355. *A Synthesis of Pyrylium Salts of Anthocyanidin Type. Part XXI. The 6-Hydroxy-derivatives of the Chief Anthocyanidins.*

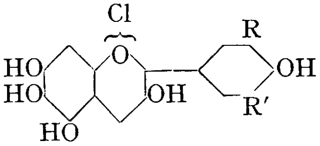
By E. H. Charlesworth and Robert Robinson.

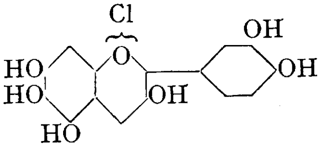
If naturally occurring anthocyanidins, divergent from the normal series, are awaiting discovery, it seems probable that some of them will be identified with the flavylium salts described in this communication. The tetrahydroxybenzene nucleus has been proved to be a unit of the structure of flavones and flavonols, and the plant product, carajurin, is the quinone-base of a flavylium salt, although it is true that this has not been shown to be an anthocyanidin (compare Chapman, Perkin, and Robinson, J., 1927, 3015). In the course of a " Survey of Anthocyanins " (Robinson and Robinson, *Biochem. J.*, 1932, **26**, 1654) it has occasionally been observed that an anthocyanidin having certain of the characteristics of cyanidin not shared with delphinidin and also certain of those of delphinidin not shared with cyanidin, could be isolated. The 6-hydroxycyanidin (I; R = H, R′ = OH) described below fulfils the requirements and an attempt to establish its natural occurrence is in progress.

The methods employed have been the normal ones of this series, antiarolaldehyde (Chapman, Perkin, and Robinson, *loc. cit.*) being coupled with appropriate second components, and the products demethylated. Nuclear alkylation was not feared in this case because the position 6 is substituted.

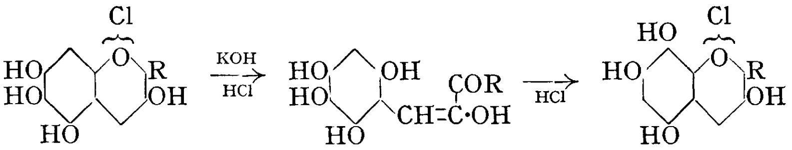
We have prepared and characterised 6-*hydroxygalanginidin chloride*, 6-*hydroxypelargonidin chloride* (I; R,R′ = H), 6-*hydroxycyanidin chloride* (II), and 6-*hydroxydelphinidin chloride* (I; R,R′ = OH). These salts are all redder (less blue) than the corresponding anthocyanidins, of which they are the 6-hydroxy-derivatives; their colour reactions in buffered solutions show that at corresponding p_H this applies also to the alkaline media. To give one concrete example, pelargonidin dissolves in aqueous sodium carbonate to a blue solution and 6-hydroxypelargonidin to a bluish-violet. The methyl ethers from which these salts are prepared have an unambiguous constitution and there is no reason to fear an isomeric change in acid solution. It must, however, be pointed out that, if the pyrylium ring were broken, isomeric change might accompany its reconstitution:

(I.)





(II.)



The distribution of the 6-hydroxyanthocyanidins in immiscible solvents, for example, the cyanidin and delphinidin reagents of Robinson and Robinson (*Biochem. J.*, 1931, **25**, 1704), is analogous to that of anthocyanidins with the same number of hydroxyl groups; hence these details will not be repeated in the experimental section.

For the purpose of comparison with its 6-hydroxy-derivative, galanginidin chloride has been synthesised by the *O*-benzoylphloroglucinaldehyde method. This salt, not yet identified as a natural anthocyanidin, has been previously prepared by Willstätter and Schmidt (*Ber.*, 1924, **57**, 1945), by Pratt and Robinson (J., 1925, **127**, 1128), and by Malkin and Robinson (J., 1925, **127**, 1190).

EXPERIMENTAL.

