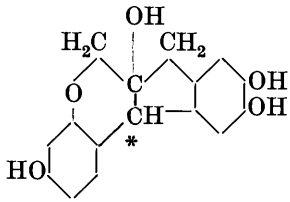
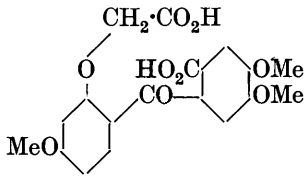
CXXXIII.—*Experiments on the Synthesis of Brazilin and Hæmatoxylin and their Derivatives. Part I. Veratrylidene-7-methoxychromanone and an Account of a New Synthesis of some Benzopyrylium Salts.*

By William Henry Perkin, jun., Jnanendra Nath Rây, and Robert Robinson.

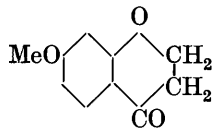
The investigation of brazilin and hæmatoxylin by analytical methods, commenced in 1901 (Part I, Gilbody, Perkin, and Yates, J., **79**, 1401) and completed in 1909 (Part X, Perkin and Robinson, J., **95**, 381), resulted in the demonstration that brazilin has the constitution (I) and that hæmatoxylin is an analogous derivative of pyrogallol. In the course of the work a number of derivatives

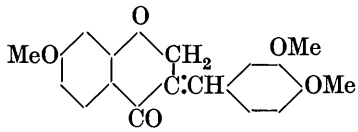
of brazilin and hæmatoxylin were synthesised, the more important being anhydrobrazilic acid, brazilinic acid, and the lactones of dihydrobrazilinic and dihydrohæmatoxylinic acids (Perkin and Robinson). Brazilinic acid (II) is an example of a derivative containing all the carbon atoms of trimethylbrazilin, and the correctness of the carbon skeleton of (I) was further confirmed by the

(I.) 

 (II.)

synthesis of *iso*brazilein and of *iso*hæmatein (Crabtree and Robinson, J., 1918, **113**, 859; 1922, **121**, 1033), substances which contain intact the ring-system of brazilin. There exists, however, no synthetical * proof of the position of the hydroxyl group in (I), since the production of 3 : 7-dihydroxychromone, an oxidation product of brazilein (Schall and Dralle, *Ber.*, 1888, **21**, 3016), could be explained in a natural manner by several brazilein formulæ and, for example, by that in which the hydroxyl is in the position denoted by an asterisk in (I). Apart from this consideration an obvious interest attaches to the synthesis of brazilin, an interest which is only heightened by the difficulty of the problem and by the probable necessity of devising new methods for its solution. In 1911, Tschitschibabin and Nikitin (*J. Russ. Phys. Chem. Soc.*, **43**, 1185) published a note on 7-methoxychromanone (III), and this led two of us to submit a preliminary note (P., 1912, **28**, 7) on the experiments which had been made on the same subject with the object of synthesising trimethylbrazilin.

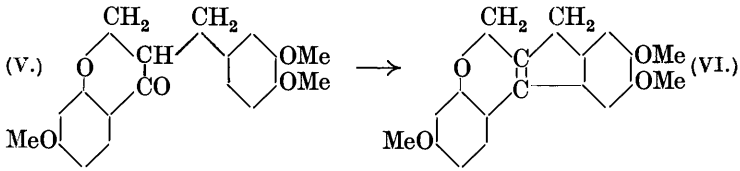
(III.) 

 (IV.)

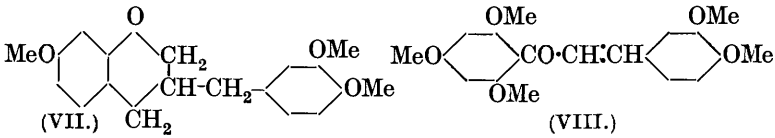
3-Veratrylidene-7-methoxychromanone (IV), m. p. 140°, was described in the note of 1912 and comment was made on its close relationship to trimethylbrazilin. Pfeiffer and Grimmer (*Ber.*, 1917, **50**, 911) then announced their intention of attacking the problem of the synthesis of brazilin and its derivatives and selected the method indicated in the above-mentioned note of 1912. These

* The position assigned to the hydroxyl in (I) is indicated by the fact that tetramethyldihydrobrazileinol yields trimethylbrazilone on oxidation (Engels, Perkin, and Robinson, J., 1908, **93**, 1130).

authors reported the preparation of anisylidene-7-methoxychromanone, and in consequence the fact that a nearer relative of brazilin, namely, veratrylidene-7-methoxychromanone, had been prepared was pointed out in a footnote to a paper in this *Journal* (1918, **113**, 859). Undeterred by this, Pfeiffer and Emmer (*Ber.*, 1920, **53**, 945) proceeded to the preparation of veratrylidene-7-methoxychromanone, m. p. 140°, and stated that they had succeeded in reducing the substance to a dihydro-derivative (V) by means of hydrogen in the presence of platinum black.



