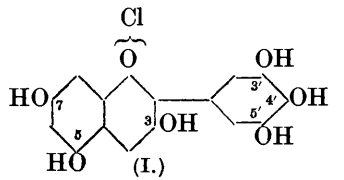
CCCIII.—*A Synthesis of Pyrylium Salts of Anthocyanidin Type. Part XVIII. A Synthesis of Malvidin Chloride.*

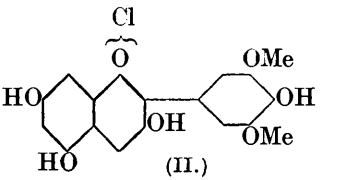
By WILLIAM BRADLEY and ROBERT ROBINSON.

WILLSTÄTTER and MIEG (*Annalen*, 1915, **408**, 122) found that malvin, the anthocyanin of the violet flowers of the wild mallow (*Malva silvestris*, L.), on account of the facility with which its sparingly soluble salts crystallise, could be isolated with particular ease.

Malvin chloride was shown to be the diglucoside of malvidin chloride, itself a dimethyl ether of delphinidin chloride (I), and it is noteworthy that of the various mono- and di-methyl ethers of



(I.)



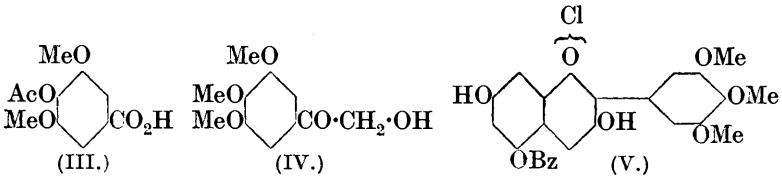
(II.)

delphinidin chloride examined by Willstätter and his collaborators, only malvidin and petunidin gave analytical figures indicating complete homogeneity. The status of malvidin as a chemical individual is unchallenged and it seems probable that petunidin also is a pure substance, namely, delphinidin 3′-methyl ether. Willstätter and Burdick (*Annalen*, 1916, **112**, 217), who isolated and examined petunin chloride, commented on the homogeneity of the pigment and emphasised its importance in connexion with our knowledge of the delphinidin methyl ethers. According to Karrer and Widmer (*Helv. Chim. Acta*, 1927, **10**, 5), however, myrtillidin and œnidin are mixtures containing malvidin, which is evidently one of the more widely distributed anthocyanidins.

Gatewood and Robinson (Part X, J., 1926, 1959) first suggested that malvidin chloride should be represented by the formula (II),

basing their argument on the reactions of delphinidin chloride 3-methyl ether and of other polyhydroxyflavylium salts related to delphinidin.

Then Anderson and Nabenhauer (*J. Amer. Chem. Soc.*, 1926, **48**, 2997) isolated a pigment from *Isabella* grapes which they considered should be identical with Willstätter and Zollinger's œnin. The related anthocyanidin gave an amorphous product on acetylation, but this was oxidised by potassium permanganate in acetone solution with formation of *O*-acetylsyringic acid (III). This result



could be brought into line with Gatewood and Robinson's view of the constitution of malvidin chloride only on the basis of the hypothesis that specimens of œnidin contain malvidin. A direct proof of the occurrence of the pyrogallol 1 : 3-dimethyl ether group in malvidin was furnished by Karrer and Widmer (*loc. cit.*), who obtained syringic acid by the fission of malvidin with 10% aqueous barium hydroxide and in other ways. These authors propose the name *syringidin* for delphinidin 3′ : 5′-dimethyl ether, but as malvidin is pure syringidin we have retained the name given to the substance by its discoverers, especially since our synthetical material has been identified with the anthocyanidin from malvin chloride.

We take this opportunity of thanking Professor P. Karrer for very kindly supplying specimens of malvin chloride and syringidin chloride which have greatly assisted us in this investigation. The methods that have been devised for the preparation of the benzoylcarbinol derivatives required for the synthesis of other anthocyanidins are not applicable to the intermediate for malvidin, chiefly because the Friedel–Crafts and analogous reactions applied to pyrogallol ethers lead to the formation of 4-acyl derivatives having the type of orientation characteristic of pyrogallolcarboxylic acid rather than of gallic acid. We therefore decided to seek a method of effecting the change $R{\cdot}CO_2H \longrightarrow R{\cdot}CO{\cdot}CH_2{\cdot}OH$ which could be used when gallic acid or one of its derivatives was the point of departure. Direct halogenation of acetophenone derivatives could not be employed in this instance because of the ease with which the aromatic nucleus was attacked by the reagent and for one reason or another none of the more obvious methods could be utilised.

However, an observation of Raper and Clutterbuck (*Biochem. J.*,

1926, **20**, 63), that hydroxyacetoacetic acid and acetol are among the products of oxidation of ethyl acetoacetate by hydrogen peroxide in the presence of alkalis, suggested an application to the preparation of benzoylcarbinols, and we developed our attack of this problem in this direction in the first instance. The action of hydrogen peroxide on ethyl 3 : 4 : 5-trimethoxybenzoylacetate and 3 : 4 : 5-trimethoxydibenzoylmethane in the presence of sodium hydroxide gave rise to substances which reduced Fehling's solution in the cold, but use could not be made of the reaction as a method of preparing trimethoxybenzoylcarbinol. It was desirable to introduce a modification in which the use of aqueous solutions could be avoided and the hydroxyl group could be protected.

These requirements are fulfilled by a method depending on the interaction of acyl peroxides and the sodium derivatives of β-ketonic esters in benzene suspension. The reaction proceeds in accordance with the equation $R{\cdot}CO{\cdot}CH{\cdot}CO_2Et\}Na + X_2(CO{\cdot}O)_2 = R{\cdot}CO{\cdot}CH(O{\cdot}COX){\cdot}CO_2Et + X{\cdot}CO_2\}Na$. Ethyl benzoylacetate and benzoyl peroxide gave, in this way, *ethyl benzoylbenzoyloxyacetate*, $COPh{\cdot}CH(O{\cdot}COPh){\cdot}CO_2Et$ (VI), in satisfactory yield; difficulties were, however, encountered in attempting the hydrolysis of this ester. Ultimately it was found that phenacyl benzoate,

$$COPh{\cdot}CH_2{\cdot}O{\cdot}COPh,$$

could be obtained from it by heating with water in a sealed tube at 200°, but further degradation to benzoylcarbinol could only be accomplished in poor yield by means of boiling aqueous-alcoholic sulphuric acid. Zincke (*Annalen*, 1883, **216**, 308) was unable to obtain benzoylcarbinol by the hydrolysis of its benzoate.

Similarly, the sodio-derivative of ethyl 3 : 4 : 5-trimethoxybenzoylacetate and benzoyl peroxide furnished *ethyl* 3 : 4 : 5-*trimethoxybenzoylbenzoyloxyacetate*, $C_6H_2(MeO)_3{\cdot}CO{\cdot}CH(O{\cdot}COPh){\cdot}CO_2Et$ (VII), and ω-*benzoyloxy*-3 : 4 : 5-*trimethoxyacetophenone*,

$$C_6H_2(MeO)_3{\cdot}CO{\cdot}CH_2{\cdot}O{\cdot}COPh \text{ (VIII)},$$

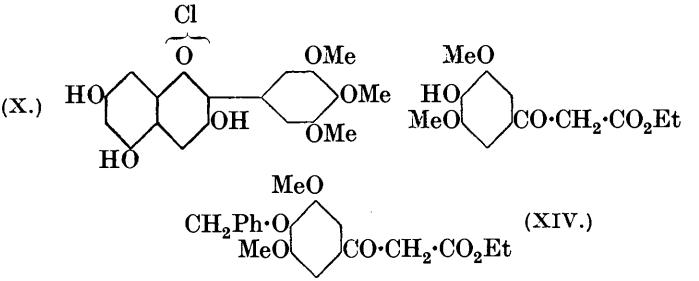
but the latter could neither be condensed with *O*-benzoylphloroglucinaldehyde to a flavylium salt nor hydrolysed to trimethoxybenzoylcarbinol. In view of the fact that the hydrolysis of phenacyl acetate presents little difficulty, we next substituted acetyl peroxide for benzoyl peroxide and thus obtained *ethyl* 3 : 4 : 5-*trimethoxybenzoylacetoxyacetate*,

$$C_6H_2(MeO)_3{\cdot}CO{\cdot}CH(OAc){\cdot}CO_2Et \text{ (IX)},$$

and by direct hydrolysis with hot dilute sulphuric acid, 3 : 4 : 5-*trimethoxybenzoylcarbinol* (IV).

This ketone condensed very readily with *O*-benzoylphloroglucinaldehyde (Robertson and Robinson, J., 1927, 1710) to give 3 : 7-*dihydroxy*-5-*benzoyloxy*-3′ : 4′ : 5′-*trimethoxyflavylium chloride*

(V), which was converted by the successive action of cold aqueous sodium hydroxide and hydrochloric acid into delphinidin chloride 3′ : 4′ : 5′-trimethyl ether (X), a methyl ether of malvidin chloride (II). A comparison of the reactions of (X) with those of malvidin



serves to confirm the view, first put forward by Heilbron, that a pure blue alkali-colour-reaction in the anthocyanin series is associated with a free hydroxyl group in position 4′. Since the partial hydrolysis of pyrogallol trimethyl ether and of gallic acid trimethyl ether affords pyrogallol 1 : 3-dimethyl ether and syringic acid, respectively, we concluded that it might be possible to hydrolyse (X) to malvidin. A product having most of the properties of this anthocyanidin, and doubtless containing it in preponderating amount, was obtained from the trimethyl ether by the action of hydrogen bromide in acetic acid solution at 45—50°. This material was contaminated with delphinidin or, more probably, delphinidin 3′-methyl ether, since it exhibited a ferric chloride reaction. By taking advantage of the sparing solubility of malvidin sulphate, a small pure specimen of the salt was isolated and this exhibited the colour reactions characteristic of the natural anthocyanidin.

