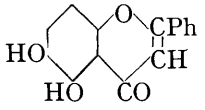
356. *Some Derivatives of Hydroxyquinol, including a Synthesis of Pyrylium Salts of Anthocyanidin Type. Part XXII.*

By (Miss) M. Healey and Robert Robinson.

Although hydroxyquinol derivatives have been recognised in nature, æsculin being the best-known example, they are not of frequent occurrence and therefore all the more interest attaches to the observations of Raistrick and Hetherington (*Phil. Trans.*, 1931, *B*, **220**, 209) and Nagai and Hattori (*Acta Phytochim.*, 1930, **5**, 1), who have investigated citromycetin and primetin respectively. The former is almost certainly a hydroxyquinol derivative related to the benzo-γ-pyrone group and the latter is probably 5 : 6-dihydroxyflavone (I). Some few years ago we commenced the preparation of reference compounds in these groups by the synthesis of 3 : 6 : 7-*trihydroxy*-2-*methylchromone* (II) and of 6 : 7-dihydroxyflavone (III), using methods which were essentially those of Allan and Robinson (J., 1924, **125**, 2192; compare Tahara, *Ber.*, 1892, **25**, 1302; Nagai, *ibid.*, p. 1287; Kostanecki and Rozycki, *Ber.*, 1901, **34**, 107).



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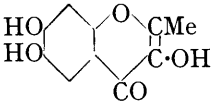

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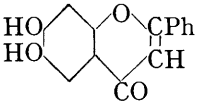
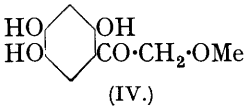


(III.)

The Hoesch reaction using hydroxyquinol and methoxyacetonitrile (compare Slater and Stephen, J., 1920, **117**, 313) results in the production of the ketone (IV) in only 5% yield under the usual conditions, but under a small pressure of hydrogen chloride this could be



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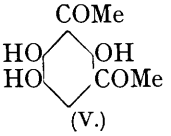

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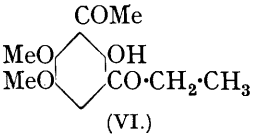


(VI.)

increased to 50% ; condensation to the methyl ether of (II) was easily effected on heating with acetic anhydride and sodium acetate and subsequent hydrolysis. The trimethyl ether of (II) could not be equated with a methylated degradation product of citromycetin, kindly supplied by Professor Raistrick, with which it is isomeric, and with which it might have proved to be identical.

In the hope of synthesising 2 : 5 : 6-trihydroxyacetophenone various modes of acetylation of hydroxyquinol have been studied; these all furnished 2 : 4 : 5-trihydroxyacetophenone (compare Badhwar and Venkataraman, J., 1932, 2420; Mauthner, *J. pr. Chem.*, 1933, **136**, 213).

The main product of the action of aluminium chloride on 2 : 4 : 5-triacetoxybenzene (compare Rosenmund and Schnurr, *Annalen*, 1928, **460**, 56) was a trihydroxydiacetylbenzene, presumably (V). Methylation of this diketone by means of diazomethane, however, gave a substance $C_{13}H_{16}O_5$ containing two methoxyl groups and exhibiting phenolic character. As methylation of the nucleus in the only remaining position, *o*- to only one hydroxyl and *op*- to two carbonyl groups, seems improbable, we suggest that the methylation may have extended one of the side-chains as shown in (VI) for one of the various possibilities. There are, of course, well-established analogous reactions (Arndt *et alia*).

Benzoylation of 2 : 4 : 5-trihydroxyacetophenone (compare Robinson and Venkataraman, J., 1929, 2219) * afforded the dihydroxyflavone (III), which is not identical with

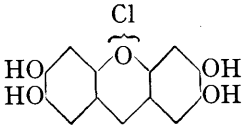
* Dr. K. Venkataraman carried out at my suggestion the first syntheses of naturally occurring flavones by the method of direct aroylation of phloracetophenone (*loc. cit.*) and when he left the laboratory it was agreed that he might continue similar researches in certain series. Unfortunately he has not respected these limitations and has now anticipated me in publication of completed work in at least four important cases, all of which are perfectly natural developments of the new synthetic method to which I drew Dr. Venkataraman's attention. One of the more recent examples is that of

primetin. No account of this work need now be submitted, as we have been anticipated in publication by Chadha and Venkataraman (J., 1933, 1073).