3-*Hydroxy*-5 : 6 : 7-*trimethoxyflavylium Chloride*.—A solution of antiarolaldehyde (5·3 g.) and ω-acetoxyacetophenone (4·5 g.) in dry ethyl acetate (75 c.c.) was saturated at 0—5° with dry hydrogen chloride. Ether was added after 4 days, and an orange-red powder (8·0 g.) isolated; this was dissolved in methyl alcohol (20 c.c.) and hydrochloric acid (20 c.c. of 20%), and the mixture refluxed for 1 hour. The crystals that separated on cooling were recrystallised from methyl alcohol by the addition of 20% hydrochloric acid, and formed brown oblique plates, many approximately rhombic and with a tendency towards convexity of the shorter side (Found in material dried in a vacuum over sulphuric acid : C, 59·2; H, 5·3; Cl, 9·8; MeO, 24·6; loss at 110° in a high vacuum over phosphoric oxide, 11·2. $C_{18}H_{17}O_5Cl,H_2O$ requires C, 58·9; H, 5·2; Cl, 9·7; 3MeO, 25·4; H_2O, 4·9%). The high value for loss on drying is due to loss of hydrogen chloride as well as water, the dry material containing Cl, 4·2% instead of the calculated amount (10·2%).

Alcoholic and aqueous hydrochloric acid solutions are yellowish-brown and weak alkalis discharge the colour and precipitate a pseudo-base. The amyl-alcoholic solution is orange-yellow and, on addition of aqueous sodium acetate or sodium carbonate, it becomes light yellow.

3 : 5 : 6 : 7-*Tetrahydroxyflavylium Chloride*.—3-Hydroxy-5 : 6 : 7-trimethoxyflavylium chloride (5·0 g.) was demethylated by boiling for 2 hours with a mixture of hydriodic acid (165 c.c., *d* 1·7) and phenol (21 g.) in an atmosphere of carbon dioxide. On the addition of much ether, a small quantity (1·1 g.) of crystalline iodide separated. This was changed to chloride in the usual manner, by treating the alcoholic solution with freshly precipitated silver chloride and adding to the filtrate an equal volume of 15% hydrochloric acid; the chloride then separated as a nearly black mass of elongated rectangular plates. These were twice recrystallised from alcohol and 15% hydrochloric acid and dried in a vacuum over sulphuric acid (Found : C, 51·9; H, 4·7; Cl, 10·2; loss at 110° in a high vacuum over phosphoric oxide, 13·3; MeO, 0·0. $C_{15}H_{11}O_5Cl,2H_2O$ requires C, 52·5; H, 4·4; Cl, 10·4; $2H_2O$, 10·5%). A second specimen, either crystallised under slightly different conditions, or dried for a longer period in the desiccator, gave an analysis indicating a monohydrate. In both specimens the loss on drying at 110° in a vacuum indicates loss of hydrogen chloride as well as water.

The 1% aqueous hydrochloric acid solution is yellow-brown and the acid alcoholic solutions are brownish-red. The addition of ferric chloride to the alcoholic solution gives a dull purple colour. When aqueous sodium acetate is added to the yellow-brown solution in amyl alcohol, the colour of the alcoholic layer deepens to a reddish-brown. Alkaline solutions all have a decided red colour, aqueous potassium bicarbonate quite a pure red, sodium carbonate a reddish-purple, and sodium hydroxide a red shade easily destroyed by aerial oxidation.

The following colour reactions were observed in a series of buffered solutions of graded p_H (for the p_H and compositions corresponding to the numbers, see Robertson and Robinson, *Biochem. J.*, 1929, **23**, 35). On mixing : 1% and 20% hydrochloric acid, yellow; (1) brownish-yellow; (3)—(9) reddish-brown, progressively redder; (11) reddish-brown, at first more intense than (7) and (9), but in 2 minutes faded to a weaker shade; (13) reddish-brown, fading within 2 minutes; (15) reddish-violet; (17) reddish-violet, more intense colour than (15) and does not fade so quickly at first, later more rapidly.

