[CONTRIBUTION FROM THE INSTITUTE OF MATERIA MEDICA, NATIONAL ACADEMY OF PEIPING]

Conversion of Peimine into Peiminine and Vice Versa

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In a previous paper,[1] the preparation and properties of peimine and peiminine were reported. Peimine has the composition $C_{26}H_{43}O_3N$, contains two alcoholic hydroxyl groups, and on acetylation yields a diacetyl derivative. Peiminine differs from peimine by 2 atoms of hydrogen and is better represented by the empirical formula $C_{26}H_{41}O_3N$. It contains one alcoholic hydroxyl group and one carbonyl group, forming easily a monoacetyl derivative and an oxime. These two alkaloids are convertible into each other by the oxidation of one case and reduction of the other. The present paper describes the results of oxidation and reduction. Peiminine forms easily, in addition to the oxime already described, a semicarbazone and a phenylhydrazone.

Experimental

I. Oxidation of Peimine into Peiminine.—A quantity of 0.3 g. of peimine is dissolved in 5 cc. of water on the addition of 3 drops of concentrated sulfuric acid and 0.5 cc. of Beckmann mixture containing 0.071 g. of potassium dichromate (1 atom oxygen). There appears a yellow precipitate which dissolves to form a clear, green solution. When cooled, it is made alkaline with potassium carbonate, the precipitate extracted with ether, and the ethereal solution dried and distilled. The basic residue is taken up with alcohol and converted into its hydrochloride by neutralizing with hydrochloric acid in alcohol. On addition of acetone, the first fraction of crystallization comes out as unchanged peimine hydrochloride, but the mother liquid, on concentration, gives nearly pure peiminine hydrochloride as the main product. The latter is recrystallized from a mixture of alcohol and ether, and converted into its free base as usual. Recrystallized from acetone and ether, peiminine so obtained forms fine needles, m. p. 212–213°, when dried at 110° in vacuum over phosphorus pentoxide. It is identical in every respect with the authentic sample of peiminine.

II. Reduction of Peiminine into Peimine.—A solution of 0.3 g. of peiminine in 10 cc. of absolute alcohol is treated carefully with 0.4 g. of metallic sodium cut into small pieces and the mixture refluxed on the water-bath for half an hour. The whole is neutralized with dilute hydrochloric acid and evaporated to dryness. The residue is taken up with water and the precipitate obtained on rendering the solution alkaline with potassium carbonate, is extracted with ether. The ethereal solution is dried and distilled. The residue crystallizes from acetone in minute crystals, m. p. 223°, identical with an authentic sample of peimine in all respects.

III. Semicarbazone and Phenylhydrazone of Peiminine.—A. Semicarbazone.—It is obtained by warming a mixture of 0.3 g. of peiminine hydrochloride, 0.2 g. of semicarbazide hydrochloride, 0.2 g. of sodium acetate and 10 cc. of water on the water-bath for an hour. Semicarbazone separates out on standing in the form of its hydrochloride. When recrystallized from dilute alcohol, it forms prismatic needles, m. p. over 295°, containing five molecules of water of crystallization.

Anal. Calcd. for $C_{27}H_{44}O_3N_4 \cdot HCl \cdot 5H_2O$: H_2O, 15.05. Found: H_2O, 14.78.

The free base of the semicarbazone, when liberated from its hydrochloride in the usual way, crystallizes from alcohol in needles, melting at 255–256°.

Anal. Calcd. for $C_{27}H_{44}O_3N_4$: C, 68.59; H, 9.39; N, 11.85. Found: C, 68.49; H, 9.57; N, 11.65.

B. Phenylhydrazone is obtained in the form of its hydrochloride by warming on the water-bath for a while a water solution containing 0.3 g. of peiminine hydrochloride, 0.15 g. of phenylhydrazine hydrochloride and 0.29 g. of sodium acetate. When crystallized from alcohol, it forms slightly colored prismatic needles, m. p. 266°.

Anal. Calcd. for $C_{32}H_{47}O_2N_3 \cdot HCl \cdot H_2O$: H_2O, 3.20. Found: H_2O, 3.11. Calcd. for $C_{32}H_{47}O_2N_3 \cdot HCl$: C, 70.88; H, 8.93; N, 7.75. Found: C, 70.59; H, 9.10; N, 7.71.

Summary

Peimine is easily oxidized to peiminine by means of Beckmann mixture, and peiminine can be converted again to peimine by reduction with metallic sodium in alcohol. Peimine easily forms a semicarbazone and a phenylhydrazone.

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(1) Chou and Chu, THIS JOURNAL, **63**, 2936 (1941).