In any case, this synthesis suffers from the defect that it does not determine the constitution of the product, but merely limits it to one of two alternatives, and we therefore turned our attention to a method free from such ambiguity.

O-*Acetylsyringoyl chloride*, $C_6H_2(OAc)(OMe)_2\cdot COCl$ (XI), and ethyl sodioacetoacetate gave rise to *ethyl acetylsyringoylacetoacetate*, $C_6H_2(OAc)(OMe)_2\cdot CO\cdot CHAc\cdot CO_2Et$ (XII), and this on hydrolysis yielded *ethyl syringoylacetate* (XIII). These esters could not be transformed into acyloxy-derivatives.

Ethyl O-*benzylsyringoylacetate* (XIV) was therefore prepared by condensing O-*benzylsyringoyl chloride*, $CH_2Ph\cdot O\cdot C_6H_2(OMe)_2\cdot COCl$ (XV), with ethyl sodioacetoacetate and hydrolysing the product, and this ester could be oxidised normally by means of benzoyl peroxide. The primary product could not be purified, but on hydrolysis it yielded ω-*benzoyloxy*-4-*benzyloxy*-3 : 5-*dimethoxyaceto*-

phenone, $CH_2Ph{\cdot}O{\cdot}C_6H_2(OMe)_2{\cdot}CO{\cdot}CH_2{\cdot}O{\cdot}COPh$ (XVI), which, however, like other ω-benzoyloxyacetophenone derivatives, did not condense readily with *O*-benzoylphloroglucinaldehyde to a flavylium salt. A small quantity of a by-product was once obtained in the course of the preparation of (XVI), and this was doubtless *benzylsyringoylcarbinol*, $CH_2Ph{\cdot}O{\cdot}C_6H_2(OMe)_2{\cdot}CO{\cdot}CH_2{\cdot}OH$ (XVII), since it reduced Fehling's solution in the cold and condensed with *O*-benzoylphloroglucinaldehyde to a salt which, in the light of later experience, we regarded as benzoylmalvidin chloride.

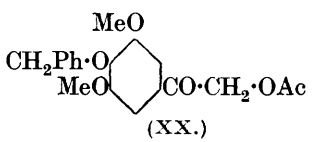
Under conditions similar to those which we were able to employ in the case of trimethoxybenzoylacetic ester the interaction of ethyl sodiobenzylsyringoylacetate and acetyl peroxide would without doubt proceed smoothly. These conditions, however, involve the handling of solid acetyl peroxide, which is capriciously and dangerously explosive. At this stage one of us had an unpleasant experience, a quantity of the peroxide exploding with extreme violence without any apparent cause that can be recalled. When it was possible to resume these experiments the use of the crystallised reagent was barred, but unfortunately the employment of the crude peroxide in solution never gave entirely satisfactory results. These are described in the experimental section (p. 1558).

Oxidation of ethyl benzylsyringoylacetate (XIV) by means of lead tetra-acetate in acetic acid solution gave *ethyl di(benzylsyringoyl) succinate*, $[CH_2Ph{\cdot}O{\cdot}C_6H_2(OMe)_2{\cdot}CO{\cdot}CH(CO_2Et){\cdot}]_2$ (XVIII), which was also obtained by the action of iodine on the potassium derivative of (XIV).

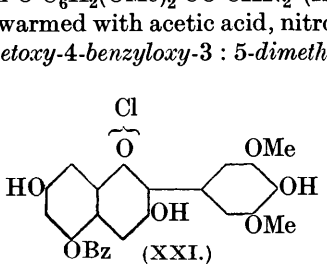
Apart from the use of pure acetyl peroxide, these oxidation experiments gave us little hope of a successful outcome and we therefore turned our attention to a method developed by Nierenstein. According to this author the action of diazomethane on acid chlorides is to produce related ω-chloro-ketones :

$$R{\cdot}COCl + CH_2N_2 \longrightarrow R{\cdot}CO{\cdot}CH_2Cl + N_2.$$

The interaction of diazomethane and benzylsyringoyl chloride (XV) in ethereal solution gave rise, however, to *ω-diazo-4-benzyloxy-3 : 5-dimethoxyacetophenone*, $CH_2Ph{\cdot}O{\cdot}C_6H_2(OMe)_2{\cdot}CO{\cdot}CHN_2$ (XIX) in excellent yield. When this was warmed with acetic acid, nitrogen was readily evolved and *ω-acetoxy-4-benzyloxy-3 : 5-dimethoxyacetophenone* (XX) was produced.



(XX.)



(XXI.)

We have recently shown that benzoyl chloride and diazomethane yield diazoacetophenone and our further work has confirmed the general character of the reaction, which has a wide scope as a synthetic method.* The condensation of *O*-benzoylphloroglucinaldehyde with (XX) in cold ethyl acetate solution by means of hydrogen chloride yields benzoylmalvidin chloride (XXI), the acetoxy- and benzyloxy-groups being hydrolysed. The alkali-colour-reaction of this 5-benzoylmalvidin chloride closely resembles that of malvin chloride. De-benzoylation was effected by means of cold aqueous sodium hydroxide and subsequent treatment with hydrochloric acid reconstructed the pyrylium ring broken by the alkali. The product (II) had all the characteristic properties and reactions of malvidin chloride as described by Willstätter and Mieg (*loc. cit.*) and careful comparison with a specimen obtained by the hydrolysis of natural malvin chloride showed that the two were identical.

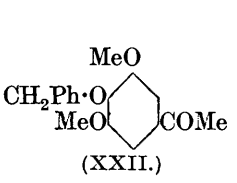
Certain flavylium salts closely related to malvidin chloride have also been synthesised with the object of eliciting further evidence in regard to the constitution of malvin chloride. The results indicate that malvin is a malvidin 5- or 7-diglucoside, whereas Karrer and Widmer (*Helv. Chim. Acta*, 1927, **10**, 729) consider it to be malvidin 3-diglucoside. If the methylation experiments of Karrer and Widmer may be interpreted in the manner suggested by Robertson and Robinson (this vol., p. 1463), the 7-diglucoside configuration can be excluded and malvin should be the 5-diglucoside of malvidin.

Briefly our argument is that a free hydroxyl group not only in position 4′ but also in position 3 is essential for the exhibition of a pure greenish-blue alkali-colour-reaction in the malvidin series; 3-des-hydroxymalvidin and malvidin 3-methyl ether give alkali-colour-reactions divergent from those of malvin, malvidin, and 5-benzoylmalvidin. It might be objected that the effects of the methoxyl and diglucosidoxyl groups in position 3 on the colour reaction might be very different, but there is evidence that this is

* (*Added, June 9th.*) Arndt, Eistert, and Partale (*Ber.*, 1927, **60**, 1364) found that the interaction of *o*-nitrobenzoyl chloride and diazomethane gave a compound $C_8H_5O_3N_3$ which they suggested might be ω-diazo-*o*-nitroacetophenone. Simultaneously with the present authors, Arndt and Amende (*Ber.*, 1928, **61**, 1222) showed that benzoyl chloride and diazomethane yield diazoacetophenone, and the German chemists also prepared diazoacetone and diazochloroacetone analogously. Arndt and his colleagues have been hampered by the effort to accommodate the contrary results of Dale and Nierenstein (*Ber.*, 1927, **60**, 1026) and this accounts for their provisional recognition of the substance $C_8H_5O_3N_3$ as diazonitroacetophenone; it is clear, however, that they were the first to offer a correct interpretation of the reaction between an acid chloride and diazomethane.

not the case. In the first place the diglucosides have the same alkali-colour-reactions as the monoglucosides to which they give rise on step-wise hydrolysis. For instance, Willstätter and Bolton (*Annalen*, 1916, **412**, 136) found that pelargonenin (pelargonidin monoglucoside) had almost the same reactions as pelargonin (pelargonidin diglucoside); chrysanthemin (cyanidin monoglucoside) and mecocyanin (cyanidin diglucoside) provide a further example. Secondly Robertson and Robinson have prepared pelargonidin 3-methyl ether (J., 1927, 1715) and pelargonidin 3-glucoside (this vol., p. 1460), and the alkali-colour-reactions of these substances closely resemble one another.

Ethyl *O*-benzylsyringoylacetate (XIV) was hydrolysed by means of water at 175—180° with formation of 4-*benzyloxy*-3 : 5-*dimethoxyacetophenone* (XXII). This ketone condenses with *O*-benzoylphloroglucinaldehyde in ethyl acetate solution in the presence of hydrogen chloride to produce what is apparently a mixture of the anticipated flavylium salt with a de-benzylated derivative. On complete de-benzoylation and de-benzylation, pure 5 : 7 : 4′-*trihydroxy*-3′ : 5′-*dimethoxyflavylium chloride* (XXIII) was obtained.



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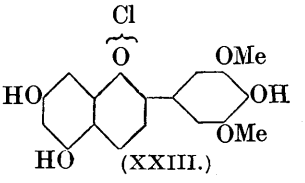
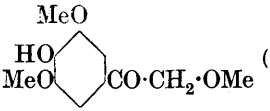
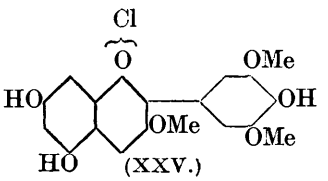


(XXIII.)

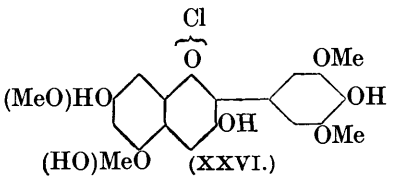


(XXIV.)

O-Acetylsyringoyl chloride reacted with ethyl sodio-αγ-dimethoxyacetoacetate (Pratt and Robinson, J., 1925, **127**, 168) to form a product which on hydrolysis afforded 4-*hydroxy*-ω : 3 : 5-*trimethoxyacetophenone* (XXIV). This ketone condensed normally with *O*-benzoylphloroglucinaldehyde and hydrogen chloride to give 7 : 4′-*dihydroxy*-5-*benzoyloxy*-3 : 3′ : 5′-*trimethoxyflavylium chloride*, and on debenzoylation 5 : 7 : 4′-*trihydroxy*-3 : 3′ : 5′-*trimethoxyflavylium chloride* (XXV) could be isolated.