The experiments on this subject, interrupted at the time because of other interests, have now been resumed, and in this communication we bring together some observations arising out of work as yet unfinished. The preparation of (V) was one of the primary objects of the investigation, since dehydration to (VI) should be feasible. We are, however, of the opinion, for various reasons, that the product of the catalytic * hydrogenation of veratrylidene-7-methoxychromanone is 3-homoveratryl-7-methoxychroman (VII) and not the ketone (V) as suggested by Pfeiffer and Emmer (*loc. cit.*).

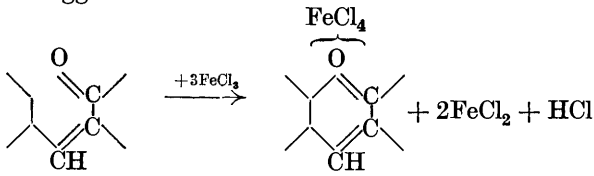


This result is by no means unique, since Freudenberg (*Ber.*, 1920, **53**, 1416) has shown that the pentamethoxychalkone (VIII) is reduced to the related diphenylpropane derivative by hydrogen in presence of spongy platinum.

Further attempts to reduce veratrylidene-7-methoxychromanone to a dihydro-derivative will be made. Our objects in making certain further experiments are explained in the sequel (pp. 947, 948, 950). In the presence of acid condensing agents veratrylidene-7-methoxychromanone (IV) might be expected to undergo internal condensation with formation of *iso*brazilein salts, readily recognisable on account of the intense green fluorescence which they exhibit. Under several sets of conditions it was, in fact, noticed that substances exhibiting intense green fluorescence could be derived from

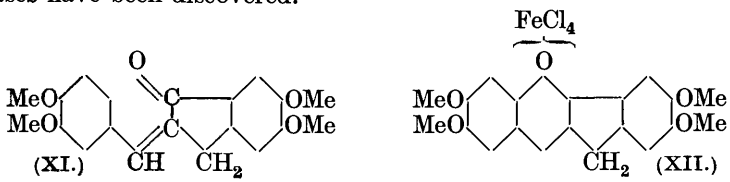
* We employed palladium as the catalyst, but it should be noted that platinum is usually regarded as even more efficient.

veratrylidene-7-methoxychromanone. The yield was usually very small, but when the unsaturated ketone was dissolved in acetic anhydride and anhydrous ferric chloride added, a relatively considerable amount of an oxonium ferrichloride was produced. The new salt was readily purified and exhibited an even more striking fluorescence than *iso*brazilein chloride trimethyl ether. It has the composition $C_{19}H_{15}O_5Cl_4Fe$ and is therefore derived from veratrylidenemethoxychromanone, $C_{19}H_{16}O_5$, by some process of oxidation. In considering this matter it seemed possible that the pyrylium ring, which the salt obviously contained, might be produced, not by modification of the heterocyclic system already present, but by attachment of the oxygen of the carbonyl group to carbon of the veratrole nucleus. The following partial formulæ will serve to make this suggestion clear :



Such a reaction, leading to the formation of a benzopyrylium salt, has not been previously observed, but it is similar, both in principle and in method, to Dilthey's synthesis of pyrylium salts (*J. pr. Chem.*, 1916, **94**, 53) and it also resembles many methods of preparation of oxazine, thiazine and azine dyestuffs. The simplest analogy is furnished by an observation recently made by Gomberg and Nishida (*J. Amer. Chem. Soc.*, 1923, **45**, 190) : *o*-hydroxytriphenylcarbinol in solution above 100° yields 9-phenylxanthane (X), no doubt through the intermediate (IX).

We found support for this view of the reaction in the fact that veratrylidene-5 : 6-dimethoxyhydrindone (XI) could be similarly oxidised to an oxonium ferrichloride (XII), and several further cases have been discovered.



