233–234°. The original filtrate upon dilution with the wash water gave a crystalline precipitate. This was washed with cold glacial acetic acid and then recrystallized from glacial acetic acid to yield 18.7 g. of very light yellow needles of vanillil melting at 233–234°. The yield was 68%. The ultraviolet absorption spectrum in ethanol was identical with that of the vanillil isolated from the cupric oxide oxidation of fermented spent sulfite liquor,[4] and in alkaline ethanol it was identical with that found earlier[4] and that reported by Johnson and Marshall.[3]

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APPLETON, WISCONSIN

[CONTRIBUTION FROM THE INSTITUTE OF PAPER CHEMISTRY]

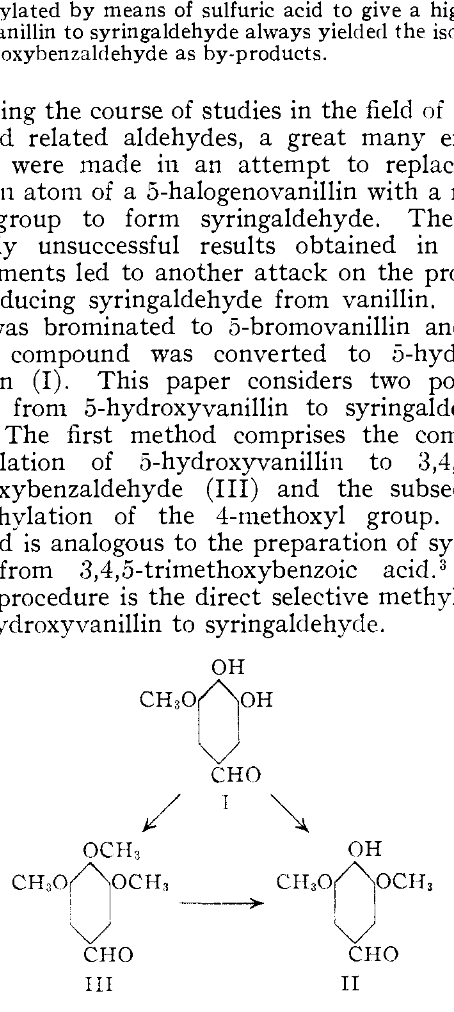
Reactions of Vanillin and its Derived Compounds. XVII.[1] A Synthesis of Syringaldehyde from Vanillin[2]

BY IRWIN A. PEARL AND DONALD L. BEYER

RECEIVED MARCH 19, 1952

Vanillin was brominated to 5-bromovanillin which in turn was hydrolyzed to 5-hydroxyvanillin. 5-Hydroxyvanillin was completely methylated with dimethyl sulfate and alkali and the resulting 3,4,5-trimethoxybenzaldehyde was partially demethylated by means of sulfuric acid to give a high yield of syringaldehyde. Attempts to selectively methylate 5-hydroxyvanillin to syringaldehyde always yielded the isomeric 5-hydroxyveratraldehyde and the completely methylated 3,4,5-trimethoxybenzaldehyde as by-products.

During the course of studies in the field of vanillin and related aldehydes, a great many experiments were made in an attempt to replace the halogen atom of a 5-halogenovanillin with a methoxyl group to form syringaldehyde. The universally unsuccessful results obtained in these experiments led to another attack on the problem of producing syringaldehyde from vanillin. Vanillin was brominated to 5-bromovanillin and the latter compound was converted to 5-hydroxyvanillin (I). This paper considers two possible routes from 5-hydroxyvanillin to syringaldehyde (II). The first method comprises the complete methylation of 5-hydroxyvanillin to 3,4,5-trimethoxybenzaldehyde (III) and the subsequent demethylation of the 4-methoxyl group. This method is analogous to the preparation of syringic acid from 3,4,5-trimethoxybenzoic acid.[3] The other procedure is the direct selective methylation of 5-hydroxyvanillin to syringaldehyde.



5-Hydroxyvanillin was methylated in high yield to 3,4,5-trimethoxybenzaldehyde by means of dimethyl sulfate and alkali. The 3,4,5-trimethoxybenzaldehyde was treated with concentrated sulfuric acid at room temperature to give an almost quantitative yield of the desired syringaldehyde. Thus syringaldehyde becomes a derivative of vanillin and obtainable from the latter in four steps, all in good yield.

