mixture of 3.0 g. (0.0064 mole) of methyl (*o*-carbomethoxyphenyl 2,3,4-tri-*O*-acetyl-β-D-glucopyranosid)uronate (II), 3 ml. of ether, 8.16 g. (0.0354 mole) of hydrated barium hydroxide, and 225 ml. of boiled deionized water was shaken for 15 hours and filtered. The filtrate was warmed to 50° and saturated with carbon dioxide; the barium carbonate was filtered and the filtrate was concentrated *in vacuo* to about 100 ml. The barium salts of acetic acid and the glucuronide were precipitated by the addition of several volumes of absolute ethanol, filtered, and dissolved in the minimum volume of cold water. The barium was precipitated as the sulfate with 4 *N* sulfuric acid and centrifuged (*p*H 3). The supernant was concentrated *in vacuo* to about 10 ml., treated with 40 ml. of acetone and filtered. The filtrate was concentrated at reduced pressure, and the gummy residue was crystallized from an acetone-ether mixture. Yield 1.0 g. (50%); m.p. 145–146° (d.); $[\alpha]_D^{23}$ −75.9° (*c*, 6, water). The material is soluble in water, does not reduce Fehling's or Tollen's solution at room temperature, and gives a negative test with ferric chloride.

Anal. Calc'd for $C_{13}H_{14}O_9$: C, 49.69; H, 4.49; Equivalent weight, 157 mg./m. eq. Found: C, 49.61; H, 4.70; Equivalent weight, 160 mg./m. eq.

The conversion of I *to* II. A solution of 2.64 g. (0.0084 mole) of I in 15 ml. of methanol was cooled in ice to 0° and ethereal diazomethane[7] was added until the yellow color persisted. The excess diazomethane was destroyed with a drop of acetic acid and the colorless solution was concentrated to dryness at reduced pressure. The residue was dissolved in 15 ml. of pyridine and cooled to 0°, and 8.0 g. of acetic anhydride was added. The reaction mixture was allowed to warm to 30° and was maintained there until the exothermic reaction was complete. Then it was heated at 80° for three minutes and poured into 100 g. of crushed ice. The gum which separated was extracted with two 50-ml. portions of ether, and the ethereal extract was washed, dried over sodium sulfate, and concentrated. The residual oil was crystallized from aqueous ethanol. Yield 2.6 g. (66%); m.p. 111.5–113°. When mixed with authentic methyl (*o*-carbomethoxyphenyl 2,3,4-tri-*O*-acetyl-β-D-glucopyranosid)uronate (II) the melting point was not depressed.

Methyl (salicyloyl 2,3,4-tri-O-acetyl-β-D-glucopyranosid)uronate.[8] A mixture of 12.0 g. (0.03 mole) of methyl 1-bromo-2,3,4-tri-O-acetyl-α-D-glucuronate[2] and 9 ml. of isoquinoline was ground together in a mortar with a pestle, while cooling the mortar in an ice-bath, and 7.8 g. (0.03 mole) of silver salicylate was added in small portions with continuous mixing. After complete addition mixing was continued for 20 minutes, and the resulting mixture was allowed to stand in a desiccator for two hours and was extracted continuously with 500 ml. of ether for 15 hours. The ether extract was concentrated and the residue was crystallized from 95% ethanol. Yield, 8.6 g. (63%); m.p. 168.5–169°; $[\alpha]_D^{25}$ −31.9° (*c*, 6, chloroform). An alcoholic solution gives a reddish-brown color with ferric chloride.

Anal. Calc'd for $C_{20}H_{22}O_{12}$: C, 52.86; H, 4.88. Found: C, 52.94; H, 4.90.

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(7) Arndt, *Org. Syntheses*, Coll. Vol. II, 165 (1943).

(8) Arredondo, *et al.* (Ref. 4) have reported the synthesis of this compound (m.p. 166–170°) but have reported no analysis. The magnitude of the rotation ($[\alpha]_D^{20}$ +32.5) agrees with that reported here.

Some Derivatives of 5-Hydroxy-1-naphthylamine

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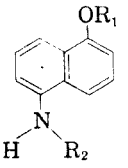
In the course of other work in these laboratories we had the occasion to prepare some derivatives of 5-hydroxy-1-naphthylamine. Since no further work with these compounds is planned in the immediate future it seems appropriate to report their preparation now.