(XXV.)



(XXVI.)

This malvidin 3-methyl ether is isomeric with hirsutidin, a new anthocyanidin obtained by Karrer and Widmer (*Helv. Chim. Acta*, 1927, **10**, 758) from the diglucosidic anthocyanin of *Primula hirsuta*. The presence of the syringic acid group in hirsutin was demonstrated by Karrer and Widmer and since the carbohydrate residues in malvin and hirsutin were supposed to be attached to position 3, these authors considered that hirsutidin must have one of the constitutions represented by (XXVI). The reactions of (XXV) show that it is not identical with hirsutidin and therefore from a different point of view we confirm the conclusions of Karrer and Widmer in regard to the constitution of this anthocyanidin.

Experimental.

Ethyl Benzoylbenzoyloxyacetate (VI).—The action of benzoyl peroxide (1 mol.) on ethyl sodioacetoacetate (1 mol.) gave rise to sodium benzoate (1 mol.) and an oil containing only a trace of ethyl acetoacetate. This was doubtless ethyl benzoyloxyacetoacetate, but as it did not crystallise the further investigation of the reaction was postponed.

Benzoyl peroxide (12·1 g.; m. p. 106° with decomp.), dissolved in benzene (130 c.c.), was added in four portions at intervals of 10 minutes to ethyl sodiobenzoylacetate (from 9·6 g. of the ester and 1·15 g. of sodium powder) in ethereal suspension and solution at 0°. After a short time an aqueous extract of the ethereal solution was neutral and this indicated the completion of the reaction. The product was isolated by the addition of water and subsequent washing of the benzene solution (5·2 g. of benzoic acid were obtained on evaporation and acidification of the aqueous solutions), which was dried and evaporated. The residue crystallised in contact with light petroleum and the substance was twice recrystallised from the same solvent, forming rosettes of slender, colourless prisms, m. p. 61° (Found : C, 69·1; H, 5·0. $C_{18}H_{16}O_5$ requires C, 69·0; H, 5·0%).

Ethyl benzoylbenzoyloxyacetate is readily soluble in cold methyl alcohol and benzene and sparingly soluble in light petroleum. It slowly reduces Fehling's solution in the cold. Its alcoholic solution gives no coloration with ferric chloride, and no copper derivative could be isolated. Moreover the ester is considerably more difficult to hydrolyse to a related ketone than is ethyl benzoylacetate, neither acid nor alkaline catalysts being effective : the best process is the following. The crude substance (9 g.) was heated with water (9 c.c.) in a sealed tube at 200° for 2 hours. On cooling, the oil solidified; after being washed in ethereal solution with aqueous sodium carbonate, it crystallised from 95% alcohol in prisms, m. p. 114—115°, identified as ω-benzoyloxyacetophenone by comparison

with the product obtained from silver benzoate and ω-bromoacetophenone.

A mixture of ω-benzoyloxyacetophenone (6 g.), sulphuric acid (10 g.), water (20 c.c.), and enough alcohol to give a clear solution was refluxed for 12 hours. From the product, benzoylcarbinol was isolated in unsatisfactory yield; it had m. p. 71—73° after crystallisation from aqueous alcohol and reduced Fehling's solution in the cold.

Ethyl 3 : 4 : 5-*Trimethoxybenzoylacetate*,

$$C_6H_2(MeO)_3\cdot CO\cdot CH_2\cdot CO_2Et.$$

—This ester has been obtained by Perkin and Weizmann (J., 1906, **89**, 1655) and by Mauthner (*J. pr. Chem.*, 1910, **82**, 278). The following modification of Perkin and Weizmann's method gave good results.

Gallic acid (150 g., crystallised) gave 120—130 g. of the trimethyl ether, m. p. 163—164°, or 100—110 g. of material, m. p. 168° (Graebe and Martz, *Annalen*, 1905, **340**, 219; Bogert and Isham, *J. Amer. Chem. Soc.*, 1914, **36**, 514). A solution of sodium ethoxide (from 16·1 g. of sodium) in alcohol (270 c.c.) was prepared and 135 c.c. of this were added to a mixture of ethyl acetoacetate (47·5 g.) and ether (280 c.c.) cooled in ice. When the temperature had fallen below 2°, a suspension of finely powdered 3 : 4 : 5-trimethoxybenzoyl chloride (40 g. of distilled material, b. p. 183—185°/18 mm., m. p. 76—78°) in ether (100 c.c.) was added in three portions with vigorous shaking. After 1 hour, the reaction appeared to be finished and further quantities of the sodium ethoxide solution (65 c.c., 33 c.c., 17 c.c., remainder) and of trimethoxybenzoyl chloride (20·2 g., 10·2 g., 5·1 g., and 5·0 g.) suspended in ether were added alternately and under the same conditions as before. After 12 hours, the precipitate was collected, washed with ether, and mixed with crushed ice, and the whole was acidified with dilute hydrochloric acid. The crystalline product (125 g.) was isolated by means of ether. It was hydrolysed in portions of 41 g. by mixing it with water (1000 c.c.) and ammonium chloride (70 g.) and adding concentrated aqueous ammonia (175 c.c.). The clear yellow solution deposited ethyl 3 : 4 : 5-trimethoxybenzoylacetate, which crystallised from methyl alcohol in colourless plates, m. p. 94—95° (total yield, 54 g.).

Ethyl 3 : 4 : 5-*Trimethoxybenzoylbenzoyloxyacetate* (VII).—In the preparation of this substance the use of potassium in place of sodium had a double advantage; the metal could be pulverised under benzene and the formation of the sodium derivative of the ester was found to be very slow. Ethyl 3 : 4 : 5-trimethoxybenzoylacetate (42 g.), dissolved in benzene (100 c.c.), was added to potassium powder (5·8 g.) and benzene (100 c.c.). A gentle reaction ensued

and the potassium derivative separated. After 15 minutes the semi-solid mass was heated on the steam-bath until the evolution of hydrogen ceased and then cooled in ice during the gradual addition of a solution of benzoyl peroxide (36 g.) in benzene (400 c.c.). When an aqueous extract was neutral in reaction, water was added, the benzene layer was washed and dried, and the solvent was removed. The pale yellow residue crystallised in contact with methyl alcohol and on recrystallisation from the same solvent formed colourless rhombs, m. p. 107° (Found : C, 62·8; H, 5·4. $C_{21}H_{22}O_8$ requires C, 62·7; H, 5·5%). The yield of material, m. p. 106—107°, was 39 g., and a further quantity (5—6 g.) was obtained from the mother-liquors.

The ester is readily soluble in most organic solvents and gives no coloration with alcoholic ferric chloride. It reduces Fehling's solution on warming and dissolves in sulphuric acid to an orange-yellow solution.

This ester is much more stable to hydrolysing agents than ethyl benzoylbenzoyloxyacetate (above). After heating with water at 200° for 4 hours, unchanged substance, m. p. 105—107°, was recovered (Found : C, 62·6; H, 5·8%). Neither alkaline nor acid agents could be employed to effect the hydrolysis.

ω-Benzoyloxy-3 : 4 : 5-trimethoxyacetophenone (VIII).—A mixture of the foregoing ester (10 g.) and water (6 c.c.) was heated in a sealed tube at 200° for 14 hours. On cooling, a little benzoic acid separated; the aqueous solution strongly reduced Fehling's solution in the cold. The pale brown oil crystallised in contact with methyl alcohol. A solution of it in ether was washed with aqueous sodium carbonate, dried, and concentrated to 15—20 c.c. The crystals that separated were recrystallised from methyl alcohol; faintly yellow parallelepipeds, m. p. 98—100°, were obtained, and colourless needles, m. p. 97—100°, from the mother-liquor. The mixture had m. p. 97—100° and when the prisms were recrystallised the m. p. 98—100° was unchanged and again colourless needles separated from the mother-liquor (Found : C, 65·3; H, 5·2. $C_{18}H_{18}O_6$ requires C, 65·4; H, 5·5%). The substance dissolves in sulphuric acid to a bright yellow solution. It does not reduce Fehling's solution in the cold, but does so rapidly on heating. Hydrolysis of this substance by means of alkaline solutions yielded only benzoic and trimethoxybenzoic acids, and on treatment with aqueous-alcoholic sulphuric acid it (3 g.) gave only 0·1—0·2 g. of the carbinol. It is remarkable that ω-benzoyloxytrimethoxyacetophenone exhibited scarcely any tendency to condense with *O*-benzoylphloroglucinaldehyde to a flavylium salt.

Ethyl 3 : 4 : 5-Trimethoxybenzoylacetoxyacetate (IX).—Acetyl peroxide was prepared by the method of Clover and Richmond (*Amer.*

Chem. J., 1903, **29**, 182); 40 g. of acetic anhydride gave 10—11 g., m. p. 27—29°. The instability of this substance renders it unsuitable for general use in the absence of special precautions.

Ethyl 3 : 4 : 5-trimethoxybenzoylacetate (8·0 g.) was converted into its potassium derivative (1·1 g. of potassium powder) in benzene, and to this, cooled in ice, acetyl peroxide (3·2 g.) dissolved in a little benzene was added in one portion. The reaction was still incomplete after 4 hours, and the mixture was heated at 30—40° for 1 hour; an aqueous extract then had a neutral reaction. Water was added and the benzene layer was washed, dried, and evaporated, leaving a residue which was crystallised from methyl alcohol. The yield was 4·5 g., m. p. 85—87°, and 3·5 g. of a somewhat less pure material were obtained from the mother-liquor.

Ethyl trimethoxybenzoylacetoxyacetate is sparingly soluble in light petroleum but readily soluble in benzene and methyl alcohol, from which it crystallises in colourless prisms, m. p. 88° (Found : C, 56·4; H, 5·7. $C_{16}H_{20}O_8$ requires C, 56·4; H, 5·9%). The reactions of the ester resemble those of the corresponding benzoyloxy-derivative, from which it is distinguished by its much more ready reduction of Fehling's solution and by its capacity for hydrolysis to trimethoxybenzoylcarbinol.

