Preparation of Dodecylamine and 6-Aminohexanoic Acid from Petroselinic Acid[1]

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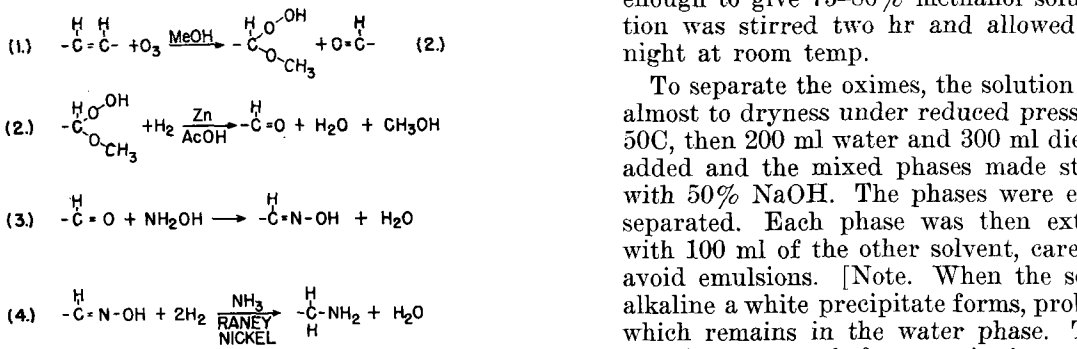
Abstract

A procedure is given for the ozonization of petroselinic acid, chemical reduction of the ozonides to aldehydes, formation of oximes, and catalytic hydrogenation of the oximes using Raney nickel in the presence of ammonia, to yield 48% dodecylamine and 44% 6-aminohexanoic acid calculated on the amounts theoretically available from the wt of petroselinic acid. The ultimate analyses, melting points, and distribution coefficients between ethyl ether and water of lauraldehyde and adipaldehydic acid oximes were determined. The infrared spectra of lauraldehyde oxime, adipaldehydic acid oxime, and 6-aminohexanoic acid are given and interpreted.

Introduction

SEED OIL of the *Umbelliferae* (parsley, carrots, anise, etc.) contain petroselinic (*cis*-6-octadecenoic) acid, an acid peculiar to the seed oil of members of this family. The acid has interesting possibilities for industrial utilization and because of its presence in the seed oil, members of this family are potential oilseed crops.

One of the possibilities for making useful derivatives from petroselinic acid is fission at the double bond and conversion of the fragments to 6-aminohexanoic acid and to dodecylamine. Both 6-aminohexanoic and dodecylamine can be made from petroselinic acid by the following series of reactions where only the carbon atoms joined by the double bond are shown:



By these reactions the 1–6 and 7-18 carbon fragments would yield ammonium 6-aminohexanoate

$$[H_2N(CH_2)_5COONH_4]$$

and dodecylamine

$$[CH_3(CH_2)_{11}NH_2],$$

respectively, and the ammonium 6-aminohexanoate could then be converted to the free 6-aminohexanoic acid.

English (6) and Japanese patents (14) cover the preparation of 9-aminononanoic acid from oleic acid or from any of the unsaturated acids with the first unsaturation at the 9–10 position. This paper reports a procedure for the preparation of 6-aminohexanoic acid and dodecylamine from petroselinic acid by a similar process.

Experimental

Petroselinic Acid. Petroselinic acid of at least 96% purity was prepared from parsley *(Petroselinum sativum)* seed oil by method of Fore et al. (8).

Ozonization. Ozonization was done in methanol with a Welsbach Model T-23 Laboratory Ozonizer at −10C. Petroselinic acid (20 g) was dissolved in 200 ml of methanol. The end point of the ozonization was determined by the darkening of an acidified solution of potassium iodide in a trap.

Reduction of Ozonides. The methanol solution of the ozonides was immediately transferred to a beaker in an ice bath containing a magnetic stirrer. For each 20 g of petroselinic acid, 25 ml of glacial acetic acid was added, then 10 g of zinc dust was slowly added, keeping the temp between 10C and 15C. Stirring was continued until the solution gave a negative test for peroxides with acetic acid, chloroform, and a saturated KI solution.

Preparation of Oximes. The methanol solution was immediately filtered to free it of the zinc sludge. Then for each 20 g of petroselinic acid, 12.3 g hydroxylamine hydrochloride dissolved in a small amount of water was added with stirring, followed by addition of 14.5 g sodium acetate in a small amount of water. The amount of water used for dissolving the salts was enough to give 75–80% methanol solution. The solution was stirred two hr and allowed to stand overnight at room temp.

