with benzyl alcohol has been prepared by the direct addition of the alcohols to mesityl oxide with the aid of an acid catalyst. Characteristic derivatives of the keto group and reduction and oxidation products give proof of the structure.

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[CONTRIBUTION FROM THE UNITED STATES DEPARTMENT OF AGRICULTURE]

THE PREPARATION OF CHLOROVANILLIN AND SOME OF ITS DERIVATIVES[1]

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A search of the available chemical literature brought to light only a preliminary note concerning the preparation and properties of a chlorinated derivative of vanillin[2] (3-methoxy-4-hydroxybenzaldehyde). The present paper describes the preparation and properties of chlorovanillin and some of its commoner aldehydic derivatives.

The position occupied by the chlorine atom has not been definitely ascertained, although orientation experiments indicate that it enters the 5 position, *ortho* to the phenolic hydroxyl. This conclusion would be the normal one on the basis of the directing influence of the groups already present. Furthermore, bromine under an environment similar to that used in the experiments here reported enters the 5 position.[3] Finally, it has been observed that while vanillin readily couples with *p*-nitrobenzene diazonium chloride in the *ortho* position to the phenolic hydroxyl, chlorovanillin fails to couple under identical experimental conditions, an indication that the position *ortho* to the hydroxyl is occupied. None of these facts can be held as more than an indication of the position of the chlorine atom. Further study is being made of this phase of the problem.

Experimental Part

Chlorovanillin.—Seventeen g. of vanillin was dissolved in 150 cc. of glacial acetic acid, and a stream of dry chlorine was bubbled through the solution at room temperature. The chlorine was rapidly absorbed, hydrochloric acid copiously evolved and the reaction mixture warmed perceptibly. After absorption had continued for 15 minutes, glistening crystals began to separate from the solution. At this point the passage of gas was discontinued. After standing for several hours the solid was separated by suction and dried. The crude yield was 18 g. A further 3 to 4 g. may be recovered from the mother liquors. The compound is practically pure, but may be completely separated

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[1] Presented at the Los Angeles meeting of the American Chemical Society, August 3-8, 1925.

[2] Menke and Bentley, THIS JOURNAL, **20,** 316 (1898).

[3] Bromovanillin has been oriented by Brady and Dunn [*J. Chem. Soc.*, **107,** 1861 (1915)] through hydrolysis of the benzonitrile from *syn.*-bromovanillin oxime to 3-methoxy-4-hydroxy-5-bromobenzoic acid previously described by Robertson [*J. Chem. Soc.*, **93,** 792 (1908)].

from traces of impurities by recrystallization from glacial acetic acid in which it is readily soluble when hot and only sparingly so when cold.

Chlorovanillin is a colorless, odorless solid, crystallizing in square plates of the tetragonal system. Optical examination showed the indices of refraction to be: $\omega = 1.662$, $\epsilon = 1.700$, $\epsilon - \omega = 0.038$, making the optical sign +. The birefringence is strong and the extinction is parallel. Heated in a capillary tube, the substance melts at 165° to a clear, colorless oil.

Anal. (Parr Bomb Method). Subs., 0.2080: AgCl, 0.1599. Calcd. for $C_8H_7O_3Cl$: Cl, 19.00. Found: 18.97.

Derivatives of Chlorovanillin.—By the usual methods a number of derivatives of chlorovanillin (Table I) have been prepared.

TABLE I

DERIVATIVES OF CHLOROVANILLIN

Compound	Anal. for N (Kjeldahl-Gunning-Arnold) Subs., g.	0.1 *N* acid consumed, cc.	N found, %	N calcd., %	M. p., °C. (corr.)	Remarks
Oxime	0.1073	5.3	6.92	6.95	172–173	Colorless, brilliant needles
Oxime hydrochloride	.1262	5.2	5.77	5.84	168–169 (decomp.)	Colorless, microcrystalline needles
Oxime hydrobromide	.1171	4.0	4.79	4.96	153–154 (decomp.)	Unstable, colorless compound, decomp. on standing
	Anal. for Cl (Parr Bomb) Subs., g.	AgCl, g.	Cl found, %	Cl calcd., %		
Hydrazone[a]	0.1061	0.0761	17.74	17.68	248–249 (decomp.)	Slightly yellow, microscopic needles
Phenylhydrazone[a]	.1132	.0621	12.81	12.82	106–107	Brilliant, orange-yellow plates
Diphenylhydrazone[a]	.0877	.0378	10.66	10.55	155–156	Hexagonal, colorless plates
Semicarbazide[a]	.1036	.0600	14.33	14.56	198–199 (decomp.)	Colorless, crystalline powder
Thiosemicarbazide[a]	.1377	.0756	13.58	13.66	216–217	Colorless needles

[a] The compounds were recrystallized from alcohol.

