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A NEW METHOD FOR THE RING ISOMERIZATION OF isoFLAVONES. DIRECT SYNTHESIS OF TECTORIGENIN, 4'-METHYL-TECTORIGENIN, CAVIUNIN AND OTHER isoFLAVONES.

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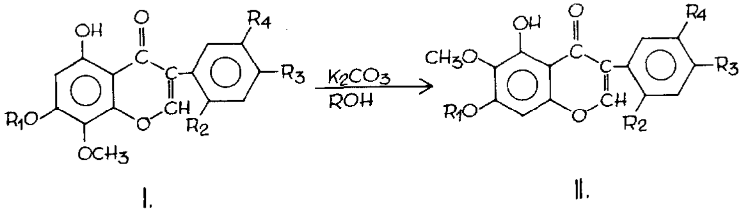
For ring isomerisation of isoflavones under alkaline conditions alcoholic potash and alcoholic potassium ethylate have been used, respectively, by Mahesh and Seshadri [1] and us [2], these methods not being suitable for the isomerization of polyhydroxy-isoflavones [2,3,4], only for that of their properly methylated or



a: $R_1=R_2=R_3=R_4=H$

b: $R_1=R_2=R_4=H,\ R_3=OH$

c: $R_1=CH_3,\ R_2=R_4=H,\ R_3=OH$

d: $R_1=R_2=R_4=H,\ R_3=OCH_3$

e: $R_1=CH_3,\ R_2=R_4=H,\ R_3=OCH_3$

f: $R_1=CH_2-C_6H_5,\ R_2=R_4=H,\ R_3=OCH_2-C_6H_5$

g: $R_1=H,\ R_2=R_3=R_4=OCH_3$

benzylated derivatives [3,5,6,7].

We have now found that, by refluxing polyhydroxy-isoflavones in alcohols of suitable boiling point /ethyl-, amyl-, cyclohexyl-, benzylalcohol etc./ in the presence of potassium carbonate under anhydrous conditions, they become directly isomerized just as well as their methylated or benzylated derivatives.

By this method 5,7-dihydroxy-8-methoxy-isoflavone /Ia/ has been isomerized to 5,7-dihydroxy-6-methoxy-isoflavone /IIa/, 5,7,4'-trihydroxy-8-methoxy-isoflavone /isotectorigenin, Ib/ to 5,7,4'-trihydroxy-6-methoxy-isoflavone /tectorigenin, IIb/, 5,4'-dihydroxy-7,8-dimethoxy-isoflavone /7-methyl-isotectorigenin, Ic/ to 5,4'-dihydroxy-6,7-dimethoxy-isoflavone /7-methyl-tectorigenin, IIc/, 5,7-dihydroxy-8,4'-dimethoxy-isoflavone /4'-methyl-isotectorigenin, Id/ to 5,7-dihydroxy-6,4'-dimethoxy-isoflavone /4'-methyl-tectorigenine, IId/, 5-hydroxy-7,8,4'-trimethoxy-isoflavone /Ie/ to 5-hydroxy-6,7,4'-trimethoxy-isoflavone /IIe/, 5-hydroxy-8-methoxy-7,4'-dibenzyloxi-isoflavone /If/ to 5-hydroxy-6-methoxy-7,4'-dibenzyloxy-isoflavone /IIf/, and 5,7-dihydroxy-8,2',4',5'-tetramethoxy-isoflavone /isocaviunin, Ig/ to 5,7-dihydroxy-6,2',4',5'-tetramethoxy-isoflavone /caviunin, IIg/, the yield being in most cases almost quantitative.

We attempt to apply the method described also for the ring isomerization of flavones.

Experimental details shall shortly be published in Acta Chim. Acad. Sci. Hung.

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