I	R_1 = H	R_2 =	$COCH_3$
II	R_1 = $(CH_2)_5CH_3$	R_2 =	$COCH_3$
III	R_1 = C_2H_5	R_2 =	$COCH_3$
IV	R_1 = $(CH_2)_5CH_3$	R_2 =	H
V	R_1 = $(CH_2)_5CH_3$	R_2 =	$COOC_2H_5$
VI	R_1 = H	R_2 =	H
VII	R_1 = $COOC_2H_5$	R_2 =	$COOC_2H_5$

5-Acetamidonaphthol (I) was etherified with *n*-hexyl bromide using the Claisen method.[2] The homologous ethyl ether (III) was prepared by the same method. Ether II was hydrolyzed to the amine IV, which was acylated with ethyl chloroformate to give V.

Acylation of the unsubstituted 5-hydroxy-1-naphthylamine (VI) with ethyl chloroformate yielded the diacyl product VII.

EXPERIMENTAL

1-Acetamido-5-n-hexoxynaphthalene (II): A solution of 10 g. (*m*/20) of 5-acetamido-1-naphthol (I)[3] in 100 ml. of methyl ethyl ketone, 7.5 g. (slight excess) of anhydrous pulverized potassium carbonate, and 8.75 g. (slight excess) of *n*-hexyl bromide was refluxed (oil bath 110°) with mechanical stirring for 10 hours. After cooling the inorganic material was separated by suction filtration; 12.15 g. (85%) of the ether crystallized from the solution, m.p. 155–158°. The residue from the mother liquor was added to the inorganic material and was extracted with ethyl acetate. After washing the ethyl acetate solution with an ice cold 4% sodium hydroxide solution and water and drying with sodium sulfate a second small crop was obtained. Recrystallization from 96% ethanol after treatment with Norit yielded colorless hexagonal platelets, m.p. 157–158°.

Anal. Calc'd for $C_{18}H_{23}NO_2$: C, 75.76; H, 8.12; N, 4.91. Found: C, 75.60; H, 7.99; N, 5.04.

1-Acetamido-5-ethoxynaphthalene (III). In a similar way, 2 g. (*m*/100) of I was refluxed on a steam-bath during 4.5 hours with 1.5 g. of potassium carbonate and 1.7 g. of ethyl iodide in 50 ml. of acetone. The solvent was distilled off under reduced pressure and the residue was extracted with ethyl acetate and water. The ethyl acetate solution was extracted three times with an ice cold 4% sodium hydroxide solution with water and then was dried with sodium sulfate. After acidification with dil. hydrochloric acid, 400 mg. of starting material (needles, m.p. 176–177°) was recovered from the

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(2) Houben-Weyl, *Methoden der Organischen Chemie*, Vol. III, 3rd ed., p. 144, G. Thieme, Leipzig, 1930.

(3) Lockett and Short, *J. Chem. Soc.*, 787 (1939).

alkaline solution. The ethyl acetate solution yielded 1.3 g. (71% calculated on the basis of recovered material) of crystalline phenol ether. After sublimation in a high vacuum (oil-bath, 120–150°) and two recrystallizations from 96% ethanol, the m.p. of the short colorless prisms was 204–205°.

Anal. Calc'd for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.59; N, 6.11. Found: C, 73.21; H, 6.74; N, 6.20.

1-Amido-5-n-hexoxynaphthalene (IV). (*a*) *Hydrochloride.* A mixture of 1 g. (*m*/285) of II, 2 ml. of conc'd hydrochloric acid, and 7.5 ml. of 96% ethanol was refluxed for 2 hours on a steam-bath. The hydrochloride crystallized from the mixture and was washed on the funnel with dry ether; yield, 950 mg. (97%) of long fine needles. An analytical sample was recrystallized from acetone-water which contained a trace of 2 *N* HCl; m.p. 190–196° (with decomposition in a sealed capillary).

Anal. Calc'd for $C_{16}H_{22}ClNO$: C, 68.68; H, 7.93; N, 5.01; Cl, 12.67. Found: C, 68.64; H, 7.81; N, 5.21; Cl, 12.60.

(*b*). *Free amine.* The mother liquors from the recrystallizations of the hydrochloride were combined and the acetone was removed under reduced pressure. Solid sodium carbonate was added until the solution was basic to phenolphthalein. A black oil precipitated which was slightly soluble in ether. The oil was extracted with ethyl acetate and was washed with water until it was neutral. The solution was dried with magnesium sulfate and concentrated under reduced pressure. The resulting dark oil could not be crystallized. This unstable oil was distilled twice at a pressure of 0.02 mm. in an oil-bath at 90–100°.

Anal. Calc'd for $C_{16}H_{21}NO$: C, 78.97; H, 8.70; N, 5.76. Found: C, 79.40; H, 8.44; N, 6.18.

