SYNTHETICAL EXPERIMENTS IN THE CHROMONE GROUP

Part XXIII. A New Synthesis of Rhamnazin and a Synthesis of 3: 4′-Dihydroxy-7-methoxyflavone

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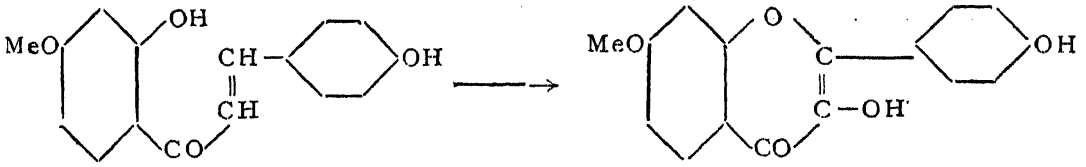
Among the methods which have been described for the synthesis of partially methylated hydroxyflavonols with a free hydroxyl in the 3-position, two convenient procedures are the preferential demethylation of the 3-methoxyl group by means of aluminium chloride[1] or hydrobromic acid[2] and the oxidation of *o′*-hydroxychalkones with alkaline hydrogen peroxide.[3] Since there are several naturally occurring flavonols (*e.g.*, rhamnazin, rhamnocitrin) in which a hydroxyl group in the 2-phenyl ring is unmethylated, we have examined the utility of Algar and Flynn's method[3] for their synthesis. It has been found that in the oxidation of *o′*-hydroxychalkones to flavonols by alkaline hydrogen peroxide a free hydroxyl group in the 4-position does not interfere. Thus, the oxidation of 2-hydroxy-4-methoxyphenyl 4-hydroxystyryl ketone (I), prepared by the condensation of resacetophenone 4-methyl ether and *p*-hydroxybenzaldehyde, readily yields 3: 4′-dihydroxy-7-methoxy-



flavone (II) in one step. The isomeric 4′-ether has been prepared by Heap and Robinson,[4] and the 3-ether (pale yellow needles, m.p. 289°) by Gulati[5] who used the Robinson reaction between ω-methoxyresacetophenone and *p*-benzyloxybenzoic anhydride, followed by debenzylation.

Condensation of phloracetophenone-4: 6-dimethyl ether with vanillin gave the chalkone (III), which on oxidation with alkaline hydrogen peroxide yielded the flavonol (IV), the 5-methyl ether of rhamnazin (V). Rhamnazin (V) was then obtained by the action of aluminium chloride in nitrobenzene on (IV) at about 100°. Kuhn, Low and Trischmann have synthesized rhamnazin by a much longer procedure, involving the condensation of