

These values indicated that it was a mixture of derivatives containing about 1.2 moles of trimethylenediamine per mole of petroselinylamine with the ratio of primary:secondary:tertiary amine groups $\cong$ 1.2:0.8:0.2 (6:4:1). Analyses of samples which were stored at room temperature or at −20C indicated almost complete disappearance of the primary amine after two weeks. The evolution of ammonia became noticeable after only 24 hr at room temperature. However this mixture of N-substituted petroselinyl-1,3-trimethylenediamine derivatives could be stored at room temperature unaltered over an indefinite period of time when converted to the corresponding solid hydrochloride salts.

The hydrochloride salt mixture was next subjected to recrystallizations from 50, 75, and 95% aqueous ethanol solutions respectively. The shiny white flakes obtained from the final recrystallization were thoroughly dried in a desiccator over concentrated sulfuric acid under high vacuum. This product was the pure N-petroselinyl-1,3-trimethylenediamine dihydrochloride which showed first signs of decomposition at 205C and completely melted at 215C. The yield amounted to about 50% of the crude product or about 30%, when based on the original amount of petroselinic acid used in the reaction.

Analytical. Calculated for $C_{21}H_{46}N_2Cl_2$: C, 63.4; H, 11.7; N, 7.1; Cl, 17.8; IV, 63.8; total AV, 282.3; primary or secondary AV, 141.1; NE, 198.8. Found: C, 63.5; H, 11.6; N, 7.2; Cl, 17.9; IV, 63.6; Total AV, 282.5; primary AV, 140.7; secondary AV, 141.8; NE, 198.0.

Preparation of Petroselinylamine-Ethylene Oxide Adduct

A 500-ml pressure bottle was charged with 50 g of petroselinylamine hydrochloride, 200 ml of *bis*(2-methoxyethyl) ether solvent, and a solution of 8 g of sodium hydroxide in 20 ml of water. The pressure bottle was equipped with a fritted-glass, gas-dispersion tube and an outlet tube leading to a trap and mercury manometer. The reaction solution was magnetically stirred, and the entire system was thoroughly flushed with nitrogen before ethylene oxide was introduced. The mixture was heated on an oil-bath and the addition of ethylene oxide so regulated that the pressure in the reaction flask and on the manometer would not exceed 760 mm above the atmospheric pressure. When the temperature of the reaction solution reached about 150C, a noticeable absorption of ethylene oxide was observed by a drop of pressure in the reaction system, and the temperature continued to rise to 170C even after heating of the solution was discontinued. The addition of ethylene oxide was continued for 2 hr while the pressure in the reaction system was maintained between 600 and 760 mm pressure above the atmospheric and while the temperature of the solution remained between 170 and 150C.

When the reaction mixture cooled to room temperature, it was again thoroughly flushed with nitrogen, then filtered under vacuum to remove the turbidity and the small amount of solid which had formed during the reaction. The solvent was removed by distillation under reduced pressure, and the semi-solid product was dried in a rotary evaporator on an oil-bath at 200C under high vacuum. The crude product, which was very hygroscopic, weighed 77.5 g, and analyses indicated that it contained an average of 4.5 moles of ethylene oxide per mole of petroselinylamine and that only tertiary amine groups were present. Infrared spectra also disclosed a small amount of amide-carbonyl absorption. Since all attempts to produce a solid hydrochloride salt were unsuccessful, the crude hydrochloride salt of the oxyethylated petroselinylamine product, dissolved in ether, was shaken in a separatory funnel with portions of 50, 75, and 95% aqueous ethanol respectively.

Analyses of the small amounts of material, isolated from the lower aqueous layers, indicated that the progressively less aqueous portions of ethanol removed fractions of the ethylene oxide-petroselinylamine hydrochloride derivatives which contained progressively smaller ratios of ethylene oxide to the petroselinylamine. Their average neutral equivalents were 616, 578, and 535 from the 50%, 75%, and 95% aqueous ethanol portions respectively. From the remaining ether portion was isolated a thick pasty material, light brown in color, which liquefied at about 140C. This product was also very hygroscopic and required exhaustive drying under high vacuum in a desiccator over concentrated sulfuric acid and hot oil-bath before it was subjected to each analytical procedure.