ω-Hydroxy-3 : 4 : 5-trimethoxyacetophenone (IV).—Ethyl trimethoxybenzoylacetoxyacetate (2·2 g.) was hydrolysed by boiling 10% sulphuric acid for 3 hours. A portion of the product (0·4 g.) separated on cooling and an equal amount was isolated by means of ether. The *keto-alcohol* crystallised from benzene–light petroleum in long, colourless needles, m. p. 87—88° (Found : C, 58·1; H, 6·7. $C_{11}H_{14}O_5$ requires C, 58·4; H, 6·2%). This substance is readily soluble in alcohol and benzene and moderately readily soluble in water; cold Fehling's solution is rapidly reduced. The *diphenylhydrazone* of 3 : 4 : 5-*trimethoxyphenylglyoxal*, obtained in dilute acetic acid solution, crystallised from aqueous pyridine in stellate clusters of serrated, yellow plates, m. p. 137—138°. The *carbinol* obtained as mentioned above from ω-benzoyloxy-3 : 4 : 5-trimethoxyacetophenone was identified by conversion into this derivative.

3 : 5 : 7-*Trihydroxy-3′ : 4′ : 5′-trimethoxyflavylium Chloride* (X).—A solution of ω-hydroxy-3 : 4 : 5-trimethoxyacetophenone (0·77 g.) and *O*-benzoylphloroglucinaldehyde (0·87 g.) in absolute ether was cooled in melting ice and saturated with hydrogen chloride. After 3 hours the product was isolated (0·44 g.) as a maroon powder exhibiting a greenish-yellow lustre. The salt crystallised from aqueous-alcoholic hydrochloric acid in crimson needles; it was readily soluble in methyl alcohol, less readily in ethyl alcohol, to

crimson solutions tinged with violet. On dilution, the pseudo-base was readily formed and the colour was restored by the addition of hydrochloric acid.

When this dihydroxybenzoyloxytrimethoxyflavylium chloride (0·32 g.) was dissolved in cold 10% aqueous sodium hydroxide (3 c.c.), air being excluded by hydrogen, the violet solution became red and then deep orange. After 6 hours, a buff-coloured solid was precipitated by the addition of water and concentrated hydrochloric acid (2 c.c.) and on heating a crimson colour developed and soon the pyrylium salt separated in hair-like needles. This delphinidin chloride trimethyl ether crystallised from aqueous-alcoholic hydrochloric acid in deep red, elongated prisms (Found : C, 54·4; H, 4·8. Calc. for $C_{18}H_{17}O_7Cl,H_2O$: C, 54·2; H, 4·8%).

In mass, this salt has a deep crimson-brown colour and a yellow lustre; it is readily soluble in alcohol and moderately readily soluble in dilute hydrochloric acid to bluish-red solutions. The red amyl-alcoholic extract from acid aqueous solutions becomes violet-red on the addition of sodium acetate, and the solution in aqueous sodium carbonate is strongly dichroic, being crimson in thick layers and bluish-violet in thin layers.

Acetic acid (3 c.c.) was saturated with hydrogen bromide at 60° and cooled, and 3 : 5 : 7-trihydroxy-3′ : 4′ : 5′-trimethoxyflavylium chloride (0·1 g.) added; when the temperature was slowly raised to 45—50°, the salt dissolved completely to a clear red solution. The colour developed on the addition of a drop of the liquid to aqueous sodium carbonate was tested at frequent intervals and even after a few minutes the pure blue malvidin reaction was observed. After 10 minutes, the liquid was cooled and a portion crystallised; less satisfactory material was obtained on dilution of the mother-liquor with water. The purer fraction had many of the properties of a malvidin salt, but it gave a ferric chloride reaction and was therefore contaminated with delphinidin or more probably a delphinidin monomethyl ether. It was dissolved in a little 0·5% hydrochloric acid, and 7% sulphuric acid added so as to give a 2% concentration of sulphuric acid; the process was repeated with the brown deposit obtained after a few hours' keeping. A very small quantity of a sulphate giving a pure blue alkali-colour-reaction and a very weak ferric chloride reaction was thus isolated. This was undoubtedly crude malvidin sulphate, but the process was not satisfactory and a synthesis of a more precise nature was undertaken. The experience gained was, however, valuable, since it was learned that the methoxyl in position 4′ is preferentially attacked by acids.

O-*Acetylsyringoyl Chloride* (XI).—The method for the preparation

of syringic acid indicated by Alimanchandi and Meldrum (J., 1920, **117**, 967) was not described in sufficient detail to permit of repetition. The following conditions gave consistent results (yield, about 80%). A solution of 3 : 4 : 5-trimethoxybenzoic acid (23 g.) in 96—98% sulphuric acid (92 c.c.) was heated at 50° for 6 hours and then added to water (200 c.c.). The silky needles, m. p. 199—201°, obtained were recrystallised from water and then melted at 205° (yield, 17 g.; methyl ester, m. p. 85°). Syringic acid was also prepared by the method of Bogert and Isham (*J. Amer. Chem. Soc.*, 1914, **36**, 519) as improved by Bogert and Ehrlich (*ibid.*, 1919, **41**, 798) and in this process we found it very important to use gallic acid trimethyl ether of m. p. not lower than 163—164°.

Syringic acid may be acetylated by boiling with an excess of acetic anhydride for 4 hours, or in a shorter period of heating on the steam-bath if zinc chloride or pyridine is employed as a catalyst; the latter method gave a 92% yield of material of m. p. 186°. After several crystallisations from benzene the m. p. remained constant at 187° (Found : C, 54·8; H, 5·0. Calc. for $C_{11}H_{12}O_6$: C, 55·0; H, 5·0%). Anderson and Nabenhauer (*J. Amer. Chem. Soc.*, 1926, **48**, 2997) give the m. p. 190°.

The *chloride* was obtained by means of phosphorus pentachloride, acetyl chloride or benzene being used as a diluent. (1) *O*-Acetylsyringic acid (12 g.) was covered with acetyl chloride (15 c.c.), and phosphorus pentachloride (12 g.) gradually added; the reaction was completed by gentle heating for 1 hour and, on keeping, the chloride crystallised in prisms. It was recrystallised from benzene–light petroleum, forming long, colourless prisms, m. p. 126° (Found : C, 51·2; H, 4·4. $C_{11}H_{11}O_5Cl$ requires C, 51·1; H, 4·3%). The yield was 7 g. A further quantity (2 g.) was obtained from the mother-liquor. (2) The acid (50 g.) and phosphorus pentachloride (45 g.) in benzene (30 c.c.), heated in the steam-bath for only 10 minutes, gave a crude product (33 g.), m. p. 114—120° (after one recrystallisation, the chloride had m. p. 121—123° and was sufficiently pure for most purposes), and a further 9 g. were obtained from the mother-liquor. The reaction could also be carried out in the cold in 5 hours, about 4 times the volume of benzene here prescribed being used; the product, m. p. 123—124°, was purer, but the yield was smaller.

Ethyl O-*Acetylsyringoylacetoacetate* (XII).—A solution (80 c.c.) of sodium methoxide (6·9 g. of sodium) in methyl alcohol was prepared and half of it was added to a mixture of ethyl acetoacetate (19·5 g.) and ether (60 c.c.) cooled in ice. A suspension of powdered acetylsyringoyl chloride (19·5 g.) in ether (50 c.c.) was then introduced in three portions with vigorous shaking. Further additions of the

sodium methoxide solution (20 c.c., 10 c.c., 5 c.c., remainder) and of acetylsyringoyl chloride (9·75 g., 4·9 g., 2·45 g., 2·4 g.) were then made alternately. Next day the salts were collected, washed with ether, and added to ice-cold dilute hydrochloric acid; the new ester was then precipitated and quickly crystallised. It was recrystallised from methyl alcohol (yield, 23 g.; m. p. 112—114°); the pure *substance* separated in glistening, colourless leaflets or elongated plates, m. p. 114° (Found: C, 58·3; H, 5·8. $C_{17}H_{20}O_8$ requires C, 58·0; H, 5·7%). The analysis does not exclude the possibility that the substance is ethyl syringoylacetoacetate ($C_{15}H_{18}O_7$ requires C, 58·1; H, 5·8%). It is soluble in aqueous sodium carbonate to a pale yellow solution, and a red coloration is developed on the addition of ferric chloride to its alcoholic solution. The substance described in the next section gives an abnormal ferric chloride reaction, probably on account of the presence of the phenolic hydroxyl in the benzene nucleus, and therefore the normal behaviour of the ester now under discussion is evidence in favour of the constitution (XII).

Ethyl Syringoylacetate (XIII).—Finely powdered ethyl acetylsyringoylacetoacetate (12 g.) was added to a mixture of water (250 c.c.), concentrated aqueous ammonia (15 c.c.), and ammonium chloride (20 g.). Within a few minutes, the ester dissolved to a yellow solution, from which a new substance quickly separated (an aqueous solution of this yielded ethyl syringoylacetate on acidification); after 30 minutes, the colourless solution was acidified, and the product collected (8·5 g.). The *ester* crystallised from methyl alcohol in slender, colourless prisms or rods, m. p. 92° (Found: C, 58·4; H, 6·0. $C_{13}H_{16}O_6$ requires C, 58·2; H, 6·0%). Again analysis does not exclude the formula $C_{15}H_{18}O_7$.

The substance crystallises from hot water in colourless prisms; it is moderately readily soluble in ether and very readily soluble in alcohol or benzene. It gives with ferric chloride in alcoholic solution a bright emerald-green coloration, which changes quickly through olive to brownish-red. The association of this curious reaction with the presence of the phenolic group was confirmed by the observation that Schotten–Baumann benzoylation of the ester furnished a product that gave a crimson coloration with ferric chloride in alcoholic solution. The addition of copper acetate to an aqueous solution of the ester gave an insoluble brown copper salt, and this behaviour also is suggestive of the presence of a free phenolic hydroxyl group.