To separate the oximes, the solution was evaporated almost to dryness under reduced pressure at less than 50C, then 200 ml water and 300 ml diethyl ether were added and the mixed phases made strongly alkaline with 50% NaOH. The phases were equilibrated and separated. Each phase was then extracted 4 times with 100 ml of the other solvent, care being taken to avoid emulsions. [Note. When the solution is made alkaline a white precipitate forms, probably $Zn(OH)_2$, which remains in the water phase. This precipitate was filtered out before continuing with the extractions.] The ether solution was dried with Na_2SO_4 and the ether evaporated to give lauraldehyde oxime.

The water phase, after separation of the lauraldehyde oxime, was made strongly acid with HCl and extracted 8–10 times with equal vol of ether. The ether extractions were not back-washed with water to avoid re-extraction of the adipaldehydic acid oxime into the water. The combined ether extracts were dried with Na_2SO_4 and evaporated under reduced pressure to yield crude adipaldehydic acid oxime.

Aminative Reduction of Oximes. Both the lauraldehyde oxime and the adipaldehydic acid oxime were reduced in absolute ethanol with Raney nickel prepared by Adkin and Billica's method for Raney nickel W-5 (1), except that the catalyst was more thoroughly

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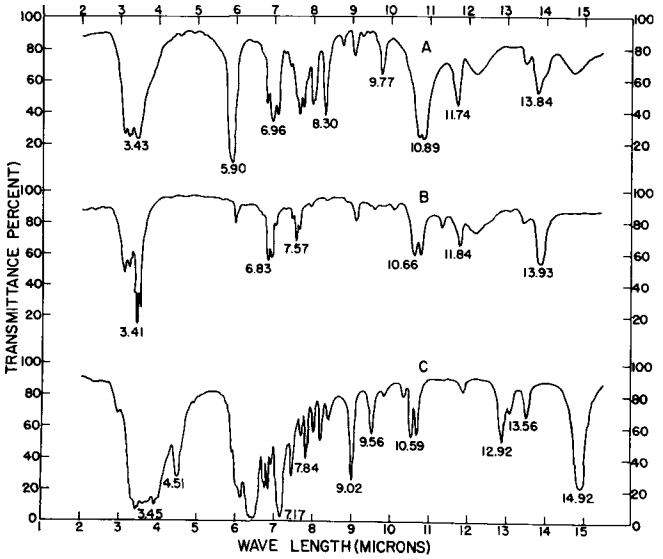

FIG. 1. Infrared spectra in KBr discs. (A) Adipaldehydic acid oxime, (B) lauraldlehyde oxime, (C) aminohexanoic acid.

washed. After digestion the catalyst was filtered out on a 90 mm medium porosity fritted glass funnel, washed with 8 liters of distilled water and then with 2 liters of absolute ethanol, not allowing the catalyst at any time to be sucked dry. The catalyst was stored under absolute ethanol and used within 10 days.

The hydrogenation vessel containing the alcohol solution of the oxime was chilled in a dry ice chamber. Then 10–15 equivalents of liquid ammonia and the catalyst were added, roughly 15% of catalyst on wt of oxime. Reduction was carried out in a rocking hydrogenator for 4 hr at 1000 lb pressure at 95–105C. After reduction, the hydrogenation vessel was allowed to cool to room temp, the catalyst filtered out, and the ethanol solution evaporated to dryness under reduced pressure, at less than 50C for the preparation of dodecylamine.

Purification of Final Products. In the case of the dodecylamine, the dry crude product was dissolved in anhydrous diethyl ether and the ether solution was saturated with HCl gas to precipitate the dodecylamine hydrochloride. The precipitate was filtered on a fritted glass funnel, rinsed with cold ether, and dried in a vacuum desiccator in the presence of sodium hydroxide. The dry hydrochloride was weighed, and its primary dodecylamine content determined by the method of Ralston and Hoerr (16). The primary amine content was 92–95%. The remainder of the nitrogen in the hydrochloride was attributed to secondary and tertiary amines.

The crude ammonium hexanoate was a very viscous greenish liquid in which crystals formed very slowly. It was purified and converted to the free amino acid by use of ion exchange resins. The ammonium salt in aqueous solution was absorbed on a column of Dowex 50 resin in the hydrogen form and the column washed thoroughly. The amino acid was absorbed as a cation then eluted with dilute ammonia yielding the ammonium salt. Similarly, the ammonium salt was then absorbed on Dowex 1 resin in the hydroxyl form as an anion, the column washed, and the amino acid eluted with dilute hydrochloric acid to yield the hydrochloride of the acid. Finally the hydrochloride was passed through an IR-4B resin column in the hydroxyl form to split off the hydrochloric acid (11). The elution of the amino acid from the columns was followed by testing the eluate with ninhydrin paper, the strips being heated several minutes at 95C to rapidly develop the color.

