

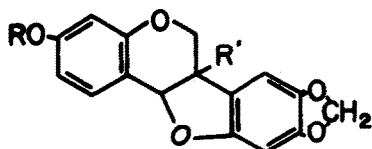
TOTAL SYNTHESIS OF (+)-PTEROCARPIN AND (+)-PISATIN

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(-)-Pterocarpin had been isolated from the heartwood of red sandalwood tree (Pterocarpus santalinus)(1). Its chemical structure (I) was established initially on the basis of n.m.r. spectral analysis (2) and later by comparison of synthetic (+)-dihydropterocarpin methyl ether ((+)-7,2'-dimethoxy-4',5'-methylenedioxyisoflavan)(II)(3), with the (-)-compound derived from natural pterocarpin. On the other hand, medicagol (7-hydroxy-5',6'-methylenedioxybenzofurano-(3',2':3,4)coumarin)(III)(4), which had been isolated from alfalfa (Medicago), has a resemble structure to I differing in a ring system of coumarin instead of chroman. This fact indicates that I may be derived from III or methyl ether (IV) of III. In previous papers, the authors were reported the synthesis of III (5) and IV (6). This communication

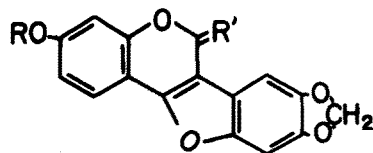
describes the synthesis of (+)-pterocarpin ((+)-maackiain methyl ether)(I)(7) via anhydropisatin (V)(8).



I R = Me, R' = H

II R = Me, R' = OH

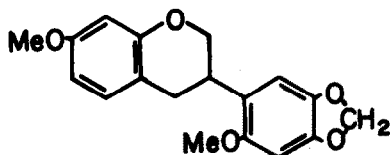
III R = R' = H



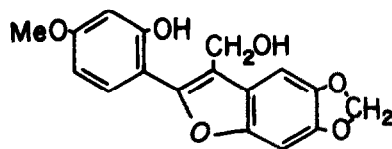
IV R = H, R' = O

V R = Me, R' = O

VI R = Me, R' = H<sub>2</sub>



II



VI

The reduction of IV with lithium aluminum hydride in tetrahydrofuran yielded 2-(2-hydroxy-4-methoxyphenyl)-3-hydroxymethyl-5,6-methylenedioxybenzofuran (VI) in 60% yield, m.p. 186-187°C; IR, 3350, 3100 (OH), 1026, 941cm<sup>-1</sup> (O-CH<sub>2</sub>-O)(Nujol); UV  $\lambda_{\max}^{\text{EtOH}}$  m $\mu$  (log  $\epsilon$ ), 271(4.11), 322(4.36); Found: C, 65.03, H, 4.64. Calcd. for C<sub>17</sub>H<sub>14</sub>O<sub>6</sub>: C, 64.96, H, 4.49%. The cyclisation of VI in boiling diethylene glycol gave 7-methoxy-5',6'-methylenedioxybenzofurano(3',2':3,4)chromen in 56% yield, m.p. 179-180°C;

IR, 1658, 1619, 1570, 1518, 1500 (phenyl), 1023, 920 $\text{cm}^{-1}$  (O-CH<sub>2</sub>-O)(Nujol); UV  $\lambda_{\text{max}}^{\text{EtOH}}$   $m\mu(\log \epsilon)$ , 215(4.49), 232<sub>i</sub> (4.22), 243<sub>i</sub>(4.13), 251(4.09), 294(3.82), 340(4.54), 359 (4.57); Found: C, 69.02, H, 4.14. Calcd. for C<sub>17</sub>H<sub>12</sub>O<sub>5</sub>: C, 68.91, H, 4.08%. The identity of this compound with anhydropisatin (3,4-dehydropterocarpin)(V)(lit.(8), m.p. 179-180°C) which had been obtained from (+)-pisatin (VII) by the action of acid, was confirmed by ultraviolet and infrared spectral comparisons. Then, V was reduced with Pd-C catalytic hydrogenation, to ( $\pm$ )-pterocarpin (I) in 60% yield, m.p. 185-186°C; IR, 1614, 1585, 1503, 1493 (phenyl), 1027, 930 $\text{cm}^{-1}$  (O-CH<sub>2</sub>-O)(Nujol); UV  $\lambda_{\text{max}}^{\text{EtOH}}$   $m\mu(\log \epsilon)$ , 281(3.60), 287(3.66), 311(3.89); Found: C, 68.55, H, 4.79. Calcd. for C<sub>17</sub>H<sub>14</sub>O<sub>5</sub>: C, 68.45, H, 4.73% (lit. (7), m.p. 185-186°C; UV  $\lambda_{\text{max}}^{\text{EtOH}}$   $m\mu(\log \epsilon)$ , 280(3.58), 286(3.65), 310(3.87)). The synthetic product was identical with ( $\pm$ )-maackiain methyl ether (( $\pm$ )-pterocarpin), which had been derived from natural ( $\pm$ )-maackiain (VIII), in mixed melting point and spectral characteristics. Moreover, by catalytic hydrogenolysis followed by methylation, ( $\pm$ )-I was converted into II, m.p. 117-118°C; IR, 1033, 939 $\text{cm}^{-1}$  (O-CH<sub>2</sub>-O)(Nujol); UV  $\lambda_{\text{max}}^{\text{EtOH}}$   $m\mu(\log \epsilon)$ , 291(3.86), 301(3.82); Found: C, 68.73, H, 5.89. Calcd. for C<sub>18</sub>H<sub>18</sub>O<sub>5</sub>: C, 68.78, H, 5.77% (lit. m.p. 111-113°C (3), 110-111°C (9)). Since the partial synthesis of ( $\pm$ )-pisatin from (-)-pterocarpin had already been carried out by Bevan et al. (9), the total synthesis of ( $\pm$ )-pisatin was now accomplished.

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