

show that veratraldehyde is converted to vanillin in at least 30% yield by nitrobenzene and 2 *N* alkali at 160°, and this reaction therefore competes with the Cannizzaro oxidation-reduction change known to be produced by alkali alone.⁶ This observation is not inconsistent with the view that the *p*-hydroxyl group in vanillin may be present as an ether in the lignin precursor, and that cleavage of a 3-carbon side chain in the precursor may produce a para-substituted vanillin by the reverse of an aldol condensation.⁵

Experimental

The directions of Stone and Blundell⁷ were followed. Pure veratraldehyde, 10.0 mg., nitrobenzene, 0.06 cc., and 1.0 cc. of 2 *N* aqueous sodium hydroxide were heated together in a stainless steel micro-bomb for three hours at 160°. This bomb had a metal to metal seal with no gasket. After isolation, 0.01-cc. aliquots of the centrifuged liquor were spotted on filter paper for chromatography, the spots were made acidic with the vapor of glacial acetic acid and were then dried in the air. *n*-Butyl ether saturated with water was the developing agent, and the ascending chromatographic technique was used for 11 to 12 hr., since the descending method was inconveniently rapid. After having been located with a 2,4-dinitrophenylhydrazine spray, aldehydes were extracted with ethanol from the proper parts of the chromatogram.

The content of vanillin in the ethanol extract, 25 cc., was determined according to Lemon⁸ by adding 4 cc. of 0.2% ethanolic potassium hydroxide, diluting to 50 cc. with absolute ethanol, and examining the absorption of the solution at wave length 354 m μ . A Beckman Model DU spectrophotometer with a tungsten tube light source was used; plots were made at 5 m μ intervals over the range 320 to 400 m μ against the logarithm of the % transmission, and were assessed against calibration plots for pure vanillin at three different, known concentrations. Other control experiments showed that the recovery of vanillin by the chromatographic technique used was about 87%. Duplicate experiments gave 29.7 and 34.2% recoveries (uncorrected for the chromatographic loss) of vanillin from veratraldehyde.

The above oxidation of veratraldehyde with alkaline nitrobenzene was repeated on a 100-fold scale in another bomb. After being centrifuged, the alkaline liquors were extracted with ether to remove impurities, were acidified, and again extracted with ether to remove phenolic and acidic substances. Phenolic aldehydes were recovered from this extract in a saturated solution of sodium bisulfite, which was then acidified and extracted with ether. The residue left on evaporation of the ether was dissolved in ethanol and was used to prepare a crystalline 2,4-dinitrophenylhydrazone.⁹ After recrystallization (yield 0.276 g. or 14%), the product had the correct m.p. 270–271°, not depressed by admixture with a sample of the same m.p. made from pure vanillin.

(6) H. Decker and R. Pschorr, *Ber.*, **37**, 3403 (1904).

(7) J. E. Stone and M. J. Blundell, *Anal. Chem.*, **23**, 771 (1951).

(8) H. W. Lemon, *ibid.*, **19**, 846 (1947).

(9) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 171.

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Reaction of Acetoin and Hydroxyacetaldehyde with Cyclohexylamine¹

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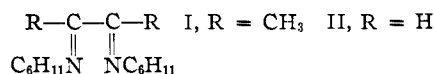
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The non-enzymatic browning of vegetables which is generally attributed to reaction of amino groups

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of amino acids or proteins with reducing sugars is being investigated by the use of simple α -hydroxy-carbonyl compounds and aliphatic amines as models for sugars and amino acids. In particular the reactions of acetoin and hydroxyacetaldehyde with primary aliphatic amines have been studied with the idea that α -hydroxyimino compounds might be isolated which would be analogous to the open chain formulas of the 1-amino-1-desoxy sugars.²

When acetoin is dissolved in anhydrous primary aliphatic amines at room temperature in the absence of air and allowed to stand several days, removal of excess amine by distillation yields colorless oils generally soluble in hydrocarbons. Short exposure to dry air produces darkening and precipitation of resin. With cyclohexylamine, however, two oxidative products could be isolated, crystalline cyclohexylamine salt of acetic acid and the new crystalline diimine, diacetyldicyclohexylimine I (R = CH₃). The mechanism whereby the primary condensation product of acetoin and amine is split to acetic acid and also oxidized to a derivative of diacetyl has not been investigated. Hydroxyacetaldehyde and cyclohexylamine in a similar way yield small quantities of the crystalline glyoxaldicyclohexylimine II (R = H). No acid has been isolated from this reaction.



The structures of the two diimines were established by ultimate analysis and by acid hydrolysis to yield diacetyl or glyoxal and cyclohexylamine. The diimines, on catalytic hydrogenation with platinum oxide, each absorb two moles of hydrogen to yield oily diamines. In the ultraviolet in methanol solution, diacetyldicyclohexylimine shows a strong absorption maximum at 213 m μ and a weak, broad inflection in the range 245–260 m μ . Glyoxaldicyclohexylimine has a maximum at 218 m μ and a second weak maximum at 267 m μ . The principal maxima are near the range where conjugated dienes absorb.

Reaction of diacetyl with cyclohexylamine yields only small quantities of the diimine, the bulk of product being of a different nature.³ Glyoxaldicyclohexylimine, however, could be prepared in good yield by reaction of 30% aqueous glyoxal solution with cyclohexylamine in alcoholic or aqueous solution.⁴ Simple crystalline aliphatic 1,2-diimines have not heretofore been described.

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(2) The importance of 1-amino-1-desoxy sugars as possible intermediates in Maillard browning reactions has been emphasized by J. Hodge and C. Rist (*THIS JOURNAL*, **74**, 1494 (1952); **7**, 316 (1952)) and A. Gottschalk and S. M. Partridge (*Nature*, **165**, 684 (1950)).

(3) J. F. Carson, *THIS JOURNAL*, **75**, 4300 (1953).

(4) K. Maurer and E. H. Woltersdorf (*Z. physiol. Chem.*, **254**, 18 (1938)) have shown that the reaction of glyoxal bisulfite with aliphatic amines in alcohol yields the corresponding *N*-alkyl- α -amino acid-*N*-alkylamide. In our experience, the diimine is obtained in quantity only with free glyoxal. Reaction of glyoxal bisulfite with cyclohexylamine in refluxing ethanol yielded only traces of the diimine and resinous material; no amide was isolated.