We have also synthesised flavylium salts containing a hydroxyquinol nucleus for comparison with isomeric anthocyanidins. The effect of the transposition of the hydroxyl from position 5 to 6 is large and the new salts are much yellower (less blue) than the anthocyanidins in acid and in alkaline solution. Thus the pelargonidin analogue gives only an orange-coloured solution in acidified alcohol, whereas pelargonidin is bluish-red under these conditions. The preparation of these salts did not proceed smoothly owing to the pronounced tendency of the hydroxyquinol derivatives to undergo condensation to xanthylium salts and other substances. These were therefore investigated as a preliminary and some curious results were the outcome. In some of the earlier experiments we had used 80% formic acid as a solvent in attempted condensations of 2 : 4 : 5-trihydroxybenzaldehyde and methyl aryl ketones in the presence of hydrogen chloride; the products were found to be obtained independently of the added ketone. This led to a study of the simpler cases and it was found that formic acid itself may enter into the condensation.

Pratt and Robinson (J., 1923, **123**, 740) condensed phloroglucinol and other phenols with ethyl formate under the influence of hydrogen chloride and obtained xanthylium salts in high yield. We have found that formic acid may be employed in place of its ester in many cases, and a more general account of the work in this field will be submitted later.

The condensation of hydroxyquinol by means of hydrogen chloride in 80% formic acid solution leads to the production of 2 : 3 : 6 : 7-*tetrahydroxyxanthylium chloride* (VII). The properties of this salt are divergent from those of 1 : 3 : 6 : 8-tetrahydroxyxanthylium chloride (Pratt and Robinson, *loc. cit.*). 2 : 4 : 5-Trihydroxybenzaldehyde, when similarly



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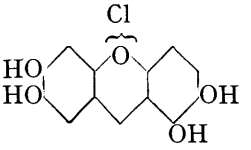

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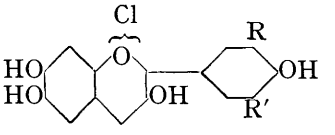

(IX.)

treated, yields a different xanthylium salt, apparently also of the composition $C_{13}H_9O_5Cl$; the nature of this isomeride has not been fully elucidated, but (VIII) is perhaps a plausible suggestion. When hydrogen chloride is passed into a solution of hydroxyquinol and 2 : 4 : 5-trihydroxybenzaldehyde in 80% formic acid, the two salts already mentioned are produced and in addition a third oxonium salt, the reactions of which recall those of the anthocyanidin group; this also is an unsolved problem.

In the condensations leading to the polyhydroxyflavylium salts (IX) the production of xanthylium derivatives could not be avoided but pure specimens of the isomerides of pelargonidin, cyanidin, and delphinidin were ultimately obtained.

The distribution of these salts between immiscible solvents such as *iso*amyl alcohol–water, ether–picric acid–0·5% hydrochloric acid, and the special reagents introduced by Robinson and Robinson (*Biochem. J.*, 1931, **25**, 1704) closely resembles that of the naturally occurring isomeric anthocyanidins. The colour reactions are, however, widely divergent.

Experimental.

Hydroxyquinol.—The triacetate was readily obtained by the modification of Thiele's method (*Ber.*, 1898, **31**, 1298) described in " Organic Syntheses " (**4**, 35). The hydrolysis of the triacetate, however, was found to be a difficult operation and neither Thiele's original process nor one depending on the use of alkalis in oxygen-free media was convenient. A modification of Thiele's method was finally adopted.

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the flavone *tricin*, which has been synthesised in this laboratory and also by Gulati and Venkataraman (J., 1933, 942). The method used by these authors is identical with that devised for the synthesis of the related flavonol, namely, syringetin (Heap and Robinson, J., 1929, 67), and it is, of course, identical with the method used in this laboratory in a parallel investigation which cannot now be published. Dr. Venkataraman has not informed me of his intention to undertake such investigations and the result has been a considerable waste of labour, time, and material.—R. R.

