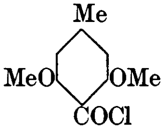
CCXCIII.—*A Synthesis of Pyrylium Salts of Anthocyanidin Type. Part XIV.*

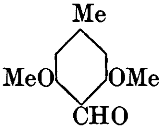
By ALEXANDER ROBERTSON and ROBERT ROBINSON.

ALL the anthocyanins derived from cyanidin chloride (3 : 5 : 7 : 3′ : 4′-pentahydroxyflavylium chloride) which have been described by Willstätter and his collaborators give a strong ferric chloride reaction, and hence the attachment of the sugar residues to positions 3′ and 4′ is highly improbable. Moreover, we know that the free hydroxyl-group combination (3 : 7 : 3′ : 4′) leads to the exhibition of an alkali colour-reaction practically identical with that due to the combination (3 : 5 : 7 : 3′ : 4′), whilst, on the other hand, the combination (5 : 7 : 3′ : 4′) produces a different effect. The evidence would clearly be much more complete if the effect of the combination (3 : 5 : 3′ : 4′) could be estimated, and the present communication includes a description of flavylium salts containing free hydroxyl groups in these positions. The results may be stated as follows. The combination (3 : 5 : 3′ : 4′) is intermediate between (3 : 7 : 3′ : 4′) and (5 : 7 : 3′ : 4′), and whilst it is closer to the former in one substance, it is closer to the latter in another; thus the influences of small constitutive variations are sufficiently pronounced to diminish the value of the argument from the colour-reactions. The present results are, however, in complete agreement with the conclusions of Pratt and Robinson (J., 1925, **127**, 1131) regarding the constitution of the anthocyanins. In order to obtain 3 : 5 : 3′ : 4′-tetrahydroxyflavylium salts by the usual methods, we required 2 : 6-dihydroxybenzaldehyde or a suitable derivative. The first line of attack was through *p*-orsellinic acid, the method for the preparation of which has been greatly improved. The acid could not be reduced directly by means of sodium amalgam in the presence of boric acid and *p*-toluidine (or sodium bisulphite), although Weil

(*Ber.*, 1922, **55**, 224, 301, 2664) has applied this process with satisfactory results to the reduction of derivatives of salicylic acid. Next, 2 : 6-*dimethoxy*-4-*methylbenzoyl chloride* (I) could not be reduced directly by Rosenmund's method, neither could the *iminochloride* derived from the related p-*toluidide* be reduced by following the conditions prescribed by Sonn in analogous cases (*Ber.*, 1919, **52**, 1927). The *nitrile* corresponding to (I) could, however, be reduced by an application of the method due to Stephen (J., 1925, **127**, 1874), although the aldehyde (II) was obtained in poor yield and was found to be useless for the special purpose in view. Finally, we succeeded in obtaining a substituted 2 : 6-dihydroxybenzaldehyde, namely, m-*xylorcylaldehyde* (III), by applying the Gattermann synthesis to *m*-xylorcin. The aldehyde is a bright yellow substance, and for this reason it may be best represented by the constitution (IV).



(I.)



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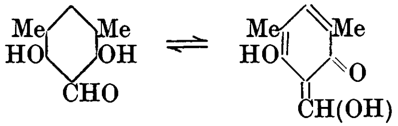
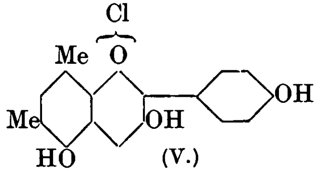


(III.) (IV.)

On condensation with ω : 4-dimethoxyacetophenone and ω-methoxyacetoveratrone in formic acid solution under the influence of hydrogen chloride, the *m*-xylorcylaldehyde readily yielded *flavylium* salts which, after demethylation, had the formulæ (V) and (VI), respectively.



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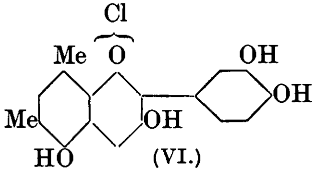
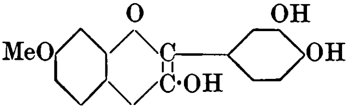


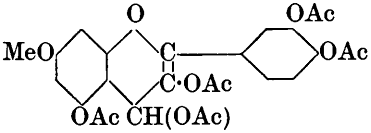
(VI.)

