TABLE II

EFFECT OF SOME COMPOUNDS ON THE RELATIVE RATE OF[a] COLOR FORMATION IN 1% FURFURAL

Sample + cpd.	pH	Acceleration of color formation[b]
0.05 *M* NH_4Cl	6.7	4.0
.01 *M* sodium pyruvate	6.8	7.5
.01 *M* biacetyl[c]	6.6	25.0
.01 *M* crotonaldehyde	6.8	1.0
.005 *M* CH_2O	6.8	0
.1 *M* H_2O_2[d]	3.9	8.0
.2 *M* $NaHSO_3$	6.1	0
.2 *M* $NaHSO_3$ + 0.05 *M* glycine	6.1	0.5
.05 *M* morpholine[e]	6.7	43.0

[a] Optical densities were measured after heating samples four hours at 80° except in the case of crotonaldehyde where measurement was after twenty-four hours. [b] Values for the acceleration of color formation represent the ratios of optical densities with the compound to samples without it. [c] The optical density was corrected for the initial slight color of the solution due to the biacetyl itself. [d] In the case of hydrogen peroxide, the relative rate of color formation varies inversely with pH. [e] The sample turned yellow on mixing the two colorless components of the solution.

samples were dialyzed against 0.01 *M* sodium chloride until no more colored material could be removed from the solution. The results indicated that the yellow colored material formed in the early stages of the color reaction was freely dialyzable. However, when dark brown solutions were dialyzed, a light orange colored material remained in the dialyzate and small amounts of brown material precipitated from the solution. This indicates that the formation of the brown colored material involves a polymerization reaction. Spectrophotometric analyses of heated furfural solutions disclosed the fact that only a negligible amount of furfural is involved in forming the colored material in the system.

The colored material from several furfural-amino acid systems prepared by the method previously described was characterized. The samples were indistinguishable by spectrophotometric means, all showing the typical end-absorption curves found for products obtained from "browning" reactions. They were all relatively insoluble in water, glacial acetic acid, 95% ethanol and ether. Alkaline solutions of the products tended to disintegrate as shown by the decreased amount of material precipitable by acid with increased age of the solution. The material precipitated by acid from aged alkaline solutions is soluble in 95% ethanol.

Bromine decolorized the brown precipitates.

Summary

1. The effect of pH on the relative rate of color formation in 1% furfural at 80° is slight over the range pH 3.3 to 6.8.

2. Glycine, aspartic acid and arginine are excellent accelerators for the color reaction in furfural solutions. Their effect increases markedly with pH over the range 3.3 to 6.8.

3. In the range 1 to 4%, doubling the furfural concentration increases the relative rate of color formation in the system at 80° roughly two-fold.

4. Under the conditions examined, ammonium chloride, pyruvate, biacetyl, hydrogen peroxide and morpholine also accelerate the formation of color. Sodium bisulfite and formaldehyde decrease the relative rate of the reaction.

5. The color reaction in the studies reported involves changes of a very small magnitude with reference to the amount of furfural. Fractions of colored material isolated from several furfural systems were indistinguishable by the methods used.

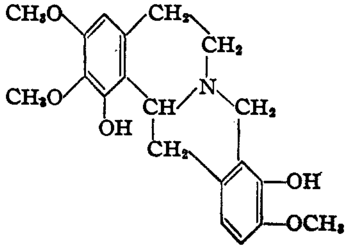
GENEVA, N. Y. RECEIVED DECEMBER 9, 1946

[CONTRIBUTION FROM THE RESEARCH LABORATORY, DOMINION RUBBER CO. LTD.]

The Alkaloids of Fumariaceous Plants. XLI. The Constitution of Capaurimine

BY RICHARD H. F. MANSKE[1]

Capaurimine is an alkaloid isolated by the author from *Corydalis pallida* Pers.[2] and from *C. Montana* (Engelm.) Britton.[3] It contains three methoxyl and two phenolic hydroxyl groups and when methylated with diazomethane, it yields capaurine O-methyl ether. Since the constitution of capaurine is already known[4] there remains only the location of the hydroxyl groups on the protoberberine skeleton. For this purpose the alkaloid was ethylated and the resulting nonphenolic base oxidized with permanganate. The expected fragments, namely, a 3,4-dialkoxyphthalic acid and a 3,4,5-trialkoxyphthalic acid, were isolated as their respective N-ethylimides. The former proved to be identical with the imide of 3-ethoxy-4-methoxyphthalic acid, a product already obtained by the author from the O-ethyl ether of scoulerine[5] and the latter was identical with the imide of 3-ethoxy-4,5-dimethoxy-phthalic acid obtained from the O-ethyl ether of capaurine.[4] The structural formula of capaurimine is therefore unambiguously represented by (I).



I

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[1] Director of Research.

[2] Manske, *Can. J. Research*, 18B, 80–83 (1940).

[3] Manske, *ibid.*, 20B, 49–52 (1942).

[4] Manske and Holmes, THIS JOURNAL, 67, 95 (1945).

[5] Manske, *Can. J. Research*, 18B, 414–417 (1940).