A mixture of 2 : 4 : 5-triacetoxybenzene (50 g.), methyl alcohol (100 c.c.), and concentrated hydrochloric acid (10 c.c.) was refluxed for 1 hour and then distilled under diminished pressure below 30° until the dark green liquid acquired a brown colour; on cooling, the hydroxyquinol separated in small grey crystals (20 g. or 80%).

2 : 4 : 5-Trihydroxybenzaldehyde was prepared from this material by Gattermann and Köbner's method (*Ber.*, 1899, **32**, 282) in 70% yield.

The *triacetyl* derivative was obtained by shaking a mixture of the trihydroxybenzaldehyde (2 g.), ether (150 c.c.), acetic anhydride (14 c.c.), and potassium carbonate (7 g.) for 1 hour. The product crystallised from alcohol in colourless prisms, m. p. 115° (Found: C, 55·6; H, 4·3. $C_{13}H_{12}O_7$ requires C, 55·7; H, 4·2%). The derivative is insoluble in dilute aqueous alkalis and gives no iron reaction in alcoholic solution.

The *monobenzoyl* derivative was obtained as follows. A solution of 2 : 4 : 5-trihydroxybenzaldehyde (5·2 g.), aqueous potassium hydroxide (20·2 c.c. of 10%), and water (108 c.c.) was cooled to 0°, and benzoyl chloride (4·2 c.c.) added very gradually with vigorous shaking. When the odour of benzoyl chloride had disappeared, sodium hydrogen carbonate was added in excess and, after stirring for 30 minutes, the solid was collected, again triturated with sodium bicarbonate solution, collected, and dried (8 g.). The crude product was dissolved in hot alcohol (charcoal), the filtered solution concentrated (*ca.* 50 c.c.), and hot water added to the hot solution until it clouded; alcohol (0·5 c.c.) was then added to clear the liquid, which was kept for 12 hours and deposited crystals; after recrystallisation from aqueous alcohol, pinkish irregular plates (1·5 g.), m. p. 184°, were obtained (Found: C, 64·9; H, 3·9. $C_{14}H_{10}O_5$ requires C, 65·1; H, 3·9%). This derivative is soluble in acetone and alcohol, and sparingly soluble in benzene, chloroform, and light petroleum.

A dark green coloration is obtained on the addition of ferric chloride to an alcoholic solution and this may be taken as an indication that the benzoyl group is in position 2 or 4. If the hydroxyl in position 5 had been benzoylated, we would anticipate that the resulting resorcinol derivative should exhibit a violet iron reaction. The following experiment shows that the benzoyloxy-group is not in position 2. Hence we consider that the derivative is 2 : 5-*dihydroxy*-4-*benzoyloxybenzaldehyde*.

A solution of *O*-monobenzoylhydroxyquinolaldehyde (0·1 g.) and ω : 3 : 4-triacetoxyacetophenone (0·1 g.) in 80% formic acid (10 c.c.) was saturated with hydrogen chloride during 3 hours and next day the flavylium salt (clusters of tiny needles) was collected and washed with ether. This salt was easily soluble in alcohol to a purplish-red solution; the very dilute solution in methyl alcohol was pure blue. When an equal volume of water was added to the purplish-red methyl-alcoholic solution, the colour faded instantly and was fully restored by the addition of acid. A clear blue solution resulted when a drop of aqueous sodium carbonate was added to a freshly prepared alcoholic solution of the salt; on standing, the solution became mauve and then pink. The salt dissolved in aqueous sodium carbonate, but the blue initial coloration rapidly faded to green and then yellow. These and other reactions which were noted establish that this salt is a flavylium salt and that it is different from the isomeride of cyanidin described below. Hence it is probably a benzoyl derivative of the latter. This method of synthesis of the salts herein described will be reinvestigated at an early opportunity.