After 20 minutes : (1) faded considerably, less yellow; (3)—(9) only slight fading; (11)—(15) light brown; (17) lemon-yellow, lighter and yellower than 1% hydrochloric acid.

After 24 hours : 1% and 20% hydrochloric acid unchanged : (1) and (3) colourless; (5)—(15) light brown, slightly redder towards (15); (17) lemon-yellow.

A comparison with the data for galanginidin chloride shows that 6-hydroxygalanginidin chloride is the yellower in acid solutions.

5-O-*Benzoylgalanginidin Chloride*.—A solution of 2-*O*-benzoylphloroglucinaldehyde (4·2 g.) and ω-acetoxyacetophenone (3·0 g.) in a mixture of ethyl acetate (75 c.c.) and absolute alcohol (5 c.c.) was saturated with hydrogen chloride at 0°. After a week an orange-brown deposit (4·0 g.) was collected, dissolved in methyl alcohol (100 c.c.) containing a little hydrogen chloride, and concentrated to about 20 c.c.; the salt then separated in slender orange needles (2·0 g.), which were dried in a vacuum over sulphuric acid (Found : C, 66·7; H, 3·9; Cl, 9·2. $C_{22}H_{15}O_5Cl$ requires C, 66·8; H, 3·8; Cl, 9·0%).

O-*Benzoylgalanginidin chloride* is practically insoluble in hot 1% hydrochloric acid; the alcoholic acid solution is orange-yellow. Aqueous sodium carbonate dissolves it to a bright violet solution, which on the addition of acetone changes to a beautiful pure blue. The reaction recalls the similar behaviour of pelargonin and it is equally characteristic. Aqueous sodium hydroxide gives a violet solution, but the colour quickly fades. The addition of aqueous sodium acetate to the orange amyl-alcoholic solution causes the alcoholic layer to become violet.

Galanginidin Chloride.—Benzoylgalanginidin chloride (2·0 g.) was dissolved in a mixture of alcohol (22 c.c.) and aqueous sodium hydroxide (15 c.c. of 20%), air having been displaced by hydrogen which was slowly passed through the liquid for 5 hours, during which the colour changed from green to deep reddish-brown. Concentrated hydrochloric acid (15 c.c.) was added, and the mixture heated at 70° for an hour. After keeping over-night in the ice chest, the solid (1·2 g.) was collected, washed with 5% hydrochloric acid, and recrystallised by dissolving it as far as possible in boiling 0·5% hydrochloric acid (300 c.c.) and adding concentrated hydrochloric acid (35 c.c.) to the filtered solution. On cooling, elongated red prisms (0·5 g.) separated (Found in material dried in a vacuum over sulphuric acid : C, 58·7; H, 4·3; Cl, 11·2; loss at 110° in a high vacuum over phosphoric oxide, 4·6. $C_{15}H_{11}O_4Cl,H_2O$ requires C, 58·3; H, 4·2; Cl, 11·5; H_2O, 5·8%). Willstätter and Schmidt (*loc. cit.*) described a dihydrate losing $1H_2O$ in a vacuum; Pratt and Robinson (*loc. cit.*) also described a dihydrate and the colour reactions are in agreement with those previously described. The amyl-alcoholic solution is bluish-red, the addition of aqueous sodium acetate giving a reddish-purple shade in the alcoholic layer, while the addition of sodium carbonate gives the characteristic violet coloration in the aqueous layer.

The following colour reactions were observed in a series of buffered solutions. On mixing : 1% and 20% hydrochloric acid, orange; (1) and (3) orange-red, fading to a violet-pink and in 5 minutes almost colourless; (5) reddish-mauve, light permanganate shade in 5 minutes; (7) reddish-mauve, does not fade as rapidly as (5); (9) reddish-mauve, little fading in 5 minutes; (11) violet; (13)—(17) blue-violet.