By chromatographing the amino acid on paper along with a known sample of 6-aminohexanoic acid it was shown that no other amino acid was present in the product. When developed in butanol: acetic acid: water = 25:6:25 v/v on Whatman No. 1 paper (4) 6-aminohexanoic acid had a Rf value of 0.62.

In some cases the final product was analyzed by the ninhydrin colorimetric method for amino acid (12). However, if the final product readily crystallized in colorless crystals which had the correct melting point (200–203C) for 6-aminohexanoic acid it was considered pure acid.

TABLE I

Infrared Absorption Spectra of Lauraldehyde Oxime

Position of band, maxima μ	Vibrating group most probably giving rise to observed absorption bands	Reference
3.10	Bonded O—H .... stretching	15
3.22	Bonded O—H .... stretching	15
3.41	C—H stretching	13
3.50	C—H stretching	13
5.99	C=N stretching (oxime)	15
6.83	CH_2 scissors	13
6.93	C—H deformation	13
7.04	C—H deformation	13
7.57	C—H bending	13
7.65	O—H bending (oxime)	15
9.14	Unassigned	
10.66	Unassigned	
10.83	N—OH stretching	15
11.36	Unassigned	
11.84	C—H=N—OH skeletal	See text
12.20	C—H=N—OH skeletal	See text
13.49	C—H=N—OH skeletal	See text
13.93	CH_2 in phase rocking	13

Results and Discussion

The oximes from some of the earlier preparations were purified by recrystallization from absolute ethanol. Their melting points, ultimate analyses, infrared spectra in KBr discs, and distribution coefficients between ethyl ether and water, were determined.

Lauraldehyde oxime: Found C, 72.5%; H, 12.6%; N, 8.2% (calculated C, 71.9%; H, 12.6%; N, 8.0%), mp 76.6C. The distribution coefficient between ether and water was nearly infinite; i.e., when the phases were in equilibrium all the lauraldehyde oxime was in the ether phase.

Adipaldehydic acid oxime: Found C, 49.6%; H, 7.6%; N, 9.6% (calculated C, 49.4%; H, 7.6%; N, 9.6%), mp 116.6C. Distribution coefficient between ether and water was 0.86.

The infrared spectrum of 6-aminohexanoic acid was also determined. Since the spectra of lauraldehyde oxime, adipaldehydic acid oxime, and 6-aminohexanoic acid have not heretofore appeared in the literature they are reproduced in Fig. 1. The spectra were obtained as KBr discs at a concentration of 1 mg to 350 mg KBr with a Perkin-Elmer Infrared Spectrophotometer Model 21. The principal absorption bands and the groups probably giving rise to them are listed in Tables I, II, and III.

The absorption bands observed in the spectrum of lauraldehyde oxime (Table I) would be expected to be a summation of those correlated with the vibrating groups of long-chain compounds plus those characteristic of the oxime moiety. The bands arising from the long-chain portion of the molecule can readily be assigned from previous reviews of long-chain fatty acids and related compounds (13). A search of the literature reveals that very little has been published on the infrared spectra of oximes and that most investigations have been concerned mainly with the O—H stretching vibrations in the 3-μ and the near-infrared regions (5,7,9,15). Palm and Werbin (15)

list the following bands as characteristic of the oxime group: 3.08 and 3.21 μ, bonded O—H . . . . stretching (these authors admit that it is not certain whether the bonding is through the O or the N atom); 6.10 μ, C=N stretching; 7.69 μ, O—H bending; and 10.87 μ, N—OH stretching. These bands agree very well with bands found in the spectrum of lauraldehyde oxime and together with the bands accounted for as arising from the long-chain moiety, account for most of the observed bands in the spectrum below 12 μ. In the 12 and 13 μ region of this spectrum are observed three sharp, clearly definable bands. As these bands are not found in the spectra of long-chain fatty acids they would appear to arise from oxime moiety. However, none of the workers reporting on the infrared spectra of oximes mention them. As indicated in Table I they are assumed to rise from a skeletal vibration of the oxime group although an alternate assignment for one or more of them could be a deformation of the C—H group about the C=N, analogous to the bending of this group about the *trans* C=C group.

