13-AMINOTRIDECANOIC ACID FROM ERUCIC ACID

JOSEPH L. GREENE, JR.,1 AND ROBERT E. BURKS, JR.
Southern Research Institute, Birmingham, Ala. 35205

IVAN A. WOLFF
Northern Regional Research Laboratory, Peoria, Ill. 61604

13-Aminotridecanoic acid, the monomer for nylon 13, was synthesized from commercial erucic acid or its derivatives by several methods in a study to determine the method of choice, which involved oxidative ozonolysis of eruconitrile, followed by esterification before isolation to give methyl 12-cyanododecanoate. The cyano ester was then catalytically reduced and hydrolyzed, without isolation of intermediates, to give very pure 13-aminotridecanoic acid in 55 to 60% yield from the eruconitrile. Almost equally convenient was a method starting with oxidative ozonolysis of methyl erucate to the half ester of brassyllic acid, which was then converted successively to the amide-ester, nitrile-ester, amino ester, and amino acid. Other methods tried were significantly less desirable because of low yields and difficult purifications.

Since this research was done to synthesize the pure amino acid from readily available material, all the work described utilized commercial grades of erucic acid, ester, or nitrile. Each material was a product of Humko Products Division, National Dairy Products Corp., Memphis, Tenn., and was 85 to 90% pure by GLC. Yields would presumably have been higher if purified erucic acid or its derivatives had been employed as starting materials.

A one-step reductive amination of the ozonide of methyl erucate, by the method of Foster and Schroeder (1953), gave only 5 to 7% of the theoretical amount of amino acid (Figure 1).

A two-step reductive amination of the methyl erucate ozonolysis product led to the amino acid in 14% overall yield (Figure 1). Methyl 12-formyldodecanoate was prepared in 50% yield according to the method of Anders et al. (1965). Working with highly purified methyl erucate, they reported an 87% yield of the desired aldehyde-ester of 99.1% purity by GLC. Reduction of the aldehyde-ester as prepared here with hydrogen in the presence of ammonia and Raney nickel catalyst gave methyl 13-aminotridecanoate, isolated in 32% yield as the hydrochloride salt. The amino ester hydrochloride upon basic hydrolysis, followed by careful adjustment of the pH of the system to 7.75, gave 91% yield of 13-aminotridecanoic acid.

The oxime of methyl 12-formyldodecanoate was obtained in 21% yield from the ozonide of methyl erucate (Figure 1). Hydrogenation over Raney nickel in the presence of ammonia gave a 51% yield of methyl 13-aminotridecanoate. The procedure followed was that of Otsuki and Funabashi (1958). They reported no yields, described no intermediates, and cited a melting point of 161–63°C for the amino acid. The pure amino acid prepared in this work by each procedure melted at 177–78°C.

Results and Discussion

Crambe abyssinica is one of the richest known sources of erucic acid, which makes up 55 to 60% of the seed oil fatty acids. Erucic acid may be obtained from crambe oil by fractional distillation of the free fatty acids from hydrolysis of the glycerides. Alternatively, the oil may be converted to methyl esters, which are then separated by distillation and hydrolyzed to the free acids. Interest in Crambe abyssinica as an oil seed crop for the United States is based, in part, on its potential value as a source of industrial chemicals (White and Wolff, 1966). These include brassyllic acid and 1,13-diaminotridecanoic, which are the monomers for nylon 1313 (Greene et al., 1967), and 13-aminotridecanoic acid, which is the monomer for nylon 13.

1 Present address, Chemistry Department, Auburn University, Auburn, Ala.
Partial hydrogenation of brassylonitrile was also investigated as a route to 13-aminotridecanoic acid (Figure 2). Brassylic acid was prepared by ozonolysis of erucic acid in 60% yield (Greene et al., 1967). The ammonium salt of brassylic acid was converted to the nitrile by dehydration with ammonia and polyphosphoric acid (Sorensen and Campbell, 1961). Alkaline hydrolysis of the hydrogenation product, followed by separation of its components, gave brassylic acid in 70% yield, 1,13-diaminotridecane in 20.2% yield, and the desired 13-aminotridecanoic acid in 5.7% yield.