The process is nevertheless not a very general one and up to the present we have only found it to succeed with the veratrylidene, *o*-veratrylidene or piperonylidene derivatives of cyclic ketones. Thus veratrylideneacetoveratrone and *m*- or *p*-methoxybenzylidene-5 : 6-dimethoxyhydrindone gave negative results.

EXPERIMENTAL.

m-*Methoxyphenol.*—The conditions for the semi-methylation of resorcinol have been studied and the following process has been devised. Potassium hydroxide (40 g.) dissolved in water (100 c.c.) was gradually added to a mixture of resorcinol (110 g.), alcohol (100 c.c.), and methyl sulphate (120 c.c.), which was frequently shaken and cooled in running water. An hour afterwards, an equal quantity of aqueous potassium hydroxide was gradually introduced and finally the mixture was heated on the steam-bath for 45 minutes. The solution was then acidified, extracted with benzene and the separated benzene layer was washed with aqueous sodium hydroxide until nothing more was removed. The alkaline solutions were acidified and again extracted with benzene. This process removes unchanged resorcinol and resorcinol dimethyl ether may be recovered from the first benzene solution. The second benzene extract was dried and distilled, 50 g., b. p. 240—242°, being obtained.

β-m-*Methoxyphenoxypropionic Acid.*—This substance was originally obtained from *m*-methoxyphenol in aqueous alkaline solution by interaction with β-iodopropionic acid. The use of β-bromopropionic acid results in rather improved yields, but β-chloropropionic acid is still better. A solution of β-chloropropionic acid (60 g.) in water (225 c.c.) and sodium bicarbonate (45·3 g.) was mixed with one of *m*-methoxyphenol (67·5 g.) in aqueous potassium hydroxide (100 c.c. of 30%), and the liquid heated on the steam-bath for 3 hours. After acidification, the mixture was extracted with ether, and the acid removed from the extract by means of aqueous sodium bicarbonate. β-*m*-Methoxyphenoxypropionic acid (30 g.) and recovered *m*-methoxyphenol (28—30g.) were ultimately isolated.

We refrain from detailed descriptions of the substances mentioned in the note of 1912 (*loc cit.*), the properties of which have since been placed on record by Pfeiffer and his colleagues.

m-β-Hydroxyethoxyanisole, b. p. 290°/15 mm., was prepared from *m*-methoxyphenol, sodium ethoxide, and ethylene chlorohydrin in alcoholic solution. In an attempt to replace the hydroxyl group in this substance by bromine with the ultimate object of preparing β-*m*-methoxyphenoxypropionitrile, a curious result was

obtained. The glycol ether (11 g.) was dissolved in benzene and phosphorus tribromide (20 g.) added, causing a copious evolution of hydrogen bromide. The mixture was gently heated in the steam-bath for 2 hours, and the neutral product isolated. This was dissolved in alcohol, and the solution boiled for 3 hours after the introduction of a concentrated aqueous solution of potassium cyanide (5 g.). On addition of water, a solid (6 g.) was precipitated and the substance crystallised from alcohol in long, colourless needles, m. p. 65° (Found: C, 70·1; H, 6·6. $C_{16}H_{18}O_4$ requires C, 70·1; H, 6·5%). The substance appears to be the ethylene ether of *m*-methoxyphenol, $MeO{\cdot}C_6H_4{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}C_6H_4{\cdot}OMe$.

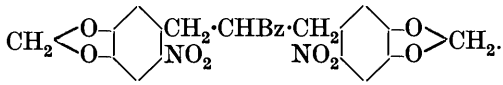
7-*Methoxychromanone* (III) has been prepared by several methods but, although it is not satisfactory, the original process of dehydration of methoxyphenoxypropionic acid in benzene solution by means of phosphoric anhydride is still the best. Phosphoric anhydride (80—90 g.) was gradually added to a gently boiling solution of methoxyphenoxypropionic acid (30 g.) in benzene (200 c.c.). After heating for 4 hours, the neutral ketone was isolated and purified by distillation. The yield was 6—8 g., b. p. 197°/30 mm., m. p. 56° after crystallisation from light petroleum. The semicarbazone separates from alcohol in glistening plates, m. p. 222° (decomp.).

3-*Veratrylidene*-7-*methoxychromanone* (IV).—This substance was at first prepared by condensation of 7-methoxychromanone and veratraldehyde in methyl-alcoholic solution in presence of potassium hydroxide, but the following is a much improved method. A rapid stream of hydrogen chloride was passed for one hour through a solution of methoxychromanone (5 g.) and veratraldehyde (5 g.) in acetic acid (10 c.c.) cooled in a freezing mixture. Next day the deep red solution was filled with a red crystalline mass of the *hydrochloride* of the unsaturated ketone and this was collected and decomposed with crushed ice. The substance was finally crystallised from much methyl alcohol, separating in colourless needles, m. p. 141°. The yield was 5·6 g.

