crystallized from benzene; tiny white crystals, m. p. 218–219° (cor.).

Anal. Calcd. for $C_{34}H_{26}O_2$: C, 87.52; H, 5.62. Found: C, 87.41; H, 5.88.

1,3-Dixenyl-5,6-dimethylisobenzofuran.—It was prepared similarly to the 1,3-dixenylisobenzofuran in 78% yields; bright orange needles from toluene, m. p. 245–247° (cor.).

Anal. Calcd. for $C_{34}H_{26}O$: C, 90.67; H, 5.82. Found: C, 90.42; H, 6.01.

Summary

The preparation of certain dixenyldihydroisobenzofurans and isobenzofurans is described.

The absorption spectra and fluorescence spectra of various diphenyl and dixenyldihydroisobenzofurans and isobenzofurans were compared. The substitution of xenyl for phenyl groups in absorption spectra shifts the band maxima toward the visible by about 200–300 Å.; and in fluorescence spectra shifts the wave length at which emission begins about 375 Å. toward the red.

A discussion of fluorescence change in relation to the tendency of the molecules to give free radicals is given.

URBANA, ILLINOIS RECEIVED JUNE 3, 1940

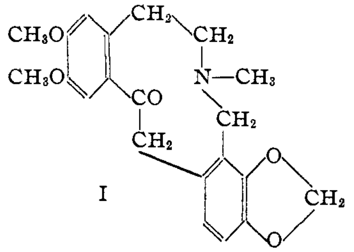
[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY, NATIONAL RESEARCH LABORATORIES]

The Alkaloids of Fumariaceous Plants. XXIX. The Constitution of Cryptocavine[1]

BY RICHARD H. F. MANSKE AND LÉO MARION

The alkaloid for which the name cryptocavine has been suggested has thus far been isolated from *Fumaria officinalis*,[2] *Dicentra chrysantha*,[3] *Corydalis ophiocarpa*[4] and *C. ochotensis*,[5] it being most abundant in the last named species.

Cryptocavine (m. p. 223°)[6] shows no optical activity in chloroform solution and yields analytical figures which agree equally well with $C_{21}H_{23}O_5N$ or with $C_{22}H_{25}O_5N$. It contains two methoxyl groups and a methylenedioxy group. Since cryptopine (I) $C_{21}H_{23}O_5N$, m. p. 221°, is not identical with cryptocavine, a mixture of the two alkaloids being liquid at 205°, the latter was at first considered by us to be $C_{22}H_{25}O_5N$. In view of the color reaction, which is that given by the protopine type of alkaloids, expression (II) seemed a reasonable one for cryptocavine. The alternative formula in which the positions of the methylenedioxy group and the two methoxyl groups are reversed has been shown to apply to corycavidine.[7]



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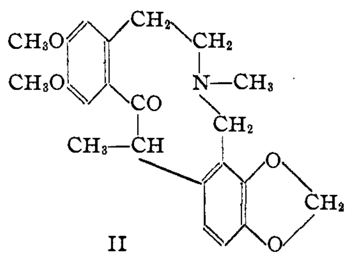

II

Degradation of a substance having formula II by Perkin's method,[8] should yield 4,5-dimethoxy-2-β-dimethylaminoethylbenzaldehyde and 2-methyl-3-acetopiperone. The former degradative base was obtained by Perkin[8] from cryptopine which also yielded instead of a ketone an aldehyde, namely, 5,6-methylenedioxy-*o*-toluic aldehyde. Our degradation experiments followed Perkin's procedure in detail. In order to obtain reference compounds we carried out the degradation of cryptopine in parallel experiments and obtained in addition to small amounts of secondary derivatives the two main fragments mentioned above, namely, the amino-aldehyde and the toluic aldehyde. Furthermore and this could not have been anticipated, cryptocavine yielded the same two degradation products. It is to be pointed out that the two degradation fragments of cryptopine together contain the nitrogen atom and all of the carbon atoms of the alkaloid plus an extra N-carbon introduced by methylation. We have looked in vain for a

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(1) Published as N. R. C. No. 917.

(2) Manske, *Can. J. Research*, **B16**, 438 (1938).

(3) Manske, *ibid.*, **B15**, 274 (1937).

(4) Manske, *ibid.*, **B17**, 51 (1939).

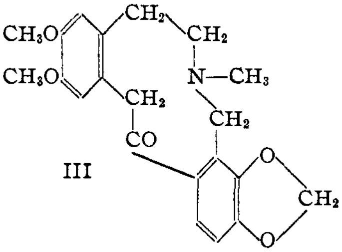
(5) Manske, *ibid.*, **B18**, 75 (1940).

(6) All melting points are corrected.

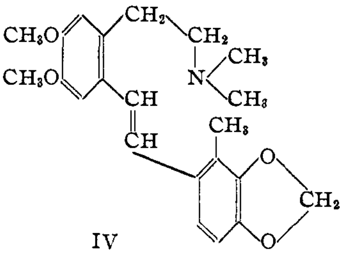
(7) Bruchhausen, *Arch. Pharm.*, **263**, 570 (1925).