Experimental

A suspension of 0.12 g. of capaurimine in a small volume of ethanol was treated with an excess of an ethereal solution of diazoethane and the mixture set aside until the alkaloid had completely dissolved and the evolution of nitrogen had ceased. The solvents were then evaporated and the amorphous residue dissolved in a small volume of dilute hydrochloric acid. The solution was treated with sodium bicarbonate until the turbidity was just permanent. The cooled mixture was treated with an aqueous solution of potassium permanganate until the color of the latter persisted for two hours. A slight excess of the oxidant was destroyed with a little methanol and the heated solution filtered. The filtrate was then acidified with hydrochloric acid and exhausted with ether. The residue from the ether extract was dissolved in dilute ammonia and a small amount of oxalic acid precipitated by adding calcium chloride. The filtrate from the calcium oxalate was acidified and again exhausted with ether. The residue from the latter was sublimed from a small tube, the sublimate of mixed anhydrides dissolved in ethanol, and treated with an excess of ethylamine. The mixture was evaporated to dryness, heated to 200° for several minutes and then sublimed *very* slowly *in vacuo* at 1 mm. from a small tube in an air-bath. A small forerun of liquid material was discarded. The temperature of the air-bath was then raised to 135°. In the course of about three hours there was obtained a small amount of crystalline sublimate which when washed with pentane and recrystallized from the same solvent, melted at 84°.[6] When this was admixed with varying amounts of N-ethyl-3-ethoxy-4-methoxy-phthalimide[5] (m. p. 91°) the mixture invariably melted above 84°. A mixture containing approximately equal amounts melted at 86°. There was insufficient to admit of further purification.

A second fraction of distillate was obtained when the temperature of the air-bath was raised to 150°. The semi-solid product was extracted with several successive portions of pentane, the solvent removed from the extract and the residue recrystallized twice from hot water. The colorless fine needles thus obtained melted not quite sharply at 73° and admixture with a specimen of N-ethyl-3-ethoxy-4,5-dimethoxyphthalimide (m. p. 76°) raised this melting point by one degree. It may be added that the separation of these imides is possible primarily because the trialkoxy derivative is respectively less volatile and more soluble in pentane than the dialkoxy compound.

Summary

The constitution of capaurimine has been determined. It is a dihydroxytrimethoxytetrahydroprotoberberine.

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[6] All melting points are corrected.

GUELPH, ONTARIO RECEIVED MARCH 19, 1947

[CONTRIBUTION FROM THE DEPARTMENT OF RESEARCH IN PURE CHEMISTRY, MELLON INSTITUTE]

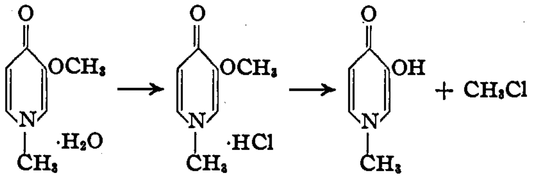
On the Structure of Leucaenine (Leucaenol) from *Leucaena Glauca* Bentham. I.

BY A. F. BICKEL[1]

Leucaenine is an amino acid obtained from the leaves and seeds of the tropical plant, *Leucaena glauca* Bentham. On methylation of leucaenine with dimethyl sulfate in alkaline medium, Bickel and Wibaut[2] obtained a decomposition product, $C_7H_{11}O_3N$(I), to which the structure of a methoxy-oxo-dihydropyridine N-hydroxymethylate was assigned. By heating the "chloro derivative" of I, ($C_7H_{10}O_2NCl$) (Ia), methyl chloride was split off and an N-methylhydroxypyridone, $C_6H_7O_2N$ (II), was formed. The N-methyl-3-hydroxypyridone-4 synthesized by Wibaut and Kleipool[3] proved to be identical with II. According to Bickel and Wibaut, therefore, I should be 4-methoxy-3-oxo-2,3-dihydropyridine N-hydroxymethylate.

In the present investigation, however, it has been shown that I is N-methyl-3-methoxypyridone-4 monohydrate; this compound has now been synthesized by heating together 3-methoxypyrone-4 and methylamine, in aqueous solution. It proved to be identical with I. This result was confirmed by identity of the picrates prepared from I and from the synthetic product, respectively.

The structures of both I and II being now definitely established, the conversion of I into II may be represented by the formulas



I Ia II

I and Ia may also be represented as 3-methoxy-4-hydroxypyridine N-hydroxymethylate and N-chloromethylate, respectively. The pyridone formula, however, accounts more readily for the addition by I of one molecule of bromine, as well as for the fact that a molecule of water may be removed from I by drying over phosphorus pentoxide at 80° (1 mm.). At first sight, the mechanism whereby methyl chloride splits off is not quite clear. In order to elucidate the course of this reaction, N-*ethyl*-3-methoxypyridone-4 was synthesized from 3-methoxypyrone-4 and ethylamine; this compound, prepared under conditions similar to those used for I, does *not* form a hydrate, thus providing further proof that I has the pyridone structure. The hydrochloride of N-ethyl-3-methoxypyridone-4, when heated, yielded N-ethyl-3-hydroxypyridone-4, thus indicating that, in the conversion of Ia into II, the methyl group attached to nitrogen does not wander. These processes, therefore, must be regarded as *intramolecular* reactions of the methoxy group with the

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[1] Visiting Fellow, Netherland-America Foundation.

[2] Bickel and Wibaut, *Rec. trav. chim.*, 65, 65 (1946).

[3] Wibaut and Kleipool, *ibid.*, 66, 24, (1947). Wibaut, *Helv. Chim. Acta*, 29, 1669 (1946).