3-*Homoveratryl*-7-*methoxychroman* (VII).—A solution of veratrylidene-7-methoxychromanone (7 g.) in acetic acid (200 c.c.) was mixed with aqueous palladous chloride (30 c.c. of 1%) and agitated in an atmosphere of hydrogen until absorption of the gas slackened. The temperature was then raised to 50—60° and the agitation in hydrogen continued for about 6 hours. Most of the acetic acid was removed from the filtered solution by distillation under diminished pressure, and the residue neutralised with aqueous sodium carbonate. The colourless solid which was precipitated was collected and when once crystallised from methyl alcohol had m. p. 89°. This is the m. p. assigned by Pfeiffer and Emmer (*loc. cit.*)

to the supposed ketonic product of the catalytic hydrogenation of veratrylidenemethoxychromanone. After three or four successive crystallisations from methyl alcohol or from aqueous acetone, the substance is obtained in slender, colourless needles, m. p. 96—97° (Found: C, 72·2; H, 7·2. $C_{19}H_{22}O_4$ requires C, 72·6; H, 7·0%). The substance dissolves in sulphuric acid to a pale rose solution and is inactive towards reagents for the carbonyl group. We do not go so far as to assert that the products of the hydrogenation of veratrylidenemethoxychromanone in presence of platinum (Pfeiffer and Emmer) and of palladium are identical, although we think it probable that this will prove to be the case.* We have not been able to isolate any product of the reduction other than that here described and it is noteworthy that, whereas the semicarbazone of the reduction product of anisylidenemethoxychromanone was described (Pfeiffer and Emmer, *loc. cit.*), no proof, other than analysis, was offered of the ketonic nature of the reduction product, m. p. 89°, of veratrylidenemethoxychromanone.

*Di-ω-6-nitropiperonyl*isobutyrophenone,



—Attempts are in progress to introduce the homoveratryl group into 7-methoxychromanone by a direct process and preliminary experiments on the interaction of the sodium derivative of acetophenone and homopiperonyl † bromide have been made. Powdered sodamide (2 g.) was added to acetophenone (6 c.c). dissolved in dry ether (75 c.c.) and, after the mixture had been occasionally shaken during an hour, homopiperonyl bromide (11 g.) was added to the clear solution. The mixture was heated on the steam-bath for 1 hour, water was added, and ether and acetophenone were removed in

* It would be anticipated that the m. p. of a chromanone should be higher than that of the related chroman.

† Possibly on account of its close relation to piperonal the alcohol $CH_2O_2{:}C_6H_3{\cdot}CH_2{\cdot}OH$ has been called piperonyl alcohol, and consequently the amine, $CH_2O_2{:}C_6H_3{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$, has been named homopiperonylamine. This nomenclature is, however, erroneous and its continuance must necessarily create confusion. The historical case for regarding the group $CH_2O_2{:}C_6H_3{\cdot}$ as piperonyl is overwhelming; thus Ladenburg termed

$$CH_2O_2{:}C_6H_3{\cdot}CH{:}CH{\cdot}CHO,$$

piperonylacrolein and the words piperonyl, veratryl, and anisyl have been very widely employed to indicate the corresponding substituted phenyl groups. The compound often called piperonyl alcohol is really homopiperonyl alcohol and the base for which the usual name is homopiperonylamine is best termed β-piperonylethylamine. It is obviously undesirable to employ one and the same word to denote two different radicals (compare Robinson and Robinson, J., 1914, **105**, 1461; Oberlin, *Arch. Pharm.*, 1925, **9**, 10).

