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CERTAIN AMINO DERIVATIVES OF LAURIC ACID

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The literature records a few amino derivatives of lauric acid. By coupling lauryl chloride with certain amino acids, Bondi[1] prepared lauryl-glycine and lauryl-alanine. By the same procedure, Guerin[2] obtained lauryl-toluidines. Condensing α-bromolauryl chloride with certain amino acids in the presence of sodium hydroxide and displacing the halogen atom with an amino group through the action of ammonia, Hopwood[3] and Weizmann prepared certain dipeptides. A search in the literature reveals the lack of reference on the preparation of α-aminolauric acid. This paper describes the preparation, characteristics of α-aminolauric acid and other amino derivatives of this long chain fatty acid.

Experimental Part

Source and Preparation of Lauric Acid.—Lauryl glyceride is the principal constituent of coconut oil, a Philippine produce of great importance. The mixed methyl esters of the fatty acids in the oil were prepared and fractionated under reduced pressure. The portion distilling at 148–155° under 18 mm. pressure was collected. This fraction was redistilled and the water-white liquid ester was preserved for use. The acid obtained from the ester melted at 43–44°.[4]

Preparation of α-Aminolauric Acid.—The method adopted by Adams and Marvel[5] in preparing α-amino-*n*-caproic acid was found applicable in the synthesis of α-aminolauric acid. To fifty grams of melted lauric acid were added 7.5 cc. of phosphorus trichloride and 11 cc. of bromine. The solution was refluxed in an all-glass apparatus provided with a trap to dispose of the escaping hydrobromic acid. Digestion was continued for eight hours, increasing the temperature of the bath to 100° toward the end. The yellow precipitate of phosphorous acid was allowed to settle and the clear liquid product was decanted gently.

Ten grams of the brominated acid chloride was hydrolyzed to obtain the free α-bromolauric acid. The acid was extracted with ether and after evaporating the solvent, a liquid residue was obtained. When cooled the product solidified but at room temperature it became liquid; 9.2 g. of this liquid product was treated with ammonia at 58° for several hours. A white precipitate separated. It was filtered by suction, washed with distilled water and afterward with methyl alcohol. The colorless powder was dried in the oven at 100° and about a 51% yield was obtained.

Acetyl-α-aminolauric Acid.—A trial experiment was undertaken to see whether acetic anhydride has any effect on α-aminolauric acid. A solid was obtained which melted

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[1] Bondi, *Biochem. Z.*, **17**, 543 (1909).

[2] Guerin, *Bull. soc. chim.*, **29**, 1121 (1903).

[3] Hopwood and Weizmann, *J. Chem. Soc.*, **99**, 571–576 (1911).

[4] Taylor and Clark, THIS JOURNAL, **49**, 2829 (1927), recorded 43–44° as the melting point of lauric acid. Guerin[2] reported 44° as its melting point.

[5] Adams and Marvel, *ibid.*, **42**, 319 (1920); Fischer, *Ber.*, **36**, 2982 (1903); *ibid.*, **33**, 2381 (1900); Abderhalden, Ref. 1; Auwers and Benhardi, *Ber.*, **24**, 2222 (1891).

very much lower than the original compound. The experiment was repeated using 2 g. of the amino acid. It was digested for a few minutes with an excess of acetic anhydride. When all the solid amino acid had dissolved, the volume of solution was doubled by adding water. An oil separated which solidified. The solid was filtered, washed with water, crystallized from alcohol and dried.

Picrate of α-Aminolauric Acid.—Two grams of α-aminolauric acid was treated with 10 cc. of a concentrated alcoholic solution of picric acid. After digestion for a few minutes, the solid amino acid was completely dissolved. After diluting the alcoholic solution to twice its volume with water, a solid compound precipitated. It was filtered and washed with dilute alcohol. It was crystallized from 50% alcohol, giving pale yellowish crystals.

TABLE I

CONSTANTS AND ANALYTICAL DATA[a]

Compound	M. p., °C.	Formula	Nitrogen analyses, %	
			Calcd.	Found
α-Aminolauric acid	263 (dec.)	$C_{12}H_{25}O_2N$	6.50	6.60 6.66
Acetyl-α-aminolauric acid	93–94	$C_{14}H_{27}O_3N$	5.44	5.46 5.50
α-Aminolauric acid picrate	255–256 (dec.)	$C_{18}H_{27}O_9N_4$	12.60	12.20
Methyl α-aminolaurate	241–242 (dec.)	$C_{13}H_{27}O_2N$	6.11	6.27
Isopropyl α-aminolaurate	250–252 (dec.)	$C_{15}H_{31}O_2N$	5.38	5.39
n-Propyl α-aminolaurate	246 (dec.)	$C_{15}H_{31}O_2N$	5.38	5.23
Isobutyl α-aminolaurate	248–249 (dec.)	$C_{16}H_{33}O_2N$	5.16	5.17
Lauryl *p*-nitranilide	80	$C_{18}H_{28}O_3N$	8.75	8.55
Lauryl *m*-nitranilide	78	$C_{18}H_{28}O_3N$	8.75	8.74

[a] The writer is indebted to Professor Alfredo Santos of the School of Pharmacy, University of the Philippines, for the determination of nitrogen by micro analysis for the last six compounds.

