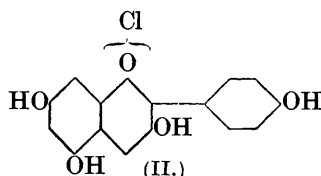
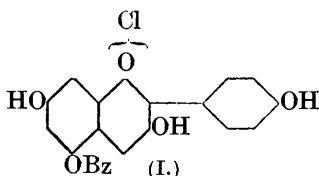


CCl.—*A Synthesis of Perylium Salts of Anthocyanidin Type. Part XVI. The Synthesis of Pelargonidin Chloride by Means of O-Benzoylphloroglucinaldehyde.*

By ALEXANDER ROBERTSON, ROBERT ROBINSON, and JIRO SUGIURA.

THE condensation of *O*-benzoylphloroglucinaldehyde and  $\omega$ :4-di-acetoxyacetophenone in ethyl acetate solution in the presence of hydrogen chloride leads to the formation of 3:7:4'-trihydroxy-5-benzoyloxyflavylium chloride (5-*O*-benzoylpelargonidin chloride) (I), which on de-benzoylation is changed to pelargonidin chloride (II).



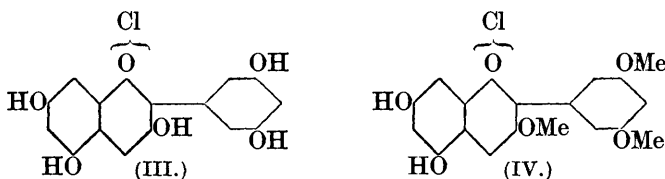
The reactions of (I) resemble those of pelargonenin and pelargonin chlorides, not only in connexion with the colours of acid and alkaline solutions but also because the alcoholic solutions exhibit a green fluorescence.

This evidence tends to confirm the view that pelargonenin is a pelargonidin 5- or 7-glucoside. Phloroglucinol derivatives seldom exhibit intense fluorescence, unless in sulphuric acid solution; on the other hand, resorcinol derivatives frequently fluoresce brightly in aqueous or alcoholic solutions and we consider that the presence of the benzoyl group in (I) makes the nucleus virtually equivalent to that of a resorcinol derivative.

The suggestion is that the sugar groups in pelargonenin and pelargonin (also in the *Salvia* series of anthocyanins) exercise a similar function and must therefore be in one of the positions 5 and 7. It should be clearly understood that all remarks in this series of memoirs on the constitution of anthocyanins are based on the assumption that these substances are homogeneous. For example, in regard to pelargonin our definite conclusion is that it is a 5- or 7-diglucoside of pelargonidin or that it is a mixture containing sufficient of the 5- or 7-substituted pelargonidin (not necessarily diglucosidoxy-substituted) to enable it to exhibit certain characteristic properties. We consider that pelargonin cannot be pure pelargonidin 3-diglucoside. Naturally it is not possible to express an opinion in regard to this question of the homogeneity of the

anthocyanins without very careful independent examinations, which we have not yet had the opportunity to make in a sufficiently detailed manner.

An account of an attempt to prepare 3 : 5 : 7 : 3' : 5'-pentahydroxyflavylium chloride (III) is included in this communication. We desired to obtain this salt in order to estimate the importance of the part played by the hydroxyl in position 4' in determining the reactions of delphinidin.



Employing the methods developed in this series of papers, we obtained without difficulty the *trimethyl ether* (IV), but this salt decomposed on attempted demethylation by means of hydriodic acid in the presence of phenol. Indications of the production of (III) were obtained in some experiments.