a current of steam. The residual yellow oil could not be crystallised but, on nitration in acetic acid solution, it yielded a compound which crystallised from benzene in needles, m. p. 193° with sintering at 175° (Found: C, 51·5; H, 3·5. $C_{16}H_{13}O_8N_3$ requires C, 51·2; H, 3·5%). The substance appears to be *dinitrodihomopiperonylamine*, $CH_2O_2{:}C_6H_2(NO_2)\cdot CH_2\cdot NH\cdot CH_2\cdot C_6H_2(NO_2){:}O_2CH_2$, obtained from homopiperonyl bromide and ammonia followed by nitration. The experiment was therefore repeated under the same conditions with the single exception that ammonia was removed from the ethereal solution by means of a current of nitrogen before introduction of the homopiperonyl bromide. In this case also the product was an oil which gave a nitro-derivative, crystallising from benzene in slender needles, m. p. 160—161° (Found: C, 60·4, 60·3; H, 3·9, 4·0; N, 6·0. $C_{24}H_{18}O_9N_2$ requires C, 60·3; H, 3·8; N, 5·9%). The composition of this substance is in agreement with the hypothesis that it is the ketone figured at the head of this section. We have not yet completed our experiments on the homoveratrylation of methoxychromanone, but it may be mentioned that in the course of the preparation of homoveratryl alcohol a further case of the production of a derivative of cinnamic acid in a Cannizzaro reaction, carried out in the presence of ethyl alcohol, has been observed (compare Perkin and Stoyle, J., 1923, **123**, 3174). Potassium hydroxide (30 g.) dissolved in ethyl alcohol (75 c.c. of 98%) was added to veratraldehyde (20 g.) dissolved in the same solvent (25 c.c.). Next day, the crystals which had separated were collected and found to consist of potassium 3 : 4-dimethoxycinnamate and to yield 7·8 g. of the corresponding acid. Veratric acid and homoveratryl alcohol were isolated from the filtrate in the usual manner.

2-Bromo-5 : 6-dimethoxy-1-hydrindone, $C_6H_2(OMe)_2\langle\begin{matrix}CO\\CH_2\end{matrix}\rangle CHBr$. —A portion (18 c.c.) of a solution of bromine (1 c.c.) in carbon tetrachloride (20 c.c.) was gradually added to 5 : 6-dimethoxyhydrindone (3·0 g.) dissolved in warm carbon tetrachloride (30 c.c.). After 1 hour the thick paste that had been produced (3·0 g.) was washed with carbon tetrachloride; it crystallised from alcohol in very pale yellow, rectangular plates, m. p. 157° (Found: Br, 28·3. $C_{11}H_{11}O_3Br$ requires Br, 29·5%).

2-Cyano-5 : 6-dimethoxy-1-hydrindone, $C_6H_2(OMe)_2\langle\begin{matrix}CO\\CH_2\end{matrix}\rangle CH\cdot CN$. —This substance was prepared in order to attempt the synthesis of a coumarin derivative by condensation with resorcinol. Such a substance would be closely related to trimethylbrazilin. A mixture of 2-bromo-5 : 6-dimethoxy-1-hydrindone (3 g.), alcohol (40 c.c. of 95%), potassium cyanide (1·5 g.), and water (20 c.c.) was boiled

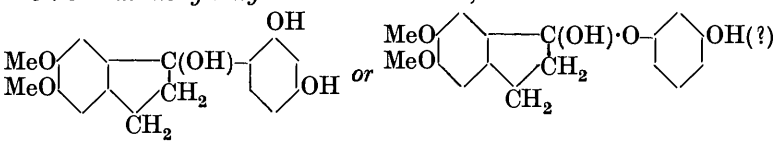
under reflux for 3 hours, then cooled, acidified with acetic acid, and extracted with ether. The residue left after removal of the solvent from the extract crystallised from alcohol in clusters of radiating needles (1—1·5 g.), m. p. 174° (Found : C, 66·1 ; H, 4·8. $C_{12}H_{11}O_3N$ requires C, 66·3 ; H, 5·0%). The substance dissolves in dilute aqueous potassium hydroxide to a very pale yellow solution and gives no coloration with alcoholic ferric chloride. On hydrolysis with boiling 50% sulphuric acid, 5 : 6-dimethoxyhydrindone, identified by conversion into its piperonylidene derivative, m. p. 245°, was obtained. In a subsequent experiment, the proportion of water employed was reduced, and in this case, in addition to the above-described nitrile, a polymeric modification or condensation product of it was obtained. Bromo-5 : 6-dimethoxyhydrindone (10 g.), absolute alcohol (60 c.c.), potassium cyanide (3·5 g.), and water (5 c.c.) were mixed and then boiled under reflux for 2 hours, water (10 c.c.) being gradually introduced during this period. The product was added to water, and the solid (5 g.) collected. On acidification the filtrate gave 1·5 g. of the normal nitrile. The main product was sparingly soluble in most organic solvents and crystallised from glacial acetic acid in needles, m. p. 256—257° to a red liquid (Found : C, 66·4 ; H, 5·4%). The substance is insoluble in dilute aqueous potassium hydroxide.

