MODIFICATIONS IN THE IODINE OXIDATION OF HYDROXY FLAVANONES AND THEIR METHYL ETHERS

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In a previous publication the action of iodine and silver acetate on flavanones in absolute alcoholic solution was discussed. Naringenin (Ia) and hesperetin (Ib) were found to yield the corresponding 3-acetoxy-flavanones while naringenin dimethyl ether (IIa) and 5:7-dimethoxy-flavanone (IIIa) yielded the corresponding 3-iodo-compounds (IVa and IIIb). Considerable difference was recorded regarding the behaviour of these 3-iodo-compounds towards alcoholic potash. The 3-iodo-5-hydroxy-7:4'-dimethoxy flavanone (IVa) on treatment with this reagent yielded the corresponding flavone, apigenin-7: 4'-dimethyl ether (Va) while the 3-iodo-5: 7-dimethoxy flavone was reported to yield the corresponding flavonol, galangin-5: 7-dimethyl ether (VIa). A more detailed study of these reactions has now been made.

\[ \text{I} \]
\[ \text{II} \]
\[ \text{III} \]

(a) \( R = \text{H}, \ R' = \text{OH} \)
(b) \( R = \text{OH}, \ R' = \text{OCH}_3 \)
(a) \( R = \text{H} \)
(b) \( R = \text{OCH}_3 \)
(a) \( X = \text{H} \)
(b) \( X = \text{I} \)
Modifications in Iodine Oxidation of Hydroxy Flavanones

In the original procedure of Goel, Narasimhachari and Seshadri, iodine was added to a boiling absolute alcoholic solution of the hydroxy flavanone and silver acetate. The method has not proved to be satisfactory as appreciable quantities of by-products are formed, making the purification of the main product difficult. During the course of the present work it has been found that if iodine is added at room temperature with shaking instead at the temperature of boiling alcohol and the addition is followed by refluxing for two hours, the purification of the product is simpler. Using this modified method naringenin (Ia), naringenin-7:4'-dimethyl ether (IIa) and 5:7-dimethoxy-flavanone (IIIa) have given good yields of 3-acetoxy-naringenin, 3-iodo-5-hydroxy-7:4'-dimethoxy flavanone (IVa) and 3-iodo-5:7-dimethoxy flavanone (IIIb) respectively. Similarly hesperetin (Ib) gives a good yield of 3-acetoxy hesperetin and hesperetin 7:3'-dimethyl ether forms the 3-iodo-compound (IVb).

Treatment with pyridine or with alcoholic potash of 3-iodo-naringenin-7:4'-dimethyl ether (IVA) and of 3-iodo-hesperetin-dimethyl ether (IVb) yielded apigenin-7:4'-dimethyl ether (Va) and luteolin-7:3':4'-trimethyl ether (Vb) respectively. 3-Iodo-5:7-dimethoxy-flavanone (IIIb) behaved somewhat differently; when treated with pyridine it yielded chrysin dimethyl ether (VIb), whereas on treatment with alcoholic potash it gave a mixture of chrysin dimethyl ether (VIb), 3-hydroxy-5:7-dimethoxy flavone (VIa) and 2-hydroxy-2-benzyl-4:6-dimethoxy coumaranone (VII). The separation of this mixture has been effected by using the difference in the solubilities of the components in aqueous alkali of different concentrations.

(a) R = H.
(b) R = OCH3.

(a) R = OH.
(b) R = H.