After 20 minutes : (1) and (3) colourless; (5) light permanganate; (7) permanganate; (9) redder than (7); (11)—(17) unchanged.

After 2 hours : 1% and 20% hydrochloric acid unchanged; (1) and (3) colourless; (5) and (7) light pink; (9) light mauve; (11)—(15) practically unchanged; (17) greenish-violet.

After 24 hours : 1% hydrochloric acid unchanged; 20% hydrochloric acid light orange-pink; (1) and (3) colourless; (5) almost colourless; (7) and (9) light reddish-mauve; (11) light mauve; (13) and (15) violet; (17) almost colourless, faint yellow-green tinge.

3 : 4′-*Dihydroxy*-5 : 6 : 7-*trimethoxyflavylium Chloride.*—A solution of antiarolaldehyde (5·3 g.) and ω : 4-diacetoxyacetophenone (5·9 g.) in dry ethyl acetate (100 c.c.) was cooled in ice and saturated with dry hydrogen chloride. The flask was kept stoppered for 4 days; the semi-crystalline orange-coloured material (6·2 g.) was then collected and washed with ethyl acetate–ether; addition of ether to the mother-liquor afforded additional material (1·5 g.). It crystallised from 1% aqueous hydrochloric acid as red rhombic plates and was recrystallised by dissolution in hot 2% methyl-alcoholic hydrogen chloride and addition of half the volume of 20% aqueous hydrochloric acid; it then separated in elongated oblique prisms with a tendency to form rosettes (Found in material dried in a vacuum over sulphuric acid : C, 56·5; H, 5·0; Cl, 8·6; MeO, 22·8; loss at 110° in a high vacuum over phosphoric oxide, 5·3. $C_{18}H_{17}O_6Cl,H_2O$ requires C, 56·5; H, 5·0; Cl, 9·3; 3MeO, 24·3; H_2O, 4·7%. Found in material dried at 110° : C, 59·2; H, 4·7; Cl, 9·8; MeO, 23·5. $C_{18}H_{17}O_6Cl$ requires C, 59·3; H, 4·7; Cl, 9·7; 3MeO, 25·5%); some loss of methoxyl by part hydrolysis is indicated.

The solutions in alcoholic and in aqueous hydrochloric acid are orange-red, with a faintly blue tinge in thin layers. The salt is not easily soluble in methyl alcohol and if the concentration of hydrogen chloride is low, change into a pseudo-base occurs. In aqueous sodium carbonate it gives a bright bluish-red solution; sodium hydroxide gives a purplish-red which fades immediately. The addition of aqueous sodium acetate to the orange amyl-alcoholic solution produces a reddish-blue coloration in the alcoholic layer; the iron reaction was negative.

3 : 5 : 6 : 7 : 4′-*Pentahydroxyflavylium Chloride* (I; R, R′ = H).—A mixture of 3 : 4′-dihydroxy-5 : 6 : 7-trimethoxyflavylium chloride (5·0 g.), phenol (25 g.), hydriodic acid (240 c.c., *d* 1·7), and acetic anhydride (30 c.c.) was gently boiled for 2 hours in an atmosphere of carbon dioxide. The cooled solution was diluted with an equal volume of water and kept in the ice-chest for 24 hours; an iodide (4·4 g.) then separated, which was collected and converted into the chloride in the usual manner, by treatment of an alcoholic solution (75 c.c.) at 60° for 15 minutes

with an excess of freshly precipitated silver chloride and a piece of silver gauze. Hydrochloric acid (40 c.c. of 20%) was added to the filtered solution, and the alcohol partly evaporated by boiling; on cooling, the chloride (2·8 g.) separated in an apparently amorphous condition. The substance crystallised, when hydrogen chloride was passed into its solution in methyl alcohol, in dark mauve-red prisms (Found : C, 52·8, 53·0; H, 4·0, 4·0; Cl, 10·2. $C_{15}H_{11}O_6Cl,H_2O$ requires C, 52·9; H, 3·8; Cl, 10·4%). The salt is freely soluble in 1% aqueous hydrochloric acid to an orange-red solution; the alcoholic solutions in marked contrast are bluish-red. Ferric chloride added to a neutral alcoholic solution gives a purplish-violet coloration which is relatively stable. The solution in aqueous sodium carbonate is blue-violet, slowly changing to red; sodium hydroxide gives the same colorations but the change is more rapid. The red solution in amyl alcohol becomes bluer on the addition of sodium acetate.

