Tetrahedron Letters No.3, pp. 185-187, 1964. Pergamon Press Ltd.
Printed in Great Britain.

SYNTHESIS OF 7-METHYLTECTORIGENIN

A. Ghanim, A. Zaman and A.R. Kidwai

Department of Research in Unani Medicine, Tibbiya College,

and Department of Chemistry, Aligarh Muslim University,

Aligarh, India.

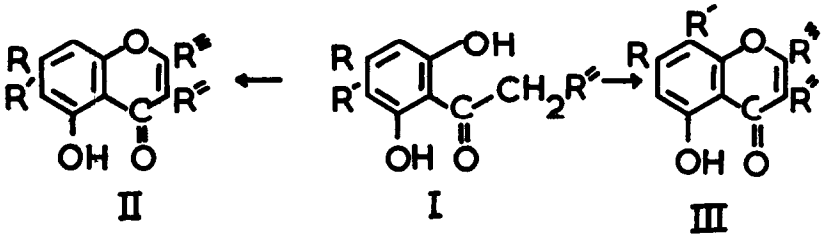
(Received 7 November 1963)

5,4'-dihydroxy-6,7-dimethoxyisoflavone (7-methyl-tectorigenin) was recently isolated from Dalbergia sisso[1] and its structure was determined by ultraviolet studies and by comparison with product obtained by selective methylation of tectorigenin in the 7 position. We report here a direct synthesis of this compound from 4,5-dimethoxyresorcinol and p-hydroxybenzyl cyanide.

4,5-dimethoxyresorcinol prepared by the method of Baker and Robinson[2] and was condensed with p-hydroxybenzyl cyanide. Condensation took place exclusively at the free position para to the methoxyl group to give benzyl o-hydroxy phenyl ketone (I; R = R' = OMe, R" = p-OH.C_6H_4) in agreement with the observations of Baker et al[2,3] and others[3] on the Hoesch condensation of substituted resorcinols of this type. Cyclisation of the above ketone gave the 2-carbethoxy derivative of the desired product along with some quantity of

1. A.Banerji, V.V.S.Murti, T.R.Seshadri and R.S.Thakur, Indian J.Chem., 1, 25 (1963).
2. W.Baker and R.Robinson, J.Chem.Soc., 152 (1929).
3. W.Baker, R.Nodzu and R.Robinson, J.Chem.Soc.,74 (1929), R.L.Shriner and R.W.Stephenson, J.Am.Chem.Soc., 64,2737 (1942).

the 8-methoxy isomer. No variation in the relative yields of the two isomers could be obtained when the cyclisation was carried out at different temperatures. It is interesting to note that in the synthesis of caviunin[4] cyclisation took place exclusively with the 6-hydroxyl group of the deoxybenzoin to give caviunin, and not even a trace of the 8-methoxy isomer could be detected whereas, as pointed out by the same authors, in the synthesis of irigenin and tectorigenin[5] exactly the reverse results were obtained and the 8-isomer was the predominant product. In a recent publication W. Rahman and his co-workers[6] have discussed the mechanism of ethoxalylation reaction and have suggested steric hindrance and hydrogen bonding as factors responsible for formation of 8-isomer as the main product in reactions involving deoxybenzoins of this type. Formation of the 6-isomer as main product in the present case does not fit into the mechanisms and explanations suggested by them.



II I III

4. S.F.Dyke, W.D.Ollis, and M.Sainsbury, J.Org.Chem., 26, 2453 (1961).
5. W.Baker, D.F.Downing, A.Y.Floyd, Gilbert, W.D.Ollis and R.C.Russell, Tetrahedron Letters, No. 5,6 (1960).
6. M.O.Farooq, W.Rahman and Kh.Takrimullah Nasim, J.Org. Chem., 27, 944 (1962).

Condensation of p-hydroxybenzyl cyanide with 4,5-dimethoxyresorcinol yielded the deoxybenzoin (I; R = R' = OMe, R" = p-OH.C_6H_4) m.p.199-200°. This deoxybenzoin when treated with ethoxalyl chloride and pyridine yielded the 2-carbethoxyisoflavones (II and III; R = R' = OMe, R" = p-OH.C_6H_4 R"' = CO_2 Et., m.p.234-36 and 213-15° respectively) which could be hydrolysed and decarboxylated smoothly to give the corresponding 5,4'-dihydroxy-6,7-dimethoxy and 5,4'-dihydroxy-7,8-dimethoxyisoflavones (II and III; R = R' = OMe, R" = p.OH.C_6H_4, R"' = H, m.p.231-33 and 170-71° respectively). Identity of the 6-isomer was established by its complete methylation to tri-O-methyltectorigenin.

Mixed melting points of the synthetic 7-methyltectorigenin and its acetate with the product isolated by Seshadri et al[1] were undepressed.