2 : 4 : 5-*Trihydroxy*-ω-*methoxyacetophenone* (IV).—A mixture of hydroxyquinol (28 g.), methoxyacetonitrile (17 g.), and ether (100 c.c.) along with powdered zinc chloride (10 g.) was saturated with hydrogen chloride under a pressure of 1·5 atm. and the whole was kept for 5 days in the ice-chest. The supernatant liquid was decanted from the ketimine hydrochloride, which was decomposed by the minimum of hot water; the *ketone* separated, on cooling, in greenish needles. It crystallised from water in colourless needles, m. p. 95° (yield, 50%) (Found: C, 50·0; H, 5·6; MeO, 14·1. $C_9H_{10}O_5,H_2O$ requires C, 50·0; H, 5·6; 1MeO, 14·3%).

6 : 7-*Dihydroxy*-3-*methoxy*-2-*methylchromone*.—2 : 4 : 5-Trihydroxy-ω-methoxyacetophenone (7·1 g.), fused sodium acetate (9·8 g.), and acetic anhydride (13 g.) were heated together (oil-bath at 170°) for 5 hours, and the reaction product then added to hot 6*N*-hydrochloric acid (400 c.c.); the acetoxy-groups suffered hydrolysis under these conditions. The sandy powder crystallised from methyl alcohol (charcoal) in colourless needles (6·2 g.), m. p. 272° (decomp.) (Found: C, 59·3; H, 4·4. $C_{11}H_{10}O_5$ requires C, 59·5; H, 4·5%). The solution in alcohol fluoresces green and gives a green coloration on the addition of ferric chloride.

Diacetate. The dihydroxymethoxymethylchromone (1 g.) was heated with acetic anhydride (4 c.c.) and pyridine (2 drops) for 2 hours on the steam-bath, and the mixture decomposed by ice-water; colourless plates, m. p. 129—130° (Found: C, 58·7; H, 4·6. $C_{15}H_{14}O_7$ requires C, 58·8; H, 4·6%).

Dimethyl ether. The dihydroxy-compound was shaken with 8% aqueous sodium hydroxide and methyl sulphate at first in the cold, finally on the steam-bath. The colourless needles that separated, crystallised from methyl alcohol, had m. p. 185·5—186° (Found : C, 62·3; H, 5·6; MeO, 36·9. $C_{13}H_{14}O_5$ requires C, 62·4; H, 5·6; 3MeO, 37·2%).

3 : 6 : 7-*Trihydroxy*-2-*methylchromone.*—Dihydroxymethoxymethylchromone (1 g.) was refluxed with hydriodic acid (20 c.c., *d* 1·7) for 45 minutes, and dilute sulphurous acid added, precipitating a brown powder. The substance crystallised from methyl alcohol (charcoal) in colourless needles (0·6 g.), having no definite m. p. (Found : C, 53·4; H, 4·3. $C_{10}H_8O_5,H_2O$ requires C, 53·1; H, 4·4%).

2 : 4 : 5-*Trihydroxyacetophenone.*—The Hoesch reaction cannot be satisfactorily applied in this case; hydroxyquinol (6 g.), acetonitrile (4 g.), zinc chloride (4 g.), and ether (40 c.c.) saturated with hydrogen chloride for 5 hours and kept for 3 days afforded on working up only 0·4 g. of the trihydroxyacetophenone, m. p. 201° (Found : C, 57·0; H, 4·9. Calc. for $C_8H_8O_4$: C, 57·1; H, 4·8%). The ketone is best obtained by Bargellini's method (*Gazzetta*, 1910, **40**, 347) and suitable conditions consist in heating (20 minutes) hydroxyquinol triacetate (30 g.) with acetic acid (45 g.) and zinc chloride (45 g.); the product is separated by means of benzene into a readily soluble and a very sparingly soluble constituent, the latter being the trihydroxyacetophenone, which is recrystallised from water. The product soluble in benzene is hydroxydiacetoxyacetophenone and we found it necessary to modify the prescription for its hydrolysis. The diacetate (16 g.) was refluxed with concentrated sulphuric acid (50 c.c.) and water (150 c.c.) for 2 hours; on cooling, the trihydroxyacetophenone separated in reddish needles and was recrystallised from water, m. p. 201° (m. p. 206° on repeated crystallisation; compare Mauthner, *loc. cit.*).