The following colour reactions were observed in the series of buffered solutions. On mixing : 1% and 20% hydrochloric acid, yellow-orange; (1) orange; (3) reddish-orange; (5) redder than (3); (7) red with faint blue tinge; (9) permanganate shade, contrasts with (7); (11) violet; (13) blue-violet, both (1) and (13) fade quickly to a permanganate shade, not so bright as (9); (15) violet-blue fading to mauve; (16) blue fading to mauve; (17) greenish-blue.

After 24 hours : 1% and 20% hydrochloric acid, unchanged; (1) almost colourless; (3) and (5) colourless, small reddish-violet precipitate; (7) very light mauve; (9)—(16) light yellow-green; (17) light greenish-yellow. The addition of concentrated hydrochloric acid dissolves the precipitate in (3) and (5) giving an orange solution. The colour is not restored in the other solutions.

3 : 3′ : 4′-*Trihydroxy*-5 : 6 : 7-*trimethoxyflavylium Chloride*.—A moderate stream of dry hydrogen chloride was passed for 5 hours through an ice-cold solution of antiarolaldehyde (5·3 g.) and ω : 3 : 4-triacetoxyacetophenone (7·4 g.) in ethyl acetate (120 c.c.). The stoppered flask was kept at room temperature for 6 days; after 2 days the solid (6·5 g.) was collected, washed with ethyl acetate and then ether, and crystallised by dissolution in hot 1% hydrochloric acid (1200 c.c.) and addition of sufficient 20% hydrochloric acid to give a hydrogen chloride concentration of approximately 8%. The substance (5·0 g.) separated in thin thread-like clusters which formed a bright red powder on drying; it darkened at 140° and decomposed without melting at 210°. A specimen was recrystallised by adding half its volume of 10% hydrochloric acid to its solution in hot methyl alcohol (Found in material dried in a vacuum over sulphuric acid : C, 52·8; H, 5·0; Cl, 8·7; MeO, 22·0; loss at 110° in a high vacuum over phosphoric oxide, 6·7. $C_{18}H_{17}O_7Cl,1{\cdot}5H_2O$ requires C, 53·0; H, 4·9; Cl, 8·7; 3MeO, 22·8; H_2O, 6·6%. Found in material dried at 110° : C, 57·1; H, 4·7; Cl, 8·4; MeO, 23·6. $C_{18}H_{17}O_7Cl$ requires C, 56·7; H, 4·5; Cl, 8·4; 3MeO, 24·4%).

The above are micro-analyses (Schoeller); a macro-estimation of methoxyl in the hydrate gave MeO, 22·9% and 2 hours' boiling was necessary for the complete elimination of methyl iodide.

An aqueous hydrochloric acid solution was orange-red and the bluish-red alcoholic solution became deep blue with slight red tinge on the addition of ferric chloride. Aqueous sodium carbonate gave a purple-blue, and sodium hydroxide a pure blue solution that was resistant to aerial oxidation for a short time. The addition of aqueous sodium acetate to the blue-red solution in amyl alcohol produced a violet colour in the alcoholic layer.

