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HEXA-1, 3, 5-TRIYNE - A METABOLITE OF *FOMES ANNOSUS*

A. T. Glen, S.A. Hutchinson and N.J. McCorkindale

Joint Mycological Laboratory
Departments of Botany and of Chemistry,
The University, Glasgow, W.2.

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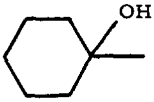
As part of a systematic survey (1) of the nature and biological effects of volatile products emitted by fungi we have found that the Basidiomycete *Fomes annosus* produces hexa-1, 3, 5-triyne (I). We have shown that this is the major constituent of the volatile products, and that the observed biological effects of culture effluents can be accounted for by the presence of this substance.

Filtered air was passed over cultures on 5% Malt Extract agar grown in diffuse light in an air conditioned room at 23°C for 7 days; the effluent vapours were condensed at -70°C. After purification, either by preparative gas-liquid chromatography of an ether extract or more simply by passing through a tube filled with phosphorus pentoxide, colourless crystals were obtained which decomposed slowly at -20° and explosively at room temperature. Solutions in pentane or ether, however, were stable for several days, even at room temperature.

Syringe reactions (2) showed that the compound was neutral and lacked carbonyl or hydroxyl functions. It did, however, absorb hydrogen readily to give a product subsequently identified as n-hexane.

$R_1 - (C \equiv C)_3 - R_2$

I $R_1 = R_2 = H$

II $R_2 = R_2 =$ 

III $R_1 = CH_3-$; $R_2 = -CH{=}CH{-}CO_2H$

IV $R_1 = HO_2C-$; $R_2 = CONH_2$

The presence of three conjugated triple bonds [characteristic u.v. spectrum (3)] with at least one ethynyl hydrogen (precipitate with ethanolic silver nitrate) strongly suggested that the product was hexa-1, 3, 5-triyne (I). Confirmation was provided by comparison with a synthetic sample (4) [u.v. spectrum, retention time*; melting point and mixed melting point of the corresponding crystalline cyclohexanone derivative (II)].

The mass spectrum of hexa-1, 3, 5-triyne (I) was very simple, being dominated by the parent ion $^m/e$ 74 together with doubly and triply charged ions. Only one other ion had an abundance more than 5% of the base peak, namely the ion at $^m/e$ 73 (again accompanied by a doubly charged ion). This cracking pattern closely parallels that of buta-1, 4-diyne (5).

* g.l.c. was carried out on 6' x $^1/8$" s.s. columns of 15% dinonyl phthalate and 20% Carbowax 1500 both on 60-80 Chromosorb W used at 60° and 75° respectively.

With the identification of hexa-1, 3, 5-triyne, a new minimum chain length is set for naturally occurring polyacetylenes. One sequence by which this compound might be derived from a C_{10} precursor of the dehydromatricaria acid (III) type (6) involves the C_8 dicarboxylic acid corresponding to the antibiotic agrocybin (IV)(7).

Hexa-1, 3, 5-triyne (I) (in a concentration comparable with that found in culture gases) showed activity against fungi (Aspergillus niger, Chaetomium globosum) and cress seedlings. Details of this work will appear elsewhere.

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