The Synthesis of the Pterocarpin Ring System[1]

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The structures of pterocarpin and homopterocarpin, the minor principles of *pterocarpus santalinus*, were elucidated in 1940 by Robertson and Whalley and by Späth and Schläger[2] as III, $R_1=R_4=OMe$, R_2, $R_3=-O-CH_2-O-$, and III, $R_1=R_3=OMe$, $R_2=R_4=H$, respectively. However, the syntheses of pterocarpin and homopterocarpin have not been hitherto completed.

This paper presents the syntheses of the

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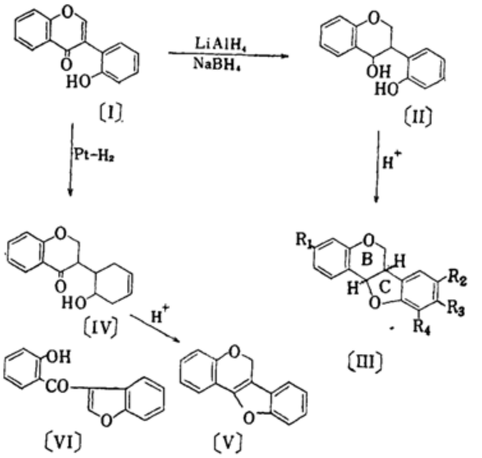
[1] Oxygen heterocycles. (II). Previous paper in this series, Hiroshi Suginome, *J. Org. Chem.*, **24**, 1655 (1959).

[2] A. Robertson and W. B. Whalley, *J. Chem. Soc.*, **1940**, 787; **1954**, 1440; E. Späth and J. Schläger, *Chem. Ber.*, 73, 1 (1940).

simple core of pterocarpin, III, $R_1=R_2=R_3=R_4=H$, and compound V, as shown in the annexed chart, which establish a synthetic route to DL-pterocarpin and DL-homopterocarpin or their isomers.

In view of a possible biogenetic link[1,3,4] of pterocarpin and homopterocarpin to naturally occurring 2′-hydroxyisoflavonoids, the synthetic sequence, I→II→III, is of particular interest.



Mild acid hydrolysis of 2, 2′-bis(methoxymethoxy) benzoin, m. p. 104～104.5°[5]. (Found: C, 64.79; H, 5.59. Calcd. for $C_{18}H_{20}O_6$: C, 65.09; H, 6.02%) afforded 2, 2′-dihydroxybenzoin, m. p. 161～163°C[6] (Found: C, 68.48; H, 5.02. Calcd. for $C_{14}H_{12}O_4$: C, 68.84; H, 4.95%), accompanied by a small amount of an unidentified substance, m. p. 156～157°C, I. R. bands at 1627 cm^{-1} (conjugated carbonyl) and 3200 cm^{-1} (broad hydroxyl band).

2, 2′-Dihydroxydesoxybenzoin, m. p. 102～103°C, readily prepared from above 2, 2′-dihydroxybenzoin and from the unidentified substance, m. p. 156～157°C, by zinc-alkali reduction, was converted into 2′-hydroxyisoflavone (I), m. p. 153°C (Found: C, 75.67; H, 4.45. Calcd. for $C_{15}H_{10}O_3$: C, 75.62; H, 4.23%), I. R. bands at 1621 cm^{-1} (γ-pyrone carbonyl) and 3187 cm^{-1} (phenolic hydroxyl), with ethyl formate and sodium. No isomeric 3-benzoylcoumarone (VI) could be isolated from the reaction mixture. The isoflavone (I) was reduced to an amorphous stereoisomeric mixture of 2′-hydroxyisoflavan-4-ol (U. V. spectrum: λ_{max}(ethanol) 275 mμ) by $NaBH_4$[7] or $LiAlH_4$.

The successful intramolecular dehydrocyclization of this amorphous diol by mild treatment in acidic medium, led to compound III, $R_1=R_2=R_3=R_4=H$, m. p. 125～126.5° (Found: C, 79.83; H, 5.49. Calcd. for $C_{15}H_{12}O_2$: C, 80.33; H, 5.39%) (U. V. spectrum; λ_{max}(ethanol) 278 mμ(ε; 3260). I. R. No band in the region 3000～3500 cm^{-1}), without any proof of stereochemical assignment of B/C ring junction.

On the other hand, catalytic hydrogenation of 2′-hydroxyisoflavone (I) in glacial acetic acid with Adams's platinum oxide as a catalyst, gave the corresponding 2′-hydroxyisoflavanone, m. p. 118～122°C. I. R. bands at 1660 cm^{-1} (conjugated carbonyl) and 3297 cm^{-1} (associated phenolic hydroxyl), which was converted into anhydro-compound V,[1] m. p. 80～83°, U. V. spectrum; λ_{max}(ethanol) 331, 299, 286, and 239 mμ (ε; 11190, 7350, 7240, and 11740), in a good yield by treatment in acidic medium.

The synthesis of homopterocarpin along the above synthetic line is now in progress.

Full details of this work will appear shortly.

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[3] W. B. Whalley, *J. Chem. Soc.*, **1956**, 3224.

[4] Also cf. R. Robinson, "The Structural Relations of Natural Products", Oxford Univ. Press, London (1955), p. 41.

[5] F. B. Laforge, *J. Am. Chem. Soc.*, **55**, 3040 (1933). F. B. Laforge records b. p. 200～210°C/1 mmHg.

[6] F. B. Laforge records m. p. 142～149°C. (Ref. 4).

[7] M. Miyano and M. Matsui, *Chem. Ber.*, **91**, 2044 (1958).