hydrate. This crude material contained 96% of the theoretical electropositive chlorine content. When it was distilled at 76–78° (10 mm.) this chlorine content was found to be 99% of theoretical. The distilled product melted at 4–4.5° cor., d^{20}_4 1.544. Since the crude material is sufficiently pure for most purposes, the distillation, which is dangerous, ought to be avoided.

i-**Propyldichloramine** was prepared by a modification of the above procedures. To an ice-cooled concentrated aqueous solution of 95 g. (1 mole) of *i*-propylamine hydrochloride (prepared *in situ*) was added slowly 2.25 moles of aqueous sodium hypochlorite (prepared by adding chlorine to cold 15% aqueous sodium hydroxide, 1.6 moles hypochlorous acid per liter). Simultaneously with this addition over two to three hours was added 6 *N* hydrochloric acid at such a rate that the acidity was maintained between *p*H 5.6 and 6.6. Brom cresol green and chlor phenol red papers can be used as criteria if the solution is allowed to creep into the paper so as to give an indicator zone ahead of the bleached zone. After two hours' subsequent stirring in the cold, the heavy oil was separated, washed once with 50 cc. cold water, twice with 50-cc. portions of 5% sodium thiosulfate, once with cold water, twice with cold 50% sulfuric acid and finally twice with cold water. The crude yield (97 g., 76% of theoretical) contained 94% of the theoretical electropositive chlorine content. Distillation at 41–43° (15 mm.) resulted in 70% recovery of yellow oil (d^{20}_4 1.165; n^{23}_D 1.4572) which contained 99.8% of the calculated electropositive chlorine content.

Anal. Calcd. for $C_3H_7NCl_2$: N, 10.9. Found: N, 10.6 (av.).

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A Modification of Wenker's Method of Preparing Ethyleneimine

BY PHILIP A. LEIGHTON, WILLIAM A. PERKINS AND MELVIN L. RENQUIST

The most convenient method for laboratory preparation of ethyleneimine is that of Wenker.[1] This is a two-step process involving the preparation of β-aminoethylsulfuric acid from monoethanolamine and sulfuric acid followed by treatment of the ester with alkali. An improved technique is suggested for the first step which involves less effort, gives a better quality of the intermediate ester, and leads to higher yields.

Six moles each of ethanolamine (b. p. 169.5–170.1°) and 95% sulfuric acid are separately diluted with half their weight of water and cooled in an ice-bath. The amine is added slowly to the acid with constant stirring in a round-bottom flask also cooled in an ice-bath. The mixture is then boiled under reduced pressure using a water aspirator attached to the flask. Bumping is prevented by the addition of glass beads and the use of a full flame to maintain vigorous boiling.

When the temperature of the liquid reaches 145°, only enough heat is applied to keep the solution boiling, and when a definite turbidity appears, usually between 155 and 160°, heating is stopped unless the temperature begins to fall. Quite suddenly crystallization takes place, causing the temperature to rise sharply to about 185°. After cooling, the cake is softened with 300 cc. of 95% ethanol, removed from the flask and ground with an additional 400 cc. of ethanol followed by filtering and drying.

The yield is 90–95%. The product is white, showing no evidence of charring as was the case when the heating was carried out in an open vessel according to Wenker's directions. Approximately one hour is required to remove the water from the above quantity of material. While Wenker was able to remove only 75% of the theoretical amount of water, in the above method a trap placed between the flask and aspirator collected virtually 100% of the amount expected.

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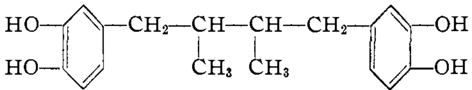
[1] H. Wenker, THIS JOURNAL, **57**, 2328 (1935).

A Synthesis of Nordihydroguaiaretic Acid

BY S. V. LIEBERMAN, GEORGE P. MUELLER AND ERIC T. STILLER

Nordihydroguaiaretic acid or 2,3-*bis*-(3,4-dihydroxybenzyl)-butane [$4,4^1$-(2,3-dimethyltetramethylene)-dipyrocatechol] (I) is of practical interest as an antioxidant used in preserving edible fats and oils.[1] It is obtained for that purpose by the alkaline extraction of dried plants of the species *Larrea divaricata*.[2]

Schroeter and his co-workers first obtained this compound from the dimethyl ether of guaiaretic acid (II) by hydrogenation and subsequent demethylation.[3] The dimethyl ether of guaiaretic acid has since been synthesized by Haworth, *et al.*[4] These two syntheses constitute a proof of the structure of nordihydroguaiaretic acid.