Ethyl α-Cyano-3-methoxy-4-hydroxy-5-chlorocinnamate.—Sixteen and four-tenths g. of chlorovanillin and 10 g. of ethyl cyano-acetate were mixed and heated on the steam-bath until a homogeneous melt was obtained. After heating to 70°, ten drops of piperidine was added. A bright yellow color was developed, the temperature rose and condensation proceeded. The beaker was heated over a free flame until a reaction began. During this reaction, which was vigorous, water as steam was given off; at its conclusion the reaction product remained as a dry, yellow powder. The crude yield was quantitative. Portions were recrystallized from alcohol and acetic acid, being obtained as light yellow, crystalline powders. Heated in a capillary tube the substance melted at 201 °C. (corr.).

Anal. (Parr Bomb). Subs., 0.1949: AgCl, 0.1011. Calcd. for $C_{13}H_{12}O_4NCl$: Cl, 12.59. Found: 12.83.

α-Cyano-3-methoxy-4-hydroxy-5-chlorocinnamic Acid.—Five g. of the ethyl ester previously described was boiled for four and one-half hours with 25 cc. of glacial acetic acid and 25 cc. of concd. hydrochloric acid. The ester gradually dissolved. At the end of this period, 25 cc. more of hydrochloric acid was added and the material allowed to stand overnight. The next day the solid material which had separated was filtered off by suction. It was purified by preparing the sodium salt (solution in 250 cc. of hot water containing 15 g. of sodium carbonate), filtering, and acidifying the cold solution with hydrochloric acid when the acid separated.

α-Cyano-3-methoxy-4-hydroxy-5-chlorocinnamic Acid is a solid, crystallizing in bright yellow needles. When heated in a capillary tube it melts at 233–234° (corr.), with decomposition.

Anal. (Parr Bomb). Subs., 0.1023: AgCl, 0.0602. Calcd. for $C_{11}H_8O_4NCl$: Cl, 13.99. Found: 14.56.

Chlorovanillal-aniline.—Three g. of chlorovanillin was dissolved in 50 cc. of warm absolute alcohol, and 1.5 g. of aniline in 12 cc. of alcohol was added. A progressive change in color took place as the reaction proceeded. After heating on the steam-bath for an hour the solution was cooled, when the Schiff base separated in yellow crystals. These were filtered by suction, washed with 50% alcohol and dried; yield, 3.5 g., or 83%. Chlorovanillal-aniline crystallizes in light yellow, prismatic crystals; m. p., 160° (corr.). The picrate, recrystallized from alcohol, melts at 226–227° to a red tar.

Anal. (Kjeldahl-Gunning-Arnold). Subs., 0.1194: 4.4 cc. of 0.1 *N* acid. Calcd. for $C_{14}H_{12}O_2NCl$: N, 5.35. Found: 5.16.

Chlorovanillal-β-naphthylamine.—This compound separates as a light yellow powder from an absolute alcohol solution containing 3 g. of chlorovanillin and 2.4 g. of naphthylamine. It may be recrystallized from alcohol or chloroform. Heated in a capillary tube it melts at 130–131° (corr.) to an orange-red oil. Treating the chloroform solution with bromine causes the separation of a brilliant orange dibromide, decomposing with evolution of gas at 150–155° (corr.).

Anal. Subs., 0.2217: 3.9 cc. of 0.1 *N* HCl. Calcd. for $C_{14}H_{12}O_2NCl$: N, 2.97. Found: 2.46.

THE PICRATE of the base was obtained as a brick-red, crystalline crust, and after recrystallization from alcohol melted at 214° (corr.), with decomposition.

Anal. (Kjeldahl-Gunning-Arnold). Subs., 0.1233: 3.8 cc. of 0.1 *N* HCl. Calcd. for $C_{24}H_{17}O_9N_4Cl$: N, 4.50. Found: 4.32.

Summary

A method has been devised for the preparation of chlorovanillin. The aldehyde is characterized by the preparation of the following derivatives: oxime, hydrazone, phenylhydrazone, diphenylhydrazone, semicarbazide and thio-semicarbazide.

Condensation of chlorovanillin with cyano-acetic ester yielded ethyl-α-cyano-3-methoxy-4-hydroxy-5-chlorocinnamate which, upon acid hydrolysis, gave the corresponding acid.

Schiff's bases were obtained by interaction of the aldehyde with aniline and β-naphthylamine.

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