1-Carbethoxyamido-5-n-hexoxynaphthalene (V). A mixture of 600 mg. (*m*/466) of the hydrochloride of IV, 600 mg. (*m*/233) of potassium carbonate powder, 500 mg. (excess) ethyl chloroformate, 40 ml. of acetone, and 0.5 ml. of water was stirred violently for 2.5 hours at room temperature. After filtering from the salts, the solution was concentrated under reduced pressure and 620 mg. (92%) of stout prisms were obtained. An analytical sample was prepared by recrystallization from methanol (Norit), m.p. 84–85°.

Anal. Calc'd for $C_{19}H_{25}NO_3$: C, 72.35; H, 7.99; N, 4.44. Found: C, 72.41; H, 8.07; N, 4.53.

1-Carbethoxyoxy-5-carbethoxyamidonaphthalene (VII). A mixture of 2 g. (*m*/80) of 5-hydroxy-1-naphthylamine (VI), 2.5 g. (excess) of powdered potassium carbonate, 50 ml. of acetone, and 2 ml. of water was prepared. Then 3.2 g. (more than *m*/40) of ethyl chloroformate in 10 ml. of acetone was added with stirring to this mixture. After an additional 4 hours stirring at room temperature, the inorganic material was removed and the solvent was evaporated under reduced pressure. The violet-colored residue was dissolved in ethyl acetate, washed with ice-cold 2 *N* HCl, washed with ice-water until neutral, and then was dried with magnesium sulfate. The solvent was removed under reduced pressure, and after the resulting residue was recrystallized from 96% ethanol, 2.5 g. (66%) of the diacyl product was obtained. An analytical sample was recrystallized from ethanol (Norit); m.p. 173–174° (tetragonal platelets).

Anal. Calc'd for $C_{16}H_{17}NO_5$: C, 63.36; H, 5.65; N, 4.62. Found: C, 63.12; H, 5.50; N, 4.67.

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N-(ω-Bromoalkyl)saccharins and N,N′-Undecamethylenedisaccharin

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Interest has recently been shown in the reaction of sodium saccharin with alkyl halides to yield N-alkylsaccharins[1–4] and with α,ω-dihaloalkanes to yield polymethylenedisaccharins.[4] To these different series we wish to add several N-(ω-bromoalkyl)saccharins (Table I). These compounds were synthesized by the condensation of sodium saccharin with α,ω-dibromoalkanes having two to ten carbon atoms in the normal hydrocarbon chain in the presence of approximately 3% by volume of dimethylformamide. The ω-(bromoalkyl)saccharins are useful as chemical intermediates, but their low melting points and the difficulties encountered in purification make them unsuitable as derivatives. In several compounds it was necessary to pass a solution of the reaction products through a silicic acid chromatographic column to prepare the analytical sample.

In each reaction a higher-melting solid was also obtained which was proved to be the polymethylenedisaccharin by independent synthesis from the same starting materials using an excess of sodium saccharin. The melting points of these compounds agree very closely with those recently reported by Reid, Rice, and Grogen.[3]

We also wish to report the synthesis of the bis-compound containing eleven carbons in the methylene chain.

EXPERIMENTAL[5]

N-(ω-Bromoalkyl)saccharins. In a flask fitted with an efficient reflux condenser were placed 5.5 g. (0.027 mole) of anhydrous sodium saccharin, 3 ml. of dimethylformamide, and the appropriate polymethylene dibromide (0.11 mole). The mixture was heated for three hours at 160–170°. The mixture was filtered, after cooling, to remove the precipitated sodium bromide and the filtrate then was poured into 50 ml. of cold water. The organic phase was extracted with three 50-ml. portions of ether and dried. After stripping off the solvent, the excess dibromide was removed by vacuum distillation. The residue was treated with diethyl ether and the ether-insoluble impurities were removed by filtration. After removal of the ether, the product was recrystallized alternately from petroleum ether and isopropyl alcohol.

N,N′-Undecamethylenedisaccharin. Anhydrous sodium saccharin, 2.25 g. (0.011 mole), dimethylformamide (10 ml.), and 1,11-dibromoundecane, 5.7 g. (0.005 mole), were placed in a flask and refluxed for one hour. The reaction mixture was cooled and filtered to remove sodium bromide. The

(1) Merritt, Levy, and Cutter, *J. Am. Chem. Soc.*, **61**, 15 (1939).

(2) Rice, Grogan, and Reid, *J. Am. Chem. Soc.*, **75**, 4304 (1953).

(3) Rice and Pettit, *J. Am. Chem. Soc.*, **76**, 302 (1954).

(4) Reid, Rice, and Grogan, *J. Am. Chem. Soc.*, **77**, 5628 (1955).

(5) Analyses by Clark Microanalytical Laboratory, Urbana, Illinois.