2 : 4 : 5-*Trihydroxy*-1 : 3-*diacetylbenzene* (V).—Bargellini (*Gazzetta*, 1913, **43**, 164) mentions in a footnote the preparation of a compound presumed to be a diketone, by the action of aluminium chloride on 2 : 4 : 5-triacetoxybenzene. We have encountered what is probably the same substance in the course of attempts to obtain isomeric methyl ketones from hydroxyquinol.

With nitrobenzene as diluent (compare Rosenmund and Schnurr, *loc. cit.*) the action of aluminium chloride on hydroxyquinol triacetate gave unchanged substance and some 2 : 4 : 5-trihydroxyacetophenone. In a similar reaction with hydroxyquinol itself (compare Rosenmund and Schulz, *Arch. Pharm.*, 1927, **265**, 308) the only ketone isolated was 2 : 4 : 5-trihydroxyacetophenone.

2 : 4 : 5-Triacetoxybenzene (5 g.) was intimately mixed with powdered aluminium chloride (32 g.) and heated (oil-bath, 140°) until evolution of hydrogen chloride ceased (about 35 minutes). The product was decomposed with dilute hydrochloric acid and ice; direct crystallisation of the separated solid from water gave clusters of pale yellow prisms, m. p. 186° (yield, 30%) (Found : C, 56·9; H, 4·7. $C_{10}H_{10}O_5$ requires C, 57·1; H, 4·8%) and extraction of the filtrate with ether afforded 2 : 4 : 5-trihydroxyacetophenone, m. p. 201° after recrystallisation.

The diketone is readily soluble in most organic solvents; it is unchanged on refluxing with aqueous methyl-alcoholic hydrochloric acid or with 60% sulphuric acid and hence does not contain acetoxy-groups. It should be noted that the presence of more acetoxy-groups would not affect the results of elementary analysis.

The *triacetyl* derivative, obtained by the use of acetic anhydride and pyridine, crystallised from ethyl alcohol in colourless clustered needles, m. p. 144° (Found : C, 57·0; H, 4·9. $C_{14}H_{14}O_7$ requires C, 57·1; H, 4·8%). The substance developed no coloration with ferric chloride in alcoholic solution.

The tribenzoyl derivative, prepared from the diketone and benzoyl chloride in dry pyridine, crystallised from methyl alcohol in colourless needles, m. p. 140·5°. With the diketone (1 mol.) and benzoyl chloride (2 mols.) a substance, m. p. 116°, was obtained. Attempts to effect the ring-closure of these derivatives were unsuccessful.

Homologue of Hydroxydimethoxydiacetylbenzene (probably VI, or MeCO and EtCO transposed, or $-CH_2{\cdot}COMe$ instead of $-COEt$).—A solution of diazomethane (from 10·7 g. of nitrosomethylurethane) in dry ether was added to one of trihydroxydiacetylbenzene (5 g.) in a little acetone and next day the solvents were removed by distillation. The residue was a complex mixture, but a pure product could be isolated by means of 95% alcohol as large rectangular prisms, m. p. 89·5—90° (Found : C, 61·7; H, 6·3; MeO, 24·6. $C_{13}H_{16}O_5$ requires C, 61·9; H, 6·3; 2MeO, 24·6%). The substance is phenolic and gives a dark green coloration on the addition of ferric chloride to its alcoholic solution.

2 : 3 : 6 : 7-*Tetrahydroxyxanthylium Chloride* (VII).—Dry hydrogen chloride was slowly passed into a solution of hydroxyquinol (2·1 g.) in 80% formic acid (100 c.c.) for 2 hours. The solution became red and then purple, and a crystalline substance separated and was collected

after 12 hours. It formed bundles of microscopic brown needles having in mass a dark, olive-green appearance (1·8 g.) and it was recrystallised from very dilute hydrochloric acid (Found : C, 48·0; H, 4·6; Cl, 19·0. $C_{13}H_9O_5Cl,2·5H_2O$ requires C, 47·9; H, 4·3; Cl, 10·9%). The salt is easily soluble in alcohol to a deep red solution and when an equal volume of water is added, a red flocculent solid is precipitated.