#### E X P E R I M E N T A L.

*5-O-Benzoylpelargonidin Chloride* (I).—A solution of *O*-benzoylphloroglucinaldehyde (7.7 g.) and  $\omega$  : 4-diacetoxyacetophenone (7.0 g.) in dry ethyl acetate (150 c.c.) was saturated with hydrogen chloride and kept for 3 days. The red crystals that separated were collected (9.5 g.), and a portion was crystallised by solution in the minimum quantity of cold methyl alcohol and addition of 10% hydrochloric acid until a turbidity appeared. In a few hours microscopic, rectangular plates, having a maroon colour in mass and a deep blue lustre, were deposited (Found in material dried over sulphuric acid and sodium hydroxide : C, 61.0; H, 4.4; Cl, 8.7.  $C_{22}H_{15}O_6Cl \cdot 1.5H_2O$  requires C, 60.3; H, 4.2; Cl, 8.1%). *Benzoylpelargonidin chloride* dissolves in alcohol to a violet solution and the pseudo-base is formed in very dilute alcoholic solution or on the addition of water. The acid alcoholic solutions resemble aqueous solutions of eosin both in colour and in fluorescence. Aqueous sodium carbonate dissolves the salt to a bright violet solution, but the colour in alcohol, even in 50% alcohol, is pure blue.

*Pelargonidin Chloride* (II).—Crude benzoylpelargonidin chloride (9.5 g.) was dissolved in a mixture of alcohol (120 c.c.) and 20% aqueous sodium hydroxide (80 c.c.), air being excluded from the apparatus by hydrogen. The intensely purplish-blue solution became dichroic (red) and then green. After 5 hours, concentrated

hydrochloric acid (100 c.c.) was added and the mixture was heated at 60° for a minute, kept for 15 minutes, then cooled, and added to a large volume of ether and 50 c.c. of water. The precipitated salt was collected and washed with 3% hydrochloric acid. The picrate was precipitated from a solution in very dilute hydrochloric acid in crimson needles, which were collected. This material dissolved in ethyl alcohol and immediately separated again; it was redissolved by heating and some picric acid added. The cooled solution deposited short, deep crimson needles. The regenerated chloride separated from the methyl alcohol-ether mixture in swallow-tailed leaflets and on recrystallisation, by addition of its filtered solution in methyl alcohol to hot 15% hydrochloric acid, it formed elongated, almost rectangular plates or flat, long prisms (Found: C, 55.8; H, 4.1. Calc. for  $C_{15}H_{11}O_5Cl \cdot H_2O$ : C, 55.6; H, 4.0%). The salt crystallised from 3% hydrochloric acid in prismatic needles and from methyl alcohol, by exposure of the solution to hydrogen chloride, in sharply cut, almost rectangular, elongated prisms. If a dilute solution of a pure specimen in methyl alcohol is added to hot 15% hydrochloric acid, rhombic plates are obtained and a large proportion of these have broad markings along the diagonals, giving the crystals the appearance of an envelope. Evaporation of a solution in a mixture of ethyl alcohol and 7% hydrochloric acid gave long, flat needles. The substance exhibited *all* the recorded properties of pelargonidin chloride and the only point not checked was the supposed conversion into a new substance by the action of hot hydrochloric acid.

When water is added to a concentrated alcoholic solution it is true that a deep red solution is formed and that the colour-base is not precipitated. On long standing, however, a colour-base having a green reflex (duller than that of cyanidin) and a violet colour by transmitted light is deposited. The colour-base is converted into the colour-salt on warming with a dilute solution of tartaric acid or citric acid. The blue solution of pelargonidin in aqueous sodium carbonate is reddish-violet when viewed in the light of a metal-filament lamp.

$\omega$ : 3:5-Trimethoxyacetophenone,  $(MeO)_2C_6H_3 \cdot CO \cdot CH_2 \cdot OMe$ .—On methylation by means of methyl sulphate and potassium hydroxide in aqueous methyl-alcoholic solution, orcinol gave a little more than its own weight of the dimethyl ether, b. p. 227—228°/751 mm., and on oxidation by hot 2% aqueous potassium permanganate (twice the theoretical quantity), 3:5-dimethoxybenzoic acid, m. p. 181—182° (lit., 180°), was obtained in 25% yield.