3 : 5 : 6 : 7 : 3′ : 4′-*Hexahydroxyflavylium Chloride* (*Quercetagetinidin Chloride*) (II).—The foregoing quercetagetinidin trimethyl ether (3·5 g.) was demethylated by boiling for 2 hours with a mixture of hydriodic acid (175 c.c., *d* 1·7, freshly distilled over red phosphorus), phenol (15 g.), and acetic anhydride (20 c.c.), a current of carbon dioxide being passed through the apparatus. The mixture was diluted with an equal volume of water and, on keeping 24 hours at 0°, an amorphous iodide (3·0 g.) separated. The iodide (2·5 g.) was dissolved in alcohol (45 c.c.) containing a drop of concentrated hydrochloric acid and treated for 15 minutes at 60° with an excess of freshly precipitated silver chloride and a small piece of silver gauze. Hydrochloric acid (30 c.c. of 20%) was added to the filtered solution, part of the alcohol evaporated, and on cooling the chloride (1·5 g.) separated, but in an amorphous condition. Considerable difficulty was experienced in the crystallisation of this material, but after repetition of the precipitation from alcoholic solution by addition of 10% hydrochloric acid, the salt was finally obtained in elongated oblique prisms, red by transmitted light and with a tendency to form twinned crosses (Found in material dried in a vacuum : C, 47·6; H, 4·4; Cl, 8·9; loss in a high vacuum at 110° over phosphoric oxide, 10·5. $C_{15}H_{11}O_7Cl,2H_2O$ requires C, 48·0; H, 4·0; Cl, 9·5; H_2O, 9·6%).

The solution in 1% aqueous hydrochloric acid is orange-red to brownish-red depending on the concentration, the blue tinge being much less in evidence than in the case of cyanidin solutions. Aqueous sodium carbonate gives a purplish coloration which becomes decidedly redder after a few minutes. Aqueous sodium hydroxide gives a blue, changing to a greenish-blue and is then moderately resistant to aerial oxidation. The alcoholic solution is bluish-red and the addition of a trace of ferric chloride gives a violet-blue coloration which quickly disappears. The addition of aqueous sodium acetate to the bluish-red amyl-alcoholic solution causes the precipitation of a flocculent violet colour-base. Aqueous sodium carbonate, when added to the amyl-alcoholic solution, gives a purplish-violet shade in the aqueous layer, but this fades quickly. The anthocyanidin is extracted from aqueous solution by means of ether in the presence of picric acid.

The following colour reactions were observed in a range of buffered solutions. On mixing: 1% and 20% aqueous hydrochloric acid, orange; (1) reddish-orange; (3) reddish-orange with slight blue tinge; (5) bluish-red; (7) permanganate; (9) bluer than (7); (11) contrasts strongly with (9), both have much the same blue-violet shade on mixing but (11) fades immediately, whereas (9) is comparatively stable for 15 minutes; (13) bright violet fading immediately to a dirty mauve; (15) blue for an instant, then dirty mauve; (17) greenish-blue, then green.

After 20 minutes: (1) unchanged; (3), (5) and (7) slight fading; (9) mauve; (11) and (13) light mauve; (15) greener than (13); (17) light yellow-green.

After 2 hours: (1) light reddish-mauve; (3) almost colourless; (5) faded only slightly; (7) and (9) light mauve; (11) and (13) light brownish-mauve; (15) and (17) light yellow-green.

After 24 hours: 1% and 20% hydrochloric acid, unchanged; (1), (3) and (5) colourless; (7), (9) and (11) very pale brown; (13) slight brownish-green; (15) and (17) very light green. Concentrated hydrochloric acid restores the colour in (1), (3) and (5) only.

