

CCLXXXIV.—*Synthetical Experiments in the Chromone Group. Part I. A New Synthesis of 7:8-Dihydroxy-2-methylchromone and 7:8-Dihydroxyflavone.*

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ALTHOUGH pyrogallol derivatives are found widespread in nature, there are few known representatives of the benzopyran group with hydroxyl groups in the positions 7 and 8 in the fused benzene nucleus. Daphnetin, hæmatoxylin, and gossypetin would appear

to be the only known examples, and of these the first is an α -pyrone, the second contains a reduced pyran ring, and the third is a derivative of tetrahydroxybenzene. True flavones related to pyrogallol in the manner indicated may well occur naturally, but they have not yet been isolated.

It seemed of interest to prepare some members of this group in order to examine their dyeing properties, Perkin and Wilkinson (J., 1902, **81**, 590) having clearly indicated the nature of the effects produced by vicinal hydroxyl groups in other positions (compare also Friedländer and Rudt, *Ber.*, 1896, **29**, 878).

The synthetical method employed is an application of that devised by Allan and Robinson (J., 1924, **125**, 2192) and by Robinson and Venkataraman (J., 1926, 2344). The condensation of gallacetophenone with acetic anhydride and sodium acetate and hydrolysis of the product led to 7 : 8-dihydroxy-2-methylchromone (I), and benzoylation of gallacetophenone with subsequent hydrolysis yielded 7 : 8-dihydroxyflavone (II). Both these substances have been previously synthesised by Kostanecki and his pupils (*Ber.*, 1903, **36**, 2192, 4242), employing a different method, but their reactions and dyeing properties have not been fully described.



A series of dye-trials was made on mordanted cotton, silk, and wool with the synthetic chromone and flavone and with chrysin for comparison. In nearly every case, 7 : 8-dihydroxy-2-methylchromone gave a darker shade than chrysin, and 7 : 8-dihydroxyflavone a still darker shade. As indicated by Perkin and Wilkinson (*loc. cit.*), wool is undoubtedly better than silk or cotton for dye-trials of flavones, and in the present instance the differences between the dyeing properties of the substituted chromones were best shown by the wool (see Table). 7 : 8-Dihydroxyflavone appears to compare favourably with luteolin, which has two more hydroxyls (see Table).

EXPERIMENTAL.

7 : 8-Dihydroxy-2-methylchromone (I).—An intimate mixture of gallacetophenone (5.0 g.) and fused sodium acetate (10.0 g.) was heated with acetic anhydride (50 g.) at 160–170° for 6 hours. The major portion of the acetic anhydride was removed by distillation under diminished pressure on the water-bath; the residue was poured into ice-cold, very dilute hydrochloric acid and kept over-night. When the precipitate obtained was crystallised from aqueous methyl

alcohol (charcoal), yellow needles of a mixture of the dihydroxy-chromone and its diacetyl derivative were obtained. This was boiled for a few minutes with alcoholic caustic potash (5%; 10 c.c.), and the precipitate (2.4 g.) obtained on the addition of dilute hydrochloric acid crystallised twice from methyl alcohol (charcoal). The felted mass of straw-coloured, long, woolly needles had m. p. 241—242° (Blumberg and Kostanecki, 243°) (Found: C, 62.3; H, 4.3. Calc. for $C_{10}H_8O_4$: C, 62.5; H, 4.2%).

The substance is insoluble in water, sparingly soluble in cold, and moderately readily soluble in boiling ethyl and methyl alcohols, in glacial acetic acid, and ethyl acetate, sparingly soluble in boiling benzene and chloroform, and insoluble in ether and light petroleum. With concentrated sulphuric acid it gives a pale yellow solution with a faint green fluorescence. It dissolves in cold sodium hydroxide solution with a colour varying from bright yellow to orange-yellow. An alcoholic solution gives with ferric chloride a bright malachite-green coloration, which is changed to reddish-violet by ammonia (pyrocatechol reaction). An alcoholic solution gives no precipitate with barium chloride, a yellow colloidal precipitate with lead acetate, no colour change with magnesium and hydrochloric acid, and a greenish-yellow coloration with sodium amalgam. On addition of saturated potassium acetate solution to an alcoholic solution of the chromone, a yellow coloration is developed and, on standing, a turbidity, but no well-defined potassium derivative could be isolated. A few drops of concentrated hydrochloric or sulphuric acid added to a solution of the substance in hot glacial acetic acid produce a bright yellow colour.