The reactions of (V), taken in conjunction with other similar data, suggest that pelargonin is a pelargonidin 5-diglucoside and callistephin a pelargonidin 3-glucoside, but in view of the problematic effect of the methyl groups, the 7-saccharide configuration is not definitely excluded in either case. The alkali colour-reaction of (VI) is similar to that exhibited by mecocyanin, but the methyl groups may have a reddening influence, as indeed the properties of rhamnetinidin (see below) suggest. A survey of commercial dyestuffs provides no certain guide as to the probable effect on the colour of the substitution of methyl for hydrogen. Thus new magenta is bluer than magenta, but phenosafranine is bluer than safranine-T, and further conflicting cases could be quoted. In order to obtain a flavylium salt with free hydroxyl groups in the positions 3 : 5 : 3′ : 4′, still more closely related to a cyanidin 7-glucoside, we have reduced the flavonol rhamnetin (VII) to the related *rhamnetinidin chloride* (IX). Rhamnetin is known to be quercetin 7-methyl ether because on fission it yields phloroglucinol monomethyl ether, and on methylation quercetin 3 : 7 : 3′ 4′-tetramethyl ether, the so-called yellow quercetin tetramethyl ether. The specimen employed was derived from xanthorhamnin and was free from quercetin and rhamnazin. The reduction of quercetin to cyanidin chloride was accomplished by Willstätter and Mallison (*Sitzungsber. K. Akad. Wiss. Berlin*, 1914, 769), who employed magnesium as the reducing agent in methyl-alcoholic hydrogen chloride solution; the yield was poor and the product was difficult to isolate. We made many unsuccessful experiments with the object of improving the direct method, and therefore had to resort to an indirect process.

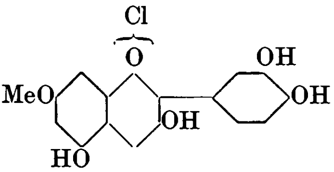
Rhamnetin was acetylated and reduced by zinc dust in boiling acetic anhydride solution (Herzig's acetylating reduction). The product [probably containing (VIII)] was then hydrolysed by means of aqueous-alcoholic hydrochloric acid with formation of rhamnetinidin chloride and other substances. This method constitutes an advance, although the yield of pure product remains unsatisfactory. The insoluble by-products probably arise from a pinacol formed in the reduction, and the optimum conditions for the process are being studied in detail in connexion with the reduction of quercetin and kaempferol. The alkali colour-reaction of rhamnetinidin is much closer to that of cyanidin and cyanin than to that of mecocyanin. This is the most definite evidence at our disposal, and it points clearly to the conclusion that mecocyanin, chrysanthenin, asterin, idaein, keracyanin, and prunicyanin are cyanidin 3-saccharides. Similarly, cyanin is indicated as a cyanidin 5-diglucoside,



(VII.)



(VIII.)



(IX.)

but we are on less safe ground here, since it is the general experience that purification of an anthocyanidin makes the alkali colour-reaction become bluer and never redder. Whilst, therefore, the fact that rhamnetinidin surpasses mecocyanin in the purity (absence of red) of the blue colour of its alkaline solutions could hardly be explained away as due to impurity of the rhamnetinidin (the presence of cyanidin in significant amount being excluded by the determination of methoxyl content and by the ascertained absence of quercetin in the rhamnetin employed), yet we could not, in view of the circumstances, be sure that further purification would not yield a rhamnetinidin having reactions identical with those of cyanin and cyanidin.

EXPERIMENTAL.

