

METABOLITES OF PYRENOAMYCETES X.¹ ISOLATION OF *p*-TOLUQUINONE AND TOLUQUINOL FROM *NECTRIA ERUBESCENS*

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We wish to report the isolation of *p*-toluquinone and its free reduced form, toluquinol, from the hypocrealean fungus, *Nectria erubescens* (Desm.) Phill. et Plow. Substituted toluquinones are present in many fungi and higher plants. Toluquinone, itself, a common metabolite of arthropods (1) occurs in plants only in its reduced form, usually as one of the glucosides, homoarbutin or isohomoarbutin. As far as we can ascertain, this is the first time that *p*-toluquinone and toluquinol have been isolated from a plant source.

EXPERIMENTAL

CULTURE.—A culture of *N. erubescens* (73-205), isolated and identified by Dr. Gary J. Samuels,² was inoculated into a dextrose yeast medium (2) in Fernbach flasks (26 x 400 ml). The still cultures were maintained at 25° in the dark and harvested after 48 days.

ISOLATION OF TOLUQUINONE AND TOLUQUINOL.—Culture liquid (6 liters) was extracted twice with 3 liters and twice again with 2 liters of ethyl acetate. The combined extracts were taken down to dryness under vacuum (ca. 10 mm). The crude extract (600 mg) was chromatographed over silica gel (30 g, 2 cm x 16 cm). The quinone was eluted with ethyl acetate-Skelly B (3:1) and the hydroquinone with ethyl acetate.

¹For Part IX see L. Ananthasubramanian, Susan T. Carey, and M. S. R. Nair, *Tetrahedron Lett.* 3527 (1978).

²We are grateful to Dr. Samuels of the Plant Disease Division, D.S.I.R., Auckland, N.Z. for the culture of *N. erubescens*.

YIELD.—Toluquinone 30 mg/liter; toluquinol 5 mg/liter of the culture liquid.

The quinone, mp 66-67° (hexane) MW 122 (CI-MS) had nmr signals at δ 2.05 (3H, d $J=1.5$ Hz), 6.63 (1H, m) and 6.73 (2H, broad). Its ir spectrum showed peaks at 1660 (broad) 1605. The nmr and ir spectra were identical with that of a recrystallized commercial sample (K & K Laboratories) of methyl *p*-benzoquinone. The hydroquinone crystallized from benzene had mp 123-4° (sublimes at 112°) and λ max 294 (ϵ 3,100). On oxidation with silver carbonate/celite, it yielded toluquinone, confirming its identity as toluquinol.

Presence of the quinone in the culture liquid was established by tlc. It is not unusual for a quinone-hydroquinone pair to occur in nature (3, 4); however, the culture was aerobic and, therefore, there is no way to eliminate the possibility that the quinone was formed by air oxidation after the hydroquinone was released into the culture medium.

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3. Ref. 1, p. 98-183.
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