CHEMICAL STUDIES OF SOME FUNGI.

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ABSTRACT.

The reaction of chloranil with various substituted phenols under basic conditions has been studied. It has been found that the yields of benzobisbenzofuranquinonoid (1) derivatives are greater when, after initial nucleophilic attack on the ketoenoid system by the oxygen atom of the phenoxide ion, the carbon atom ortho to the vinyl--aryl ether linkage is activated towards further nucleophilic attack by the presence of a suitably orientated electron releasing substituent. The other products of the reaction mixture have been isolated and characterised, and the spectral data discussed for the derivatives of 2,3-diethoxydibenzofuran-1,4-quinone which were obtained in this way.

The mass spectra of benzobisbenzofuranquinones and the corresponding quinol acetates have been examined. Facile loss of methyl radicals from aromatic methoxy groups and ketene from the acetate derivatives was observed. Decarbonylation and fragmentation involving the heterocyclic ring system resulted in peaks of only minor intensity. The ready loss of substituents as described above is explained by the resulting formation of resonance stabilized quinonoid ions.

Some chemical constituents of Peniophora gigantea have been isolated and characterised. 2',3',6'-Trimethoxy-p-terphenyl (25) was obtained which represents the first methoxylated p-terphenyl isolated from a fungus. Also obtained was a mixture comprising two compounds, $C_{30}H_{48}$ and $C_{30}H_{50}$. On mass spectral grounds these are proposed to be the pentacyclic

triterpenes, lupa-15,19(22)-diene (33) and lup--19(22)-ene (34) respectively.

14,15-Epoxy-2-ketomanoyl oxide (44) has been microbiologically hydroxylated by Calonectria decora to form 1β,7α-dihydroxy-14,15-epoxy-2--ketomanoyl oxide (45). The positions of the hydroxy groups were determined from the peaks arising from fragmentations in rings A and B in the mass spectrum. Strong intramolecular hydrogen bonding observed in the i.r. spectrum supported the equatorial conformation of the hydroxy group at C1 whilst the facile loss of water upon electron impact and the presence of a signal corresponding to an equatorial carbinol proton in the n.m.r. infers that at C7 is axial.

Finally, it has been proposed that the structures of the blue pigments, corticins A and B, isolated from Corticium caeruleum by Dean are 2,6,9-trihydroxy--3,8,12-trimethoxybenzo[1,2-b:4,5-b']bisbenzofuran and 2,3,8,9-tetramethoxybenzo[1,2-b:4,5-b']bisbenzofuran-6,12-dione respectively. The n.m.r. spectrum of corticin A triacetate and comparison of the mass spectra of these compounds and those authentic samples prepared synthetically support these structures.

Erratum p105 para 1: Should read (R = Ac).