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THE SYNTHESIS OF 4',5,6,7- AND 4',5,7,8-TETRAHYDROXYFLAVANONE AND THEIR COMPARISON WITH CARTHAMIDIN AND ISOCARTHAMIDIN

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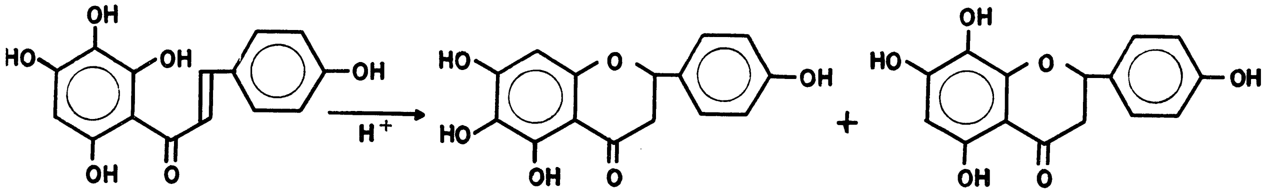
4',5,6,7- and 4',5,7,8-Tetrahydroxyflavanone (II and III) have been synthesized by the isomerization of 2',3',4,4',6'-pentahydroxychalcone (I), and the structures of carthamidin and isocarthamidin were corrected by the comparison with these synthetic flavanones.

In a previous communication,[1)] we have reported the synthesis of 2',3',4,4'-6'-pentahydroxychalcone (I) corresponding to the aglycon of carthamin,[2)] the red coloring matter of the flowers of Carthamus tinctorius. In the present paper, the synthesis of 4',5,6,7- and 4',5,7,8-tetrahydroxyflavanone (II and III) by the isomerization of I with acid, and their comparison with carthamidin and isocarthamidin, the hydrolysis products of carthamin[2)] will be described.

A mixture of II and III was obtained from I by heating with dilute hydrochloric acid in methanol, and the mixture was chromatographed on a column of silica gel to give II and III in 32 and 29% yields respectively.

The structures of II and III were confirmed by the elemental analysis, by the studies of their UV, IR, and NMR spectra, and, furthermore, by the comparison of their tetramethylethers with authentic samples of 4',5,6,7-[3)] and 4',5,7,8-tetramethoxyflavanone[4)], respectively.



(I) (II) (III)

4',5,6,7-Tetrahydroxyflavanone (II), mp 219°C (pale yellow needles from dilute methanol); Mg-HCl, deep red; $FeCl_3$, brownish green; UV, λ_{max}^{EtOH} (log ε) 300 (4.13) and 368 mμ (3.18); tetraacetate, mp 160°C (colorless prisms from methanol).

4',5,7,8-Tetrahydroxyflavanone (III), mp 248°C (pale yellow needles from methanol); Mg-HCl, deep red; $FeCl_3$, brownish green; UV, λ_{max}^{EtOH} (log ε) 299 (4.17) and 370 mμ (3.52); tetraacetate, mp 177°C (colorless needles from methanol).

While Kuroda(2) had been reported the structure of III and II for carthamidin (A) and isocarthamidin (B) on the basis of the color phenomena of their hydroxyl groups, the IR spectra of A and B which were prepared by the hydrolysis of carthamin according to Kuroda's method(2) were identical with those of the synthetic II and III.

Seshadri et al(3) have reported the synthesis of II and III by the demethylation of the corresponding tetramethoxyflavanones in the presence of anhydrous aluminium chloride in benzene solution. We have attempted the synthesis in a manner similar to that described above, but, no expected tetrahydroxyflavanones could be obtained.

The detail will be published elsewhere.

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