p-*Orsellinic Acid and some Derivatives.*—The method adopted for the preparation of the acid is based on that by means of which Brunner (*Annalen*, 1907, **357**, 321) obtained γ-resorcylic acid in 40% yield from resorcinol. A mixture of orcinol (20 g.), potassium bicarbonate (40 g.), and glycerol (40 g.) was heated (oil-bath at 115—120°) for 6 hours in an atmosphere of carbon dioxide. The *p*-orsellinic acid (16 g.) isolated from the reaction product is almost pure and, after crystallisation from boiling water (some decomposition to orcinol) and drying at 100°, had m. p. 165—166° (decomp.). The methyl ester has previously been obtained by Herzig (*Monatsh.*, 1903, **24**, 894) by the action of diazomethane on the acid. We have prepared the substance by the action of methyl iodide on silver *p*-orsellinate in boiling benzene solution. It crystallises from light petroleum in elongated, flat prisms, m. p. 93—94° (Herzig gives m. p. 98—99°) (Found: C, 59·4; H, 5·7. Calc. for $C_9H_{10}O_4$: C, 59·4; H, 5·5%). The m. p. could not be raised by repeated crystallisation. The ethyl ester has previously been obtained by Lipp and Schiller (*Ber.*, 1909, **42**, 1967) as a by-product from the condensation of ethyl sodioacetoacetate and propylene dibromide. These authors quote the m. p. 61°; we applied the silver-salt method and our ester crystallised from 60% alcohol in prismatic needles, m. p. 62°. These esters, like *p*-orsellinic acid, give a blue coloration with ferric chloride. [The publication of Wagenhofer on the complete methylation of *p*-orsellinic acid (*Monatsh.*, 1924, **45**, 223) appeared in the course of our work.] The acid (15 g.) was methylated by means of methyl sulphate (58 g.) and aqueous sodium hydroxide, giving methyl *p*-orsellinate dimethyl ether (12 g.). This ester has m. p. 86°, and on hydrolysis yields the acid, m. p. 180—182° (decomp.) (Found: C, 61·5; H, 6·3. Calc. for $C_{10}H_{12}O_4$: C, 61·3; H, 6·1%) (Herzig, *loc. cit.*, gives m. p. 178°).

2 : 4-*Dimethoxy*-6-*methylbenzaldehyde* (*Orcylaldehyde Dimethyl Ether*).—This substance, stated to melt at 62°, has been prepared by Gattermann by nuclear synthesis from orcinol dimethyl ether (*Annalen*, 1907, **357**, 372). We prepared the compound from orcylaldehyde in order to carry out certain confirmations of orientation, and because we were attempting the synthesis of the isomeric *p*-orcylaldehyde dimethyl ether. The methylation of the aldehyde (1 mol.) was effected by means of methyl sulphate (1·5 mol.) and aqueous sodium hydroxide (2 mol.). The alkali-insoluble product crystallised from light petroleum in small, colourless needles, m. p. 64—65°. On oxidation with potassium permanganate, orsellinic acid dimethyl ether was obtained in good yield. This crystallised from 20% acetic acid in glistening prisms, m. p. 143—144° (decomp.) (Found: C, 61·2; H, 6·2. Calc. for $C_{10}H_{12}O_4$: C, 61·3; H, 6·1%). The acid (m. p. given as 140°) has been previously obtained by Herzig (*loc. cit.*) by hydrolysis of the product of methylation of orsellinic acid by diazomethane. A mixture of the dimethyl ethers of orsellinic acid and *p*-orsellinic acid began to melt at 130°.

2 : 6-*Dimethoxy*-4-*methylbenz*-p-*toluidide*.—Phosphorus pentachloride (9 g.) was added to a mixture of *p*-orsellinic acid methyl ether (8 g.) and carbon tetrachloride (or benzene) (50 c.c.), and the reaction completed at 50°. The residue, left after the removal of the solvent and phosphoryl chloride under diminished pressure, was redissolved in benzene (100 c.c.) which was distilled away as before, leaving the 2 : 6-*dimethoxy*-4-*methylbenzoyl chloride* (I) as a mass of colourless needles, m. p. 84—85° (for the purest specimen obtained). The p-*toluidide* was obtained by the action of an excess of *p*-toluidine on a solution of the acid chloride in benzene. It crystallised from benzene, followed by light petroleum, in colourless needles, m. p. 168—169° (Found, in material heated at 100° for 6 hours with loss of benzene: C, 71·7; H, 6·8. $C_{17}H_{19}O_3N$ requires C, 71·6; H, 6·6%). This *p*-toluidide is moderately readily soluble in methyl or ethyl alcohol, and sparingly soluble in benzene or light petroleum. From a suspension of it in benzene (6 g. in 50 c.c.) the corresponding *imino-chloride* was prepared by the action of phosphorus pentachloride (5 g.) for 10 minutes on the steam-bath. After removal of the benzene and phosphoryl chloride, a colourless solid was obtained. On exposure to moist air, this was quickly converted into the original *p*-toluidide, m. p. 168—169°.

