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The present work forms a part of the systematic study of the chemistry of flavones and flavanones going on in the laboratory here for the past few years. It deals with (i) the synthesis of iodo-flavones and -flavanones by direct iodination ; (ii) chloromethylation of some flavones and flavanones and the conversion of the chloromethyl derivatives into formyl, acetoxymethyl and alkyl- ~~or aryl~~-aminomethyl derivatives ; (iii) synthesis of some biflavonyls by Ullmann reaction on iodoflavones ; (iv) synthesis of cyanoflavones , by Rosemund-von Braun reaction on the iodoflavones and (v) Beckmann rearrangement of the oximes of some C-acyl flavones.

In chapter I (General Introduction), the previous work on the substitution in flavones and flavanones has been briefly reviewed.

Chapter II deals with the synthesis of some iodo- flavones and -flavanones. The iodination of $7,4'$-dihydroxy-, 7-hydroxy-$4'$-methoxy-, $7,4'$-dimethoxy-, 5,7-dihydroxy- and 6-hydroxyflavone , simple-, 7-hydroxy-, 7-hydroxy-$4'$-methoxy- and $4'$-hydroxy-flavanone has been carried out, by using either (1) iodine and iodic acid or (2) iodine and ammonia or (3) iodine monochloride as iodinating agents.

$7,4'$-Dihydroxyflavone with iodine and iodic acid or with iodine and ammonia gave a mono-iodo derivative which has been assigned the 8-iodo structure as its methyl ether on alkaline hydrolysis gave the known 2-hydroxy-3-iodo-4-methoxyacetophenone. With twice the amount of iodine and ammonia 7,4'-dihydroxyflavone gave the 8,3'-di-iodo derivative. Its methyl ether on hydrolysis gave the known 2-hydroxy-3-iodo-4-methoxyacetophenone and 2-hydroxy-3-iodo-4-methoxybenzoic acid. With thrice the amount of iodine and ammonia the same flavone gave the 8,3',5'-tri-iodo derivative. Its methyl ether on alkaline hydrolysis gave 2-hydroxy-3-iodo-4-methoxyacetophenone and 3,5-di-iodo-4-methoxybenzoic acid. The latter was synthesised for comparison by iodination of 4-hydroxybenzoic acid followed by simultaneous methylation and esterification and subsequent hydrolysis of the ester formed.

7-Hydroxy-4'-methoxyflavone on iodination with different quantities of iodine and iodic acid gave the 8-iodo and the 6,8-di-iodo derivative as seen from the results of hydrolysis. No tri-iodo derivative could be obtained even with excess of iodinating reagents.

7,4'-Dimethoxyflavone on iodination with excess of iodine and iodic acid gave the 8-iodo derivative as seen by the direct comparison with the product prepared earlier.

5,7-Dihydroxyflavone on iodination with iodine and iodic acid and iodine and ammonia gave a di-iodo derivative, the methyl ether of which remained unchanged on boiling with alkali. As no coumarone derivative was formed on boiling with alkali there was no iodine in the 3-position. The 6,8-di-iodo structure has been tentatively assigned to this product. Neither a mono-iodo nor a tri-iodo derivative could be obtained under different conditions of reaction with any of the iodinating agents.

6-Hydroxyflavone on iodination with iodine and iodic acid gave a mono-iodo derivative to which the 5-iodo structure has been assigned in analogy with the previous work on substitution in 6-hydroxyflavone and on the basis of IR spectral data.

6-Methoxy- and 7,8-dihydroxyflavone could not be iodinated by any of the three iodinating agents.

Simple flavanone could only be iodinated with iodine monochloride to a mono-iodo-derivative to which the 3-iodo structure has been assigned as on refluxing with potassium acetate and acetic acid it was converted into simple flavone.

7-Hydroxyflavanone on iodination with iodine and iodic acid as well as with iodine and ammonia in different proportions gave a mono-iodo and a di-iodo derivative. These were treated with potassium acetate and acetic acid when the former gave 7-hydroxyflavone and the latter gave a mono-iodoflavone derivative, the methyl ether of which on alkaline hydrolysis gave a mixture of 2-hydroxy-4-methoxy-5-iodoacetophenone and 2-hydroxy-4-methoxy-5-iodobenzoic acid. Therefore the mono and the di-iodoflavanones have been assigned the 3-iodo- and the 3,6-di-iodo structures respectively.

7-Hydroxy-4'-methoxyflavanone on iodination with iodine and iodic acid or with iodine and ammonia gave the 3,6-di-iodo derivative. The structure has been assigned on the basis of the hydrolysis of the methyl ether of the mono-iodoflavone derivative obtained from the di-iodo-flavanone derivative by reaction with potassium acetate and acetic acid.

4'-Hydroxyflavanone on iodination with iodine and iodic acid gave the 3',5'-di-iodo derivative. Its methyl ether on alkaline hydrolysis gave 3,5-di-iodo-4-methoxybenzoic acid described earlier.