Ethyl 5 : 6-*Dimethoxy*-1-*hydrindone*-2-*carboxylate*,

$$C_6H_2(OMe)_2\langle\begin{matrix}CO\\CH_2\end{matrix}\rangle CH\cdot CO_2Et.$$

—A solution of the nitrile, m. p. 174°, described in the last section, in 20 times its weight of absolute alcohol was saturated with hydrogen chloride at the ordinary temperature for 3 hours, then boiled for 10 minutes and added to ice-cold water. The solid which separated crystallised from alcohol in colourless needles, m. p. 138° (decomp.) (Found : C, 63·9 ; H, 6·3. $C_{14}H_{16}O_5$ requires C, 63·6 ; H, 6·1%). This ester gives with ferric chloride in alcoholic solution a transient green and then a blue coloration. We have not yet prepared a coumarin derivative from either the nitrile or the ester by condensation with resorcinol, although a number of trials have been made.

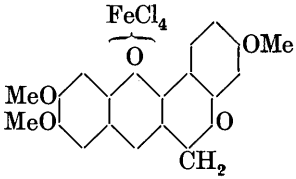
5 : 6-*Dimethoxy*-1-*hydrindone-resorcinol*,



—A solution of dimethoxyhydrindone (9·0 g.) and resorcinol (7·0 g.) in acetic acid (35 c.c.) was saturated with hydrogen chloride in the cold, kept for 1 hour, and added to water (150 c.c.). The resulting

clear liquid was neutralised with sodium carbonate; the yellow, crystalline deposit separated from boiling water in silky needles, m. p. 78° (Found: C, 67·9; H, 6·0. $C_{17}H_{18}O_5$ requires C, 67·6; H, 5·9%). A small quantity of a yellow oil was separated in the above process on account of its sparing solubility in hot water. This consists of a substance which crystallises from methyl alcohol in needles, m. p. 227°. The by-product has not yet been further examined, nor has the compound, m. p. 78°, been characterised by the preparation of derivatives. It is remarkably sensitive to alkalis, being quantitatively resolved into its components, namely, dimethoxyhydrindone and resorcinol, by means of cold aqueous sodium hydroxide. Attempts to prepare an indene derivative by dehydration of this substance were fruitless. It is not a mere molecular compound, since it is not obtained in the absence of a condensing agent.

2 : 3-[7-*Methoxychromeno* (4 : 3)]-6 : 7-*dimethoxybenzopyrylium Ferrichloride,*

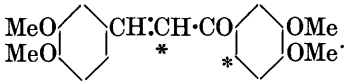


—Anhydrous ferric chloride (5·0 g.) was added to a solution of veratrylidene-7-methoxychromanone (1·0 g.) in acetic anhydride (25 c.c.) and when the reaction had subsided a further quantity of ferric chloride (3·0 g.) was added. After 10 minutes, the product was added to water (250 c.c.), and a ferrichloride precipitated by addition of a concentrated solution of ferric chloride in hydrochloric acid. The substance (yield almost quantitative) crystallised from acetic acid in crimson, prismatic needles, m. p. 213°, exhibiting a blue reflex (Found: C, 43·7, 43·4; H, 3·5, 3·2. $C_{19}H_{15}O_5Cl_4Fe$ requires C, 43·6; H, 3·3%). Solutions of this salt in all solvents and particularly those in alcohol and acetic acid exhibit an extraordinarily brilliant greenish-yellow fluorescence. The salt is very sparingly soluble in acetic acid and more readily soluble in hot formic acid.

2-m-*Methoxybenzylidene*-5 : 6-*dimethoxy*-1-*hydrindone.*—This compound was obtained by condensation of dimethoxyhydrindone and *m*-methoxybenzaldehyde in hot alcoholic solution containing a few drops of concentrated aqueous potassium hydroxide. The yield was practically quantitative and the sparingly soluble substance crystallised from ethyl acetate in pale yellow needles, m. p. 164—165° (Found: C, 73·6; H, 5·7. $C_{19}H_{18}O_4$ requires C, 73·5; H, 5·8%).

Neither this substance nor the isomeric anisylidenedimethoxyhydrindone could be converted into a pyrylium salt by means of ferric chloride in acetic anhydride solution.