2 : 6-*Dimethoxy*-4-*methylbenzamide*, $(MeO)_2C_6H_2Me{\cdot}CO{\cdot}NH_2$.—A stream of ammonia was led through a solution of 2 : 6-dimethoxy-4-methylbenzoyl chloride (10 g.) in benzene (150 c.c.), and the solid which separated was collected, washed with water, and crystallised

from benzene; slender needles, m. p. 199° (yield, 7 g.) (Found: C, 61·5; H, 6·8. $C_{10}H_{13}O_3N$ requires C, 61·5; H, 6·7%). Its solubilities resemble those of the *p*-toluidide.

2 : 6-*Dimethoxy*-4-*methylbenzonitrile*.—A solution of the foregoing amide in pure thionyl chloride was boiled for 5 minutes, and the thionyl chloride then distilled under diminished pressure; the last traces were eliminated by the addition of benzene and redistillation. The *nitrile* (yield, 65—70%) crystallises from benzene–light petroleum in prismatic rods, m. p. 138—139° (Found: C, 68·0; H, 6·5. $C_{10}H_{11}O_2N$ requires C, 67·8; H, 6·2%). The substance may also be crystallised from 60% alcohol in large, squat prisms.

2 : 6-*Dimethoxy*-4-*methylbenzaldehyde* (II).—Hydrogen chloride was led into a mixture of powdered anhydrous stannous chloride (15 g.) and ether (150 c.c.) until a homogeneous solution was obtained. 2 : 6-Dimethoxy-4-methylbenzonitrile (6 g.), dissolved in a little chloroform, was then added, and the passage of hydrogen chloride continued until the liquid was saturated. Crystals separated after 12 hours; after 14 days, the separated solid weighed 8 g. and ultimately about 1 g. more was obtained. This double tin salt crystallised in needles and was very difficult to hydrolyse. The best results were obtained by dissolution in water at 40—50°, addition of an excess of sodium acetate, and heating on the steam-bath for 3 minutes. The *aldehyde* (1·5 g.) was isolated by means of ether, and crystallised from light petroleum in long, colourless, prismatic needles, m. p. 90—91° (mixed m. p. with orcylaldehyde dimethyl ether, 50—55°) (Found: C, 66·7; H, 6·7. $C_{10}H_{12}O_3$ requires C, 66·7; H, 6·7%). This substance is readily soluble in ether and the simple alcohols, moderately readily soluble in benzene, and slightly soluble in hot water. It yields a yellow, sparingly soluble p-*nitrophenylhydrazone* and reduces an ammoniacal silver solution. All attempts to condense it with ω-methoxyacetoveratrone were fruitless, and, no doubt as the result of steric hindrance, it does not appear to form a Schiff's base by condensation with aniline.

4-*Nitro*-6-*hydroxy*-m-*xylene*.—The nitration of *m*-xylidine (100 g.) by the method of Nöelting and Collins (*Ber.*, 1884, **17**, 265) gave 4-nitro-6-amino-*m*-xylene (80 g.), and this was converted into the corresponding phenol by the following method (compare D.R.-PP. 95,339 and 97,012) which is superior to that described by Pfaff (*Ber.*, 1883, **16**, 616). A diazonium salt solution, prepared at below 0° from the nitro-amine (16·6 g.), sulphuric acid (50 g.), crushed ice and water (300—350 g.), and sodium nitrite (7 g.), was filtered and gradually added to boiling 55% sulphuric acid (350 c.c.). On cooling, the nitroxylenol separated in light brown crystals (12—

14 g.), which could be employed for the next stage. The substance crystallised from hydrochloric acid in very slender needles, m. p. 95°. The reduction to 4-amino-6-hydroxy-*m*-xylene (Pfaff, *Ber.*, 1883, **16**, 1137) was conveniently effected by means of iron in alcoholic solution (compare West, J., 1925, **127**, 494). Iron powder (80 g.) was added in portions of about 10 g. at intervals of 3 minutes to a boiling solution of the nitro-*m*-xylenol (55 g.) in alcohol (300 c.c.) and concentrated hydrochloric acid (20 c.c.), and the mixture was boiled for 5 hours, a test then showing that reduction was complete. The filtered solution was concentrated to 100 c.c., cooled, and saturated with hydrogen chloride. After keeping in an ice-chest for some hours, the hydrochloride was collected, and a further quantity could be isolated from the mother-liquor by concentration to 50 c.c. and renewed saturation with hydrogen chloride. The salt crystallised in glistening plates; total yield of practically pure substance, 45 g.