(8) Perkin, *J. Chem. Soc.*, **109**, 815 (1916).

mechanism which could account for the loss of a carbon atom in our degradation of cryptocavine and we are, therefore, committed to the formula $C_{21}H_{23}O_5N$. Furthermore, the carbon skeleton would seem to be exactly that of cryptopine. In fact, we are at a loss to account for our experimental results except by one formula in which the positions of the CO-group and the adjacent CH_2-group are reversed. It may be pointed out that during the degradation the CO-group is reduced to a secondary alcohol and then water is eliminated so that the structure of the unsaturated base does not depend upon the position of the CO-group. Our unsaturated bases from the two sources were not completely identical and we attribute this partial discrepancy to the possibility of *cis-trans* isomerism which, as shown by the configuration (IV), might be expected. We, therefore, suggest formula III as a highly probable representation of cryptocavine.



III



IV

Experimental

Anhydrotetrahydromethylcryptopine.—Cryptopine was converted into its methosulfate which was reduced with sodium amalgam in acid solution and the reduced product dehydrated with acetyl chloride according to Perkin's directions.[8] Anhydrotetrahydromethylcryptopine, recrystallized from dilute methanol, melted at 106–107°.

Oxidation of Anhydrotetrahydromethylcryptopine.—The base was dissolved in acetone and oxidized with an equal weight of potassium permanganate at 3° and the products isolated as described by Perkin. The neutral fraction yielded 5,6-methylenedioxy-*o*-toluic aldehyde which after sublimation *in vacuo* and recrystallization from ether–hexane melted at 75°. It formed an oxime, m. p. 144–145°, in agreement with Perkin.

The basic fraction was distilled, b. p. 175–180° (1 mm.), dissolved in dry ether containing a little methanol and the solution treated with methyl iodide. The methiodide, which began to separate immediately, crystallized when rubbed with a glass rod, m. p. 201°. Recrystallized from methanol it separated as colorless prismatic needles, m. p. 208°.

This aldehydic base methiodide, when dissolved in acetone containing a trace of sodium hydroxide, gradually deposited pale yellow crystals which after recrystallization from boiling methanol melted at 253°. Perkin gives m. p. 255°.

Tetrahydromethylcryptocavine.—The methosulfate of cryptocavine (prepared exactly like that of cryptopine), m. p. 210–211°, 4.54 g., was dissolved in hot 5% sulfuric acid (225 cc.) and the solution kept hot in a porcelain dish on the steam-bath. Sodium amalgam (250 g.), 2.5% was added all at once, the mixture stirred vigorously and kept strongly acid by the addition from time to time of small quantities of 25% sulfuric acid. The stirring and heating were continued for one-half hour. The cooled solution was decanted from the mercury, filtered, basified with 30% sodium hydroxide (200 cc.) and the precipitated base collected in ether. The dried, oily product recovered from the extract weighed 3.44 g., yield 97.3%.

Anhydrotetrahydromethylcryptocavine. — Tetrahydromethylcryptocavine (3.44 g.) was heated just to boiling for thirty minutes with acetyl chloride (15 cc.). A white precipitate was first formed which gradually dissolved, and after *ca.* fifteen minutes a crystalline solid began to separate. After completion of the reaction the excess acetyl chloride was distilled off and the crystalline cake dissolved in boiling water. On cooling the hydrochloride of anhydrotetrahydromethylcryptocavine gradually separated as clusters of prismatic needles. These began to char at 258° and melted at 264°. The crystalline cake was redissolved in hot water and the solution basified with an excess of strong aqueous sodium hydroxide. The base, which separated as an oil, crystallized on cooling and was recrystallized from dilute methanol from which it separated as long, soft, white, silky needles, m. p. 111°, 2.6 g. (Calcd. for $C_{22}H_{27}O_4N$: C, 71.5; H, 7.3. Found: C, 70.86, 71.50; H, 7.31, 7.39.)

Oxidation of Anhydrotetrahydromethylcryptocavine.—Anhydrotetrahydromethylcryptocavine (2.2 g.) was dissolved in purified acetone (100 cc.) and the stirred and cooled (3°) solution oxidized with finely ground potassium permanganate (2.2 g.) added in small quantities at a time. When the solution had finally become discolored, the mixture was filtered and the solid washed with acetone. The combined filtrate and washings were distilled under diminished pressure and the viscous residue dissolved in ether. The filtered ether solution was extracted with several small quantities of dilute acid (1 vol. hydrochloric acid:3 vol. water), washed with water, dried over sodium chloride and distilled. The crystalline residue which was sublimed *in vacuo* produced two fractions: one boiling at 95–105° (1 mm.) and another subliming at 130° (1 mm.). The first fraction, after recrystallization from ether–hexane, melted at 75° either alone or in admixture with a specimen of 5,6-methylenedioxy-*o*-tolualdehyde (wt. 0.38 g.). It yielded an oxime, m. p. 144–145°. The second fraction was recrystallized from hexane and melted at

221°. Admixture with 5,6-methylenedioxy-*o*-toluic acid failed to depress the melting point.

