The Chemistry of the "Insoluble Red Woods." Part V. Pterocarpin and an Oxidation Product of Homopterocarpin.*

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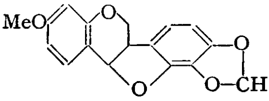
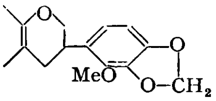
The structure assigned to pterocarpin (*J.*, 1940, 787) has been confirmed by the synthesis of (±)-7 : 2′-dimethoxy-3′ : 4′-methylenedioxy*iso*flavan (II), *i.e.*, the methyl ether of (±)-dihydropterocarpin.

The oxidation product, $C_{15}H_9O_3(OMe)_3$, of homopterocarpin (*loc. cit.*) has been shown to be 3-hydroxy-7 : 2′ : 4′-trimethoxy*iso*flavan-4-one (VI).

THE constitution (I) assigned to pterocarpin from an examination of its degradation products (Part I, *J.*, 1940, 787) has now been supported by a synthesis of (±)-7 : 2′-dimethoxy-3′ : 4′-methylenedioxy*iso*flavan (II) of which *O*-methyldihydropterocarpin is the (—)-form. 2-Hydroxy-4 : 2′-dimethoxy-3′ : 4′-methylenedioxydeoxybenzoin ((III; R = Me) was prepared from resorcinol and 2-methoxy-3 : 4-methylenedioxybenzyl cyanide by the Hoesch method followed by partial methylation of the product. Reaction of this deoxybenzoin with ethyl formate and sodium gave 2-hydroxy-7 : 2′-dimethoxy-3′ : 4′-methylenedioxy*iso*flavanone (IV) (cf. Whalley, *J. Amer. Chem. Soc.*, 1953, **75**, 1059) which on dehydration furnished 7 : 2′-dimethoxy-3′ : 4′-methylenedioxy*iso*flavone. Hydrogenation of this *iso*flavone gave the (±)-flavan (II) which, by comparison of the infra-red absorption spectra, was found to be structurally identical with the natural (—)-*O*-methyldihydropterocarpin; *inter al.*, both compounds showed bands at 1037 cm.$^{-1}$ and 1165 cm.$^{-1}$, characteristic of the methylenedioxy-group, the presence of which is thus definitely established in pterocarpin (cf. Part I, *loc. cit.*).



(I)



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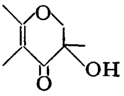
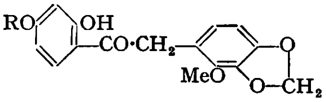


(VI)



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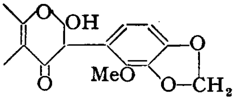
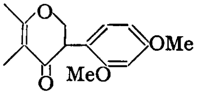


(IV)



(V)

Formed by the oxidation of *O*-methyldihydrohomopterocarpin, the readily racemised *iso*flavanone (V) gave, on further oxidation, an optically inactive product, $C_{15}H_9O_3(OMe)_3$ (Part I, *loc. cit.*), not identical with 4-hydroxy-7 : 2′ : 4′-trimethoxy-3-phenylcoumarin (Part II, *J.*, 1948, 174), or with 2-hydroxy-7 : 2′ : 4′-trimethoxy*iso*flavanone, the synthesis of which is now described. The compound $C_{15}H_9O_3(OMe)_3$, however, has now been found to be readily dehydrated in a mixture of boiling acetic acid and sulphuric acid, yielding 7 : 2′ : 4′-trimethoxy*iso*flavone, and clearly, therefore, must be 3-hydroxy-7 : 2′ : 4′-trimethoxy*iso*flavanone (VI), the formation of which from (V) is strictly analogous to the oxidation of deoxybenzoins to benzoins under similar conditions (Part IV, *J.*, 1950, 2961).

EXPERIMENTAL

2-*Methoxy*-3 : 4-*methylenedioxybenzyl Cyanide* (WITH G. B. SMITH).—Prepared from 2-methoxy-3 : 4-methylenedioxybenzaldehyde (Brownell and Weston, *J. Amer. Chem. Soc.*, 1951, **73**, 4971) (5 g.), hippuric acid (6·5 g.), sodium acetate (3 g.), and acetic anhydride (10 ml.) by the standard method, the *azlactone* (6·7 g.) separated from benzene in bright yellow prisms, m.p. 190° (Found: C, 67·4; H, 4·1; N, 4·3. $C_{18}H_{13}O_5N$ requires C, 66·9; H, 4·0; N, 4·3%).

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* Part IV, *J.*, 1950, 2961.

Hydrolysis of this product (6·5 g.) with boiling 10% sodium hydroxide solution (40 ml.) for 5 hr., followed by isolation in the usual manner, furnished 2-methoxy-3 : 4-methylenedioxyphenylpyruvic acid (4·3 g.) which was converted directly into the oxime (4·0 g.). A mixture of the crude air-dried oxime (4·0 g.) and acetic anhydride (10 ml.) was warmed on the steam-bath and, after the initially vigorous reaction had subsided, the solution was diluted with water and 24 hr. later the crystalline precipitate was isolated and purified from alcohol, giving 2-*methoxy*-3 : 4-*methylenedioxybenzyl cyanide* in almost colourless plates (2·1 g.), m. p. 100° (Found : N, 7·1. $C_{10}H_9O_3N$ requires N, 7·3%).