The selective methylation of 5-hydroxyvanillin was not so straight forward. Methylation with one mole of potassium hydroxide and one mole of dimethyl sulfate gave a mixture of the desired syringaldehyde with 3,4,5-trimethoxybenzaldehyde, 5-hydroxyveratraldehyde (3,4-dimethoxy-5-hydroxybenzaldehyde) and unchanged 5-hydroxyvanillin. These compounds were easily separated by adsorption chromatography. Methylation with one mole of methyl iodide and two moles of alkali in accordance with the procedure employed by Bertram[4] for the preparation of vanillin from protocatechualdehyde yielded the same products, but the yield of the desired syringaldehyde was much less. Several other experiments with a variety of methylating conditions indicated that chances for a selective methylation of 5-hydroxyvanillin to syringaldehyde alone are not very good.

For the preparation of 5-hydroxyvanillin in this study the process of Bradley, Robinson and Schwarzenbach,[5] who heated 5-bromovanillin with a solution of sodium hydroxide in the presence of copper bronze,[6] was employed. Attempted hydrolysis of the 5-bromovanillin without the bronze catalyst resulted in a small yield of 5-hydroxyvanillin and the recovery of the unchanged bromovanillin. Substitution of the bronze by an active copper catalyst gave interesting side reactions. In addition to the desired 5-hydroxyvanillin, guaiacol, vanillin, vanillic acid and 5-bromovanillic acid were obtained.

Expermental

All melting points are uncorrected.

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[1] For paper XVI of this series, see THIS JOURNAL, **74**, 4260 (1952).

[2] This paper represents a portion of the results obtained in the reearch program sponsored by the Sulphite Pulp Manufacturers' Research League and conducted for the League by The Institute of Paper Chemistry. Acknowledgment is made by the Institute for permission on the part of the League to publish these results.

[3] M. T. Bogert and B. B. Coyne, THIS JOURNAL, **51**, 569 (1929).

[4] J. Bertram, German Patent 63,007 (Aug. 19, 1890); *Ber.*, **25**, R823 (1892).

[5] W. Bradley, R. Robinson and G. Schwarzenbach, *J. Chem. Soc.*, 793 (1930).

[6] The bronze powder employed was a bronze pigment, Copper Brilliant 104, manufactured by the Crescent Bronze Powder Co., Chicago, Ill.

3,4,5-Trimethoxybenzaldehyde.—5-Hydroxyvanillin was methylated with dimethyl sulfate and alkali following the procedure employed by Buck[7] for the methylation of vanillin to veratraldehyde, and the product was recrystallized from water to give 77% of pure 3,4,5-trimethoxybenzaldehyde melting at 74–75° and not depressing a mixed melting point with authentic 3,4,5-trimethoxybenzaldehyde prepared by methylating gallaldehyde according to Rosenmund and Zetzsche.[8]

Syringaldehyde.—A mixture of 10 g. of recrystallized 3,4,5-trimethoxybenzaldehyde and 56 g. of concentrated sulfuric acid was maintained at 40° in a water-bath for 8 hours and then allowed to stand overnight at room temperature. The mixture was stirred into 100 cc. of cold water and cooled. The clear solution was decanted from the little tar that separated and was extracted with ether. The ether was dried and distilled to yield 8.9 g. (96%) of almost pure (as indicated by chromatography) syringaldehyde which, upon crystallization from petroleum ether (b.p. 65–110°), melted at 109° and did not depress the melting point of a mixture with authentic syringaldehyde.[9]

The use of crude 3,4,5-trimethoxybenzaldehyde or of longer reaction times resulted in poorer yields and in much cruder products.

Reaction of 5-Hydroxyvanillin with One Mole of Potassium Hydroxide and One Mole of Dimethyl Sulfate.—5-Hydroxyvanillin (16.8 g., 0.1 mole) was treated with 7.7 g. (0.1 mole) of potassium hydroxide in 60 cc. of water and with 12.6 g. (0.1 mole) of dimethyl sulfate in the same manner employed for the complete methylation noted above. The cooled reaction mixture was extracted with ether and the ether was washed with 5% sodium hydroxide solution and then with water. The alkaline solution and washings were acidified and extracted with ether to yield 16.0 g. of oily product. The original ether solution, when dried and distilled, yielded 3.3 g. of crude 3,4,5-trimethoxybenzaldehyde melting at 70°. Recrystallization from petroleum ether (b.p. 65–120°) yielded crystals melting at 74–75° which did not depress a mixed melting point with authentic 3,4,5-trimethoxybenzaldehyde.

The oily phenolic product was chromatographed from benzene on acid-washed Magnesol and developed with benzene–ethanol (100:1). The bands were located by streaking with 2,4-dinitrophenylhydrazine, potassium permanganate and ferric chloride.[10] The leading band was eluted with acetone to yield 40% of 5-hydroxyveratraldehyde melting at 63–64° and not depressing a mixed melting point with authentic 5-hydroxyveratraldehyde.[11] The next band, upon elution, yielded 13% syringaldehyde melting at 109–110°, and the upper band yielded 20% of unchanged 5-hydroxyvanillin melting at 132–133°.