In aqueous sodium carbonate, the cobalt-blue solution initially produced fades almost immediately to purple, red and then brownish-yellow; these colour changes are also brought about on dilution and are due to aerial oxidation. The reaction in aqueous sodium hydroxide is similar and the Prussian-blue solution behaves in the manner described on dilution. The addition of solid sodium acetate to the freshly prepared alcoholic solution precipitates a purple solid.

The red aqueous solution on large dilution is yellow and exhibits an intense green fluorescence.

Condensation of 2 : 4 : 5-*Trihydroxybenzaldehyde with Hydroxyquinol in Formic Acid Solution.*—A solution of the aldehyde (0·5 g.) and hydroxyquinol (0·5 g.) in 80% formic acid (10 c.c.) was saturated with hydrogen chloride during 5 minutes. On filtration, a small amount of a red crystalline product (A) was obtained. Hydrogen chloride was passed for 1 hour and the solution became filled with a dark green solid, which was collected and washed with dry ether (100 c.c.). The solid consisted of a mixture of (A), which was very sparingly soluble in water, and 2 : 3 : 6 : 7-tetrahydroxyxanthylium chloride (B), which was readily soluble in water and was identified by direct comparison with an analysed specimen. The filtrate was kept for 60 hours and deposited dark brown needles having a bluish-black appearance in mass (C) (Found : C, 55·8; H, 4·3; Cl, 9·0. $C_{19}H_{15}O_8Cl$ requires C, 56·1; H, 3·7; Cl, 8·7%).

The product (C) dissolved in methyl alcohol to give a ruby-red solution, and on the addition of sodium acetate a bright red solid was precipitated. Its solution in aqueous sodium hydroxide was purplish-blue and on dilution the colour changed through red to pink. It dissolved in aqueous sodium carbonate to give a violet-red solution; on dilution the colour changed to orange. The attractive possibility that this salt is 2 : 3 : 6 : 7 : 2′ : 4′ : 5′-heptahydroxy-9-phenylxanthylium chloride is not in agreement with the estimation of hydrogen ($C_{19}H_{13}O_8Cl$ requires H, 3·2%). However, the value for hydrogen found was high for the suggested formula also.

The product (A) was identified by its reactions as the condensation product obtained when hydrogen chloride is passed into a solution of 2 : 4 : 5-trihydroxybenzaldehyde in 80% formic acid. It was obtained in the course of many attempted condensations to flavylium salts, especially when methyl ketones were used as second components. It separated as characteristic maroon crystals (Found : C, 51·6, 51·8; H, 3·8, 3·9; Cl, 11·5, 11·7, 11·1. $C_{13}H_9O_5Cl,H_2O$ requires C, 52·3; H, 3·7; Cl, 11·5%). Some specimens have a higher value for carbon content (up to C, 53·8. $C_{13}H_9O_5Cl,0·5H_2O$ requires C, 54·0%), indicating variable hydration. All the specimens had identical properties and colour reactions.

The substance is sparingly soluble in alcohol to an orange solution exhibiting a green fluorescence that is intensified on dilution with water. The solution in aqueous sodium carbonate is red with a purplish tinge, that in aqueous sodium hydroxide is cherry-red and lacks the purple tinge.

In aqueous 2*N*-hydrochloric acid, a greenish-yellow solution is obtained; this is non-fluorescent and correspondingly the addition of a drop of concentrated hydrochloric acid to the orange fluorescent aqueous alcoholic solution changes the colour to yellow and destroys the fluorescence. Evidently it is an orange fluorone that exhibits fluorescence.

The condensation of 2 : 4 : 5-trihydroxybenzaldehyde and hydroxyquinol in ethyl acetate solution under the influence of hydrogen chloride afforded a crystalline solid which consisted of brown needles having a dark green appearance in mass. It was identified by comparison as 2 : 3 : 6 : 7-tetrahydroxyxanthylium chloride.

