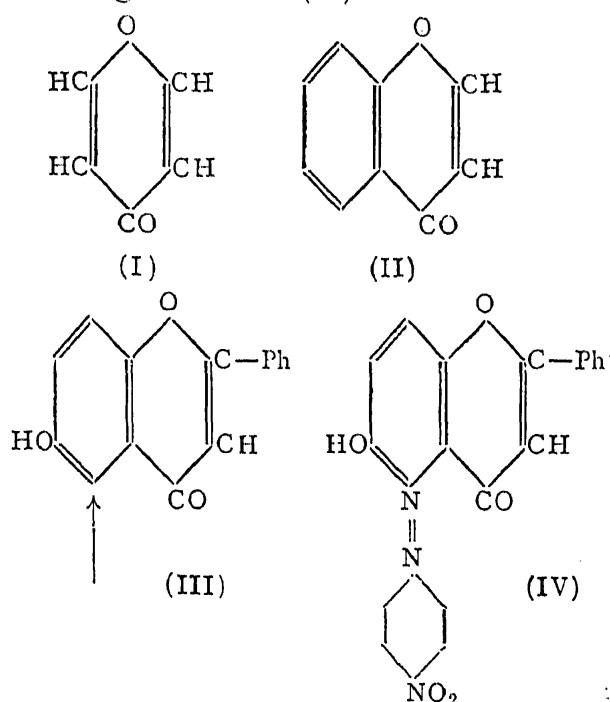


### The Coupling of 6-Hydroxyflavone with Diazo Salts.

THE reactivity of natural colouring matters derived from resorcinol and phloroglucinol towards diazo salts has been the subject of several investigations by Perkin,<sup>1</sup> and Ramachandran and one of us<sup>2</sup> have recently utilised the coupling of catechin with diazo salts for altering the shades of cutch dyeings. While Perkin found that chrysin, apigenin, euxanthone and catechin all gave diazo dyes, the coupling of 6-hydroxyflavone<sup>3</sup> has yielded a mono-azo derivative. *p*-Nitraniline (2 g.) was diazotised with sodium nitrite (1.2 g.) and 50 per cent. hydrochloric acid (9 c.c.) and the solution made up to 50 c.c. To the sparingly soluble sodium salt prepared from 6-hydroxyflavone (0.5 g.) and 1 per cent. caustic soda solution (10 c.c.), sodium acetate (4 g.) in water (10 c.c.) was added, followed by the diazo solution (7.5 c.c.) the temperature of the reactants being maintained at 0°. On leaving overnight in the ice chest, the dye was collected and twice crystallised from glacial acetic acid. The deep orange prisms (0.2 g.) melted at 256°. (Found: N, 10.9; C<sub>21</sub>H<sub>13</sub>O<sub>5</sub>N<sub>3</sub> requires N, 10.9 per cent.)

Fusion with the  $\gamma$ -pyrone ring (I) must be presumed to stabilise one of the Kekule forms of the benzene ring in chromone, the double bonds being fixed as in (II). This is confirmed



by Baker's observation<sup>4</sup> that the Fries reaction on 7-acetoxy-3-acetyl-2-methylchromone leads exclusively to the 8-acetyl compound.

Mills and Nixon<sup>5</sup> regarded the coupling of phenols with diazo salts as evidence of double linkage between the carbon atoms, to which the hydroxyl and the azo group were attached, the hydroxyl activating only the doubly linked carbon atom. Ability to couple with diazo salts has also been used by Fieser and Lothrop<sup>6</sup> to examine the permanent fixation of links in the aromatic nucleus. Conversely it would appear therefore that 6-hydroxyflavone (III) can couple only in position 5 as shown, the *p*-nitrobenzeneazo derivative having the structure (IV). A route to the synthesis of primetin (5:6-dihydroxyflavone) thus becomes possible.

Several attempts to synthesise primetin have been recorded. Sugawara<sup>7</sup> found that the debenzoylation of 2:3-dimethoxy-6-benzyloxyacetophenone did not proceed normally; the action of benzoic anhydride and sodium benzoate on the oily product, assumed to contain 2:3-dimethoxy-6-hydroxyacetophenone, gave an impure 5-hydroxy-8-methoxyflavone. By the action of potassium acetate on 2:4-diacetylresorcinol dibenzoate Baker<sup>8</sup> obtained a poor yield of 5-hydroxy-6-acetylflavone, which also resulted from a Fries reaction on 5-acetoxyflavone; but the Dakin oxidation of 5-hydroxy-6-acetylflavone did not yield primetin. Baker<sup>8</sup> also noticed that 6-acetoxyflavone did not undergo the Fries change, the action of aluminium chloride merely leading to the removal of the acetyl group.

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<sup>1</sup> Perkin, *J. Chem. Soc.*, 1895, **67**, 933; 1896, **69**, 1439; 1897, **71**, 186; 1898, **73**, 666.

<sup>2</sup> Ramachandran and Venkataraman, *Indian Patent Application*, No. 24056 of 1937.

<sup>3</sup> Chadha and Venkataraman, *J. Chem. Soc.*, 1933, 1075.

<sup>4</sup> Baker, *ibid.*, 1934, **73**; see also Wittig, Baugert and Richter, *Ann.*, 1925, **446**, 184.

<sup>5</sup> Mills and Nixon, *J. Chem. Soc.*, 1930, 2510.

<sup>6</sup> Fieser and Lothrop, *J. Amer. Chem. Soc.*, 1936, **58**, 2050.

<sup>7</sup> Sugawara, *J. Pharm. Soc., Japan*, 1934, **54**, 295.

<sup>8</sup> Baker, *J. Chem. Soc.*, 1934, 1953.