Experiments on the acetoxylation of ethyl syringoylacetate and ethyl acetylsyringoylacetoacetate through the interaction of their sodium salts with acetyl peroxide gave small quantities of reducing substances, but the yields were uniformly inadequate.

Mr. Leslie R. Ridgway, M.Sc., collaborated with us in the preparation of the derivatives of syringic acid described above.

Methyl 4-*Benzyloxy*-3 : 5-*dimethoxybenzoate* (*Methyl* O-*Benzylsyringate*), $CH_2Ph{\cdot}O{\cdot}C_6H_2(OMe)_2{\cdot}CO_2Me$.—A solution of potassium hydroxide (11·2 g.) in methyl alcohol (100 c.c.) was added to one of methyl syringate (46 g.) and benzyl chloride (25·3 g.) in methyl alcohol (50 c.c.); the potassium salt crystallised. The mixture was boiled for 5 hours, the reaction then being neutral, and the filtered solution on cooling deposited elongated prisms (35 g.); a further quantity was obtained from the mother-liquor. The *ester* crystallised from 95% alcohol (yield, 38 g.; m. p. 69—71°) in pointed, hexagonal prisms, m. p. 71° (Found: C, 67·3; H, 5·9. $C_{17}H_{18}O_5$ requires C, 67·5; H, 6·0%). It is readily soluble in most organic solvents; its bright yellow solution in concentrated sulphuric acid changes rapidly through emerald-green to bluish-green. Attempts to prepare (XIV) by condensing this ester with ethyl acetate by means of sodium were not successful.

O-*Benzylsyringic Acid and its Chloride* (XV) *and Amide*.—(A) Benzyl chloride (6·3 g.) was added to a solution of syringic acid (5 g.) in 10% aqueous sodium hydroxide (20 c.c.), and the mixture boiled until it became neutral; a further quantity (10 c.c.) of 10% sodium hydroxide was then added drop-wise. The isolated acids were separated by taking advantage of the more sparing solubility of the benzylated derivative in hot water; 4—4·5 g. of benzylsyringic acid, m. p. 140—150°, were obtained. It is better to prepare the acid by the hydrolysis of its methyl ester (above).

(B) The solution obtained by heating a mixture of methyl *O*-benzylsyringate (96 g.) and 10% aqueous sodium hydroxide (140 c.c.) for 2 hours on the steam-bath was cooled, diluted to 500 c.c., and acidified. The crude *acid* was crystallised from 95% alcohol (yield, 87 g.; m. p. 155—157°) and then from water or more dilute aqueous alcohol, forming slender, colourless prisms, m. p. 157° (Found: C, 66·7; H, 5·6. $C_{16}H_{16}O_5$ requires C, 66·6; H, 5·6%). A solution of the acid in sulphuric acid is bright yellow and soon becomes bluish-green.

Graebe and Martz (*Ber.*, 1903, **36**, 217) describe the formation of syringic acid from gallic acid trimethyl ether by the action of concentrated hydrochloric acid at 150°. Debenzylation of *O*-benzylsyringic acid is much more facile, occurring to a large extent in 3 or 4 minutes under the influence of boiling 20% hydrochloric acid.

Owing to this ease of debenzylation some difficulty was experienced in finding the conditions for the preparation of O-*benzylsyringoyl chloride*. Powdered phosphorus pentachloride (41·6 g.) was added during 30—40 minutes to a suspension of powdered *O*-benzyl-

syringic acid (57·6 g.) in benzene (200 c.c.) efficiently cooled by ice. The mixture was occasionally shaken during 4—5 hours and the solid had then passed into solution. Crushed ice was added to decompose the phosphoryl chloride and in sufficient amount to keep the mixture near 0°. The separated benzene layer was washed with ice-water, aqueous potassium bicarbonate, and ice-water and dried with calcium chloride, and the solvent was removed, finally under diminished pressure. The residual pale yellow oil crystallised to a nearly colourless mass (46 g.), m. p. 35—40°, sufficiently pure for many purposes.

The chloride is readily soluble in most organic solvents and separates from light petroleum in colourless needles, m. p. 45° (Found : C, 62·9; H, 5·0. $C_{16}H_{15}O_4Cl$ requires C, 62·6; H, 4·9%).

When an emulsion of the chloride (1 g.) and water was shaken with 15% aqueous ammonia (10 c.c.), the *amide* was at once precipitated. It crystallised from alcohol in colourless, elongated plates, m. p. 152° (Found : C, 66·4; H, 5·9. $C_{16}H_{17}O_4N$ requires C, 66·9; H, 6·0%).

Ethyl O-*Benzylsyringoylacetoacetate and Ethyl* O-*Benzylsyringoylacetate* (XIV).—Sodium (9·2 g.) was dissolved in alcohol, and the solution made up to 150 c.c. Half of the ethoxide was added to a mixture of ethyl acetoacetate (26 g.) and ether (50 c.c.) well cooled in ice. *O*-Benzylsyringoyl chloride (30·6 g.) in ether (50 c.c.) was then gradually introduced with shaking and continued cooling. After 1 hour the alternate addition of the sodium ethoxide solution (38 c.c., 19 c.c., 9·5 c.c., remainder) and of benzylsyringoyl chloride (15·3 g., 7·7 g., 3·8 g., 3·8 g.) in ether was commenced under conditions similar to those previously observed. After 12 hours, the mixed sodium salts were collected, washed with ether, and added to ice-cold, dilute hydrochloric acid in the presence of ether. The ethereal solution was dried and the solvent removed, leaving a residue which solidified to an almost colourless mass (67 g.). After one crystallisation from methyl alcohol the m. p. was 74—84° and after three further crystallisations fine, colourless needles, m. p. 97—102°, were obtained (Found : C, 65·9; H, 5·7. $C_{22}H_{24}O_7$ requires C, 66·0; H, 6·0%). The *ester* is readily soluble in benzene, chloroform and methyl alcohol and separates very slowly from its saturated solution in the last solvent; it is sparingly soluble in boiling light petroleum. An alcoholic solution develops a crimson coloration with ferric chloride, and the orange solution in sulphuric acid soon becomes crimson. The ester is soluble in aqueous sodium carbonate and is precipitated unchanged on acidification.

Finely powdered ethyl *O*-benzylsyringoylacetoacetate (50 g.) was added to water (2000 c.c.), ammonium chloride (80 g.), and con-

centrated aqueous ammonia (200 c.c.). The solution became opalescent and deposited an oil; after 2 hours the original ester had passed into solution and the hydrolysed product had separated completely from the clear liquid. The ester was crystallised from methyl alcohol (yield, 32 g.; m. p. 64—66°) and finally obtained in prisms, m. p. 67° (Found: C, 67·2; H, 6·0. $C_{20}H_{22}O_6$ requires C, 67·0; H, 6·2%).

Ethyl O-*benzylsyringoylacetate* is readily soluble in methyl alcohol and very readily soluble in benzene or chloroform; it is sparingly soluble in light petroleum and separates from this solvent in iridescent plates. A crimson coloration is developed with alcoholic ferric chloride.

Copper derivative. Under the usual conditions, many derivatives of ethyl benzoylacetate are difficult to transform into their copper salts, but we have found (compare J., 1926, 2364) that the derivatives are readily obtained by the interaction of the esters and copper acetate in pyridine solution. The *copper* derivative of ethyl benzylsyringoylacetate prepared in this way and precipitated on the addition of water, crystallised from benzene in pale green needles, m. p. 212° (Found: Cu, 8·3. $C_{40}H_{42}O_{12}Cu$ requires Cu, 8·2%).

ω-*Benzoyloxy*-4-*benzyloxy*-3 : 5-*dimethoxyacetophenone* (XVI).—Ethyl *O*-benzylsyringoylacetate (7·2 g.) was converted into its potassium salt by means of pulverised potassium (0·78 g.) in benzene suspension. The mixture was then cooled in ice during the addition of benzoyl peroxide (4·85 g.), dissolved in a little benzene. The reaction evidently proceeded smoothly, since the aqueous washings were neutral, and the product was a viscous, pale yellow oil, which gave only a very weak ferric chloride reaction and reduced Fehling's solution very readily on warming. It could not be crystallised and was therefore directly hydrolysed by heating with an equal volume of water in a sealed tube at 160—170° for 8 hours. The resulting oil was dissolved in benzene and washed with dilute aqueous sodium hydroxide. This dissolved about 30—40% of the material, and the acid obtained on acidification was, rather unexpectedly, benzylsyringic acid; no syringic acid could be isolated and only a small quantity of benzoic acid was present. The benzene solution was washed with water and dried, and the solvent removed, leaving an oil that partly crystallised and was allowed to remain in contact with porous porcelain. The substance crystallised from methyl alcohol in slender, colourless prisms, m. p. 105° (Found: C, 70·6; H, 5·5. $C_{24}H_{22}O_6$ requires C, 70·9; H, 5·5%). The *ketone* is readily soluble in benzene, sparingly soluble in the simple alcohols, and very sparingly soluble in light petroleum. It appeared to condense with *O*-benzoylphloroglucinaldehyde, although in a

sluggish fashion, and the behaviour of the substance in this and other respects was somewhat anomalous.

In one experiment, the aqueous solution from the hydrolysis of the crude benzoyloxylated product deposited a crystalline substance, m. p. 87—89°, which reduced Fehling's solution in the cold and condensed readily with *O*-benzoylphloroglucinaldehyde to a flavylium salt. This substance was doubtless ω-hydroxy-4-benzyloxy-3 : 5-dimethoxyacetophenone (XVII), but the conditions for its preparation could not be ascertained. The flavylium salt (from 0·08 g. of the carbinol) was debenzoylated in the usual manner and furnished a salt agreeing with malvidin in regard to the colour of acid solutions, the behaviour with ferric chloride, and the alkali-colour-reaction.