3 : 6 : 7 : 4′-*Tetrahydroxyflavylium Chloride* (IX; R, R′=H).—A rapid stream of hydrogen chloride was passed through a solution of 2 : 4 : 5-trihydroxybenzaldehyde (0·3 g.) and ω : 4-diacetoxyacetophenone (0·2 g.) in 80% formic acid, and after 10 minutes the red xanthylium salt was collected and hydrogen chloride was passed into the filtrate for 3 hours. After 2 days the crystalline homogeneous flavylium salt was collected and washed with dry ether. Under the microscope it was observed to consist of irregular amber plates; in mass it had a bright green lustre. It was recrystallised, by distilling an alcoholic solution containing a few drops of concentrated hydrochloric acid, in twinning elongated leaflets (Found : C, 55·6; H, 4·2; Cl, 10·7. $C_{15}H_{11}O_5Cl,H_2O$ requires C, 55·6; H, 4·0; Cl, 10·8%). The ferric reaction is cherry-red in alcoholic solution, brown-red on the addition of water.

The salt dissolved readily in methyl alcohol to an orange-red solution; on dilution with an

equal volume of water, the blue tinge increased and a reddish-purple flocculent solid was precipitated. The pink solution in water is decolorised on warming, and the colour is at once restored on acidification. The dilute acid solutions are orange-coloured, in striking contrast with the normal series of anthocyanidins. The salt dissolves in aqueous sodium carbonate and sodium hydroxide to give purplish-red solutions. The addition of sodium acetate to the freshly prepared alcoholic solution of the salt precipitated the colour-base. These reactions are so characteristic that it is thought unnecessary to record the colours obtained in buffered solutions of graded p_H, and the same comment applies to the isomerides of cyanidin and delphinidin mentioned below.

3′ : 4′ : 3 : 6 : 7-*Pentahydroxyflavylium Chloride* (IX; R=OH, R′=H).—Dry hydrogen chloride was passed rapidly into a solution of 2 : 4 : 5-trihydroxybenzaldehyde (1·0 g.) and ω : 3 : 4-triacetoxyacetophenone (2·0 g.) in 80% formic acid (50 c.c.). After 2 minutes the crystalline xanthylium salt appeared, and after 5 minutes the mixture was filtered. Dry hydrogen chloride was passed into the filtrate for a further period of 6 hours, during which time no more of the red xanthylium salt, but a dark green flavylium salt separated. This was collected, washed with dry ether, and so obtained in clusters of red-brown needles having in mass a dark sparkling green appearance (Found : C, 47·8; H, 3·7; Cl, 9·8. $C_{15}H_{11}O_6Cl,3H_2O$ requires C, 47·8; H, 4·0; Cl, 9·5%). A different hydrate was obtained by distilling an alcoholic solution containing concentrated hydrochloric acid until crystallisation occurred in the hot liquid. The slender needles obtained were brown-red by transmitted light, dark violet-brown in mass and exhibited a metallic lustre (Found : C, 52·7; H, 3·8; Cl, 10·3. $C_{15}H_{11}O_6Cl,H_2O$ requires C, 52·9; H, 3·8; Cl, 10·4%). The ferric reaction in both aqueous and alcoholic solutions is a rich intense violet (cyanidin, pure blue in alcohol). This salt is easily soluble in alcohol to a violet-red solution, which becomes purple on dilution with more alcohol or with an equal volume of water, and on heating a purple colour-base is precipitated. A purplish-blue colour results when a drop of aqueous sodium carbonate is added to a freshly prepared alcoholic solution; this fades slowly to purple and then red in an hour. Sodium acetate added to the methyl-alcoholic solution of the salt gives a stable purple coloration and the purple colour-base is precipitated. The salt dissolves in aqueous sodium carbonate to give a purplish-blue solution which rapidly fades (5 minutes) to a grey-green colour; in aqueous sodium hydroxide, the Prussian-blue colour, initially produced, fades completely in one hour.