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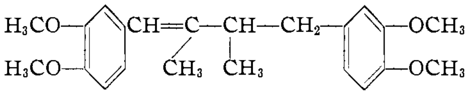

II

The new synthesis described here confirms this structure. The first step involves the coupling of two molecules of 1-piperonyl-1-bromoethane, yielding the corresponding dimethylene ether of nordihydroguaiaretic acid (IV), a compound reported by Orcutt and Bogert as a crystalline solid, m. p. 74°.[5] Apparently a mixture of the diastereoisomers of this compound is produced by the reaction of 1-piperonylethylmagnesium bro-

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[1] U. S. Patent 2,373,192; Higgins and Black, *Oil & Soap*, **21**, 277 (1944).

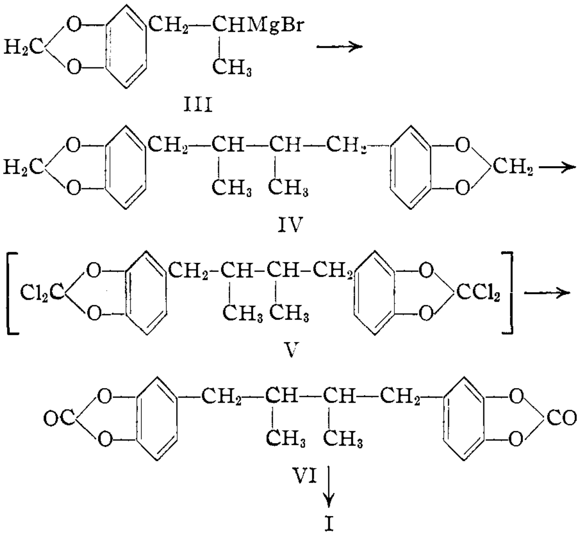
[2] U. S. Patent 2,382,475.

[3] Schroeter, Lichtenstadt and Irineu, *Ber.*, **51**, 1587 (1918).

[4] Haworth, Mavin and Sheldrick, *J. Chem. Soc.*, 1423 (1934).

[5] Orcutt and Bogert, THIS JOURNAL, **58**, 2057 (1936).

mide (III) in ethereal solution with one equivalent of iodine. While treatment with iodine gave a yield of 30%, the use of silver bromide instead of iodine gave a 21% yield. Our product was a heavy oil, b. p. 175–185° (0.1 mm.), having the correct analytical values for the dimethylene ether of nordihydroguaiaretic acid. Attempts to couple two molecules of the bromide with sodium or zinc dust in dry benzene, and with copper–bronze in decalin proved to be unsuccessful.



The dimethylene ether (IV) yielded nordihydroguaiaretic acid (I) by the following series of steps: the dimethylene ether (IV) was converted to the corresponding tetrachloro derivative (V), not isolated, which yielded the dicarbonic ester (VI) on mild hydrolysis; on saponification with acid, the dicarbonic ester (VI) yielded crystalline nordihydroguaiaretic acid (I). This product showed no depression of the melting point when mixed with an authentic sample of optically inactive nordihydroguaiaretic acid.[6]

1-(3,4-Dimethoxybenzyl)-1-bromoethane reacted with magnesium with difficulty and incompletely, yielding only 6% of the coupled product upon treatment with iodine. The phenylmagnesium bromide–cobaltous chloride free radical coupling method of Kharasch was applied.[7] None of the expected tetramethyl ether of nordihydroguaiaretic acid was obtained. The failure here, as compared to the success of this method when applied by Kharasch to the coupling of two molecules of anethole hydrobromide, may be attributed to the inactivity of the halogen in the β-position relative to its activity when adjacent to the benzene ring. The action of copper–bronze in decalin on 1-(3,4-dimethoxybenzyl)-1-bromoethane formed a small amount of heavy oil which was not further identified.

