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Reactions of Vanillin and its Derived Compounds. XX.¹ The Reduction of Vanillil²

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Vanillil was subjected to the action of a number of reducing agents in an attempt to prepare all of its monomolecular reduction products. In addition to the already known hydrovanilloin, three new vanillil reduction products, namely, vanilloin, desoxyvanilloin and bivanillyl were prepared in high yield directly from vanillil. 4,4'-Dihydroxy-3,3'-dimethoxystilbene could not be prepared directly from vanillil by reduction but was easily prepared in good yield by reduction of desoxyvanilloin.

A number of years ago it was shown that benzil could be reduced to almost any of its possible reduction products by the use of different reducing agents.³ Recently vanillil (4,4'-dihydroxy-3,3'-dimethoxybenzil) has been synthesized from vanillin⁴ and has become available in large quantities. The only reduction products of vanillil known heretofore were hydrovanilloin⁵ and 4,4'-dihydroxy-3,3'-dimethoxystilbene.⁶ The present paper reports the reduction of vanillil under a variety of conditions and the preparation of some of the missing members of the bivanillyl series. These vanillil reduction products will be employed as model compounds for lignin oxidation studies.

It became obvious almost immediately that there was no correlation between the reduction of vanillil and the reduction of benzil.³ Reducing agents yielding a certain reduction product with benzil either caused no reduction or gave a different reduction product when applied to vanillil. Conditions were found for the reduction of vanillil to any of its possible monomolecular reduction products except 4,4'-dihydroxy-3,3'-dimethoxystilbene and 4,4'-dihydroxy-3,3'-dimethoxyphenylbenzylcarbinol. However, these compounds could be prepared by further reduction of isolated desoxyvanilloin.

The new compounds, vanilloin (4,4'-dihydroxy-3,3'-dimethoxybenzoin), desoxyvanilloin (4,4'-dihydroxy-3,3'-dimethoxydesoxybenzoin) and bivanillyl (4,4'-dihydroxy-3,3'-dimethoxybiphenyl) were isolated in high yields and converted into their methyl ethers. The methyl ethers are all known compounds.

Ultraviolet absorption spectra of the new compounds prepared in this study were determined in 95% ethanol with a Beckman spectrophotometer at minimum slit width and are shown in Fig. 1. The ultraviolet absorption spectra of vanilloin and of desoxyvanilloin are almost identical, indicating the same configuration between the guaiacyl nuclei and verifying both assigned structures. The same is true for the ultraviolet absorption spectra for hydrovanilloin⁴ and biphenyl.

Experimental

All melting points are uncorrected.

(1) For paper XIX of this series, see *Anal. Chem.*, in press.

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(3) I. A. Pearl and W. M. Dehn, *THIS JOURNAL*, **60**, 57 (1938).

(4) I. A. Pearl, *ibid.*, **74**, 4260 (1952).

(5) H. D. Law, *J. Chem. Soc.*, **89**, 1512 (1906).

(6) H. Richtzenhain and C. von Hofe, *Ber.*, **72B**, 1890 (1939).

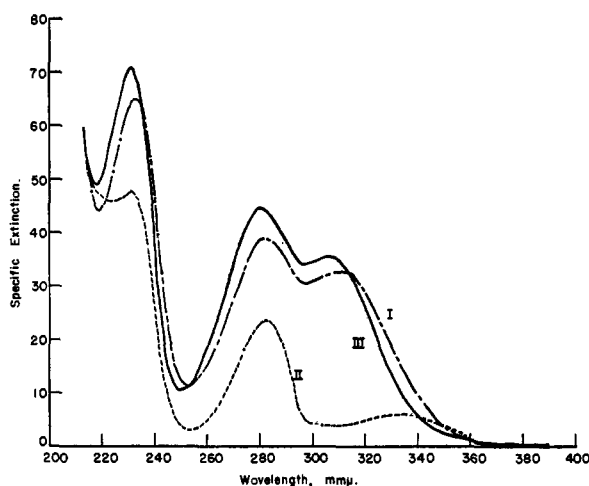


Fig. 1.—Ultraviolet absorption data for: I, vanilloin; II, bivanillyl; III, desoxyvanilloin.