m-*Xylorcin*.—The method of Pfaff (*loc. cit.*) for the preparation of this phenol gave unsatisfactory results, and we adopted the following procedure: 4-Amino-6-hydroxy-*m*-xylene hydrochloride (16 g.) was dissolved in 10% sulphuric acid (200 c.c.) by heating, and crushed ice (200 g.) was added after sudden cooling and shaking to ensure the separation of small crystals. Sodium nitrite (6·4 g.), dissolved in a little water, was then introduced, and the mixture stirred until the sulphate had disappeared. A little charcoal was added, and the diazo-solution filtered and gradually added to 600 c.c. of boiling 10% sulphuric acid. Very little tarry matter was produced, and the filtered solution (charcoal), which was almost colourless, was saturated with ammonium sulphate. Part of the xylorcin crystallised and was collected; the remainder was isolated by six extractions with ether. The product crystallised from benzene in colourless, hexagonal plates, m. p. 124—125° (yield, 8—10 g.). The substance has the properties attributed to it by Pfaff.

m-*Xylorcylaldehyde* (III).—A mixture of *m*-xylorcin (10 g.), anhydrous hydrogen cyanide (15 c.c.), and ether (150 c.c.) was saturated with hydrogen chloride, and the aldimine-hydrochloride separated in almost colourless, prismatic needles in 1 hour. After keeping over-night, the salt was collected, washed with ether, dried, and dissolved in cold water (200 c.c.). The solution was heated at 80—90° for 15 minutes, and a part of the *aldehyde* crystallised, the remainder separating in long, yellow needles on cooling. The substance was recrystallised from 40% ethyl alcohol (charcoal); bright yellow, prismatic needles, m. p. 155—156° (Found: C, 64·8; H, 6·0. $C_9H_{10}O_3$ requires C, 65·1; H, 6·0%). So far as we are able to judge, the striking colour of this substance is not due to impurity, and Gattermann has noted the yellow colour of 4 : 8- and 2 : 7-dihydroxynaphthaldehyde (Annalen, 1907, **357**, 341).

3 : 4′-*Dimethoxyflavylium Chloride.*—Bright scarlet needles (changing to orange-red on contact with air) separated when hydrogen chloride was passed into a solution of salicylaldehyde (2·2 g.) and ω : 4-dimethoxyacetophenone (3·4 g.) in ether (80 c.c.). The *chloride* recrystallised from 8% hydrochloric acid in glistening, red, prismatic needles (yield, 5·7 g.) (Found, in material dried over sulphuric acid in a high vacuum for 12 hours : C, 60·0; H, 5·7. $C_{17}H_{15}O_3Cl,2H_2O$ requires C, 60·3; H, 5·6%). The substance is sparingly soluble in cold dilute hydrochloric acid, but easily soluble in the hot solvent. The ferrichloride crystallised from acetic acid in small, dull orange, prismatic needles, m. p. 151—152°. Pratt and Robinson described (J., 1923, **123**, 751) hair-fine, orange-red needles, m. p. 135°, so that it is possible that this substance exists in two modifications. The crystalline form, colour, and melting point are different, and in repeating the preparation through the unsaturated ketone we obtained the salt, m. p. 151—152°.

3 : 4′-*Dihydroxyflavylium Chloride.*—This salt is of interest inasmuch as it contains hydroxyl groups in the two positions considered to have the greatest effect on the alkali colour-reactions of the anthocyanidins. Thus, a comparison of the colour of alkaline solutions of this salt and of 7 : 3′ : 4′-trihydroxyflavylium chloride and the representative of the 5 : 3′ : 4′-hydroxylated series described below demonstrates the relatively feeble hypsochromic character of the hydroxyl groups in positions 7 and 5. A mixture of 3 : 4′-dimethoxyflavylium chloride (2·5 g.), phenol (10 g.), and hydriodic acid (60 c.c.; *d* 1·7) was boiled for 30 minutes in an atmosphere of carbon dioxide. After cooling, the phenolic layer was separated, and the demethylated *iodide* was obtained in slender, bright red needles by the addition of ether (yield, 0·7 g.). The *chloride*, obtained in the usual manner by means of silver chloride in methyl-alcoholic solution, was precipitated, after concentration, by dilute hydrochloric acid as a mass of bright red plates, and crystallised from 5—6% hydrochloric acid in red plates exhibiting a golden reflex. Rapid cooling causes the separation of needles (Found, in material dried over soda–lime for 12 hours : C, 59·6; H, 5·1.