Partial hydrolysis of brassylonitrile (Figure 2) gave excellent yields (90%) of 12-cyanododecanamide, but the conversion was low (40%). The reaction of nitriles with concentrated sulfuric acid, followed by hydrolysis to amides, is well known (Cook and Cox, 1949; Jenkins et al., 1930; Turner, 1946). It was expected that slow addition of sulfuric acid to an excess of brassylonitrile would result in the reaction of only one nitrile group in most of the molecules and that subsequent hydrolysis of the adduct would yield 12-cyanododecanamide (Lamb and White, 1939) in preference to brassylic acid diamide (Stetter and Dierichs, 1952). When 1.0 mole of dinitrile was treated with 0.5 mole of concentrated sulfuric acid and the adduct was hydrolyzed, 12-cyanododecanicot acid amide was obtained in 90% yield with 20 to 40% conversion. Brassylic acid diamide was produced in 10 to 20% conversion and the rest of the dinitrile was recovered unchanged. The cyano-amide was hydrogenated catalytically in the presence of ammonia to 13-aminotridecanoic acid amide, which was isolated as its hydrochloride in 90% yield. The amino amide was hydrolyzed to the free amino acid. Several hundred grams of 13-aminotridecanoic acid was prepared in this fashion.

Methyl erucate (Figure 1) was ozonized oxidatively to 12-carbomethoxydodecanoic acid in 57.5% yield. This monomethyl ester of brassyllic acid was converted to 12-carbomethoxydodecanoyl chloride by treatment with thionyl chloride. The crude acid chloride was converted in 95% yield to 12-carbomethoxydodecanamide. Dehydration of the amide-ester with thionyl chloride (Soffer et al., 1947) gave methyl 12-cyanododecanamide in 92% yield. Alternatively, methyl 12-cyanododecanate was realized from eruconitrile (Figure 3) in a more direct manner and in higher over-all yields. Pasero et al. (1963) showed that olefinic nitriles can be oxidatively ozonized without harmful effect to the nitrile function. Oxidative ozonolysis of eruconitrile gave 12-cyanododecanoic acid in 26% yields when isolation of the acid, as such, from the reaction mixture was attempted. However, when the mixture of crude ozonolysis products was esterified by the method of Clinton and Laskowski (1948), the yield of desired methyl ester was 65 to 70%.

Catalytic reduction of the methyl 12-cyanododecanato with cobalt-on-kieselguhr and excess ammonia was followed by basic hydrolysis of the crude reduction product (Figure 3). The pH of the hydrolyzed material was adjusted to 7.75, and very pure 13-aminotridecanoic acid separated out in 90% yield. The over-all yield of amino acid from a commercial grade of eruconitrile was 63%.

---

**Figure 1.** Conversion of methyl erucate to 13-aminotridecanoic acid

**Figure 2.** Conversion of brassylonitrile to 13-aminotridecanoic acid
Several pounds of 13-aminotridecanoic acid of analytical purity was prepared from eruconitrile by this route.

**Experimental**

**Reductive Amination of Methyl Erucate Ozonide.** Methyl erucate (88.2 grams, 0.25 mole) dissolved in methanol (500 ml.) was maintained at 3° ± 2°C. and stirred vigorously while a stream of oxygen containing 3.5% ozone by weight was passed in until slightly more than 0.25 mole of ozone had been absorbed. The cold reaction mixture was transferred to a chilled stainless steel autoclave; liquid ammonia (160 ml., 7.5 moles) and Raney nickel (18.7 grams) were added, and the autoclave was charged with hydrogen to 1400 p.s.i.g. The autoclave was heated with shaking to 100°C. and maintained at that temperature for 2 hours. After the autoclave had cooled, the catalyst was removed by filtration, and the methanol was removed in vacuo. The residue was refluxed for several hours with 10% sodium hydroxide solution, and the cloudy hydrolysate mixture was subjected to steam distillation until all volatile material was removed. The hot residue was extracted three times with hot benzene; the aqueous layer was evaporated to dryness in vacuo and treated with all volatile material was removed. The remaining solid was collected on a filter, washed with water, and dissolved in warm methanol (60 ml.). The residue was triturated with water; and then water, and dissolved in warm methanol (60 ml.). The crystalline precipitate that formed upon standing was recrystallized twice from methanol (50 and 40 ml.). Yield was 3.1 grams or 20.8% (m.p. 168-69°C, λ_max 3440, 2925, 2855, 1740 cm⁻¹).

