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1,3,6,8-TETRAHYDROXYANTHRAQUINONE FROM *ASPERGILLUS VERSICOLOR*

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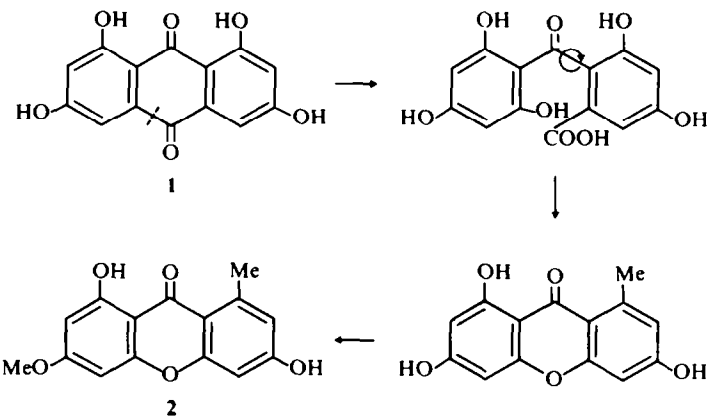
Key Word Index—*Aspergillus versicolor*; fungal metabolite; 1,3,6,8-tetrahydroxyanthraquinone; ^{13}C NMR studies.

Continuing our investigation [1–4] of *Aspergillus versicolor* (Vuillemin) Tiraboschi, we now report the isolation of 1,3,6,8-tetrahydroxyanthraquinone (**1**), a synthetic compound [5] isolated from a natural source for the first time. The identification of this compound from the mycelium of *A. versicolor* is particularly interesting biosynthetically. In fact, all anthraquinone metabolites previously isolated from this fungus are C_{18}- or C_{20}-anthraquinone derivatives, namely versicolorin A, B and C [6] and averufin [7]. Moreover, **1** is possibly the precursor of 3,8-dihydroxy-6-methoxy-1-methylanthrone (**2**) [8], since, on the basis of an aflatoxin biosynthesis [9–10], we can propose the following biosynthetic pathway (Scheme 1): the oxidative ring cleavage in **1** followed by reduction of CO_2H, recyclization and methylation, leads to **2**. The coupled ^{13}C NMR spectrum of **1** recorded in DMSO-d_6 after addition of a small amount of D_2O, reveals a wealth of fine structure. The observed long-range coupling constants confirm the assignments established on chemical grounds [12].



Scheme 1. Possible relationship between 1,3,6,8-tetrahydroxyanthraquinone and 3,8-dihydroxy-6-methoxy-1-methylanthrone.

EXPERIMENTAL

Isolation. A. versicolor (strain ATCC 34508 ex IRSAC 2172) was cultured on Czapek-Dox formule II at 25° for 25 days. The dried pigmented mycelium (480 g) was extracted with petrol and with Et_2O. The Et_2O extract was concd and chromatographed on Si gel using toluene with increasing amounts of EtOAc as eluent. The main fractions obtained were crystallized in Me_2CO to yield averufin (510 mg), versicolorin B (380 mg) and 1,3,6,8-tetrahydroxyanthraquinone (32 mg).

Identification. 1,3,6,8-Tetrahydroxyanthraquinone was identified by spectral data [5, 12] and by direct comparison with a synthetic sample. High resolution NMR spectra give: ^{1}H NMR (DMSO-d_6): δ 6.65 (2H, *d*, J = 2.5 Hz, H-2, 7), 7.19 (2H, *d*, J = 2.5 Hz, H-4, 5), 11.37 (2H, *br.s*, OH-3, 6), 12.14 (2H, *s*, OH-1, 8); ^{13}C NMR (DMSO-d_6 with D_2O): δ 108.2 (*dd*, ^1J = 162.8, ^3J = 4.6 Hz, C-2, 7), 108.8 (*d*, ^2J = 4.2 Hz, C-11, 14), 108.9 (*dd*, ^1J = 166.5, ^3J = 4.8 Hz, C-4, 5), 134.9 (*t*, ^3J = 5.5 Hz, C-12, 13), 164.4 (*d*, ^2J = 4.2 Hz, C-1, 8), 165.2 (*t*, ^2J = 4.3 Hz, C-3, 6), 181.3 (*d*, ^3J = 4.5 Hz, C-10), 188.6 (*s*, C-9).

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