3′ : 4′ : 5′ : 3 : 6 : 7-*Hexahydroxyflavylium Chloride* (IX; R, R′=OH).—Dry hydrogen chloride was passed slowly into a solution of 2 : 4 : 5-trihydroxybenzaldehyde (0·2 g.) and ω : 3 : 4 : 5-tetra-acetoxyacetophenone (0·4 g.) in 80% formic acid (10 c.c.) for 6 hours at room temperature. Next day the purple solution contained in suspension the maroon crystals of the aldehyde self-condensation product and also a dark green micro-crystalline flavylium salt. As purification of these salts by chemical means presented difficulty, they were separated mechanically. The flavylium salt was much more dense than the xanthylium compound; accordingly a mixture of the two solids was repeatedly shaken with dry ether in a flask, and the ether, which then contained the greater part of the xanthylium salt in suspension, was decanted. After many repetitions of this process a specimen of flavylium salt was obtained which on microscopic examination proved to be homogeneous (Found : C, 51·9; H, 4·2; Cl, 9·1. $C_{15}H_{11}O_7Cl,0{\cdot}5H_2O$ requires C, 51·9; H, 3·6; Cl, 10·2%).

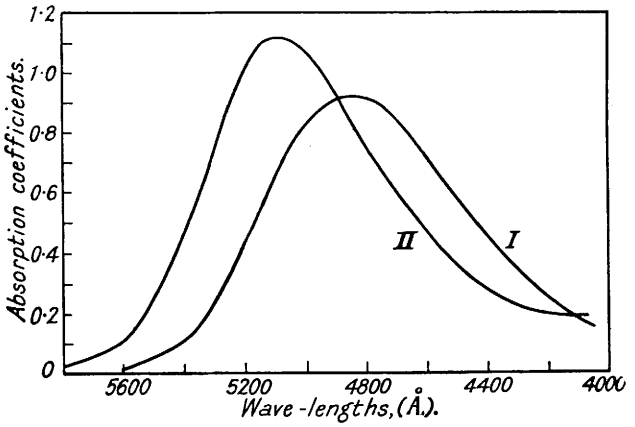
The salt was obtained in clusters of reddish-brown prisms having a dark green appearance in mass. It is easily soluble in alcohol to a ruby-red solution with a purple tinge, increasing on dilution; when an equal volume of water or solid sodium acetate is added the purple colour-base is precipitated. The very dilute methyl-alcoholic solution is violet and a purple coloration results when a drop of aqueous sodium carbonate is added. The salt dissolves in aqueous sodium carbonate, but the purple colour initially produced fades quickly to red; in aqueous sodium hydroxide a cobalt-blue solution, which fades to purple and then to red in about an hour, is obtained.

It is sparingly soluble in cold water, and dissolves readily on heating to a purplish-red solution which is soon decolorised, the colour being restored on acidification. In dilute aqueous acids it dissolves to brown-red solutions and on great dilution the brown tinge disappears and the solution becomes bluish-red. The ferric reaction in alcoholic solution is a rich violet-blue, red-violet in thin layers.

The addition of a saturated aqueous solution of picric acid to an aqueous solution of the salt precipitates the *picrate* in clusters of slender red-brown needles which may be recrystallised from half-saturated aqueous picric acid (Found in material dried at 80° in a high vacuum over phosphoric oxide : C, 47·7; H, 2·6; N, 7·6. $C_{21}H_{13}O_{14}N_3$ requires C, 47·5; H, 2·4; N, 7·9%).

The chloride was recovered from this derivative and found to have the colour reactions already described.

Absorption in the Visible Region.—The salts were examined in $0{\cdot}25N/10^4$-solution in 0·1%



I. 3 : 6 : 7 : 4′-*Tetrahydroxyflavylium chloride.* II. 3 : 6 : 7 : 3′ : 4′ : 5′-*Hexahydroxyflavylium chloride.*

methyl-alcoholic hydrogen chloride. The effect of the hydroxyl in the 6-position, replacing that in the 5-position of the anthocyanidins, is to make the transmitted light much yellower (less blue). We are indebted to Mrs. A. M. Robinson for kindly making these observations.

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