$$C_{15}H_{11}O_3Cl,1{\cdot}5H_2O$$

requires C, 59·7; H, 4·7%). The salt crystallises from ethyl-alcoholic hydrogen chloride in flat, pointed prisms. It is moderately soluble in 4—6% hydrochloric acid and very readily soluble in hot dilute or concentrated hydrochloric acid, giving orange to orange-red solutions. When it is treated with much water, a colourless solution of the pseudo-base is obtained, addition of acids restoring the orange-yellow colour of the flavylium salt. Aqueous or aqueous-alcoholic sodium carbonate dissolves the salt to a red solution, tinged with violet.

5-*Hydroxy*-3 : 4′-*dimethoxy*-6 : 8-*dimethylflavylium Chloride*.—A solution of *m*-xylorcylaldehyde (2 g.) and ω : 4-dimethoxyacetophenone (3 g.) in formic acid (25 c.c.) was saturated with hydrogen chloride, kept for 48 hours, and mixed with an excess of dry ether. The precipitated dark brown, prismatic needles were collected and crystallised from 8% hydrochloric acid as a dark brown, matted mass of slender, woolly needles (3 g.) (Found, in material dried over soda-lime for 12 hours : C, 57·1 ; H, 6·2. $C_{19}H_{19}O_4Cl,H_2O$ requires C, 57·4 ; H, 6·3%).

The *ferrichloride* crystallised from acetic acid in spherical aggregates of brown, prismatic needles, m. p. 211—212° after darkening at 190°.

3 : 5 : 4′-*Trihydroxy*-6 : 8-*dimethylflavylium Chloride* (V).—The foregoing dimethyl ether (2 g.) was demethylated by boiling hydriodic acid (60 c.c.; *d* 1·7) and phenol (20 g.) in 40 minutes (passage of carbon dioxide). The iodide was precipitated from the separated phenolic layer by means of ether in purple rods (1 g.), and converted into the *chloride* in the usual way. This salt separated from its concentrated aqueous methyl-alcoholic hydrochloric acid solution in violet, prismatic needles, and was recrystallised from 8% hydrochloric acid; glistening, violet needles (Found, in material dried in a high vacuum over sulphuric acid for 24 hours : C, 63·9 ; H, 5·1. $C_{17}H_{15}O_4Cl$ requires C, 64·1 ; H, 4·7%). This salt is very sparingly soluble in cold dilute hydrochloric acid but dissolves freely in the hot solvent to a reddish-brown solution. Unlike most flavylium salts, the anhydrous material is not hygroscopic and, as the crystals suffered no change in appearance on drying, it would appear that they separated in the anhydrous condition. The alcoholic solutions are not fluorescent, and on dilution with water give almost colourless solutions of the pseudo-base. The colour of the solution in aqueous sodium carbonate is reddish-violet, and in aqueous-alcoholic sodium carbonate, bluish-violet.

5-*Hydroxy*-3 : 3′ : 4′-*trimethoxy*-6 : 8-*dimethylflavylium Chloride*.—The condensation of *m*-xylorcylaldehyde and ω-methoxyacetoveratrone was carried out as in the analogous case (above) and the yield was almost quantitative. A hot solution of the crude salt in 0·5% hydrochloric acid was filtered, and the acid concentration increased to 8%. The dark red, woolly needles which separated were collected, and when dried exhibited a green reflex. The solutions in hot 7—8% hydrochloric acid are deep crimson, and on cooling, the separation of the salt is almost complete. The *ferri-*

chloride crystallised from acetic acid in reddish-brown, elongated, rhombic plates, exhibiting a bluish-green reflex; m. p. 200—203° (Found: C, 44·6; H, 3·9. $C_{20}H_{23}O_5Cl_4Fe$ requires C, 44·5; H, 3·9%). This derivative is readily soluble in hot acetic acid, and separates almost completely on cooling the solution.