3 : 4-*Dimethoxystyryl Veratryl Ketone*,



—An ethyl-alcoholic solution of equivalent quantities of veratraldehyde and acetoveratrone, together with a few drops of concentrated aqueous potassium hydroxide, was boiled for 10 minutes. The oil then precipitated by water solidified on repeated washing with cold water and aqueous alcohol. The substance crystallised from alcohol in flat, yellow prisms, m. p. 116° (Found : C, 69·3; H, 6·1. $C_{19}H_{20}O_5$ requires C, 69·5; H, 6·1%). The compound is not changed to a pyrylium salt by the action of ferric chloride in acetic anhydride solution. This fact may be compared with the ready conversion of veratrylidenedimethoxyhydrindone into an oxonium ferrichloride by oxidation with ferric chloride. In the latter case, the carbon atoms in the asterisked positions in the above formula are connected by a methylene group.

2-*Veratrylidene*-4 : 6-*dimethoxycoumaranone*,

$$C_6H_2(OMe)_2\langle\begin{matrix}O\\CO\end{matrix}\rangle C{:}CH{\cdot}C_6H_3(OMe)_2.$$

—A solution of equivalent quantities of veratraldehyde and 4 : 6-dimethoxycoumaranone (Sonn, *Ber.*, 1917, **50**, 1265) in five times their weight of acetic acid was cooled in a freezing mixture and saturated with hydrogen chloride. The liquid was filled with a mass of deep red crystals of a hydrochloride in 1·5 hours; these were collected and decomposed by water, giving a bright yellow substance which crystallised from alcohol in needles, m. p. 175° (Found : C, 66·1; H, 4·9. $C_{19}H_{18}O_6$ requires C, 66·6; H, 5·2%). No pyrylium salt could be isolated from the product of the action of ferric chloride and acetic anhydride on this substance.

2-*Veratrylidene*-1-*hydrindone*, $C_6H_4\langle\begin{matrix}CO\\CH_2\end{matrix}\rangle C{:}CH{\cdot}C_6H_3(OMe)_2$.—An ice-cold mixture of veratraldehyde (4·5 g.), α-hydrindone (3 g.), and acetic acid (15 c.c.) was saturated with hydrogen chloride and after 3 hours the scarlet hydrochloride was collected, washed with acetic acid, and decomposed with water; the resulting yellow compound crystallised from acetic acid in prisms, m. p. 175° (Found : C, 76·6; H, 5·8. $C_{18}H_{16}O_3$ requires C, 77·2; H, 5·7%).

2 : 3-*Indeno*(1 : 2)-6 : 7-*dimethoxybenzopyrylium Ferrichloride* (formula similar to XII).—Anhydrous ferric chloride (15 g.) was added in portions of about 3 g. during an hour to a solution of

veratrylidene-1-hydrindone (2 g.) in acetic anhydride (35 c.c.). After 2 hours, the dark red mixture was added to a concentrated solution of ferric chloride in hydrochloric acid, and the precipitate was collected, dried, and extracted with acetic acid; the chocolate residue crystallised from absolute formic acid in brownish-red prisms, m. p. 237—238°, twinning characteristically with formation of a symmetrical cross (Found: C, 45·4; H, 3·2. $C_{18}H_{15}O_3Cl_4Fe$ requires C, 45·5; H, 3·1%). A similar, even more sparingly soluble, ferrichloride may be obtained analogously from piperonylidene-hydrindone.

2 : 3[5 : 6-*Dimethoxyindeno*(1 : 2)]-6 : 7-*dimethoxybenzopyrylium Ferrichloride* (XII).—Anhydrous ferric chloride (10 g.) was gradually added to a mechanically stirred solution of 2-veratrylidene-5 : 6-dimethoxy-1-hydrindone (Perkin and Robinson, J., 1907, **91**, 1073) (3·7 g.) in acetic anhydride (50 c.c.) cooled in melting ice. After ½ hour, the vessel was removed from the cooling bath and a further equal quantity of sublimed ferric chloride added. After 15 minutes, the vessel was immersed in water at 40—50° and stirring continued for 20 minutes. Next day, decomposition with aqueous hydroferrichloric acid gave a gelatinous precipitate, which was collected and became crystalline on boiling with acetic acid. The substance crystallised from formic acid in deep brownish-crimson needles, m. p. 246—247°, with bluish-green reflex (Found: C, 45·0; H, 3·7. $C_{20}H_{19}O_5Cl_4Fe$ requires C, 44·9; H, 3·6%). Solutions of this salt in alcohol or formic acid exhibit a phenomenal, greenish-yellow fluorescence. The substance is insoluble in cold acetic acid and sparingly soluble in formic acid.

