

OXYGENATION OF TRYPTAMINE AND TRYPTOPHAN DERIVATIVES

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Irradiation (253.7 nm) of N_a, N_b -dimethyltryptamine and pyridine N-oxide produced 1,8-dimethyl-3a-hydroxy-2,3,3a,8,8a-hexahydropyrrolo[2,3-b]indole, whilst with visible light N_b -(4-cyanobutadienyl)- N_a, N_b -dimethyltryptamine was obtained. Irradiation (300W flood lamp) of tryptophan methyl ester in benzene-MeOH for 15 hr in the presence of Rose Bengal under a stream of O_2 gave 2-carbomethoxy-3a-hydroxy-1-methyl-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-b]indole (3.7 %). Photooxygenation of N_b -methyltryptamine under similar reaction conditions for 7 hr (200W Halogen lamp) produced 4a-hydroxy-2-methyl-2,3,4,4a,9,9a-hexahydro-1,2-oxazino[6,5-b]indole, providing new evidence for the intermediacy of a hydroperoxyindolenine in singlet oxygen oxidation of indoles. Our results show that both dioxygenases and monooxygenase model reactions produce the 3a-hydroxy-pyrrolo[2,3-b]indole ring system, suggesting possible pathways in the biogenesis of a number of 3a-hydroxy tricyclic pyrroloindoles.