Vanilloin.—A solution of 10 g. of vanillil in a boiling mixture of 400 ml. of 95% ethanol and 25 ml. of glacial acetic acid was removed from the hot-plate and treated with 10 g. of zinc dust. After a few minutes the decolorized solution was filtered and the zinc dust was extracted with boiling ethanol. The combined ethanolic extracts were concentrated under reduced pressure on the steam-bath to a volume of 100 ml. This concentrated solution was diluted with one liter of water and distilled until approximately 200 ml. of distillate was collected. The white granular precipitate which separated was filtered and washed with cold water. Recrystallization of the product (8.5 g. or 84%) from benzene gave white needles of vanilloin melting at 161–162°.

Anal. Calcd. for $C_{16}H_{16}O_6$: C, 63.15; H, 5.30; CH_2O , 20.39. Found: C, 63.18; H, 5.38; CH_2O , 20.30.

Attempted acetylation of vanilloin with acetic anhydride and pyridine gave a mixture of materials from which no pure compound could be isolated. Methylation with dimethyl sulfate in alkaline solution for a short period of time yielded veratroin as a resinous light yellow solid which could not be crystallized. The product was identical with authentic veratroin.^{7,8} Slow methylation of vanilloin in alkaline solution resulted in the formation of veratril. This finding agrees with the report of Raiford and Talbot⁷ that veratroin in alkaline solution on standing in the presence of air yields veratril.

Vanilloin was also prepared by reduction of vanillil with iron and acetic acid in 89% yield and with sodium hydro-sulfite and alkali in aqueous solution in 87% yield. The latter result was surprising because in earlier work on the oxidation of hydrovanilloin to vanillil⁴ all attempts at oxidation with alkaline agents resulted in cleavage of the "enediol" form of vanilloin to give vanillin. From this it was assumed that vanilloin was unstable in alkaline solution. The present findings prove this assumption incorrect.

Desoxyvanilloin.—A mixture of 25 g. of vanillil and 50 g. of zinc dust in 1000 ml. of 95% ethanol was heated to boiling under reflux on the steam-bath. A solution of 50 g. of am-

(7) L. C. Raiford and W. F. Talbot, *THIS JOURNAL*, **54**, 1092 (1932).

(8) G. Kubiczek, *Monatsh.*, **76**, 54 (1946).

monium chloride in 200 ml. of water at 50° was added and the mixture reheated to boiling under reflux. Decolorization took place in about 10 minutes. Boiling was continued for one hour, and the mixture was filtered. The filtrate was treated with 100 ml. of glacial acetic acid and concentrated to a small volume under reduced pressure on the steam-bath. The ethanol was replaced with water by further distillation, and the resulting mixture containing a white precipitate was diluted with water and cooled. The precipitated crystals were filtered, washed with water and dried to yield 20 g. (84%) of crude desoxyvanilloin. Recrystallization from ethanol yielded white needles melting at 154–155°.

Anal. Calcd. for $C_{16}H_{16}O_5$: C, 66.66; H, 5.60. Found: C, 66.65; H, 5.72.

Acetylation of desoxyvanilloin with acetic anhydride in pyridine and recrystallization from ethanol yielded white crystals of desoxyvanilloin diacetate (4,4'-diacetoxy-3,3'-dimethoxydesoxybenzoin) melting at 172–173°.

Anal. Calcd. for $C_{20}H_{20}O_7$: C, 64.51; H, 5.43. Found: C, 64.49; H, 5.43.

Methylation of desoxyvanilloin yielded colorless needles of desoxyveratrin melting at 100–101° which was identical with desoxyveratrin prepared by the reduction of veratril with tin and hydrochloric acid⁹ and by the reduction of veratrin with zinc and acetic acid.⁸

Desoxyvanilloin was also prepared by reduction of vanillil with iron powder and hydrochloric acid in ethanolic solution in 70% yield, with tin or tin amalgam and hydrochloric acid in ethanolic solution in 82 and 79% yields, respectively, and with zinc and aqueous sodium hydroxide in 59% yield.