Experiments on the action of acetyl peroxide in ethereal solution on the potassio-derivative of ethyl benzylsyringoylacetate were undertaken. An excess of barium peroxide was employed in the preparation of the ethereal solution, the concentration of which (9·65 g. contained 1 g. of the peroxide) was estimated by combined iodometric and acidimetric methods; acetic anhydride was not present in significant proportion. Ethyl benzylsyringoylacetate (14·9 g.) was converted into its potassio-derivative under benzene and oxidised below 15° by means of the ethereal acetyl peroxide (55 c.c.). The reaction proceeded normally, but the isolated product gave a ferric chloride reaction and therefore contained unchanged ester. This was removed in the form of its copper derivative by the pyridine–copper acetate method. The separated oil then gave no immediate ferric chloride reaction and rapidly reduced Fehling's solution on warming. A crude benzoylcarbinol derivative was obtained from this product by means of boiling 5% sulphuric acid (10 hours), together with a small quantity of a similar substance, m. p. 85—87°, that crystallised in colourless prisms from the aqueous solution. The main, more sparingly soluble, product could not be crystallised, but it condensed readily with *O*-benzoylphloroglucinaldehyde in ethyl acetate solution in presence of hydrogen chloride, the dark red flavylium salt produced forming stout parallelopipeds having a marked yellowish-green lustre. This was debenzoylated and debenzylated, but although the salts at the various stages crystallised well, the reactions were not those of pure malvidin derivatives and indicated contamination with salts not containing a free hydroxyl group in position 3.

Ethyl Di(O-*benzylsyringoyl*)*succinate* (XVIII).—(A) Powdered lead tetra-acetate (11·1 g.) (Dimroth and Schweitzer, *Ber.*, 1923, **56**, 1375) was added in several small portions to a solution of ethyl benzylsyringoylacetate (9·0 g.) in acetic acid (20 c.c., previously

crystallised and drained) with cooling in ice. After 12 hours, water was added, the product taken up in benzene and freed from acids by means of aqueous sodium carbonate, and the solution dried. The oily residue after removal of the solvent contained unchanged ester, because it gave a ferric chloride reaction, and it probably contained the α-acetoxy-derivative, because it reduced Fehling's solution; the substances responsible for these reactions were not isolated. The oil partly crystallised on keeping and, after draining on porous porcelain, the solid was recrystallised from methyl alcohol, forming flat, colourless prisms, m. p. 173—176° after softening at 168° (Found: C, 67·1, 67·3; H, 5·1, 5·5. $C_{40}H_{40}O_{12}$ requires C, 67·4; H, 5·7%). This ester is moderately readily soluble in benzene and chloroform and is sparingly soluble in methyl alcohol; it neither exhibits a ferric chloride reaction nor reduces Fehling's solution even on heating.

Conceivably the substance is $C_{40}H_{38}O_{12}$ (C, 67·6; H, 5·4%), that is, ethyl di(benzylsyringoyl)fumarate (or maleate), and this hypothesis is certainly favoured by the absence of a ferric chloride reaction. Subsequently we found that the action of lead tetra-acetate on the potassium derivative of the ester in benzene suspension afforded the succinate (or fumarate) in improved yield.

(B) Potassium (0·39 g.) was pulverised under benzene, and ethyl benzylsyringoylacetate (3·6 g.) introduced. When the formation of the metallic derivative was complete a benzene solution of iodine (1·3 g.) was added with cooling. The reaction was completed by heating on the steam-bath for 30 minutes. The product crystallised from much methyl alcohol in flat, colourless prisms, m. p. 173—176°, unchanged by admixture with the specimen prepared by method (A).

The fused ester has a yellow colour and its solution in sulphuric acid is red. All its properties are in good agreement with the "fumarate" hypothesis, but the above method of preparation harmonises better with the view that the ester is a derivative of succinic acid.

ω-Diazo-4-benzyloxy-3:5-dimethoxyacetophenone (XIX).—A solution of benzylsyringoyl chloride (14·3 g.) in anhydrous ether was added during 5 minutes to an ethereal solution of diazomethane (from 20 c.c. of nitrosomethylurethane; compare Houben–Weyl, "Die Methoden der Organischen Chemie," 1923, **3**, 124) previously distilled through an efficient column (45 cm.) and cooled to −10°. A mild evolution of nitrogen occurred and continued for 1—1½ hours and crystallisation of the product commenced 10 minutes after the reagents were mixed. Next day the pale yellow solid was collected (13·4 g., m. p. 115—120° with decomp.) and a further quantity (1·25 g., m. p. 105—108°, recryst., m. p. 118—120°) was obtained

from the ethereal solution. The new substance crystallised with great ease from a variety of solvents; it separated from benzene–light petroleum in bright lemon-yellow, quadrilateral tablets or flat prisms, m. p. 122—123° (decomp.) (Found : C, 64·7, 65·4, 65·5; H, 5·2, 4·8, 4·8; N, 8·8. $C_{17}H_{16}O_4N_2$ requires C, 65·4; H, 5·2; N, 9·0%).

This *diazo-ketone* is readily soluble in alcohol and benzene, sparingly soluble in ether, and very sparingly soluble in light petroleum. It was unchanged by boiling aqueous alcohol in a few minutes, but was rapidly decomposed by acids and by iodine in alcoholic solution with evolution of nitrogen. It gave no coloration with cold alcoholic sodium hydroxide, but on warming a crimson solution was obtained; ω-diazoacetophenone exhibits this reaction in the cold (Wolff, *Annalen*, 1902, **325**, 141). The thermal decomposition of the substance occurs vigorously at 125° or at lower temperatures with impure specimens. In *iso*amyl ether the diazo-ketone appeared to be stable at 130°, but on the addition of porous porcelain, nitrogen was evolved and a sparingly soluble oil separated. The product of decomposition in a vacuum crystallised from light petroleum in bundles of colourless, flat prisms, m. p. 58—59°.

The action of boiling dilute aqueous-alcoholic sulphuric acid on the diazo-ketone gave a compound that crystallised from light petroleum, containing a little benzene, in colourless needles, m. p. 85—86°. The substance was soluble in hot water and crystallised on cooling; it rapidly reduced Fehling's solution in the cold and was undoubtedly O-*benzylsyringoylcarbinol* (XVII). The *diphenylhydrazone* of the related phenylglyoxal derivative crystallised from aqueous pyridine in bright yellow, slender prisms, m. p. 131° after sintering at 110°.

ω-*Acetoxy*-4-*benzyloxy*-3 : 5-*dimethoxyacetophenone* (XX).—A mixture of the crude diazo-ketone (15 g., m. p. 115—120°) and acetic acid (30 c.c.) was heated at 60—70° until the evolution of nitrogen ceased and was then boiled for 2 minutes. Ether was added to the cooled liquid, and the acetic acid removed by washing with aqueous sodium carbonate; the washed and dried ethereal solution was then evaporated, and the residue extracted by means of boiling light petroleum. The first extracts readily deposited colourless crystals (5·7 g.), m. p. 58—60°, but the later extracts were contaminated with a yellow oil and crystallised much more slowly; on keeping, however, crystals were obtained from these fractions also and had the m. p. 57—60° (8·0 g.). About 2 g. of a deep yellow material remained undissolved. The *ketone* crystallised from light petroleum in colourless, fibrous, prismatic needles, m. p. 60·5—61° (Found : C, 66·1; H, 5·7. $C_{19}H_{20}O_6$ requires C, 66·2; H, 5·9%).

It is freely soluble in alcohol, benzene, or chloroform and it is rapidly oxidised by warm Fehling's solution.

5-*Benzoylmalvidin Chloride* (XXI).—Hydrogen chloride was passed into a filtered solution of ω-acetoxy-4-benzyloxy-3 : 5-dimethoxyacetophenone (2·2 g., m. p. 58—60°) and pure *O*-benzoylphloroglucinaldehyde (2·1 g., m. p. 196°) in ethyl acetate (40 c.c., distilled over phosphoric oxide) cooled to 0°. A colourless solid separated slowly during 1—1½ hours, but this did not increase in amount and after 7 hours it was collected. The filtrate was kept saturated with hydrogen chloride and next day a dark red crystalline powder had separated (1·2—1·3 g. Specimen A). A further quantity (0·61 g.) of less pure material separated on keeping for 48 hours. The salt crystallised from methyl alcohol–10% hydrochloric acid in well-formed, oblique, elongated prisms which were olive-green in mass and exhibited a strong golden lustre (Found in air-dried material : C, 56·1, 56·0; H, 4·1, 4·0. $C_{24}H_{19}O_8Cl,2·5H_2O$ requires C, 55·9; H, 4·6%). Benzoylmalvidin chloride is moderately readily soluble in methyl alcohol, more sparingly so in ethyl alcohol, to violet-red solutions which are readily decolorised on keeping or heating. The salt dissolves in hot water to a colourless solution containing the pseudo-base and even the solution in 0·5% hydrochloric acid is decolorised on boiling for a few minutes. The solution in hot 4% hydrochloric acid is stable and has a weak bluish-red colour. Aqueous sodium carbonate dissolves the salt to a pure deep blue solution, which becomes greener on dilution with water, and in alcoholic solution even the addition of sodium acetate gives a pure blue coloration. The ferric chloride reaction is negative and the violet-red solution in concentrated sulphuric acid does not exhibit fluorescence.

In a second experiment the acetoxy-ketone (3·45 g.) and *O*-benzoylphloroglucinaldehyde (3·25 g.) were condensed together in ethyl acetate (100 c.c.); after the solution had been saturated at 0°, the temperature was allowed to rise to that of the room. The colourless product (0·95 g.) that separated was collected after 5 hours and consisted of benzoylphloroglucinaldehyde. The filtrate was maintained saturated for 12 hours and the benzoylmalvidin chloride separated in dark red, flat, quadrilateral prisms, which appeared olive-green in mass and had a striking golden-yellow lustre (yield, 1·55 g.). Further quantities were obtained on keeping (24 hours, 0·8 g.; 48 hours, 0·1 g.; 96 hours, 0·15 g.) and the total yield was 2·6 g. (Specimen B).