Analytical. Calculated for $R-NH_2(CH_2CH_2O)_{x+y}$ HCl, where R is $C_{18}H_{35}$:

$R-NH_2$ $(CH_2CH_2O)_{x+y}$ HCl	%C	%H	%N	%O	%OH	%Cl	MW or NE	IV
x + y = 2	67.4	11.8	3.6	8.2	8.7	9.0	392	64.7
x + y = 3	66.1	11.6	3.2	11.0	7.8	8.1	436	58.2
x + y = 4	65.0	11.3	2.9	13.3	7.1	7.4	480	52.9
x + y = 5	64.2	11.2	2.7	15.3	6.5	6.8	524	48.4
$R-N(CH_2CH_2)_2O$ · HCl	70.6	11.9	3.5	4.3	....	9.5	374	67.9

Found: C, 66.2; H, 11.6; N, 3.3; O, 10.9; OH, 7.6; Cl, 7.3; MW, 460; NE, 480; IV, 52.4.

Discussion

In the preparation of long-chain primary amines the fatty acid is treated with ammonia and subjected to dehydration to form the nitrile, which is then reduced to the fatty amine according to the scheme outlined in Figure 1. The primary amine can be eventually modified further to produce other N-substituted derivatives.

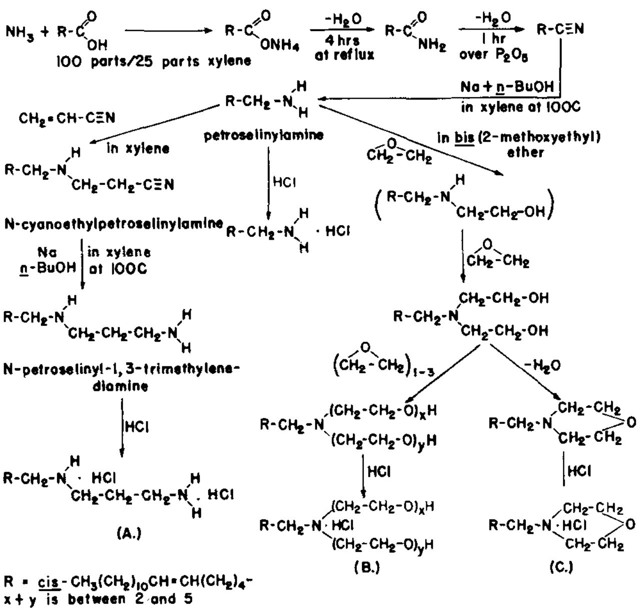

FIG. 1. Preparation of petroselinylamine and its derivatives from petroselinic acid in xylene.

The formation of amides from ammonium salts and carboxylic acids and their subsequent dehydration to nitriles are a reversible process. The rate of transformation and the final position of the equilibrium are partly influenced by the nature of the fatty acid but are mostly dependent on the conditions under which the ammonolysis-dehydration reactions are carried out. High temperatures and an efficient means of removing the water of dehydration from the reaction mixture are usually required in order to minimize the reversibility of the reaction.

In the present process the use of xylene eliminates the high reaction and distillation temperatures during which formation of various by-products can occur because of polymerization and cracking. The amount of xylene employed is sufficient to be effective as a solvent for the solid ammonium salt and the petroselinamide intermediates. Consequently it prevents the frequent clogging of the fritted-glass tube, through which ammonia is introduced into the melted petroselinic acid, and the depositing of the solid intermediates swept up by the fast stream of ammonia into the condenser when xylene is not used. Xylene also functions as an aid in the dehydration process by forcing the equilibrium to the right since the water formed during the reaction is distilled off as an azeotrope with xylene and condensed into the Dean-Stark trap. The water collected in the trap is not only a convenient means for estimating the extent of the reaction, but it also can be partially drained off to control the quantity of xylene distilled out and aid in regulating the reaction temperature at which the dehydration process is most efficient.

Infrared analyses of samples taken each hour during the reaction indicate that the petroselinic acid in xylene is converted to its ammonium salt within the first hour, even before the solution begins to reflux. When heating is continued for 3 hr more, the reflux temperature of the reaction mixture gradually rises as the xylene content is reduced and as the ammonium salt is dehydrated to petroselinamide.