2 : 3[5 : 6-*Dimethoxyindeno*(1 : 2)]-6 : 7-*methylenedioxybenzopyrylium Ferrichloride* (formula similar to XII).—Anhydrous ferric chloride (20 g.) was gradually added to a stirred solution of 2-piperonylidene-5 : 6-dimethoxy-1-hydrindone (3·5 g.) in acetic anhydride (50 c.c.) during 2 hours. The product, isolated in the usual manner, was extracted by acetic acid and crystallised from formic acid in hæmatite-red, microscopic prisms, m. p. 270° (decomp.) (Found: C, 43·6; H, 3·0. $C_{19}H_{15}O_5Cl_4Fe$ requires C, 43·8; H, 2·9%). This very sparingly soluble substance exhibits a vivid greenish-yellow fluorescence in formic acid solution.

2-(2 : 3-*Dimethoxybenzylidene*)-1-*hydrindone*,

$$C_6H_4\begin{<}{CO-}\\{CH_2}\end{>}C{:}CH\cdot C_6H_3(OMe)_2.$$

—This substance was obtained in almost theoretical yield by the methylation of 2-hydroxy-3-methoxybenzylidenehydrindone (Lawson and Robinson, J., 1924, **125**, 207) by means of methyl sulphate and potassium hydroxide in alcoholic solution. It crystallises from

alcohol in pale yellow prisms, m. p. 124° (Found : C, 77·2; H, 5·3. $C_{18}H_{16}O_3$ requires C, 77·2; H, 5·7%).

2 : 3-*Indeno*(1 : 2)-5 : 6-*dimethoxybenzopyrylium Ferrichloride* (formula after XII).—Anhydrous ferric chloride (18 g.) was gradually added to a stirred solution of 2 : 3-dimethoxybenzylidenehydrindone (3 g.) in acetic anhydride (40 c.c.) during 1·5 hours. The product, isolated in the usual manner, crystallised from acetic acid in crimson leaflets or flat needles, m. p. 168° (Found : C, 45·2; H, 3·3. $C_{18}H_{15}O_3Cl_4Fe$ requires C, 45·5; H, 3·1%). This salt does not exhibit strong fluorescence in any solution. *o*-Veratrylidenehydrindone might have given indeno-8-methoxybenzopyrylium ferrichloride, m. p. 187° (Lawson and Robinson, *loc. cit.*), by hydrolysis of the *o*-situated methoxyl group, but a mixture of the salts, m. p. 168° and 187°, melted indefinitely at about 140°.

2′ : 3′ : 5 : 6-*Tetramethoxy*-2-*benzylidene*-1-*hydrindone*,

$$C_6H_2(OMe)_2\langle\begin{matrix}CO\\CH_2\end{matrix}\rangle C{:}CH{\cdot}C_6H_3(OMe)_2.$$

—The coppery-red potassium salt, resulting from the condensation of *o*-vanillin and 5 : 6-dimethoxyhydrindone in alcoholic solution in presence of potassium hydroxide, was methylated by means of methyl sulphate. The product crystallised in glistening yellow leaflets, m. p. 183—184°, from ethyl acetate–methyl alcohol (Found : C, 70·5; H, 5·2. $C_{20}H_{20}O_5$ requires C, 70·8; H, 5·6%). Anhydrous ferric chloride and acetic anhydride convert this substance into a ferrichloride crystallising from formic acid in brick-red leaflets, m. p. 211° (decomp.). The m. p. of the salt described below is depressed by admixture with this compound, and the salt, m. p. 211°, is therefore, in all probability, 2 : 3[5 : 6-*dimethoxyindeno*-(1 : 2)]-5 : 6-*dimethoxybenzopyrylium ferrichloride*.

2 : 3[5 : 6-*Dimethoxyindeno*(1 : 2)]-8-*methoxybenzopyrylium Ferrichloride* (formula after XII).—A solution of equivalent quantities of *o*-vanillin and 5 : 6-dimethoxyhydrindone in acetic acid was saturated with hydrogen chloride for 2 hours; it was then diluted with water and a ferrichloride precipitated. The latter crystallised from much acetic acid in brownish-red needles, m. p. 250° (decomp.) (Found : C, 45·1; H, 3·6. $C_{19}H_{17}O_4Cl_4Fe$ requires C, 45·0; H, 3·3%). Solutions of this salt do not exhibit fluorescence.

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