6-Hydroxyflavanone could not be iodinated either with iodine and iodic acid or with iodine and ammonia, but with iodine monochloride a chlorinated product was obtained which has not been investigated.

Chapter III deals with the chloromethylation of some flavones and flavanones. The chloromethylation of 7-hydroxy-, 6-hydroxy-, 6-methoxy- and 6-methoxy-3-methyl-flavone and simple- and 7-methoxyflavanone has been carried out with paraformaldehyde and hydrogen chloride gas in acetic acid.

7-Hydroxy- and 6-hydroxy-flavone on chloromethylation gave the 8-chloromethyl and the 5-chloromethyl derivatives respectively. On Sommelet reaction the former gave the known 8-formyl derivative and the latter gave the known 5-formyl derivative.

6-Methoxyflavone on chloromethylation gave the 3,5-di-(chloromethyl) derivative. This on reduction gave a product which was found to be identical on direct comparison with the product synthesised as follows : Quinpropiophenone was subjected to Kostanecki-Robinson benzoylation and the 6-hydroxy-3-methylflavone obtained was methylated and then subjected to chloromethylation. A monochloromethyl derivative was obtained which was reduced. The reduced product was found to be identical with the product described above. One of the chloromethyl group is, therefore, in the 3-position. The other chloromethyl group is assigned the 5-position on the basis of the IR data.

Simple flavanone on chloromethylation gave the 3-chloromethyl derivative which on reduction and dehydrogenation with selenium dioxide gave the known 3-methylflavone.

7-Methoxyflavanone on chloromethylation gave the 8-chloromethyl derivative. On reduction and dehydrogenation with selenium dioxide it gave the known 7-methoxy-8-methylflavone.

Some of the above chloromethyl derivatives have been converted into the corresponding acetoxymethyl derivatives, and some have also been condensed with secondary amines such as dimethylamine and morpholine.

In chapter IV, the synthesis of aome biflavonyls by the Ullmann reaction on the mono-iodoflavones mentioned in chapter II has been described.

7-Methoxy-6-iodo- and 7,4'-dimethoxy-6-iodoflavone on Ullmann reaction gave 7,7''-dimethoxy-6,6''-biflavonyl and 7,7'',4',4'''-tetramethoxy-6,6''-biflavonyl respectively.

6-Methoxy-5-iodoflavone on a similar reaction gave 6,6''-dimethoxy-5,5''-biflavonyl.

With a view to synthesise unsymmetrical biflavonyls it was thought of interest to study crossed Ullmann reactions. Before proceeding with the crossed Ullmann reaction between two iodoflavones some crossed Ullmann reactions were carried out between iodoflavones and iodobenzene and 7-methoxy-6-phenyl-, 7,4'-dimethoxy-6-phenyl-, and 6-methoxy-5-phenylflavone synthesised. However, the crossed Ullmann reaction between 7-methoxy-8-iodoflavone and 7-methoxy-6-iodoflavone did not give any pure product.

Chapter V deals with the synthesis of some cyano flavones from the iodoflavones through the Rosenmund-von Braun reaction.

7-Methoxy-6-iodo- and 7,4'-dimethoxy-6-iodoflavone on Rosenmund-von Braun reaction gave the corresponding cyano derivatives. With 70 % sulphuric acid 7-methoxy-6-cyanoflavone gave 7-hydroxyflavone-6-carboxylic acid and 7,4'-dimethoxy-6-cyanoflavone gave 7-hydroxy-4-methoxyflavone 6-carboxylic acid. On alkaline hydrolysis both the cyanoflavones gave 2-hydroxy-4-methoxy-5-cyanobenzoic acid as seen by direct comparison with an authentic specimen.

6-Methoxy-5-iodoflavone on Rosenmund-von Braun reaction gave the corresponding 5-cyano derivative which on hydrolysis with sulphuric acid gave the corresponding acid and on alkaline hydrolysis gave 2-acetyl-3-hydroxy-6-methoxybenzoic acid.

7-Methoxy-3-iodoflavanone on Rosenmund-von Braun reaction gave 7-methoxyflavone.

In chapter VI, the Beckmann rearrangement of the oximes of some acetyl and formyl flavones has been described.

The oxime of 7-hydroxy-8-acetyl- and 7-methoxy-8-

acetylflavone on Beckmann rearrangement gave the corresponding 8-acetamido derivatives which on hydrolysis with sulphuric acid gave the corresponding 8-amino derivatives. 7-Hydroxy-8-aminoflavone was obtained for comparison by the reduction of the known 7-hydroxy-8-nitroflavone with stannous chloride and hydrochloric acid.

The oxime of 7-hydroxy-8-formyl and 7-methoxy-8-formylflavone on Beckmann rearrangement gave the corresponding 8-cyanoflavone which on hydrolysis gave the corresponding known flavone 8-carboxylic acids.

The oxime of 7-hydroxy-8-benzoylflavone on Beckmann rearrangement gave 7-hydroxy-8-benzamidoflavone which on hydrolysis gave the 8-amino derivative described above.