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RING ISOMERIZATION OF C-METHYL ISOFLAVONES

NEW SYNTHESES OF 2-HYDROXY ISOFLAVANONES

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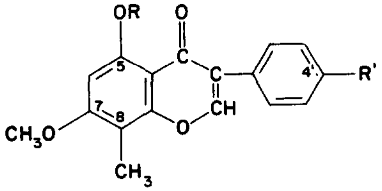
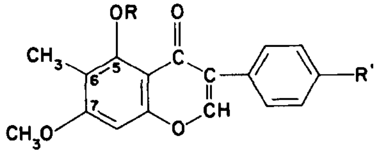
ACCORDING to our present knowledge,[1] the rearrangement of 5-hydroxy-7,4'-dimethoxy-8-methyl isoflavone catalysed by acid gives a mixture of 6- and 8-methyl-5,7,4'-trihydroxy isoflavones.

Our recent investigations proved, however, that this rearrangement takes place unequivocally in the presence of a basic catalyst.



I



II

Thus, on the effect of potassium ethylate, 5-hydroxy-7-methoxy-8-methyl isoflavone (I; R = R' = H, m.p. 169-170°) converts into 5-hydroxy-7-methoxy-6-methyl isoflavone (II; R = R' = H, m.p. 176-177°, lit. m.p.[2] 170-172).

On reacting, in turn, 5,7-dimethoxy-8-methyl isoflavone[2] (I; R = CH_3, R' = H) with potassium ethylate, ring isomerization can not take place as

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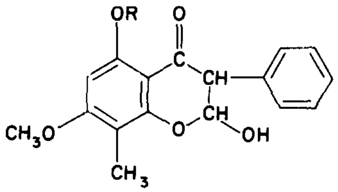
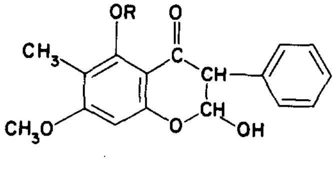
[1] W.B. Whalley, J. Chem. Soc. 3366 (1953).

[2] M.O. Farooq, W. Rahman and KH.T. Nasim, J. Org. Chem. 27, 944 (1962).

the hydroxyl group on C_5 is not free, and thus, after careful neutralization of the reaction mixture, 2-hydroxy-5,7-dimethoxy-8-methyl isoflavanone (IIIa; R = CH_3, m.p. 191-192°) was obtained.



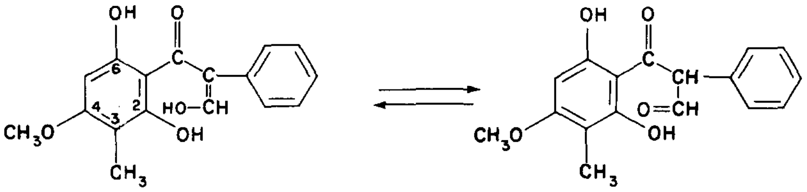
III a



III b

The same compound was prepared also from 2-hydroxy-4,6-dimethoxy-3-methyl-desoxybenzoin,[3] subjecting it to a Claisen condensation (ethyl formate, metallic sodium). Compounds IIIa (R = CH_3) prepared by both methods proved to be completely identical.

Thus, we presume that on the effect of potassium ethylate, the isoflavone ring splits also on the case of compound I (R = R' = H), and that, on cautiously neutralizing the produced α-hydroxymethylene ketone (IVa) and β-ketone aldehyde (IVb), respectively, they form, owing to free rotation,



IV a IV b

an isoflavanone ring (IIIb; R = H) with the hydroxyl group of C_6 of higher reactivity. On stronger acidification, however, this product converts, under loss of water, into isoflavone II (R = R' = H).

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[3] R. Iengar, A.C. Mehta, T.R. Seshadri and S. Varadarajan, J. Sci. Ind. Res. (India) 13B, 166 (1954).

Similary, we succeeded in unequivocally isomerizing 5-hydroxy-7,4'-dimethoxy-8-methyl isoflavone (I; R = H, R' = OCH_3, m.p. 169-170°, lit. m.p.[4] 164-166°) to 5-hydroxy-7,4'-dimethoxy-6-methyl isoflavone (II; R = H, R' = OCH_3, m.p. 204-205°, lit. m.p.[5] 200-201°) by treatment with potassium ethylate.

Our investigations in order to extend this reaction are in progress. Our communication will shortly be published in detail in Chemische Berichte.

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[4] T.R. Seshadri and S. Varadarajan, Proc. Ind. Acad. Sci. 37A, 145 (1953).

[5] A.C. Mehta and T.R. Seshadri, J. Chem. Soc. 3823 (1954).