

Alkoxyated derivatives of *o*-methoxyphenyl styryl ketones can also be preferentially demethylated to the σ -hydroxy-compounds in this manner.

W. A. HUTCHINS.
T. S. WHEELER.

Royal Institute of Science,
Bombay,
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Flavones from the Dibromides of
o-Hydroxyphenyl Styryl Ketones. A
Modified Synthesis of Apigenin and
Luteolin.

It has previously been pointed out¹ that the dibromides of certain *o*-hydroxyphenyl styryl ketones which normally yield benzylidene coumaranones only on treatment with alcoholic alkali, can be converted into flavones by simple heating. It has now been found by several workers in this laboratory that better yields of the flavones can be obtained if the hydroxy-dibromide is treated with alcoholic potassium cyanide. Further, *o*-hydroxyphenyl α -bromo- β -ethoxy- β -alkoxyphenylethyl ketones which give benzylidene coumaranones with alkali hydroxide or carbonate in presence of hot or cold acetone or alcohol, give flavones with alcoholic potassium cyanide.

2-Hydroxy-4 : 6-dimethoxyphenyl *p*-methoxystyryl ketone on bromination gives 5-bromo-2-hydroxy-4 : 6-dimethoxyphenyl $\alpha\beta$ -dibromo- β -*p*-anisylethyl ketone which on heating yields 6-bromo-5 : 7 : 4'-trimethoxyflavone; this with hydriodic acid gives apigenin (5 : 7 : 4'-trihydroxyflavone). Luteolin (5 : 7 : 3' : 4'-tetrahydroxyflavone) has been synthesised by heating 5-bromo-2-hydroxy-4 : 6-dimethoxyphenyl $\alpha\beta$ -dibromo- β -3 : 4-dimethoxyphenyl ethyl ketone with alcoholic potassium cyanide and treating the resulting bromoflavone with hydriodic acid.

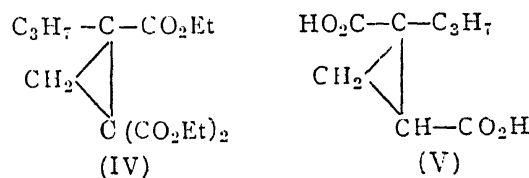
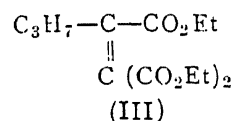
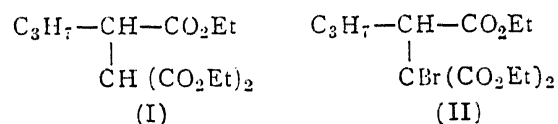
The synthesis of 5 : 7 : 2' : 4'-tetrahydroxyflavone which is thought to be lotoflavin is now in hand.

W. A. HUTCHINS.
T. S. WHEELER.

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A New Method of Synthesis of
Umbellularic Acid.

UMBELLULARIC acid, a degradation product of the naturally occurring bicyclic ketone umbellulone, has been synthesised by two methods.^{1,2} It has now been synthesised by a convenient method starting from ethyl α -isopropyl- α' -carbethoxy succinate (I) which gives readily the bromo-compound (II) (b.p. 155-56°/3 mm.; Found: Br, 21.40; Calc.: Br, 21.86 per cent.). The bromo-compound (II) loses a molecule of hydrobromic acid by the action of diethylaniline yielding ethyl isopropyl-carboxyfumarate (III), b.p. 135-40°/3 mm., which readily adds on a molecule of diazomethane to yield the cyclopropane-tricarboxylic ester (IV) (b.p. 148-50°/3 mm.; Found: C, 59.46; H, 8.34; Calc.: C, 60.0; H, 8.0 per cent.). The triester (IV) on being boiled with hydrochloric acid (18 per cent.) during eight hours got hydrolysed and decarboxylated and yielded *trans*-umbellularic acid (V) (m.p. 190-92°; Found: C, 55.63; H, 7.26; Calc.: C, 55.81; H, 7.0 per cent.). The *trans*-acid (V) has been converted into the *cis*-variety (monohydrate, m.p. 94-95°) by treating with acetyl chloride and its identity has been proved by taking mixed m.p. with a genuine sample obtained by older methods.



P. C. GUHA.
M. S. MUTHANNA.

Department of Organic Chemistry,
Indian Institute of Science,
Bangalore,
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¹ *Curr. Sci.*, 1937, 5, 475; *J.C.S.*, 1937, 1800.

¹ Rydon, *J.C.S.*, 1936, 829.

² Ranganathan, *J. Ind. Chem. Soc.*, 1936, 13, 419.
Simonsen, *J.C.S.*, 1936, 828.