3 : 3′ : 4′ : 5′-*Tetrahydroxy*-5 : 6 : 7-*trimethoxyflavylium Chloride*.—Dry hydrogen chloride was passed for 5 hours through an ice-cold solution of antiarolaldehyde (9·1 g.) and ω : 3 : 4 : 5-tetra-acetoxyacetophenone (15·2 g.) in dry ethyl acetate (200 c.c.), absolute ethyl alcohol (35 c.c.), and glacial acetic acid (15 c.c.). The flask was corked and kept for 5 days; the almost black material (10·9 g.) was then collected and washed with ethyl acetate–ether and then ether. The crude material could not be crystallised and admixture with acetyl derivatives was suspected. It was therefore dissolved in 5% hydrochloric acid (about 1500 c.c.), the solution boiled for 1 hour and filtered, and a saturated aqueous solution of picric acid added; on cooling, an amorphous picrate (13·7 g.) separated. This derivative was sparingly soluble in alcohol and was purified by extraction with boiling alcohol (200 c.c.) containing picric acid (5 g.). After cooling, the *picrate* (11·1 g.) was collected, washed with alcohol, and crystallised from alcohol, forming red spear-shaped plates (Found: C, 48·0; H, 3·8; N, 6·8; MeO, 16·9; loss at 100° in a high vacuum, 4·1. $C_{18}H_{16}O_8,C_6H_3O_7N_3,H_2O$ requires C, 47·5; H, 3·5; N, 6·9; 3MeO, 15·3; H_2O, 3·0%).

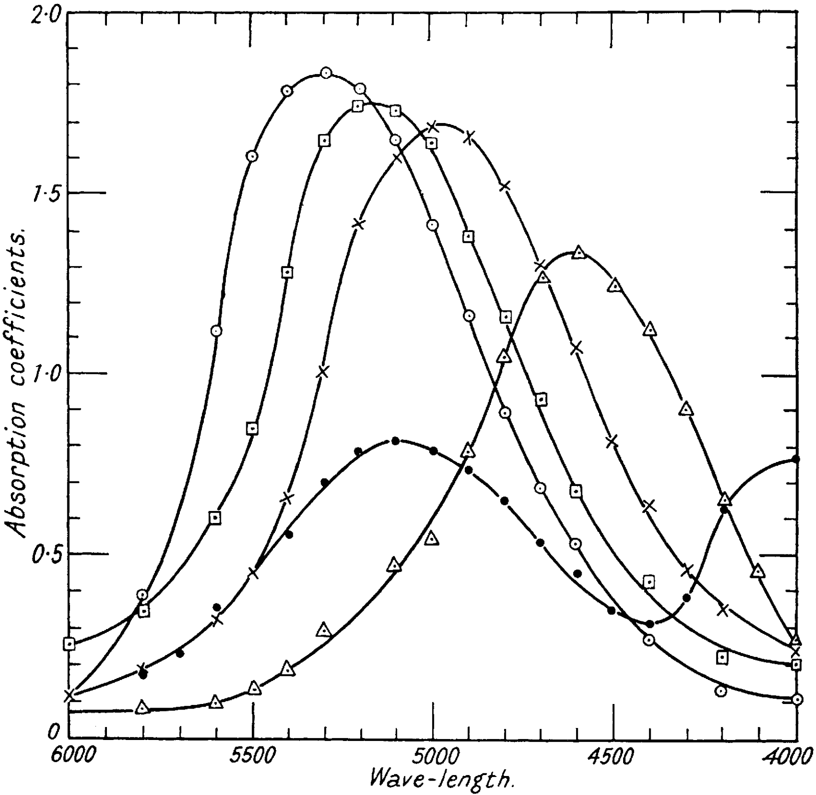
The picrate was dissolved in 5% methyl-alcoholic hydrogen chloride (100 c.c.) and, on further passage of hydrogen chloride, the chloride partly separated and precipitation was completed by means of ether. The crystalline chloride (7 g.) thus obtained was recrystallised by passing dry hydrogen chloride into its solution in hot alcohol (500 c.c.). On cooling, elongated rectangular prisms (6·6 g.) separated, which were dried in a vacuum over sulphuric acid (Found: C, 54·6; H, 4·8; Cl, 8·8; MeO, 25·2. $C_{18}H_{17}O_8Cl$ requires C, 54·5; H, 4·3; Cl, 9·0; MeO, 23·4%). The method of crystallisation perforce employed probably caused a slight etherification of hydroxyl groups and this accounts for the high figure for methoxyl content.