Bivanillyl.—A solution of 10 g. of vanillil in 500 ml. of boiling 95% ethanol was removed from the source of heat and treated first with 20 g. of zinc dust and then gradually with 30 ml. of concentrated hydrochloric acid. The colorless mixture was filtered immediately, and the spongy zinc was extracted with boiling ethanol. The combined filtrate and washings were concentrated to a small volume under reduced pressure on the steam-bath. The concentrated solution was diluted with one liter of water, and the resulting white granular precipitate was filtered to give 9.0 g. (99%) of granular crystals of bivanillyl. Recrystallization from methanol gave fine white needles melting at 161–162° which were strongly fluorescent under ultraviolet light.

Anal. Calcd. for $C_{18}H_{18}O_4$: C, 70.05; H, 6.61. Found: C, 70.10; H, 6.74.

Bivanillyl was acetylated with acetic anhydride and pyridine. The white granular precipitate obtained on pouring into water was filtered, washed with water and recrystallized from ethanol to yield white needles of bivanillyl diacetate (4,4'-diacetoxy-3,3'-dimethoxybibenzyl) melting at 138–139°.

Anal. Calcd. for $C_{20}H_{20}O_6$: C, 67.02; H, 6.19. Found: C, 66.86; H, 6.28.

Methylation of bivanillyl yielded a light yellow compound which was recrystallized from petroleum ether (b.p.

65–110°) to yield light yellow crystals of biveratryl (3,3',-4,4'-tetramethoxybibenzyl) melting at 105–106°.

Anal. Calcd. for $C_{18}H_{22}O_4$: C, 71.50; H, 7.34. Found: C, 71.50; H, 7.34.

Fodor and Szarvas¹⁰ prepared biveratryl by heating and eliminating nitrogen from azoveratryl and recorded a melting point of 110°.

Reduction of vanillil with zinc amalgam and hydrochloric acid gave results identical with those obtained above.

Hydrovanilloin.—A solution of 10 g. of vanillil in 400 ml. of *N* sodium hydroxide was treated in small portions with 5 g. of Raney nickel alloy. A vigorous reaction took place after each addition. The decolorized solution was filtered, and the nickel precipitate was washed with water. The combined filtrate and washings were acidified with sulfur dioxide. The white inorganic precipitate which first formed finally dissolved upon saturation with sulfur dioxide, and only the organic precipitate remained. This was filtered, washed with water, and dried to yield 9.5 g. (94%) of crude hydrovanilloin melting at 218–224°. Recrystallization from ethanol gave crystals melting at 222–223° which did not depress the melting point of a mixture with authentic hydrovanilloin.⁴

4,4'-Dihydroxy-3,3'-dimethoxystilbene.—Reduction of 10 g. of desoxyvanilloin with Raney nickel alloy and alkali in the same manner yielded upon acidification with sulfur dioxide a mixture of oil and crystalline solid weighing 8.5 g. Recrystallization of the entire mixture from benzene yielded a white powder melting at 188–209° which was apparently a mixture of the *cis*- and *trans*-stilbenes. Recrystallization of the mixture from either ethanol or glacial acetic acid yielded fine crystals melting at 210–211° and not depressing a mixed melting point with authentic 4,4'-dihydroxy-3,3'-dimethoxystilbene.⁴

Acetylation of the original reaction product gave a quantitative yield of the diacetate of 4,4'-dihydroxy-3,3'-dimethoxystilbene melting at 226–227° and not depressing the melting point of a mixture with authentic 4,4'-diacetoxy-3,3'-dimethoxystilbene.⁶ Hydrolysis of the diacetate with ethanolic sodium hydroxide yielded only the *trans*-stilbene melting at 211–212°.

All attempts to isolate the pure intermediate phenylbenzylcarbinol derivative of the pure *cis*-stilbene were unsuccessful.

Unsuccessful Reductions of Vanillil.—Attempted reductions of vanillil with sodium and ethanol, zinc and ammonia in ethanolic solution, magnesium and either hydrochloric or acetic acid in ethanolic solution, and aluminum and hydrochloric acid in ethanolic solution resulted in the recovery of only the starting material. In one large scale aluminum and acid reduction, a little vanilloin was isolated.

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(9) I. Allen and S. Buck, *THIS JOURNAL*, **52**, 310 (1930).

(10) G. Fodor and P. Szarvas, *Ber.*, **76B**, 334 (1943).