**METHYL 13-OXIMIDOTRIDECANOATE.** Crude methyl 13-formyldodecanoate (14 grams) was refluxed for 2 hours with a mixture of hydroxylamine hydrochloride (14 grams), pyridine (70 ml.), and methanol (70 ml.). The solution was evaporated in a current of air until a white, waxy solid remained. The residue was triturated with water; the remaining solid was collected on a filter, washed with water, and dissolved in warm methanol (60 ml.). The crystalline precipitate that formed upon standing was recrystallized twice from methanol (50 and 40 ml.). Yield was 20 grams or 10.8% (m.p. 177-78°C). Anal. Calcd. for C₃₁H₅₈O₈: C, 58.80; H, 10.14; N, 3.53. Found: C, 58.60; H, 9.90; N, 3.51.

**From Methyl 13-Oximidotridecanoate.** Methyl 13-formyldodecanoate (55 grams) was dissolved in methylcyclohexane (600 ml.) and placed in a stainless steel autoclave. The autoclave was chilled in dry ice, and liquid ammonia (160 ml.) and Raney nickel catalyst (15 grams) were added. The autoclave was purged with and then charged with hydrogen to 1540 p.s.i.g. The autoclave was heated with shaking to 120°C over a 1-hour period and maintained at 115° ± 5°C for 6 hours. The product was removed with the aid of methylcyclohexane. After removal of the catalyst by filtration, the clear filtrate was evaporated in a rotary evaporator until essentially all the solvent had been removed. The oily residue was dissolved in anhydrous ether (600 ml.) and treated with methanolic hydrogen chloride (95 grams; 11% HCl by weight). The white precipitate, which formed at once, was collected on a filter, washed with ether, and dried. Yield was 20 grams or 31.5% (m.p. 152-54°C). Anal. Calcd. for C₃₁H₅₈O₈: C, 69.36; H, 10.81. Found: C, 69.14; H, 11.18.

**Analysis and Data.** The analyses agree equally well with the theoretical values for methyl 13-hydroxytridecanoate (calculated for C₃₁H₆O₈: C, 69.36; H, 11.18). GLC revealed that the sample was not pure; it was composed chiefly of two materials present in a 50 to 40 ratio. The infrared spectrum was compatible with that expected for a mixture of the aldehyde-ester and hydroxy-ester: λ_max 3440, 2925, 2855, and 1740 cm⁻¹. Anal. Calcd. for C₃₁H₅₈O₈: C, 69.36; H, 10.81. Found: C, 69.14; H, 11.18.

**CH₃(CH₂)₇CH=CH(CH₂)₁₁CN**

**Figure 3. Conversion of eruconitrile to 13-aminotridecanoic acid**

![Conversion of eruconitrile to 13-aminotridecanoic acid](image-url)
the reaction. The catalyst was removed by filtration, and the methanol was removed in vacuo. The residue was dissolved in anhydrous ether (200 ml.), and the solution was treated with methanolic hydrogen chloride (35 grams; 11% HCl by weight). The white crystalline precipitate was collected on a filter, washed with ether, and dried in vacuo to a constant weight. Yield was 3.8 grams or 51% (m.p. 151–153°C).

Partial Hydrogenation of Brassylic Acid Dinitrile and Subsequent Hydrolysis. Brassylic acid dinitrile (Greene et al., 1967) (100 grams) dissolved in p-dioxane (400 ml.) was placed in a stainless steel autoclave and chilled in dry ice. Liquid ammonia (170 ml.) and Girdler G-67RS (cobalt-on-kieselguhr) catalyst (30 grams) were added. The autoclave was sealed, purged with hydrogen, and pressurized to 1825 p.s.i.g. Shaking and heating were started; the temperature rose rapidly to 110 ± 5°C. and was held there until slightly less than half of the theoretical amount of hydrogen for complete reduction had been absorbed. The autoclave was cooled quickly, and the pressure was released as rapidly as possible. The contents were removed with the aid of p-dioxane, and the catalyst was removed by filtration. After the solvent was removed in vacuo, the residue was dissolved in ethanol (300 ml.), and concentrated hydrochloric acid (50 ml.) and water (100 ml.) were added to convert the amines to salts. The mixture was shaken in a separatory funnel; the aqueous layer was separated from the organic layer and evaporated to dryness; the solid residue was dissolved in methanol saturated with ammonia (200 ml.), and the resulting clear hydrolyzate was allowed to cool to room temperature. The ammonia, methanol, and water were removed in vacuo, the solid was suspended in ether (1000 ml.), washed with water, and dried to yield relatively pure 1,13-diaminotridecane dihydrochloride (28.2 grams; m.p. >250°C with decomposition; 20.2% of theory), from which the free diamine was isolated and identified.