Figure 2 illustrates the infrared spectrum in CCl_4 of a sample taken from the product after reacting petroselinic acid with ammonia for only 4 hr in the presence of xylene and at temperatures not exceeding 180C. From measurements of the absorption peaks characteristic of the amide group (the NH stretching frequencies at 2.87 μ and 2.99 μ, the amide $C = O$ absorption at 6.05 μ, and the primary amide NH_2 deformation at 6.35 μ), it is estimated (12) that the petroselinamide is present in the product in essentially quantitative yield at this time.

The infrared curve shows no evidence of bands in the region where the carbonyl groups of carboxylic acids or its ammonium salts should absorb (5.8–5.9 μ).

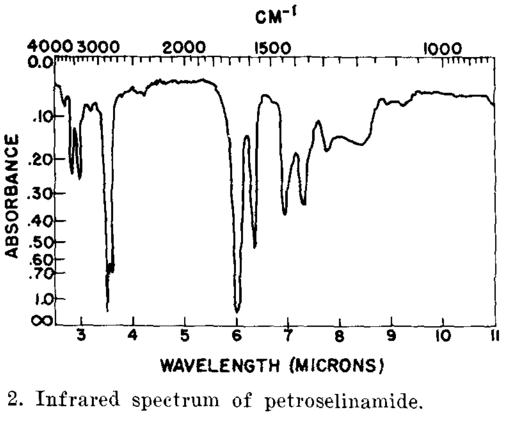

FIG. 2. Infrared spectrum of petroselinamide.

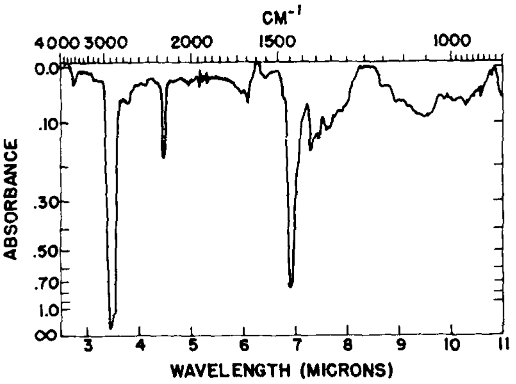

FIG. 3. Infrared spectrum of petroselinonitrile.

The absence of peaks at 10.35 μ (*trans* ethylenic CH deformation) and at 4.5 μ ($C \equiv N$ stretching) indicates that, under the condition of this method, no isomerization of the *cis* double bond to the *trans* configuration takes place and that, at this point of the process, there has been no noticeable formation of the petroselinonitrile. Yields of similar fatty acid amides have been reported up to 90% by a laboratory method which requires the preparation of the acid chloride by a separate step prior to its reaction with ammonia (15).

Apparently the dehydration of petroselinamide to the nitrile takes place at temperatures above 200C and at a very slow rate. This would prevent the use of any appreciable amount of xylene to facilitate removal of the water formed during dehydration of the amide and would allow the production of undesirable by-products caused by high temperatures. However the yields and purity of the petroselinonitrile are greatly improved and dehydration of the amide is hastened by the addition of small amounts of P_2O_5. Al_2O_3 was also tried for this purpose but was much less effective. The infrared curve reproduced in Figure 3 shows the good quality of the crude petroselinonitrile obtained in this way. There are no absorption bands which would suggest the presence of the *trans* isomer or any appreciable amounts of the unreacted amide. The product is anhydrous, pure enough, and already in a solution of xylene so that it can be subjected to reduction to the primary amine with metallic sodium and alcohol immediately after the dehydrating agent has been filtered off.

The authors have chosen the method employing sodium and alcohol for reduction of the nitrile groups in petroselinonitrile and the N-cyanoethylpetroselinylamine in order to prepare the corresponding primary amines with the best possible yields. Catalytic hydrogenation of petroselinonitrile was investigated, by employing various catalyst and solvent systems as described in an earlier publication (12), but no satisfactory conditions could be found which would produce the primary amine without partially reducing the ethylenic bond of the petroselinic moiety or without also producing some secondary and tertiary amine derivatives which were difficult to separate from the resulting mixture.