Lauramide.—The amides of lower fatty acids have been prepared by treating their methyl esters with concentrated ammonium hydroxide and it was expected that lauramide could be obtained in this way. It was found, however, that ammonia had no effect on methyl laurate either at room temperature or at 60°. The compound was finally obtained by condensing the acid chloride with ammonia. Ten grams of lauryl chloride was added in small streams to a concentrated solution of ammonium hydroxide which was continually stirred. Methyl alcohol was added to the semi-gelatinous mass. A white solid separated from the alcoholic solution and from the filtrate two more crops of crystals were obtained when the volume of solution was reduced. Recrystallization from alcohol gave a product which was found to melt at 99–100°.[6]

When the residual filtrate was evaporated, a gelatinous mass was obtained. It was dissolved in alcohol and a compound was obtained which melted at 74–75°.[7] When the mixed melting point of this compound was taken with ammonium laurate obtained by passing ammonia into an absolute alcoholic solution of lauric acid, no depression in the melting point was noted. From the filtrate a very small amount of oily substance[8] was obtained.

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[6] Blaise and Guérin, *Bull. soc. chim.*, **29**, 1209 (1903), reported lauramide as melting at 98–99°. The literature records from 97 to 103°.

[7] Falicola, *Gazz. chim. ital.*, **40**, II, 425 (1910), reported 75° as the melting point of ammonium laurate.

[8] Blaise and Guérin, Ref. 6, obtained a small quantity of oily substance when they prepared lauramide by condensing lauryl chloride and ammonia. They characterize it as lauronitrile.

Esters of α-Aminolauric Acid

Methyl α-Aminolaurate.—Methyl α-bromolaurate was prepared first by condensing 5 g. of α-bromolauryl chloride with methyl alcohol. The ester was purified by washing its ethereal solution with dilute sodium hydroxide. After evaporating the solvent, a liquid residue was obtained. The ester was acted upon by concentrated ammonium hydroxide for several hours at 58°. The white solid compound which separated was filtered, washed with methyl alcohol and dried in the oven at 100°.

Isopropyl α-Aminolaurate.—The α-bromolaurate of isopropyl alcohol was prepared by starting with 5 g. of α-bromolauryl chloride and excess alcohol. The purified liquid ester was treated with concentrated ammonium hydroxide at 58° for several hours. The white solid that separated was filtered, washed with methyl alcohol and dried in the oven at 100°.

***n*-Propyl α-Aminolaurate.**—Five grams of the α-bromolauryl chloride prepared above was treated with excess propyl alcohol. The purified liquid ester was treated with ammonia at 58° for several hours. The white solid compound was filtered, washed with methyl alcohol and dried.

Isobutyl α-Aminolaurate.—Five grams of the α-bromo acid chloride was condensed with excess isobutyl alcohol. The liquid ester was purified by washing its ethereal solution with dilute sodium hydroxide. The halogen of the ester was displaced by an amino group when the ester was acted upon by ammonia at 58° for several hours. The amino compound separated as white precipitate from the solution. It was filtered, washed with methyl alcohol and dried.

Nitranilides

Lauryl-*p*-nitranilide.—One gram of *p*-nitraniline was condensed with a little excess of lauryl chloride. Upon warming the mixture, the solid nitraniline dissolved. The product was extracted with ether and washed with dilute alkali, afterward with distilled water. When the solvent was evaporated, a solid residue was obtained. The solid was crystallized from alcohol, giving fine short white needle crystals.

Lauryl-*m*-nitranilide.—Two grams of *m*-nitraniline was condensed with a little excess of lauryl chloride. The solid *m*-nitraniline dissolved when the mixture was warmed. The ethereal solution of the compound was washed with dilute sodium hydroxide and afterward with water. A solid residue was left when the solvent was evaporated. Crystallization from alcohol gave fine short needle crystals.

Summary

1. The preparation of α-aminolauric acid has been described.
2. Nine amino derivatives of lauric acid have been prepared.

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