

L-3,4-DIHYDROXYPHENYLALANINE FROM CARPOPHORES OF *HYGROCYPE CONICA* AND *H. OVINA*

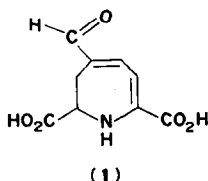
WOLFGANG STEGLICH and REGINA PREUSS

Organisch-Chemisches Institut der Technischen Universität Berlin, Germany

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Key Word Index—*Hygrocybe conica*, *H. ovina*; Hygrophoraceae; Agaricales; fungi; L-3,4-dihydroxyphenylalanine; muscaflavin.

Muscaflavin **1** has recently been isolated from yellow and red carpophores of *Hygrocybe* species [1]. The compound is considered to be derived biogenetically from 3,4-dihydroxyphenylalanine (DOPA) by metapyrocatechase [2] cleavage of the aromatic ring, followed by cyclization. Support for the correctness of this hypothesis is provided by the isolation of considerable quantities of L-DOPA from two *Hygrocybe* species. The yellow to scarlet carpophores of *Hygrocybe conica* (Scop. ex Fr.) Kummer were found to contain 3.2% of dry wt of L-DOPA together with minor amounts of muscaflavin. *Hygrocybe ovina* (Bull. ex Fr.) Kühn., a toadstool of greyish appearance, contains only L-DOPA. It is responsible for the remarkable colour changes to black and red, when the toadstools are bruised. L-DOPA appears to be rare in Basidiomycetes [3, 4] and it has only been reported in the carpophores of *Strobilomyces floccopus* [5].



EXPERIMENTAL

Carpophores of *H. conica* [6] (19.3 g, dry wt) were placed into acidified MeOH (1 litre + 5 ml N HCl) immediately after collec-

tion. Filtration and repeated extraction gave a brown-yellow solution which was adjusted to pH 7-8 with NH_4OH . Saturated aq. $\text{Pb}(\text{OAc})_2$ (25 g) was added and the mixture was kept overnight. The precipitate was centrifuged off, washed (H_2O and MeOH) and decomposed with H_2S . The resulting solution was filtered, evaporated to a small vol. and the pH brought to 3-4 with NH_4OH inducing crystallization of L-DOPA (0.62 g, 3.2%); mp > 260° (decomp.); $[\alpha]_{\text{D}}^{20} -12.2^\circ$ (c, 1 in N HCl); IR, MS, TLC and colour reactions with FeCl_3 and $\text{K}_3[\text{Fe}(\text{CN})_6]/\text{NaHCO}_3$ were identical with an authentic sample. L-DOPA was obtained from *H. ovina* [6] by the same procedure. Muscaflavin **1** was isolated in a separate experiment using the procedure of v. Ardenne *et al.* [1]. The dimethyl ester showed no differences on TLC and MS with an authentic sample.

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