The diacetyl derivative was prepared by treating the dihydroxy-chromone with boiling acetic anhydride and a few drops of pyridine during 2 hours. After isolation in the usual way, it crystallised from 50% alcohol (charcoal) in long white needles, m. p. 189° after shrinking at 110° and losing water of crystallisation (Blumberg and Kostanecki give m. p. 120°) (Found in material dried at 120°: C, 60.9; H, 4.6. Calc. for $C_{14}H_{12}O_6$: C, 60.9; H, 4.3%).

7: 8-Dihydroxyflavone (II).—To an intimate mixture of gallacetophenone (5.0 g.), benzoic anhydride (50 g.), and sodium benzoate (5.0 g.), heated at 180—185° and mechanically stirred, a further 5 g. of sodium benzoate were added in the course of an hour. After being heated for 6 hours, the mixture was dissolved in boiling alcohol (290 c.c.), a solution of caustic potash (32 g. in 30 c.c. of water) gradually added, the whole refluxed for 30 minutes, and the greater part of the alcohol then distilled off under diminished pressure. A filtered aqueous solution of the residue was saturated with carbon dioxide and the precipitate obtained was washed and

dried (3.1 g.). The substance was dissolved in boiling glacial acetic acid, a few drops of concentrated sulphuric acid were added (the brown liquid then became intensely red), and the solution was treated with an equal volume of boiling water. After boiling for a few more minutes (charcoal), the liquid was filtered and cooled, depositing a felted mass of short pinkish needles. This was recrystallised from alcohol (charcoal) and obtained as cream-coloured needles, m. p. 246° (Woker, Kostanecki, and Tambor give 239°) (Found: C, 70.6; H, 4.2. Calc. for $C_{15}H_{10}O_4$: C, 70.9; H, 3.9%).

7 : 8-Dihydroxyflavone is insoluble in water, moderately readily soluble in ethyl alcohol, and very readily soluble in boiling benzene; sparingly soluble in ethyl acetate in the cold and moderately readily soluble at the boiling point; moderately soluble in cold glacial acetic acid and readily soluble in the hot solvent; very sparingly soluble in ether and insoluble in light petroleum. The yellow solution in concentrated sulphuric acid exhibits a green fluorescence, much stronger than that shown by 7 : 8-dihydroxy-2-methylchromone. The substance dissolves in cold caustic soda solution with an orange-yellow colour. An alcoholic solution gives with ferric chloride an intense malachite-green coloration, turning violet on addition of ammonia; with magnesium and hydrochloric acid an orange coloration; with barium chloride solution a pale yellow turbidity, but no precipitate; with lead acetate solution a yellow precipitate; with sodium amalgam a slightly greenish, pale orange colour; with potassium acetate a yellow colour and, on standing, a turbidity. On addition of concentrated hydrochloric or sulphuric acid, the colourless solution of the substance in glacial acetic acid assumes a bright yellow colour, but, as in the case of the chromone, there is no separation of a mineral acid compound on cooling.

The diacetyl derivative, prepared in the usual manner, crystallised from 70% alcohol (charcoal) in long colourless needles, m. p. 194° (Woker, Kostanecki, and Tambor give 193°) (Found: C, 67.1; H, 4.1. Calc. for $C_{19}H_{14}O_6$: C, 67.5; H, 4.1%).

The dye-trials tabulated below were made, under conditions as similar as possible, with chrysin, 7 : 8-dihydroxy-2-methylchromone, and 7 : 8-dihydroxyflavone.

	Dye.	Al.	Cr.	Fe.	Sn.
Cotton	Chrysin.	Pale yellowish-brown	Light grey	Very dark brown	Light ash-grey
	Chromone.	Light snuff	Light grey with a tinge of violet	„	Heliotrope
	Flavone.	Light greyish-brown	„ but slightly heavier	„	„

	Dye.	Al.	Cr.	Fe.	Sn.
Silk	Chrysin.	Cream	Biscuit colour	Chocolate	Pale cream
	Chromone.	„	Cream	„	Cream
	Flavone.	Creamy-brown	Creamy-brown	„ slightly deeper than above	Creamy-brown
Wool	Chrysin.	Light yellow	Cream	Light brown	Light buff
	Chromone.	Light greyish-brown	Light greyish-brown	Dark brownish-grey	Pale coffee
	Flavone.	Warm brown	Warm brown	Chocolate	Coffee
	Luteolin.	Orange-yellow	Brown-orange	Olive-black	Bright yellow

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