The organic layer from this separation contained the nitrile-amine salt. It was refluxed for 20 hours with 10% sodium hydroxide solution (1000 ml.), and the resulting clear hydrolyzate was allowed to cool to room temperature. A thick, white precipitate formed and was collected on a filter. The filter cake was slurried with water (1000 ml.), and the insoluble portion was collected on a filter and washed with ice water and then with ethanol. The water-soluble portion was treated as described below. After being dried, the water-insoluble solid was dissolved in boiling water (400 ml.), and the pH of the solution was adjusted to 7.75 by the addition of hydrochloric acid. The white solid thus precipitated was collected on a filter, washed with water, and dried to yield relatively pure 13-aminotridecanoic acid (6.0 grams; or 5.7%; m.p. 172–74°C).

The water-soluble portion of the hydrolyzate was acidified with hydrochloric acid. The heavy precipitate was collected on a filter, washed with water, and dried to give relatively pure brassylic acid (67.5 grams or 70%; m.p. 104–08°C).

12-Cyanododecanamide. By Partial Hydrolysis of Brassylic Nitrile. Brassylic acid dinitrile (239 grams, 1.16 moles) was stirred while being treated dropwise with concentrated sulfuric acid (39 grams, 0.58 mole) at such a rate that the reaction temperature did not exceed 30°C. After completion of the addition, the clear mixture was stirred an additional 16 hours. The viscous solution was poured into 1000 ml. of ice and water in a high-speed blender. The resulting solid was collected on a filter and washed with water until the washings were neutral. After being dried in air, the solid was suspended in ether (1000 ml.) and stirred vigorously for 2 hours. The soluble portion contained the dinitrile (123 grams); the insoluble portion contained the diamide and the amide-nitrile. The insoluble portion was collected on a filter, washed with ether and rinsed with boiling ethanol (1000 ml.). The ethanol solution was allowed to stand overnight at 5°C., and the precipitate that formed was collected on a filter, dried, and suspended in boiling acetone (1000 ml.). The boiling acetone containing suspended material was filtered, and the insoluble portion was essentially pure brassylic acid diamide. Yield was 36.8 grams or 14% (m.p. 174–75°C). Stetter and Dierichs (1952) reported m.p. 177°C.

The clear acetone filtrate was evaporated in vacuo. The residue was crystallized twice from ethanol (900 and 700 ml.) to give 12-cyanododecanamide. Yield was 67.3 grams or 29.5% (m.p. 100–02°C).

Anal. Calcd. for C_{12}H_{23}N_{2}O·HCl: C, 69.80; H, 10.78; N, 12.49. Found: C, 69.47; H, 10.55; N, 12.80.

From Methyl 12-Cyanododecanoate. Methyl 12-cyanododecanoate (10 grams, prepared as described below), methanol saturated with ammonia (200 ml.), and aqueous ammonia (300 ml., 28% NH_{3}) were placed in a 1-liter flask containing a stirring bar. A rubber stopper was wired securely into the neck of the flask, and the solution was stirred at room temperature for 72 hours. At the end of this time the liquid contained a fine crystalline suspension. The ammonia, methanol, and water were removed in vacuo; the residue was washed with water and recrystallized from ethanol (60 ml.) to give 12-cyanododecanamide. Yield was 8.9 grams or 95% (m.p. 101–02°C).

13-Aminotridecanamide Hydrochloride. 12-Cyanododecanamide (50 grams) dissolved in p-dioxane (150 ml.) was placed in a stainless steel autoclave and cooled in dry ice. Liquid ammonia (100 ml.) and Girdler G-67RS (cobalt-on-kieselguhr) catalyst (10 grams) were added. The vessel was charged with hydrogen to 1740 p.s.i.g. when the temperature was 12°C. After heating and agitation were started, hydrogen absorption became detectable at about 50°C. The system was held at 110 ± 5°C until hydrogen absorption ceased (about 2 hours). The maximum pressure reached was 2080 p.s.i.g. The product, suspended in dioxane, was heated to boiling and filtered while hot through Celite to remove the catalyst. The solvent was removed in vacuo to leave a clear oil, which solidified to a hard glass. The yield of crude 13-aminotridecanamide was 46 grams or 92%. Efforts to recrystallize this free amino amide were not successful. A small sample of the amino amide was treated in ethanol solution with ethanolic hydrochloric acid. Upon cooling, a white, granular precipitate formed; this was separated and recrystallized from ethanol to give pure 13-aminotridecanamide hydrochloride (m.p. 178–80°C).