Ethyl  $\alpha\gamma$ -dimethoxyacetoacetate (22.8 g.) was gradually added to a suspension of granulated sodium (2.8 g.) in ether (150 c.c.) and when the formation of the sodio-derivative was complete a solution

of 3 : 5-dimethoxybenzoyl chloride (24.1 g.) in ether (95 c.c.) was introduced. The mixture was refluxed for 4 hours and kept for 12 hours. After removal of the solvent the viscous, orange residue was agitated for 12 hours with cold 2.5% aqueous potassium hydroxide (550 c.c.), and the reaction completed by heating on the steam-bath for 4 hours. The neutral product was isolated by means of ether and distilled (6.7 g., b. p. 127—137°/3 mm.). The oil soon solidified and the *ketone* crystallised from light petroleum in colourless needles, m. p. 42° (Found : C, 63.1; H, 6.6.  $C_{11}H_{14}O_4$  requires C, 62.9; H, 6.7%). The substance is readily soluble in most organic solvents. The *semicarbazone* crystallises from alcohol in colourless needles, m. p. 149—149.5° (Found : N, 16.0.  $C_{12}H_{17}O_4N_3$  requires N, 15.7%).

*7-Hydroxy-5-benzoyloxy-3 : 3' : 5'-trimethoxyflavylium Chloride* (IV with OBz in position 5).—A mixture of *O*-benzoylphloroglucin-aldehyde (2.3 g.),  $\omega$  : 3 : 5-trimethoxyacetophenone (2.0 g.), and anhydrous ether (500 c.c.) was saturated with hydrogen chloride for a few hours and then kept for 2 days. The brownish-crimson crystals that separated exhibited a green reflex and were collected (0.84 g.). The salt was recrystallised from methyl alcohol containing hydrogen chloride, forming prismatic needles (Found in material dried over sulphuric acid and sodium hydroxide : C, 59.5; H, 5.0; Cl, 6.9.  $C_{25}H_{21}O_7Cl \cdot 2H_2O$  requires C, 59.5; H, 5.0; Cl, 7.0%).

*5 : 7-Dihydroxy-3 : 3' : 5'-trimethoxyflavylium Chloride* (IV).—(A) A mixture of  $\omega$  : 3 : 5-trimethoxyacetophenone (3.2 g.), *O*-triacetylphloroglucin-aldehyde (4.5 g.), and formic acid (15 c.c.) was cooled and saturated with hydrogen chloride for 3 hours. Next day the product was precipitated by the addition of ether, collected, and hydrolysed by means of boiling alcohol (150 c.c.) and concentrated hydrochloric acid (25 c.c.) for 10 minutes. The greater part of the alcohol was removed by distillation under diminished pressure and 10% hydrochloric acid (100 c.c.) was added to the residue. The crude salt was purified by solution in 0.5% hydrochloric acid and precipitation with concentrated hydrochloric acid and then by crystallisation from methyl alcohol containing hydrogen chloride. The dark violet-brown, flat prisms are reddish-brown by transmitted light and exhibit a coppery glance (Found : C, 58.1; H, 5.2; MeO, 22.0.  $C_{18}H_{17}O_6Cl \cdot 0.5H_2O$  requires C, 58.0; H, 4.8; MeO, 24.4%). In view of the difficulty often experienced in obtaining satisfactory results for methoxyl in the flavylium salt series, the low value found in this case is without significance except that it excludes the composition  $C_{18}H_{17}O_6Cl \cdot CH_4O$  (C, 57.6; H, 5.3; MeO, 31.3%). The salt dissolves in aqueous sodium carbonate to a greenish-yellowish-brown solution; it is insoluble in cold 0.5%

hydrochloric acid, but dissolves in the hot solvent to an orange-red solution. The latter gives a dark brownish-violet colour-base on the addition of sodium acetate. The rose-coloured solution in alcohol is decolorised on the addition of water and the colour is rapidly and quantitatively restored on the addition of hydrochloric acid.

(B) The benzoyl derivative (above) was hydrolysed by means of 10% aqueous sodium hydroxide in the absence of air for 4 hours. The regenerated salt was crystallised from dilute hydrochloric acid and then from methyl alcohol containing hydrogen chloride (Found: C, 57.6; H, 5.2%). The salt was identical with that prepared as under (A). All attempts to demethylate this substance and to isolate the product in a pure condition were unsuccessful, but solutions of the pentahydroxyflavylium chloride were probably obtained in the course of the experiments. The bluest alkali-colour-reaction observed was a reddish-purple.

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THE UNIVERSITY, MANCHESTER.

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