Both petroselinylamine and N-petroselinyl-1,3-trimethylenediamine show signs of decomposition soon after their preparation even when they are stored at −20C as solids or in a xylene solution. The deterioration of these compounds becomes apparent with the liberation of ammonia and by the rise in their melting points. However both can be stored indefinitely at room temperature in the form of their corresponding hydrochloride salts.

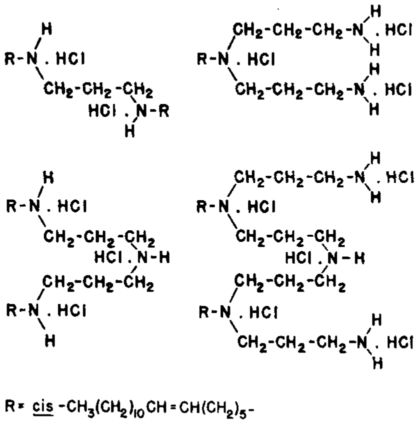

FIG. 4. N-Substituted petroselinyl-1,3-trimethylenediamine derivatives.

Analyses of the crude product obtained from the reaction of petroselinylamine with acrylonitrile and its subsequent modification to the diamine dihydrochloride salt and analysis of the residue left after removal of the major component indicated that the by-products were higher-molecular-weight, N-substituted petroselinyl-1,3-trimethylenediamine derivatives which contained mostly secondary amine groups. The tertiary amine derivatives were in the minority. This leads to a belief that, under the basic conditions of the reaction, the resulting by-products included compounds with structures such as those shown in Figure 4. However about 50% of the crude mixture was the principal product, N-petroselinyl-1,3-trimethylenediamine, which was isolated pure in the form of its solid hydrochloride salt, as illustrated in Figure 1 by structure A.

Although no single compound could be isolated in its pure form, from the reaction of petroselinylamine with ethylene oxide it was evident, from analyses of the crude product, its hydrochloride salt, and the material separated during its treatment with aqueous ethanol, that the oxyethylated product obtained was a mixture of compounds having structures such as B and C (Figure 1); the number of oxyethylene groups ranged between 2 and 5 per mole of petroselinylamine. The intermediate secondary amine, N-petroselinyl-2-hydroxyethylamine, or its polyoxyethylated derivative could not be detected at any time during the reaction.

It has been shown by other investigators (1,2,16,17) that, under similar conditions, ethylene oxide adds to primary and secondary fatty amines to give tertiary amines which are mixtures of adducts with composition similar to those reported in this paper and which are exceedingly difficult to separate into their pure components. Because of its hygroscopic nature the product must be subjected to drastic drying conditions prior to each analysis. This seems to result in the splitting off of one mole of water from the component with two moles of ethylene oxide per mole of petroselinylamine. The presence and formation of the substituted morpholine structure C (Figure 1) in an increasingly higher proportion after each subsequent drying treatment and analysis were shown by the decreasing oxygen and hydroxyl content of the mixture.

The 1,3-trimethylenediamines and the ethylene oxide derivatives of a number of fatty amines are commercially available, and it has been suggested that these derivatives prepared from unsaturated fatty acids are superior as corrosion inhibitors, when added to lubricating oils, to the corresponding derivatives from saturated fatty acids (17–19). Limited evaluations of the petroselinylamine and its N-substituted derivatives by Armour and Company disclosed that they are comparable as corrosion inhibitors to their isomeric oleylamine derivatives (20). The hydrochlorides of these amines also exhibited antimycotic activity against various types of micro-organisms (21).

It may be concluded that the new process employing xylene throughout its course is capable of producing nitrogen-containing derivatives from petroselinic acid in better yields than other methods because it eliminates losses with each isolation and purification procedure of the individual intermediates. The time necessary for the conversion of petroselinic acid to its nitrile has been shortened from some 20 hr, required by the previous method, to about 5 hr. Also the purity of the petroselinonitrile and the intermediate amide is higher than when xylene was not used, and higher temperatures over longer periods of time were necessary for the conversion.

The process can be terminated at any appropriate time to obtain the individual intermediates, or it can be continued to produce the N-substituted derivatives of petroselinylamine without removing the intermediates from the xylene solution, reserving the last step for isolation and purification of the final products.

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Screening of amine hydrochlorides for antimycotic activity performed by A. Novak of Louisiana State University.

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