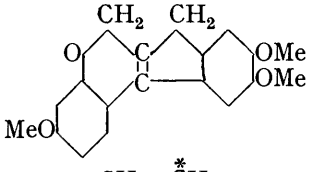
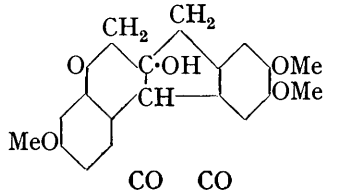
148. *Experiments on the Synthesis of Brazilin and Hœmatoxylin. Part V.*

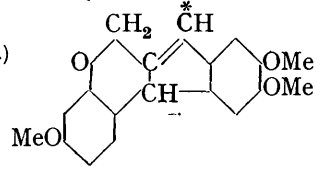
By H. Appel, Wilson Baker, H. Hagenbach, and Robert Robinson.

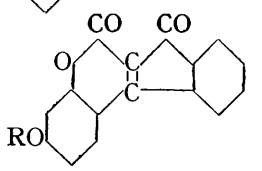
Three methods have been developed for the synthesis of substances containing the brazilane skeleton, and these lead to α-pyrones (Prescott and Robinson, 1911), to pyrylium salts (Crabtree and Robinson, 1918, 1922) or to γ-pyrans (Perkin, Ray, and Robinson; Pfeiffer and collaborators, 1912—), which are all closely related to brazilin. In the last two methods, actual brazilin derivatives have been synthesised; such are trimethoxybrazylium salts, anhydrotrimethylbrazilin (I), trimethylbrazilone, and their hæmatoxylin analogues. In spite of attempts repeated at intervals during the last fifteen years, it has not been found possible to extend any of these methods so as to accomplish the synthesis of trimethylbrazilin (II) itself, and in particular the hydration of (I) could not be effected, chiefly because it is itself the base of quinonoid oxonium salts and furthermore it is converted with remarkable ease into trimethoxybrazylium salts in the presence of acids or by means of the halogens or their equivalents.

It seems likely that the substance (III) isomeric with anhydrotrimethylbrazilin (I) would exhibit the normal character of an indene and show far less tendency than (I) to pass into a quinonoid-oxonium or pyrylium salt. We have to take the risk of indene tautomerism between the two forms; it is not certain that the system will be a mobile one. Hence we have directed attention to methods of preparation of intermediates in the synthesis of substances in which the asterisked position in (III) represents a carbonyl group. Full

(I.) 

(II.) 

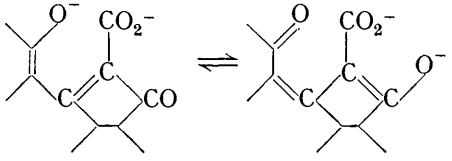
(III.) 

(IV.) 

reduction of such an intermediate should yield an isomeride of (II), from which (III), and then (II), might be accessible.

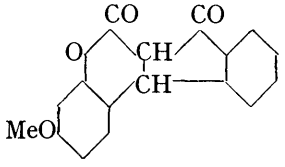
Two promising lines of investigation have been opened up in this direction and it is hoped to pursue both of them beyond the point reached in the present communication.

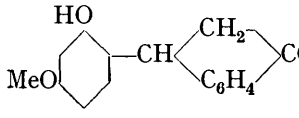
The condensation of ethyl 1 : 3-indanedione-2-carboxylate with resorcinol could only be brought about by means of hydrogen chloride in alcoholic solution (cf. Appel, J., 1935, 1031) and it then afforded a *coumarin* derivative (IV, R = H). This intensely yellow substance dissolves in aqueous sodium carbonate to a red solution, but in aqueous sodium hydroxide to a deep blue solution. Its *methyl* ether (IV, R = Me) is also yellow and gives a blue solution in alcoholic sodium hydroxide. The blue colour is therefore probably a manifestation of the *o*-hydroxyphenylindone structure in alkaline solution and the true explanation of the deep colour of salts of unsaturated hydroxy-ketones in general will apply to this particular case. The tautomerism, distribution of anionic charge, or resonance which is here possible may be represented by the expression :



On reduction with zinc and acetic acid, IV (R = Me) yields a *dihydro*-derivative, which is probably (V), and with zinc and aqueous sodium hydroxide a phenolic *ketone*, $C_{16}H_{14}O_3$, regarded as having the constitution (VI), is produced.

(V.)

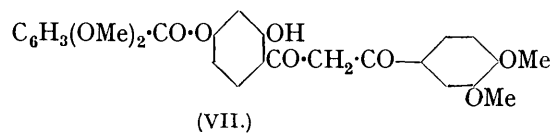




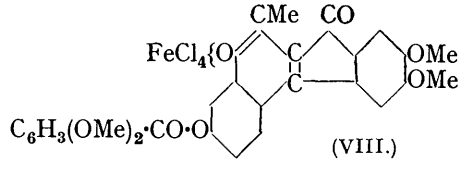
(VI.)

Experiments on the condensation of (VI) with formaldehyde derivatives give promise of realisation of the first part of the general scheme outlined above and this work is in progress; the analogous series starting with *m*-hemipinic acid instead of phthalic acid will also be studied.