Malvidin Chloride (II).—Benzoylmalvidin chloride (1·0 g. of A) was dissolved in 10% aqueous sodium hydroxide (10 c.c.) and a stream of hydrogen was used to exclude air and to agitate the

mixture. The colour changed from deep blue to green and finally to orange. After 4½ hours methyl alcohol (20 c.c.) and concentrated hydrochloric acid (4 c.c.) were added, giving a clear violet-red solution, which was heated on the steam-bath for ½ hour and kept over-night. A quantity (about 0·5 g.) of malvidin chloride crystallised in stout prisms possessing a marked steel-blue lustre when in contact with the solvent and appearing olive-green in mass (Specimen C). About 0·2 g. of less pure material was obtained from the mother-liquor on the addition of 10% hydrochloric acid.

A second specimen of the salt was prepared from benzoylmalvidin chloride (2·55 g. of B) by hydrolysis with 10% aqueous sodium hydroxide (20 c.c.) for 5 hours. Regeneration of the pyrylium salt was effected by means of concentrated hydrochloric acid (6·5 c.c.) and ethyl alcohol (20 c.c.); a portion of the malvidin chloride crystallised during the ½ hour period of heating on the steam-bath. The appearance of the product resembled that of C; it was collected after 12 hours and washed with aqueous-alcoholic hydrochloric acid and ether (yield, 0·9 g.). The substance was recrystallised by solution in a boiling mixture of ethyl alcohol (4 vols.; more than 400 c.c. were required) and 10% hydrochloric acid (1 vol.) and addition of hot 10% hydrochloric acid (3 vols.) to the filtered solution. The malvidin chloride (Specimen D) was deposited in small, flat, rhombic prisms or tablets which appeared red by transmitted light and had a green lustre in mass when dry or a steel-blue lustre when in contact with the solvent (Found in air-dried material: C, 53·0, 53·4; H, 3·7, 4·1; MeO, 15·8; loss at 110° in a high vacuum, 4·1. Calc. for $C_{17}H_{15}O_7Cl,H_2O$: C, 53·0; H, 3·9; 2MeO, 16·1; H_2O, 4·7%). The anhydrous salt was extremely hygroscopic and absorbed water from the air during weighing; hence the somewhat low value found for loss at 110° in a high vacuum. Every statement made by Willstätter and Mieg (*loc. cit.*) from "*Bei* 300° *ist die Substanz*" (p. 132) to "*rotbraunen Nädelchen aus.*" (end of p. 133) in regard to the properties of malvidin chloride was confirmed with the synthetical specimens in detail (the solubility in 7% sulphuric acid was not, however, quantitatively determined). In addition, Specimen C was directly compared with malvidin chloride obtained by the hydrolysis of the malvin chloride so kindly sent to us by Professor Karrer. This material had a chocolate-brown colour and exhibited a strong tendency to crystallise in slender needles. It dissolved in methyl alcohol and immediately crystallised again, as described by Willstätter and Mieg. This product was easily soluble in 0·01% hydrochloric acid and when warmed with 0·5—1% hydrochloric acid it also dissolved, but crystallised from the hot solution in highly characteristic, very small, hair-like needles which were very spar-

ingly soluble in cold 0·01% hydrochloric acid. This whole process had to be repeated twice in order to obtain a completely homogeneous crystallisation from the dilute hydrochloric acid. (C) behaved in the same way; it dissolved in methyl alcohol, and a blood-red crystalline powder, violet by transmitted light, soon separated. The material had the same bright reflex, resembling that of iron pyrites, as the natural specimen and, like it, consisted of obliquely cut, elongated prisms. On treatment with 0·5% hydrochloric acid it also dissolved and on heating crystallised again in needles, rather larger than those from the natural specimen. After several repetitions, the product was very sparingly soluble in cold 0·01% hydrochloric acid and its solubility in 0·5% hydrochloric acid at 55° was found (colorimetric comparison) to be within 5% of that of the specimen of natural origin. The synthetical specimen was a shade the more sparingly soluble of the two.

The solubility of malvidin chloride in cold, very dilute hydrochloric acid is entirely a question of crystalline form. Most specimens dissolve very easily in 0·01% hydrochloric acid and even in 0·1% acid to brownish-red solutions, which are possibly hydrolysed and possibly colloidal; the test with 0·01% hydrochloric acid is an extraordinarily stringent one and will succeed only with material which has been prepared as described above and found to be microscopically homogeneous. If any indefinitely crystallised aggregates are present, the 0·01% hydrochloric acid will dissolve them. The colour of alcoholic solutions at various stages of dilution and on the addition of hydrochloric acid, sodium acetate, and sodium carbonate, the rates of pseudo-base formation and oxidation by hydrogen peroxide, and the extent of recovery of the salt from the pseudo-base were directly quantitatively compared and found to be completely identical in the case of the natural and the synthetic specimen.

The only remaining point to be cleared up was the difficulty that we had never observed, nor had other authors described, the crystallisation of malvidin chloride in rhombic plates as recorded above. We attributed this to the exceptional purity of the synthesised salt and accordingly attempted the purification of the anthocyanidin. After separation from methyl alcohol, the picrate was prepared and crystallised from a methyl-alcoholic solution of picric acid. The recovered chloride was again crystallised from methyl alcohol and afterwards from a mixture of ethyl alcohol and 10% hydrochloric acid under the conditions mentioned above. At first, prismatic needles separated; a second crystallisation gave clusters of rather indefinite prisms, and a third crystallisation with slow cooling gave rhombic prisms, not quite so clear-cut as those of the Specimen D but obviously of the same crystalline habit. It was very interesting

to note the appearance of the steel-blue lustre of the crystals in suspension in the solvent and the green reflex of the dried salt. The solubility of (D) in hot aqueous alcoholic hydrochloric acid was greatly increased on the addition of a trace of peonidin chloride. The salt separated in indefinite clusters of jagged prisms and the mother-liquor deposited, on evaporation in the air, very slender needles exactly like those of natural malvidin chloride. We do not suggest that the impurity in natural malvidin is necessarily peonidin (although malvidin may contaminate peonidin), but undoubtedly malvidin chloride from natural sources does contain some persistent impurity that modifies its habit of crystallisation. This impurity does not give a ferric chloride reaction, and this fact points to peonidin. Both peonidin chloride and malvidin chloride have been obtained synthetically in a well-defined prismatic form exhibiting a characteristic lustre; on the other hand, the anthocyanidins from natural sources are usually chocolate-brown and devoid of marked lustre. Mixtures of the synthetic malvidin with a little synthetic peonidin or of the synthetic peonidin with a little synthetic malvidin also tend to crystallise in forms which when dried are almost lustreless and chocolate-brown.

4-Benzyloxy-3 : 5-dimethoxyacetophenone (XXII) *and 4-Hydroxy-3 : 5-dimethoxyacetophenone.*—The hydrolysis of ethyl *O*-benzylsyringoylacetate by means of 5% or 10% aqueous sulphuric acid did not proceed satisfactorily, but the acetophenone derivative could be readily obtained under the following conditions. Ethyl benzylsyringoylacetate (12 g.) was heated with water (10 c.c.) in a sealed tube at 175—180° for 10 hours. The product was taken up in benzene, the extract washed with aqueous sodium hydroxide and water and dried, and the solvent removed, leaving a crystalline mass (9 g., m. p. 50—59°). The ketone crystallised from light petroleum in colourless, slender prisms, m. p. 60—61° (Found : C, 71·3; H, 6·3. $C_{17}H_{18}O_4$ requires C, 71·3; H, 6·3%); it is readily soluble in other organic solvents. The orange solution in sulphuric acid slowly became greenish-brown on keeping. The *semicarbazone* crystallised from aqueous alcohol in platelets, m. p. 166°. The *2 : 4-dinitrophenylhydrazone* was prepared in dilute alcoholic solution and crystallised from benzene–alcohol in scarlet, prismatic needles, m. p. 192—193°.

The ketone (5·3 g.) was debenzylated during 7 hours by means of a cold saturated solution of hydrogen bromide in acetic acid (18 c.c.). *4-Hydroxy-3 : 5-dimethoxyacetophenone* crystallised from light petroleum in colourless, slender prisms, m. p. 117° (yield, 1·9 g.) (Found : C, 61·1; H, 6·2. $C_{10}H_{12}O_4$ requires C, 61·2; H, 6·2%). The substance was soluble in aqueous sodium carbonate solution and

gave a precipitate of a sparingly soluble sodium salt when triturated with 15% aqueous sodium hydroxide. Its solution in sulphuric acid was yellow, and ferric chloride added to an alcoholic solution developed a weak bluish-green coloration. On treatment with benzyl chloride and potassium hydroxide in boiling aqueous methyl-alcoholic solution, the original ketone, m. p. 60—61°, was regenerated. Attempts to obtain this substance directly from the accessible pyrogallol 1 : 3-dimethyl ether were unsuccessfully made by Mr. L. R. Ridgway. The phenol did not react with acetonitrile under the conditions of the Hoesch synthesis. A solution of the phenol (6 g.) and acetyl chloride in carbon disulphide was treated with anhydrous ferric chloride and kept in the cold for 16 hours. 2·1 G. of a substance, crystallising from benzene–light petroleum in shining leaflets, m. p. 110° (phenylhydrazone, m. p. 106—107°), and insoluble in aqueous sodium carbonate, were obtained. These data show that the product of this reaction was 3-acetoxy-2 : 4-dimethoxyacetophenone (compare Brand and Collischonn, *J. pr. Chem.*, 1922, **103**, 338). Even if the hydroxyl group were not first acetylated, it is doubtful whether the acetyl group would enter the desired position para to hydroxyl, since Levine (*J. Amer. Chem. Soc.*, 1926, **48**, 797, 2719) has shown that the bromination and chlorination of pyrogallol 1 : 3-dimethyl ether occur in position 4. The reaction was carried out in a neutral solvent and the result may be attributed to the absence of *active* anions and the consequent relative immunity of the proton of the hydroxyl group. In such circumstances, the directive power of hydroxyl relative to that of methoxyl is greatly diminished. Chlorination of benzyloxydimethoxyacetophenone occurred readily, but the halogen atom appeared to enter the nucleus preferentially. The most advantageous method of preparation of iso*nitroso*-4-*benzyloxy*-3 : 5-*dimethoxyacetophenone*,

