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SHORT COMMUNICATION

HEXAMETHYL ETHER OF LEUCO-THELEPHORIC ACID FROM *CORTICIUM CAERULEUM*

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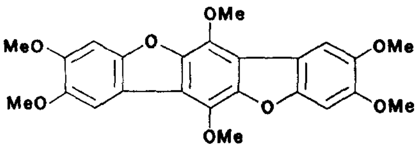
Key Word Index—*Corticium caeruleum*; Basidiomycetes; Fungi; hexamethyl ether of leucothelephoric acid.

Abstract—The hexamethyl ether of leuco-thelephoric acid has been isolated from the mycelium of *Corticium caeruleum*; its structure has been established by X-ray analysis.

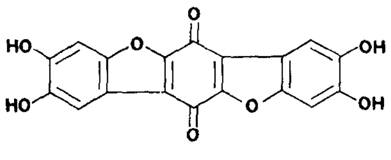
INTRODUCTION

During an examination of the deep blue mycelium of the Basidiomycete, *Corticium caeruleum* (Corticiaceae), grown on 1·5% malt agar plates, we isolated from the hexane extract a minute amount of a colorless, crystalline compound (I), m.p. 261°, by crystallization from hexane:chloroform.

An exact mass measurement (438·1315) of the molecular ion established the molecular formula $C_{24}H_{22}O_8$. This ion is the base peak in the spectrum; it is accompanied by a series of low intensity peaks separated by 15 mass units, implying the presence of several methoxyl groups. The compound was resistant to acid hydrolysis. Its IR spectrum did not show any carbonyl or hydroxyl bands. The highly characteristic UV spectrum remained unchanged on addition of acid or base; it could not be correlated with any chromophore known to us.



(I)



(II)

The very simple NMR spectrum showed signals assigned to aromatic (δ 7·62 and 7·10 ppm, singlets, 2H each) and methoxy protons (δ 4·38, 4·02 and 3·97 ppm, singlets, 6H each). On the basis of this evidence, the formula of (I) can be expanded to $C_{18}H_4O_2\ (OMe)_6$;

the simplicity of the NMR spectrum is consistent only with a very compact, highly symmetrical structure with aromatic protons and methoxyl groups occurring in pairs. The absence of any coupling in the aromatic protons precludes any *ortho* or *meta* relationship between these protons.

In view of the very small quantity of (I) available and of the well-known difficulties in the chemical degradation of such compact molecules, an X-ray crystallographic study was undertaken. A detailed account will be published elsewhere.

The compound crystallizes in space group $P2_1/c$ with cell dimensions $a = 7{\cdot}660$ Å; $b = 8{\cdot}737$ Å; $c = 15{\cdot}682$ Å; $\beta = 101{\cdot}41°$. The density, measured by flotation in KI solution, was 1·41 (± 0·01) g/cm^3 and, on a basis of two molecules in the unit cell, the calculated density was 1·415 g/cm^3. Since the space group has four-fold multiplicity, the compound must possess a center of symmetry. The structure was solved using three-dimensional diffractometer X-ray data by the direct methods of Hauptman and Karle.[1]

The crystallographic *R*-factor is about 5%, and refinement is almost complete. The constitution of (I) resulting from our work is that of the leuco-hexamethyl ether of the well-known mold and lichen terphenyl quinone, thelephoric acid[2,3] (II). This ether has not so far been isolated from any natural source; it has, however, been obtained by Gripenberg[3] on prolonged methylation of (II) with dimethyl sulfate in acetone in the presence of potassium carbonate and a small amount of pyridine.

Our observations (m.p., UV spectrum) agree acceptably with those of the literature. Comparison of our compound with a sample kindly provided by Prof. Gripenberg established their identity (m.m.p. 261–262°, identical NMR and IR (KBr) spectra). Our X-ray data thus constitute additional proof for the correctness of Gripenberg's structure of (II). It should be noted that the structure found for (I) is also entirely consistent with the deductions from nmr spectroscopy.

While several leuco-*esters* of pigments of the terphenyl-quinone group have been obtained from fungi [e.g. protoleucomelone and the leucotetrabenzoate of atromentin (Ref. 2, pp. 159 and 161, resp.)], the isolation of (I) seems to constitute the first instance of the natural occurrence of a leuco-*ether* of this series.

Corticium is usually referred to the order Polyporales (Aphyllophorales) of the class Basidiomycetes. Christiansen[4] divided this order into seven families. One of these is the family Corticiaceae which is typified by *Corticium*. Relationships among the seven families remain unclear, so that the significance of chemical similarities in different members is conjectural. Nevertheless, note should be taken that (II) was first isolated from species of *Thelephora* in the Thelephoraceae; that the same compound subsequently has been found[5] in one or two species of the other families of the order, except for the Corticiaceae; and that the closely related (I) has now been found in the Corticiaceae. Thus, all seven families that appear in Christiansen's treatment now have representatives from which either (I) or (II) has been extracted. In addition, (II) also has been found in cultures of *Clitocybe subilludens*, which is a representative of the Tricholomataceae in the order Agaricales.[6]

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[1] H. Hauptman and J. Karle, *The Solution of the Phase Problem. I. The Centrosymmetric Crystal, A.C.A. Monograph No.* 3, Polycrystal Book Service, Pittsburgh, Pa. (1953).

[2] R. H. Thomson, *Naturally Occurring Quinones*, 2nd Edition, p. 161, Academic Press, London (1971); and literature cited therein.

[3] J. Gripenberg, *Tetrahedron* **10**, 137 (1960).

[4] M. P. Christiansen, *Dansk. Botan. Ark.* **19**, 63 (1960).

[5] For literature on the occurrence of (I), see Ref. 2.

[6] G. Sullivan, R. D. Garrett and R. F. Lenehan, *J. Pharmac. Sci.* **60**, 1727 (1971).

EXPERIMENTAL

Isolation of (I). Cultures of *C. caeruleum* were grown in Petri dishes on 1·5% malt agar at room temp. After about 2 weeks, the deep blue mycelial mat was scraped off the agar surface, and extracted 3× in a Waring blendor with hexane. The hexane extracts were combined, dried (Na_2SO_4) and concentrated. Crude (I) crystallized from the concentrated extracts on standing overnight. Recrystallization from hexane: chloroform gave (I), m.p. 261° (lit.[3] 260–261°); λ_{max} (CH_3OH) 353, 338, 316, 304 and 273 nm; NMR ($CDCl_3$): 7·62 and 7·10 δ (2H each, singlets, aromatic protons), 4·38, 4·02 and 3·97 (6H each, singlets, methoxy protons). Found: M (high resolution MS) 438·1315. $C_{24}H_{22}O_8$ requires: M 438·1314.

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