SOME REACTIONS IN ALKALOIDS OF Carex brevicollis

6-AMINOBREVICOLLINE AND 6-BROMOBREVICOLLINE

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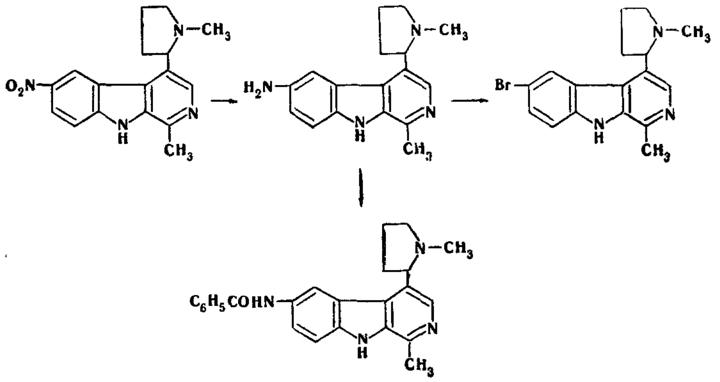
Nitro derivatives of brevicolline, brevicarpine, and methyl- and acetylbrevicarpines have been reduced to the amino compounds with stannous chloride in hydrochloric acid. 6-Aminobrevicolline, which has been isolated and characterized in the form of the benzoyl derivative, has been converted by the Sandmeyer reaction into 6-bromobrevicolline.

A few extremely unstable amino compounds of the β-carboline series are known in the literature [1, 2]. To obtain such structures by the reduction of nitro derivatives of brevicolline, brevicarpine, and methyl- and acetylbrevicarpines [3] we have used hydrogenation in the presence of Pt, Pd, and Ni under various conditions, and reduction with iron in hydrochloric acid [4], with hydrazine hydrate in the presence of Raney nickel [5], and with $SnCl_2 \cdot 2H_2O$ in hydrochloric acid solution [1]. The best results were obtained by the last method. However, because of the instability of the amino derivatives and their tendency to oxidation, it was possible to isolate only 6-aminobrevicolline in the form of the benzoyl derivative.

By the Sandmeyer reaction [1], 6-aminobrevicolline was converted into 6-bromobrevicolline.



EXPERIMENTAL

6-Aminobrevicolline. To a solution of 4.4 g of $SnCl_2 \cdot 2H_2O$ (0.02 mole) in 5 ml of conc. HCl and 20 ml of water was added 1 g (0.003 mole) of 6-nitrobrevicolline, and the mixture was heated for 2 h. The cooled and filtered solution was treated with a 10% solution of NaOH. The water was decanted from the bright yellow oil that deposited on the wall and sides of the flask, and this was dissolved in ethanol. The ethanolic solution rapidly turned red and then darkened. The small amount of precipitate that it was possible to isolate was unstable. Mp 210-214°C (subliming at 180°C).

6-Benzoylaminobrevicolline. The ethanolic solution of 6-aminobrevicolline was evaporated to dryness, and 0.2 g of the residue was suspended in a small amount of 10% NaOH. With vigorous shaking, an excess of benzoyl chloride was added until a solid precipitate had been formed, which was separated off and crystallized first from benzene and then from methanol, giving 6-benzoylaminobrevicolline dihydrochlo-

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ride, mp 212-214°C; this was converted into the base by means of concentrated ammonia. The lustrous colorless crystals of 6-benzoylaminobrevicolline, after recrystallization from methanol, melted at 175-177°C. Found, %: C 71.6; H 6.5; N 13.8. $C_{24}H_{24}N_4O \cdot H_2O$. Calculated, %: C 71.6; H 6.5; N 13.9. IR spectrum: 1650 cm^{-1} (amide band I) and 1550 cm^{-1} (amide band II) [6]. Mol. wt. 384 (mass spectrometrically).

6-Bromobrevicolline. To a solution of 1 g (3.6 mmoles) of crude 6-aminobrevicolline in 3.75 ml of water and 2.5 ml of 40% hydrobromic acid was added a solution of 0.375 g of sodium nitrite in 1.25 ml of water. This mixture was poured into a hot solution of 0.395 g of cuprous bromide in 0.75 ml of 40% hydrobromic acid, and the resulting mixture was heated in the water bath for 10 min. The precipitate that deposited on cooling was separated off and treated with ammonia. Colorless crystals with mp 240-243°C (benzene). Yield 1 g (81%). Found, %: C 59.5; H 5.3; Br 23.4; N 12.1. $C_{17}H_{18}BrN_3$. Calculated, %: C 59.3; H 5.2; Br 23.2; N 12.2. IR spectrum: 600 cm^{-1} (C–Br bond); the band at 770 cm^{-1} (ortho-substituted benzene derivatives containing four adjacent CH groups [6]) characteristic for brevicolline was absent.

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