Most of the principal bands observed in the spectrum of adipaldehydic acid oxime (Table II) can, similarly, be accounted for as arising from vibrations of the long-chain fatty acid (13) or as the bands assigned to oximes by Palm and Werbin (15). The strong C=O stretching band in this spectrum reduces the weaker C=N stretching to a mere inflection and the several C—O stretching and O—H deformation vibrations account for the main differences in this spectrum compared to that of the lauraldehyde oxime. The bands in the 12 and 13 μ region, tentatively assigned to a skeletal mode of the CH=NOH in the spectrum of lauraldehyde oxime, appear in the spectrum of adipaldehydic acid oxime, strengthening the postulation that they arise from the oxime moiety. Bands at 8.00 and 9.77 μ are unaccounted for in this spectrum. The 8.00 μ band is usually evidence for the acetate (or a short chain ester) group, and O'Connor et al. (13) used the 9.77 μ band to differentiate between a methyl and an ethyl ester, showing that this band appears in the spectra of ethyl esters but not in the spectra of methyl esters nor in those of the free long-chain fatty acids. Thus these two bands, constituting evidence for the ester group, are anomalous in the spectrum of adipaldehydic acid oxime.

Since the adipaldehydic acid oxime was purified by recrystallization from ethanol it is possible that a small amount of the acid aldehyde had been converted to the ethyl ester.

The spectrum of the 6-aminohexanoic acid (Table III) exhibits a considerably greater number of intense sharp bands than observed in the spectra of the oximes, especially in the region from about 7.0 to 8.5 μ. The observed bands, shown in Table III, can be accounted for from the previously mentioned reviews of long-chain fatty acids and derivatives and from numerous investigations of the infrared absorption of the amine group as summarized by Bellamy (3). The band at the lowest wave length, 2.94 μ, undoubtedly arises from a N—H stretching vibration as neither the bonded O—H from the COOH group nor the C—H stretching would occur at this high a frequency. The broad band extending with minor peaks from about 3.3 to 3.8 μ represents only incomplete resolution of the N—H, O—H, and C—H stretchings. The increased number of sharp bands observed in the region between about 7.0 and 8.5 μ indicates the possible appearance of the band progressions arising in solid state spectra from various CH_2 vibrations, as first described by Jones et al. (10). In solid state spectra subsequent work has shown that a series or progression of bands occurs in long-chain compounds which have an active end-group. In such a compound as 6-aminohexanoic acid, with two active end groups, such a band progression might be expected. The characteristic feature of such a band progression is the constant difference in frequency as each pair of CH_2 groups vibrates at a fixed frequency dependent upon its distance in the crystallographic structure from the active end group. The very constant difference in frequency of the bands assigned, in Table III, to such progression as shown below:

TABLE II

Infrared Absorption Spectra of Adipaldehydic Acid Oxime

Position of band, maxima μ	Vibrating group most probably giving rise to observed absorption band	Reference
3.11	Bonded O—H . . . . stretching	15
3.23	Bonded O—H . . . . stretching	15
3.43	C—H stretching	13
3.48	C—H stretching	13
5.90	C=O stretching	13
5.99I*	C=N stretching (oxime)	15
6.82	CH_2 *scissors*	13
6.96	C—H deformation	13
7.09	C—H deformation	13
7.66	O—H bending (oxime)	15
7.76	C—O stretching, O—H deformation coupling (COOH group)	13
8.00	Unassigned	See text
8.30	C—O stretching, O—H deformation coupling (COOH group)	13
8.76	C—O stretching about COOH group	13
9.07	C—O stretching about COOH group	13
9.77	Unassigned	See text
10.75	O—H bending COOH group	13
10.89	N—OH stretching (oxime)	15
11.74	C—H=N—OH skeletal	See text
12.24	C—H=N—OH skeletal	See text
13.50	C—H=N—OH skeletal	See text
13.84	CH_2 is phase rocking	13
14.79	Unassigned	....

* I = inflection.

μ	cm^{-1}	Δ cm^{-1}
6.58	1520	....
6.85	1460	60
7.17	1395	65
7.49	1335	60
7.84	1275	60
8.23	1215	60