The solution in aqueous hydrochloric acid is dark red with a slight blue tinge; the alcoholic solution is deep bluish-red and with ferric chloride gives an intense pure blue coloration. Aqueous sodium carbonate gives a pure blue and sodium hydroxide a blue-violet solution. The addition of aqueous sodium acetate to the bluish-red amyl-alcoholic solution produces an intense violet coloration in the alcoholic layer.

3 : 5 : 6 : 7 : 3′ : 4′ : 5′-*Heptahydroxyflavylium Chloride* (I; R,R′ = OH).—3 : 3′ : 4′ : 5′-Tetrahydroxy-5 : 6 : 7-trimethoxyflavylium chloride (3·6 g.) was demethylated in 2 hours by a boiling mixture of hydriodic acid (140 c.c., *d* 1·7) and phenol (18 g.) in an atmosphere of carbon dioxide. On cooling and dilution with ether, the iodide (2·9 g.) separated and it was changed into chloride (1·8 g.) in the usual way. The salt was purified by dissolution in alcohol (50 c.c.) and addition of 10% hydrochloric acid (25 c.c.) to the hot solution. After several such treatments, the product was obtained in a micro-crystalline condition and dried in a vacuum over sulphuric acid (Found: C, 46·0; H, 4·4; Cl, 8·9; loss at 110° in a high vacuum over phosphoric oxide, 11·0; MeO, 0·0. $C_{15}H_{11}O_8Cl,2H_2O$ requires C, 46·1; H, 3·9; Cl, 9·1; H_2O, 9·2%). On drying at 110° the salt loses some hydrogen chloride as well as water.

The solution in 1% aqueous hydrochloric acid is bright red with only a faint blue tinge in thin layers; the alcoholic solution is bluish-red and on the addition of ferric chloride gives an unstable violet-blue coloration. When absolute alcohol is used the solution is violet-red and the addition of ferric chloride gives a pure blue coloration much more permanent than in the presence of water. The aqueous sodium carbonate solution is blue-violet, oxidising rather quickly. Aqueous sodium hydroxide gives a pure blue, changing to a greenish-blue, soon discharged on exposure to air. The solution in amyl alcohol is bluish-red and on the addition of aqueous sodium acetate an unstable flocculent violet colour-base is precipitated.

The following colour reactions were observed in the range of buffered solutions. On mixing: 1% and 20% aqueous hydrochloric acid, reddish-orange; (1) more intense reddish-orange; (3) reddish-violet; (5) dull permanganate; (7) bright permanganate; (9), (10), and (11) blue-violet, of increasing blueness; (13) blue with faint violet tinge; (15) blue; (17) violet-blue.



○ 6-Hydroxydelphinidin chloride. ▣ 6-Hydroxycyanidin chloride.
× 6-Hydroxypelargonidin chloride. △ 6-Hydroxygalanginidin chloride.
• Galanginidin chloride.

After 20 minutes: (1)—(5) unchanged; (7) slight fading; (9) dull violet; (10) as (9); (11) contrasts strongly with (9) and (10), all were much the same shade on mixing, but the violet tinge of (11) quickly disappears leaving a pure bright blue; (13) bright blue; (15) slightly duller blue than (13).

After 24 hours: 1% and 20% hydrochloric acid, unchanged; (1) and (3) colourless solution containing a small amount of violet precipitate; (5) precipitate and very pale dull reddish-violet; (7)—(11) very light brown; (13) light blue-grey; (15) light violet; (17) light pink.

Absorption in the Visible Region.—The absorption of light in the region 4000—6000 Å. of the 6-hydroxyanthocyanidin chlorides is illustrated in the Fig. In each case a $0{\cdot}25N/10^4$-solution in 0·1% methyl-alcoholic hydrogen chloride was employed.

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