(±)-7 : 2′-*Dimethoxy*-3′ : 4′-*methylenedioxy*iso*flavan* (II).—The condensation of the aforementioned cyanide (4 g.) with resorcinol (5 g.) in ether (100 ml.) by hydrogen chloride and zinc chloride (2 g.), followed by hydrolysis of the oily ketimine complex with water (50 ml.), gave 2 : 4-*dihydroxy*-2′-*methoxy*-3′ : 4′-*methylenedioxydeoxybenzoin* (III; R = H) which separated from benzene in needles (2·5 g.), m. p. 165°, having an intense wine-red ferric reaction in alcohol (Found : C, 54·2; H, 4·3. $C_{16}H_{14}O_6$ requires C, 63·6; H, 4·6%). On methylation in acetone by the methyl iodide–potassium carbonate method for 2 hr. this ketone furnished a quantitative yield of 2-*hydroxy*-4 : 2′-*dimethoxy*-3′ : 4′-*methylenedioxydeoxybenzoin* (III; R = Me) which formed needles, m. p. 127°, from methanol, having an intense red-brown ferric reaction in alcohol (Found : C, 64·4; H, 4·8. $C_{17}H_{16}O_6$ requires C, 64·6; H, 5·1%).

The interaction of this deoxybenzoin (1·8 g.) with ethyl formate (25 ml.) and pulverised sodium (1·5 g.), and the isolation of the product by Whalley's method (*loc. cit.*), gave 2-*hydroxy*-7 : 2′-*dimethoxy*-3′ : 4′-*methylenedioxy*iso*flavanone* (IV) (1·2 g.), forming needles, m. p. 188° (decomp.), from ethyl acetate (Found : C, 62·4; H, 4·8. $C_{18}H_{16}O_7$ requires C, 62·8; H, 4·7%). On being boiled in acetic acid during 10 min. this *iso*flavanone was converted quantitatively into 7 : 2′-*dimethoxy*-3′ : 4′-*methylenedioxy*iso*flavone* which separated from methanol in needles, m. p. 203° unchanged on sublimation at 200°/0·01 mm. (Found : C, 66·2; H, 4·4. $C_{18}H_{14}O_6$ requires C, 66·3; H, 4·3%).

A solution of this *iso*flavone (0·5 g.) in acetic acid (50 ml.) containing Adams's catalyst (0·1 g.) was shaken in hydrogen at atmospheric pressure until one mol. of hydrogen had been absorbed (30 min.). On crystallisation from methanol the gummy product gave (*a*) unchanged *iso*flavone (100 mg.), (*b*) a colourless crystalline solid, m. p. 86°, and (*c*) a non-crystalline residue. Purification of fraction (*b*) from methanol gave (±)-7 : 2′-*dimethoxy*-3′ : 4′-*methylenedioxy*iso*flavan* (II) in needles (100 mg.), m. p. 86°, insoluble in 2N-aqueous sodium hydroxide and having a negative ferric reaction in alcohol (Found : C, 69·0; H, 6·0. $C_{18}H_{18}O_5$ requires C, 68·8; H, 5·8%). It did not react with 2 : 4-dinitrophenylhydrazine.

The Oxidation Product of (−)-7 : 2′ : 4-*Trimethoxy*iso*flavanone* (V).—A solution of this compound (*loc. cit.*) (0·2 g.), in acetic acid (5 ml.) containing 2N-sulphuric acid (0·5 ml.), was refluxed for 10 min., cooled, and diluted with water, giving a quantitative yield of 7 : 2′ : 4′-trimethoxy*iso*flavone, m. p. 148° after purification, identical with a synthetical specimen prepared thus. Cyclisation of 2-hydroxy-4 : 2′ : 4′-trimethoxydeoxybenzoin (1·0 g.) with sodium dust (0·3 g.) in ethyl formate (30 ml.) and isolation of product as described previously (*loc. cit.*) furnished 2-*hydroxy*-7 : 2′ : 4′-*trimethoxy*iso*flavanone* (0·3 g.), which separated from ethyl acetate in tablets, m. p. 156° and decomposing with effervescence at *ca.* 180° [Found : C, 65·7; H, 5·3; OMe, 27·6. $C_{15}H_9O_3(OMe)_3$ requires C, 65·5; H, 5·5; OMe, 28·2%]. In boiling acetic acid during 5 min. this *iso*flavanone was converted quantitatively into the 7 : 2′ : 4′-trimethoxy*iso*flavone, m. p. 148° (cf. Späth and Schläger, *Ber.*, 1940, **73**, 1).

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