Anal. Calcd. for C_{13}H_{25}N_{2}O·HCl: C, 58.96; H, 11.04; N, 10.58. Found: C, 58.31; H, 11.37; N, 10.38.

12-Carbomethoxydodecanic Acid (Monomethyl Brassylicate). Methyl erucate (706 grams, 2.0 moles) was dissolved in glacial acetic acid (2600 ml.). The solution was treated at 25°C to 30°C, with a stream of oxygen containing ozone (3.5% by weight) at 5 liters per minute until ozone appeared in the effluent gas (approximately 8 hours). Pure oxygen was then passed through the solution at a rate of 1.5 liters per minute while the solution was heated. At approximately 65°C, an exothermic reaction began, and the temperature increased spontaneously to 115°C. This temperature was maintained for 5 hours by external heating while the flow of oxygen was continued. The
Oxygen flow was stopped, and the clear, yellow reaction mixture was allowed to stand overnight at room temperature before it was distilled in vacuo through a 15-inch Widmer column. After removal of the acetic acid, a fraction consisting of essentially pure nonanoic acid (246 grams or 78%) was recovered before the main fraction of 12-carbomethoxydodecanoic acid distilled over at 175-85 °C. at 0.5 to 0.7 mm. The yield of crude product was 328 grams or 63.5%. The crude mono ester so obtained was distilled in boiling n-heptane (2000 ml.), and the resultant solution was allowed to stand overnight at 5 °C. The crystalline product was collected on a filter, washed with cold n-heptane, and air-dried. The yield was 297.5 grams or 57.5% (m.p. 54-55 °C).


12-Carbomethoxydodecanoic Acid Anilide. This derivative was prepared by a standard procedure (Shriner et al., 1964) (m.p. 73.5-74.5 °C.).


12-Carbomethoxydodecanoic Acid p-Toluidide. This derivative was prepared by a standard procedure (Shriner et al., 1964) (m.p. 84-85 °C.).


12-Carbomethoxydodecanoyl Chloride. 12-Carbomethoxydodecanoic acid (125 grams, 0.483 mole) and thionyl chloride (175 grams, 1.46 moles) were heated together at gentle reflux for 2.5 hours. Excess thionyl chloride was removed in vacuo on a rotary evaporator, and the residue was distilled in vacuo through a simple Claisen head to give 12-carbomethoxydodecanoyl chloride. Yield was 282 grams or 67% (b.p. 140-145 °C. at 0.2 to 0.3 mm.).

12-Cyanododecanoic Acid. Eruconitrile (562 grams, 1.77 moles) dissolved in glacial acetic acid (2500 grams) was treated at 25-30 °C. with a stream of oxygen containing ozone (3% by weight) at 5 liters per minute until free ozone appeared in the effluent gas stream. Ozone addition was stopped and the flow of pure oxygen was continued at 1.5 liters per minute while the system was heated. A vigorous exothermic reaction began when the temperature reached 65 °C.; the temperature then rose rapidly until the liquid refluxed (about 118 °C.). Heating and introduction of oxygen were continued for 2 hours after refluxing began. The system was allowed to cool, and the liquid was fractionally distilled in vacuo to remove the acetic acid. The clear orange-colored residue was treated with methanol (384 grams), ethylene dichloride (1200 ml.), and concentrated sulfuric acid (12 ml.). This mixture was heated at gentle reflux for 20 hours. After being cooled to room temperature, the mixture was washed until the wash water was no longer acid. The organic layer was treated with decolorizing carbon, filtered, and distilled in vacuo to remove the ethylene dichloride and methyl nonanoate. The residue was fractionally distilled through a 15-inch Widmer column to give methyl 12-cyanododecanoate. Yield was 282 grams or 67% (b.p. 140-145 °C. at 0.2 to 0.3 mm.).