Experimental

1-Piperonyl-1-bromoethane.—Safrole, 250 g., and 200 g. of 42% hydrobromic acid were mixed in a sintered disk gas-washing bottle immersed in an ice–salt-bath. A stream of hydrogen bromide was introduced, rapidly at first, and more slowly as saturation was approached. After four hours the gas inlet was removed and the mixture permitted to stand in ice overnight. It was poured into 500 cc. of cold brine. The organic layer was diluted with ether and removed. The ether solution, washed three times with cold brine, was dried with Drierite, then anhydrous magnesium sulfate and distilled. A fraction of 218 g., b. p. 154–158° (13–14 mm.), was collected; yield 62%.

Similarly, 250 g. of methyleugenol and 121 g. of hydrobromic acid gave 326 g. of 1-(3,4-dimethoxybenzyl)-1-bromoethane, b. p. 164–167° (9.5 mm.); yield 89.5%.

2,3-bis-(3,4-Methylenedioxybenzyl)-butane (IV).—A solution of 24.3 g. (0.1 mole) of 1-piperonyl-1-bromoethane in 75 cc. of anhydrous ether was added slowly to a stirred mixture of 2.43 g. (0.1 mole) of magnesium turnings and 50 cc. of ether contained under nitrogen in the conventional Grignard apparatus. A crystal of iodine and local heating initiated the reaction which continued with refluxing by the heat of reaction for thirty minutes. After an additional hour at reflux, the heat was removed and 12.7 g. (0.05 mole) of iodine in 75 cc. of ether added to the solution. The heat of the ensuing reaction caused refluxing to resume; the small amount of unreacted magnesium dissolved quickly. After an hour of heating following this addition, the solution was cooled below 15° and hydrolyzed by the slow addition of 4% hydrochloric acid. The organic material was separated with the aid of ether and dried. A viscous, amber-colored oil, 5.0 g., was collected by distillation, b. p. 175–185° (0.1 mm.); yield 31%.

Anal. Calcd. for $C_{20}H_{22}O_4$: C, 73.62; H, 6.75. Found: C, 73.50; H, 6.94.

2,3-bis-(3,4-Carbonyldioxybenzyl)-butane (VI).[8]—2,3-bis-(3,4-Methylenedioxybenzyl)-butane, 3.5 g., was dissolved in 15 cc. of toluene and heated at reflux for three hours with 14 g. of phosphorus pentachloride. The reaction mixture was protected from moisture. The amber-colored solution was cooled and poured slowly into 300 cc. of a stirred mixture of saturated sodium carbonate and ice and the white precipitate collected, washed with cold water and dried at 50° *in vacuo;* the yield was 1.2 g. of product, m. p. 165–168°. An additional 0.25 g. was recovered by removing and evaporating the toluene layer. After two recrystallizations from toluene the compound melted at 171.5–173°.

Anal. Calcd. for $C_{20}H_{18}O_6$: C, 67.80; H, 5.08. Found: C, 67.53; H, 5.41.

Nordihydroguaiaretic Acid (I).—The product from the preceding reaction, 0.68 g., was heated at reflux in an atmosphere of nitrogen with 50 cc. of 1 *N* hydrochloric acid in 80% methanol. After two and one-half hours, during which the solid slowly dissolved, the solvent was removed under reduced pressure. The residual oil was taken up in ether and extracted with 15 cc. of a 5% sodium hydroxide–3% sodium hydrosulfite solution. The aqueous layer was separated, made just acid to litmus with dilute hydrochloric acid and permitted to stand; long colorless needles, 0.16 g., separated overnight, m. p. 185.0–186.5°.

Anal. Calcd. for $C_{18}H_{22}O_4$: C, 71.52; H, 7.28. Found: C, 71.70; H, 7.43.

A mixture of this compound with a sample of nordihydroguaiaretic acid[6] melted at 185.0–186.5°. Neither the natural nor the synthetic phenol displayed any optical rotation.

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[6] Purchased from Nordigard Corporation, 2536 W. Monroe Street, Chicago 12, Ill.

[7] Kharasch and Kleiman, *ibid.*, **65**, 491 (1943).

[8] *Cf. Organic Syntheses*, Coll. Vol. II, 1943, p. 549.