$$CH_2Ph{\cdot}O{\cdot}C_6H_2(OMe)_2{\cdot}CO{\cdot}CH{:}NOH,$$

was found to be the following : Ethyl alcohol (4 g.) was added to a suspension of pulverised sodium (1·2 g.) in dry ether (70 c.c.), and when the formation of the ethoxide was complete the mixture was cooled in ice and benzyloxydimethoxyacetophenone (10 g.) and freshly distilled *iso*amyl nitrite (6·1 g.) were successively introduced, the latter in small portions during 1 hour. The amount of the yellow sodium salt that separated increased during several days and after 5 days the solid was collected, washed with ether, and dissolved in water. The crude iso*nitroso*-derivative was obtained by acidification with acetic acid and freed from 1·5 g. of benzylsyringic acid by washing its solution in benzene with aqueous sodium carbonate. The derivative (yield, 6·0 g.) crystallised from light petroleum, containing a little chloroform, in canary-yellow, flat

prisms, m. p. 107—108° (Found: N, 4·8. $C_{17}H_{17}O_5N$ requires N, 4·5%). The substance has the usual properties of its class and forms an *oxime* that crystallises from aqueous alcohol in colourless, slender, flat prisms, m. p. 141—142°. A dilute solution of this dioxime in 50% aqueous ethyl alcohol gave orange-red and reddish-brown precipitates on the addition of aqueous nickel and cobalt acetates, respectively.

5 : 7 : 4′-*Trihydroxy*-3′ : 5′-*dimethoxyflavylium Chloride* (XXIII).—A stream of dry hydrogen chloride was passed through an ice-cold solution of 4-benzyloxy-3 : 5-dimethoxyacetophenone (3·0 g.) and *O*-benzoylphloroglucinaldehyde (4·0 g.) in dry ethyl acetate (70 c.c.) for 10 hours. The reddish-bronze crystals were then isolated (4·3 g.); they possessed a marked greenish-yellow lustre. This substance, which was very probably a mixture, was debenzoylated by means of 10% aqueous sodium hydroxide (passage of hydrogen) in 6 hours. The reddish-orange alkaline liquid was then mixed with methyl alcohol and concentrated hydrochloric acid, and the flavylium salt regenerated by heating on the steam-bath for ½ hour. The crude salt was crystallised from methyl alcohol containing hydrogen chloride and then from alcohol and a few drops of concentrated hydrochloric acid. This material was next fully debenzylated, whereby the facility with which the substance crystallised was greatly increased; the crystalline habit was modified, but there was no great change in the colour reactions. The salt (0·47 g.) was dissolved in acetic acid (50 c.c.), and hydrogen chloride passed in, first at 15°, and then at 65—70° for 2 hours. Crystals remained in suspension and these together with a crop obtained on cooling were recrystallised, first from ethyl alcohol and a few drops of hydrochloric acid and then from methyl alcohol containing a little hydrochloric acid. The homogeneous product consisted of slender, pointed, hexagonal prisms, reddish-brown in colour and exhibiting a greenish-yellow lustre when rubbed, m. p. 280° (Found: C, 55·2, 55·3; H, 4·4, 4·5; Cl, 9·3. $C_{17}H_{15}O_6Cl,H_2O$ requires C, 55·4; H, 4·6; Cl, 9·6%).

5 : 7 : 4′-*Trihydroxy*-3′ : 5′-*dimethoxyflavylium chloride* is very sparingly soluble in cold water to a yellow solution, but readily soluble in hot water to a deep brownish-red solution (basic salt); it is very sparingly soluble in hot dilute hydrochloric acid. The brownish-red solution in methyl alcohol has a faint violet nuance and the colour is not discharged by dilution or by heating. In this respect, the salt exemplifies the rule that pseudo-base formation of a hydroxyflavylium salt that can give a colour-base is associated with the occurrence of the groups OH or OR in position 3. The dichroic solution in aqueous sodium carbonate is reddish-violet and

the colour remains unchanged on the addition of alcohol. The colour in aqueous sodium hydroxide is also reddish-violet, but changes through deep red to orange and yellow. Sodium acetate added to a methyl-alcoholic solution develops a reddish-violet coloration and the solution appears bluish-purple in thin layers.

4-*Hydroxy*-ω : 3 : 5-*trimethoxyacetophenone* (XXIV).—Ethyl αγ-dimethoxyacetoacetate (12·0 g.) (Pratt and Robinson, J., 1925, **127**, 168) was added to a suspension of sodium powder (1·45 g.) in anhydrous ether (100 c.c.), and when the formation of the sodio-derivative was complete powdered acetylsyringoyl chloride (15·5 g.) was added in one portion. Next day the mixture was refluxed for 4 hours. The product crystallised in sheaves of colourless plates and gave a deep red coloration with alcoholic ferric chloride.

This intermediate was mixed with water (100 c.c.), and a solution of potassium hydroxide (16·5 g.) in water (25 c.c.) introduced at intervals during 2 days. The deep orange solution was then boiled for 4 hours; on cooling, a sparingly soluble yellow potassium salt separated and more of this was obtained by the addition of potassium hydroxide (20 g.) in water (15 c.c.) to the filtrate. The derivative was collected on a sintered glass filter, washed with 20% potassium hydroxide, and added to an excess of dilute hydrochloric acid. The ketone quickly solidified (yield, 1·4 g.) and then crystallised from light petroleum in colourless, elongated prisms, m. p. 90° (Found : C, 58·4; H, 6·0. $C_{11}H_{14}O_5$ requires C, 58·4; H, 6·2%). 4-*Hydroxy*-ω : 3 : 5-*trimethoxyacetophenone* is readily soluble in most organic solvents, and forms yellow solutions in dilute aqueous alkalis. A weak green coloration (similar to that given by ω-chloroacetovanillone) is produced by alcoholic ferric chloride.

5 : 7 : 4′-*Trihydroxy*-3 : 3′ : 5′-*trimethoxyflavylium Chloride* (*Malvidin Chloride* 3-*Methyl Ether*) (XXV).—5-*Benzoyl derivative*. An ice-cold solution of 4-hydroxy-ω : 3 : 5-trimethoxyacetophenone (1·05 g.) and *O*-benzoylphloroglucinaldehyde (2·0 g.) in dry ethyl acetate (35 c.c.) was saturated with hydrogen chloride for 10 hours. Next day the dark violet oxonium salt was collected (2·1 g.): it crystallised from methyl alcohol, containing a little 8% hydrochloric acid, in glistening rhombs, deep red by transmitted light, olive-green by reflected light, and possessing a bright yellow lustre (Found : C, 57·6, 57·4. $C_{25}H_{21}O_8Cl,2H_2O$ requires C, 57·7%).

The salt dissolved readily in hot water to a red solution that rapidly became colourless; the colour was quickly and completely restored on the addition of hydrochloric acid. In cold 0·5% hydrochloric acid a pale red solution was obtained, but hot 8% hydrochloric acid was only coloured pink. The red solution in methyl alcohol had a violet tinge and was decolorised on dilution with more

methyl alcohol. The powdered salt was coloured blue by moderately concentrated aqueous sodium carbonate, but not dissolved; on the addition of methyl alcohol a blue solution resulted and this was greener than the corresponding solution of the de-benzoylated salt (below). Similarly the violet colour obtained by the addition of solid sodium acetate to a solution of the salt in methyl alcohol was slightly bluer than that given by the malvidin 3-methyl ether under the same conditions.

De-benzoylation. A stream of hydrogen was passed through ice-cold 10% aqueous sodium hydroxide (20 c.c.), and the crude benzoyl derivative (2·0 g.) stirred into the solution. The purplish-blue colour persisted for 45—50 minutes and subsequently changed through olive-green to deep orange. After 6 hours, methyl alcohol (20 c.c.) and concentrated hydrochloric acid (6 c.c.) were added, the clear red solution was heated to incipient ebullition for 30 minutes and kept for 12 hours, and the flavylium salt was then precipitated by means of concentrated hydrochloric acid. It was collected and twice separated as an amorphous violet-brown powder from hot 3% hydrochloric acid. Crystallisation from methyl alcohol under a variety of conditions was unsuccessfully attempted, but the salt crystallised easily from ethyl alcohol, containing a few drops of concentrated hydrochloric acid, as a dark violet powder having a bright yellow reflex and consisting of slender prisms that appeared deep red by transmitted light (Found in air-dried material: C, 55·7, 55·7; H, 5·2, 5·4. $C_{18}H_{17}O_7Cl,\frac{1}{2}H_2O$ requires C, 55·5; H, 4·9%). This malvidin chloride methyl ether is much more readily soluble in water and dilute hydrochloric acid than its benzoyl derivative or malvidin chloride; in cold water the solution has a blood-red colour and is decolorised on keeping, if sufficiently dilute. The cold saturated solution in 3% hydrochloric acid is deep red and even in hot 8% hydrochloric acid the salt is moderately readily soluble, but separates almost completely on cooling. It is readily soluble in methyl alcohol, but sparingly so in ethyl alcohol, and the colour of the acid alcoholic solutions resembles that of malvidin. The ease of pseudo-base formation in alcoholic solution is greater than with malvidin and the colour is immediately and fully restored on acidification. An alcoholic solution added to much water gives a solution of the damson colour-base, from which the pseudo-base is formed at a measurable rate. The solutions in aqueous sodium carbonate and aqueous sodium hydroxide are purplish-blue and change very little on the addition of alcohol; the colorations are redder than those characteristic of malvin or malvidin under the same conditions.

The colorations produced by the addition of sodium acetate to

solutions of the salt are violet, and bluer in methyl alcohol than in water. Addition of aqueous sodium acetate to a concentrated methyl-alcoholic solution precipitates the violet colour-base, insoluble in water but immediately soluble in dilute hydrochloric acid to a red solution.

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