TABLE III

Infrared Absorption Spectra of 6-Aminohexanoic Acid

Position of band, maxima, μ	Vibrating group most probably giving rise to observed absorption band	Reference
2.94	Bonded N—H . . . . stretching (primary amine)	3
3.3–3.8	Unresolved bonded N—H . . . . asymmetrical stretching, bonded N—H . . . . symmetrical stretching, bonded O—H stretching (COOH group) and C—H stretchings	
4.51	Unassigned	See text
5.94	C=O stretching (COOH group)	13
6.14	Unassigned	....
6.4–6.5	NH_2 scissors	3
6.58	CH_2 Progression band	See text
6.77	Unassigned	....
6.85	CH_2 scissors	13
6.95	CH_2 Progression band	See text
7.17	CH_2 Progression band	See text
7.49	CH_2 Progression band	See text
7.72	C—O stretching, OH deformation coupling (COOH group)	13
7.84	CH_2 Progression band	See text
8.03	C—N stretching	....
8.23	CH_2 Progression band	See text
8.44	C—O stretching, OH deformation coupling (COOH group)	13
9.02	NH_2 out-of-phase rocking	3
9.56	C—N stretching	3
10.59	Unassigned	....
10.73	O—H bending about COOH group	13
11.92	Unassigned	....
12.92	NH_2 out-of-phase twisting	3
13.14	Unassigned	....
13.56	CH_2 in phase rocking	13
14.92	Unassigned	....

constitutes confirmation for these assignments. A few bands appear in the spectrum of 6-aminohexanoic acid which cannot be accounted for from investigations on the long-chain fatty acids nor on the infrared absorption studies of the amine group.

With the exception of a few unassigned bands the spectra confirm the structures of lauraldehyde oxime, adipaldehydic acid oxime and 6-aminohexanoic acid.

The best yields of dodecylamine and of 6-aminohexanoic acid were obtained by the procedure given under Experimental. The yield of the dodecylamine was 48% of the theoretical calculated on the wt of petroselinic acid used, the yield of 6-aminohexanoic acid was 44%.

The yields of the aldehydes from the reduction of the ozonides with zinc-acetic acid was 77–85% of the theoretical. The yields of oximes was in the same range, as calculated from their weights and nitrogen contents, assuming that all the nitrogen present was in the form of oximes.

Various modifications of the procedure for the preparation of the amines were tried: using the procedure given under Experimental but without separating the oximes; using the same procedure except hydroxylamine was added before the reduction of the ozonides with zinc and acetic acid; direct catalytic aminative reduction of the aldehydes in the presence of ammonia and hydrogen; ozonizing methyl petroselinate instead of the acid; and catalytic reduction with hydrogen of the ozonides to aldehydes. None of these procedures gave as high yields as the procedure outlined above. A problem encountered in all procedures was the solubility of the adipaldehydic acid and its oxime in water, and especially in water-alcohol mixtures. For this reason more difficulty was encountered in isolating the adipaldehydic acid and its oxime than would be the case with the corresponding derivatives from oleic acid.

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Determination of Structure of Unsaturated Fatty Acids via Reductive Ozonolysis[1,2]

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Abstract

An improved method of reductive ozonolysis for the determination of structure of unsaturated fatty acids is reported.

The ozonization is carried out at −60 – −70C by adding the sample dissolved in pentane to a .02–.03 M pentane solution of ozone. The reduction is effected by the Lindlar catalyst at 0C in pentane or in other solvents, such as the methyl esters of short-chain fatty acids or in dimethyl phthalate, and the aldehydic fragments are analyzed by gas-liquid chromatography (GLC).

The method is applied to the structural analyses of methyl esters of oleic, linoleic, linolenic, and arachidonic acids. The sensitivity of the method is demonstrated by the analysis of methyl oleate containing a small amount of added methyl linolenate. Mixtures of methyl oleate and petroselinate are analyzed to demonstrate the identification of the simple aldehydes and ester-aldehydes, and to show the potential of the method for quantitative analysis of mixtures of unsaturated esters.

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[2] Presented at the AOCS meeting in Chicago, Ill., 1961.

Introduction

OZONIZATION, followed by oxidative or reductive fission of the ozonides, has been used by many investigators for the determination of structure of unsaturated fatty acids (1,3,6,9,10,11,14,16,18). However, a completely satisfactory procedure has not been developed. In general, the determination of structure by ozonolysis is complicated by side reactions which give spurious results (4,6,8). The products of the ozonization of double bonds are markedly influenced by the conditions of the reaction and may be very complex (2,7). Herein, we describe a procedure which is based on the quantitative and instantaneous formation of true ozonides and their reductive cleavage to aldehydes. The location of the double bonds is based on the analysis of the aldehyde fragments by gas-liquid chromatography (GLC).

Experimental

Methyl Ester Standards. Highly purified methyl oleate, linoleate, linolenate, petroselinate, and arachidonate were obtained from The Hormel Foundation, Austin, Minn. These esters were used without further purification, except for methyl arachidonate, which was further purified by reversed-phase partition chromatography as previously described by the authors (13). No impurities could be detected in these preparations by GLC.