The combined acid washings of the ether solution mentioned above were basified with a large excess of 50% sodium hydroxide and the precipitated base extracted with several portions of ether. The residue from the combined extracts was rapidly distilled *in vacuo*. The fraction distilling up to 200° (1 mm.) was collected and redistilled when the bulk boiled at 175–180° (1 mm.) (0.724 g.). This was dissolved in dry ether (10 cc.) containing a few drops of methanol and methyl iodide (1 cc.) was added to the solution. The methiodide which began to separate immediately, crystallized on rubbing, m. p. 225° (1.05 g.). After one recrystallization from methanol–ether, however, the melting point was 208–209°. The crystalline forms of the two products were different. The high-melting form crystallized in small prisms whereas the low-melting form separated as long prismatic needles. A mixture of the high-melting form with the corresponding cryptopine compound melted at 219° but admixture of the latter with the low-melting form did not affect the melting point.

Calcd. for $C_{14}H_{22}O_3NI$: C, 44.33; H, 5.80. Found: C, 44.64, 44.82; H, 5.76, 5.70.

Some of the methiodide (m. p. 225°) was dissolved in acetone containing a trace of potassium hydroxide and the solution allowed to stand several days. The yellow crystalline precipitate which had been deposited was recrystallized from boiling methanol. It melted at 253° either alone or in admixture with the corresponding product obtained in the cryptopine degradation.

Summary

The alkaloid cryptocavine has been found to be isomeric with cryptopine. The oxidative degradation of both alkaloids by the classical method of Perkin gave rise to identical products. It is concluded that the —CH_2CO— grouping of cryptopine is probably reversed in cryptocavine, for which a constitutional formula is suggested.

OTTAWA, CANADA RECEIVED JUNE 7, 1940

[CONTRIBUTION FROM THE NAVAL STORES RESEARCH DIVISION, BUREAU OF AGRICULTURAL CHEMISTRY AND ENGINEERING, U. S. DEPARTMENT OF AGRICULTURE]

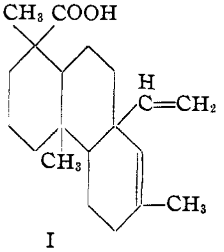
A Hydroxy-lactone from *d*-Pimaric Acid[1]

BY ELMER E. FLECK[2] AND S. PALKIN[3]

It recently has been shown[4] that concentrated sulfuric acid, at −5 to −10°, converted *d*-pimaric acid into a mixture of approximately equal parts of a non-crystalline acid and neutral substance. It has now been found that when the temperature of the sulfuric acid, in this procedure, was held at −20 to −30°, a crystalline hydroxy-lactone was obtained in 25 to 30% yields. This lactone, $C_{20}H_{32}O_3$, melted at 181–182°, $[\alpha]^{20}D$ −4°; it could be distilled unchanged at 1 mm. and it contained one active hydrogen atom. It was not found possible to prepare either the acetate or the benzoate of the indicated hydroxyl group. The tetranitromethane test showed the compound to be completely saturated.

As in the case of lactonized dihydroabietic acid[5] the lactone was only partially saponified by dilute alcoholic sodium hydroxide but was easily opened with *n*-butyl alcoholic potassium hydroxide. The free acid melted at 150–151° and contained water of crystallization. Diazomethane yielded the methyl ester, $C_{21}H_{36}O_4$, of melting point 156–157°.

Ruzicka and Sternbach[6] have recently advanced formula I for *d*-pimaric acid.



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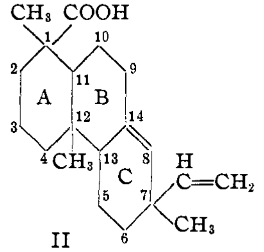

II

On the basis of this formula the point of lactonization of *d*-pimaric acid would have to be on the ethylenic side chain at C-14. This would mean the formation of an 8 or 9 membered lactone.

They also suggested formula II as a possibility wherein the double bond in ring C may be located between any of the 6, 5, 13, 14 and 8 positions. These authors regarded formula II as improbable, however, in view of the fact that only 1,7-dimethylphenanthrene and no 1-methyl-7-ethylphenanthrene could be isolated as dehydrogenation products. However, since the isolation of pure hydrocarbons from dehydrogenation

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(1) Not subject to copyright.

(2) Associate chemist.

(3) Senior chemist.

(4) Fleck and Palkin, THIS JOURNAL, **61**, 1230 (1939).

(5) Fleck and Palkin, *ibid.*, **60**, 2621 (1938).

(6) Ruzicka and Sternbach, *Helv. Chim. Acta*, **23**, 124 (1940).