12-Cyanododecanoic Acid. Eruconitrile (19.2 grams) in acetic acid (40 ml.) was cooled to 10 °C. The vigorously stirred solution was maintained at 10 ± 2 °C. while a stream of oxygen containing ozone (5% by weight) was passed through at a rate of 0.2 liter per minute. When ozone absorption ceased, the ozone generator was turned off, and pure oxygen was passed into the reactants while the temperature was gradually increased to reflux. This condition was maintained for 1 hour before the gas flow was stopped, and the system was allowed to cool to room temperature. The acetic and nonanoic acids were removed in vacuo, and the residue was dissolved in ether (150 ml.). The resulting solution was mixed with 5% sodium hydroxide solution (150 ml.) and the aqueous layer was separated and acidified to a pH of 3 by the addition of concentrated hydrochloric acid. The oily suspension thus produced was cooled before being extracted three times with 75-ml. portions of ether; the ether extracts were dried, filtered, and evaporated in vacuo to leave a residue which was recrystallized from cyclohexane to give 12-cyanododecanoic acid. Yield was 3.5 grams or 26% (m.p. 51.5-52.5 °C.).

Anal. Calcd. for C₁₄H₈NO₂: C, 69.30; H, 10.29; N, 6.22. Found: C, 69.35; H, 9.59; N, 6.08.

13-Aminotridecanoic Acid. A solution of methyl 12-cyanododecanoate (100 grams, 0.418 mole) in p-dioxane (500 ml.) was placed in a cooled 1715-ml. bomb containing Girdler G-67RS (cobalt-on-kieselguhr) catalyst (5 grams) and liquid ammonia (100 ml.). Hydrogen was introduced to 1800 ps.i.g. at 2 °C. After heating and shaking were started, apparent hydrogen absorption began at about 50 °C. The system was held at 100 to 110 °C. for 4 hours, during which time the maximum gage pressure was 2400 p.s.i.g. After the system had cooled, the contents were removed with the aid of p-dioxane. The slurry was filtered.
cold and the filtrate evaporated on a rotary evaporator to remove the solvent. A solution of sodium hydroxide (180 grams) in water (1020 ml.) was added, and the resulting suspension was heated at gentle reflux for 16 hours. The solution was chilled in an ice bath, and the granular precipitate that formed was collected on a filter and washed with a small amount of ice water. The moist precipitate was dissolved in water (3500 ml.), heated to boiling, treated with a small amount of decolorizing carbon, and filtered hot. The filtrate was diluted with water to 7000 ml. The resulting suspension was heated to boiling, and the pH was adjusted to 7.75 by the addition of dilute hydrochloric acid. When the resulting suspension had cooled to 35° C., it was filtered. The precipitate was washed repeatedly with deionized water and once with boiling ethanol before being air dried. Yield was 90.0 grams or 94% (m.p. 176-78° C).

Anal. Calcd. for C_{13}H_{21}N_2O_2: C, 68.08; H, 11.87; N, 6.11. Found: C, 68.00; H, 11.61; N, 6.27.

A similar experiment with 50 grams of the cyano-ester gave 44 grams or 92.1% of the amino acid; 190 grams of the cyano ester gave 168 grams or 93% of the amino acid.

Virtually identical yields of the amino acid resulted from the reduction and hydrolysis of 12-cyanododecanamide in the manner described, and from hydrolysis of methyl 13-aminotridecanoate hydrochloride or 13-aminotridecanamide hydrochloride.

13-Acetamidotridecanoic Acid. This material was prepared by a standard procedure (Shriner et al., 1964) (m.p. 93–94° C.).

Anal. Calcd. for C_{15}H_{29}NO_4: C, 66.38; H, 10.77; N, 5.16. Found: C, 66.16; H, 10.73; N, 5.21.

Acknowledgment

The authors thank W. L. Mayfield who provided technical assistance. The analytical determinations were performed under the direction of W. J. Barrett.

Literature Cited


Baruch, J., Ber. 26, 1870 (1893).

Baruch, J., Ber. 27, 176 (1894).


Müller, A., Krauss, P., Ber. 65, 1354 (1932).


RECEIVED for review August 30, 1968
ACCEPTED January 22, 1969

Research supported by the Northern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture, and authorized by the Research and Marketing Act of 1946. Mention of trade names or firms does not constitute an endorsement by the U. S. Department of Agriculture.