Reaction of 5-Bromovanillin with Sodium Hydroxide Solution in the Presence of Active Copper.—Active copper powder was prepared according to Brewster and Groening.[12] A mixture of 155 g. of 5-bromovanillin, 50 g. of freshly prepared active copper powder and 3000 cc. of 8% sodium hydroxide solution was placed in a one-gallon stirring autoclave, heated to 200–210° with stirring for one hour and allowed to cool with stirring. The copper was filtered, and the alkaline solution was acidified with dilute sulfuric acid. Some tar was removed by filtration, and the filtrate was concentrated to a small volume in a vacuum circulating evaporator below 50°. The tar was boiled with water and filtered hot. Cooling of this filtrate yielded 4.4 g. of crude 5-bromovanillic acid which, recrystallized from water in the presence of charcoal, yielded white needles melting at 226° and not depressing a mixed melting point with authentic 5-bromovanillic acid.[13]

The concentrated original aqueous filtrate deposited a crystalline precipitate on cooling. The crystals were filtered and recrystallized from water to yield 5.1 g. of vanillic acid melting at 210–211°. The filtrate was extracted with ether, and the ether was extracted successively with 21% sodium bisulfite, 8% sodium bicarbonate and 5% sodium hydroxide solutions. Work up of the bisulfite extract and chromatographing the residue yielded 6.6 g. of vanillin and 1.8 g. of 5-hydroxyvanillin. The bicarbonate solution yielded 0.8 g. of vanillic acid. The sodium hydroxide extract, upon acidification and extraction with ether, yielded 13.6 g. of phenolic oil which was distilled at 0.4 mm. pressure to give pure guaiacol, whose benzoate melted at 58–59° and did not depress a mixed melting point with the benzoate prepared from authentic guaiacol. Guaiacol was also recovered from the condensate of the original vacuum concentration.

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(7) J. S. Buck, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 619.

(8) K. W. Rosenmund and F. Zetzsche, *Ber.*, **51**, 594 (1918).

(9) I. A. Pearl, THIS JOURNAL, **70**, 1746 (1948).

(10) I. A. Pearl and E. E. Dickey, *ibid.*, **73**, 863 (1951).

(11) E. Späth and H. Röder, *Monatsh.*, **43**, 106 (1922).

(12) R. Q. Brewster and T. Groening, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 446.

(13) L. C. Raiford and D. J. Potter, THIS JOURNAL, **55**, 1682 (1933).

APPLETON, WISCONSIN

[CONTRIBUTION FROM THE INSTITUTE OF PAPER CHEMISTRY]

Reactions of Vanillin and its Derived Compounds. XVIII.[1] Preparation and Reactions of Lignin Model Substances Related to 5-Carboxyvanillic Acid[2,3]

BY IRWIN A. PEARL AND DONALD L. BEYER

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5-Allylvanillin was isomerized by low temperature caustic fusion to yield 5-propenylvanillin. Ethyl vanillate and ethyl orthovanillate were converted to ethyl 5-allylvanillate and ethyl 5-allylorthovanillate, respectively, and these were treated directly with fused caustic to yield 5-propenylvanillic acid and 5-propenylorthovanillic acid. Oxidation of the propenyl compounds with nitrobenzene and alkali at 160-165° gave the corresponding formyl derivatives as the major products of reaction along with other intermediates. All the formyl derivatives were oxidized by means of alkali and silver oxide to 5-carboxyvanillic acid.

The recent isolations of 5-carboxyvanillic acid and 5-carboxyvanillin from metallic oxide oxidations of lignosulfonate materials[4–6] led to a study of the preparation of these materials and of the reactions of the lignin model substances employed in their preparation. The present paper describes the preparation of the propenyl derivatives of vanillin, vanillic acid and orthovanillic acid and their oxidation with nitrobenzene and alkali to form 5-formylvanillin, 5-formylvanillic acid and 5-

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(1) For Paper XVII of this series, see THIS JOURNAL, **74**, 4262 (1952).

(2) Presented before the Division of Cellulose Chemistry at the 121st Meeting of the American Chemical Society, Milwaukee, Wisconsin, March 30 to April 3, 1952.

(3) This paper represents a portion of the results obtained in the research program sponsored by the Sulphite Pulp Manufacturers' Research League and conducted for the League by The Institute of Paper Chemistry. Acknowledgment is made by the Institute for permission on the part of the League to publish these results.

(4) I. A. Pearl, THIS JOURNAL, **72**, 1427 (1950).

(5) I. A. Pearl, *ibid.*, **72**, 2309 (1950).

(6) I. A. Pearl and D. L. Beyer, *Tappi*, **33**, 508 (1950).