3 : 5 : 3′ : 4′-*Tetrahydroxy*-6 : 8-*dimethylflavylium Chloride* (VI).—The chloride (1·5 g.) last described was demethylated under the usual conditions by hydriodic acid (80 c.c.; *d* 1·7) in presence of phenol (15 g.) in 30 minutes. Water (30 c.c.) was added, the phenolic layer separated, and the *iodide* precipitated by the addition of ether. The slender, red needles were collected and converted into the *chloride* by means of silver chloride in hot dilute hydrochloric acid solution. On standing, the cooled solution deposited dark red, microscopic, slender needles, and these were recrystallised from 10% hydrochloric acid (Found, in material dried in a high vacuum over sulphuric acid for 24 hours: C, 58·1; H, 5·1. $C_{17}H_{15}O_5Cl,H_2O$ requires C, 57·9; H, 4·8%). The salt is readily soluble in hot dilute hydrochloric acid, giving deep red solutions that deposit crystals but slowly on cooling. It dissolves in aqueous sodium carbonate to a bluish-violet solution, unchanged, in the absence of oxygen, by the addition of sodium hydroxide. In alcoholic solution, the sodium carbonate reaction is also violet, but this becomes blue on the addition of sodium hydroxide. The ferric chloride reaction in alcoholic solution is intense violet.

Rhamnetinidin Chloride (IX).—The crude rhamnetin obtained by hydrolysis of xanthorhamnin from Persian berries, was thoroughly extracted with boiling alcohol to remove quercetin, and then with hot acetic acid to remove rhamnazin. Finally it was purified through its monopotassium salt (Perkin and Wilson, J., 1903, **83**, 136). The light yellow product was dried at 140° (Found: MeO, 9·7. Calc.: MeO, 9·8%). A mixture of rhamnetin (4·6 g.), potassium acetate (5 g.), and acetic anhydride (80 c.c.) was boiled for 2—3 minutes (acetylation cannot be complete at this stage), and a large excess of zinc dust added in small portions in rapid succession. When further additions produced no change in the appearance of the solution (about 5 mins.), the liquid was boiled for 5 minutes longer, then cooled, decanted, and added to 500 c.c. of water containing concentrated hydrochloric acid (25 c.c.). The zinc was washed with a little acetic acid. The ochreous, sticky product was collected on a glass rod and on the sides of the container, washed with water, dissolved in alcohol (100 c.c.) and hydrochloric acid (30 c.c.), and the solution boiled for 20 minutes, the red colour of the flavylium salt appearing during this process. The crimson solution was concentrated in a vacuum, a little water being added from time to time. When most of the colouring matter had been precipitated, the substance was collected, thoroughly extracted with a large volume of ether, and the residue with boiling 0·5% hydrochloric acid. The salt was precipitated from the filtrates, after concentration, by concentrated hydrochloric acid, and this operation was repeated. The product was then fractionally crystallised by slow evaporation of an alcoholic solution containing 10% hydrochloric acid; some tarry matter was first eliminated and then definite prismatic crystals separated. These were collected, twice recrystallised in the same way, and air-dried (Found : C, 51·9; H, 4·7; MeO, 8·3. $C_{16}H_{13}O_6Cl,2H_2O$ requires 51·6; H, 4·6; MeO, 8·6%). After this had been exposed to a vacuum for 12 hours, the analytical results indicated a monohydrate, but were not sufficiently sharp. *Rhamnetinidin chloride* is very sparingly soluble in cold 0·5% hydrochloric acid, readily soluble in the hot solvent to a brownish-red solution; the alcoholic solutions are bluish-red. The salt crystallises from aqueous-alcoholic hydrochloric acid in clusters of elongated prisms, orange-red by transmitted light, and forming a dark purplish-brown mass exhibiting an intense green reflex. On the addition of aqueous sodium carbonate to the solid salt, a blue solution is obtained. This is bluer than that of mecocyanin and redder than that of cyanidin, cyanin, or fisetinidin under the same conditions. Thick layers are violet-red, and this dichroism is the chief distinction from fisetinidin. On progressive dilution the colour becomes violet and finally blue. In alcoholic solution, the distinction from mecocyanin is much more pronounced, since with sodium carbonate under similar conditions, rhamnetinidin gives a blue solution (on the red side by comparison with cyanidin), whereas mecocyanin gives a violet solution. On the addition of sodium hydroxide to the alcoholic solution, mecocyanin and rhamnetinidin give identical pure blue colorations. The ferric chloride reaction of rhamnetinidin is blue in alcoholic solution and violet in aqueous solution.

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