A remarkably facile synthesis of the brazilin skeleton has been encountered in the further examination of ω-veratroylresacetophenone 4-veratrate (VII) (Baker, J., 1933, 1387). When this substance is suspended in acetic anhydride and treated at room temperature with zinc chloride, stannic chloride, or ferric chloride, an intensely orange-red solution is at once obtained and eventually bright red oxonium salts separate unless very low concentrations have been employed. With each of the three metallic chlorides the products are double salts which could not be recrystallised without decomposition; the zincichloride was not obtained in a pure state, but the analyses of the *stannichloride* pointed to the formula $(C_{28}H_{23}O_8)_2SnCl_6$ and those of the *ferrichloride* to the formula $C_{28}H_{23}O_8FeCl_4$. It was apparent, therefore, that the veratroyloxy-group had not been eliminated and that the condensation, if regarded as one between diveratroylresacetophenone, acetic acid, and hydrogen chloride, involved the loss of $3H_2O$.



(VII.)



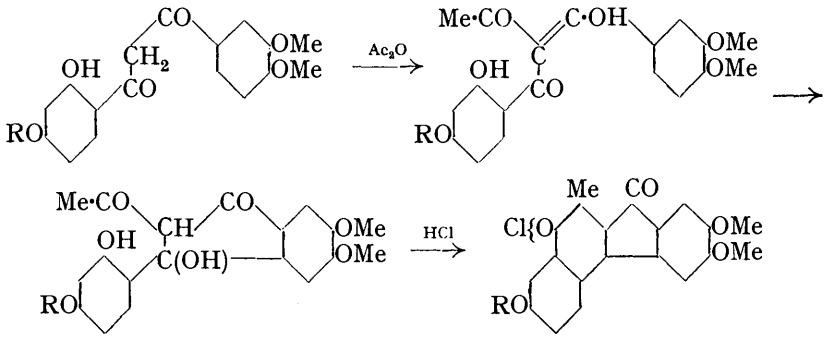
(VIII.)

Bearing in mind the syntheses of brazylium salts from homoveratrylpæanol (Crabtree and Robinson, J., 1918, **113**, 859; cf. Baker and Robinson, J., 1925, **127**, 1424, for the behaviour of homoveratrylresacetophenone) by the combined action of acetic anhydride

and zinc chloride, the brilliant red colour of the salts, and the above-mentioned analyses, it seemed very probable that they were ketohomobrazylium derivatives (VIII for the ferrichloride). This was confirmed by permanganate oxidation, which afforded veratric (from the veratroyloxy-group) and *m*-hemipinic acids.

The salts differ from the trimethoxybrazylium derivatives in that they are derived from a very weak base and in their lack of fluorescent properties. This is in accord with analogy; the direct union of the pyrylium nucleus with a carbonyl group should impair the basic function, and the non-fluorescent character of the 3-acylflavones may also be recalled in this connection.

The mechanism of the conversion of (VII) into (VIII) may be briefly considered and the chief point to note is that any satisfactory theory must include an explanation of the attack on the veratroyl nucleus, which is apparently inactivated by union with a carbonyl group. Ring-closures, such as that of benzoylbenzoic acid to anthraquinone, in the *o*-position to a keto-group are seldom accomplished with great ease and in the present case we suggest that enolisation prior to ring-closure must be assumed to occur. That reactions of this type do not proceed by way of intermediate chromones and that therefore the indene ring closure precedes that of the pyran nucleus has been demonstrated in similar cases (Baker and Robinson, *loc. cit.*) and reasons have been given for believing that *o*-hydroxydibenzoylmethanes can be directly *C*-acylated (Baker, *loc. cit.*). Hence the most probable course of the reaction is that represented in the following scheme:

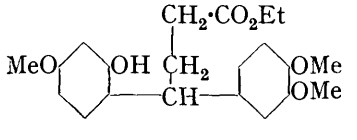


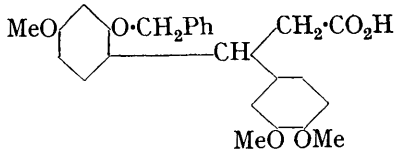
O-*Veratroylpæanol* undergoes rearrangement with far less readiness than *O*-diveratroylresacetophenone, but a 70% yield of *ω-veratroylpæanol* is obtainable by the use of sodamide instead of potassium carbonate (cf. Mahal and Venkataraman, *Current Science*, 1933, **2**, 214; J., 1934, 1767; Bhalla, Mahal, and Venkataraman, J., 1935, 868). ω-Veratroylpæanol evidently undergoes a reaction of the type discussed above, but the products do not crystallise from the solutions and so could not be isolated in a pure condition.

Attempts to employ formic acid, ethyl formate, or ethyl orthoformate in these reactions were not successful, but it is not improbable that a salt of the type (VIII) (zincichloride) could be reduced and hydrolysed with the formation of a ketone constituted like (VI), and further work will be directed to this end.

Some other possible methods of attack on this synthetical problem have been explored in a preliminary fashion. 7-Hydroxy-4-veratrylcoumarin (Mitter and Paul, *J. Indian Chem. Soc.*, 1931, **8**, 271) has been successively methylated, reduced, hydrolysed, and esterified with formation of *ethyl β-veratryl-β-(2-hydroxy-4-methoxyphenyl)propionate* (IX), but this ester could not be condensed with ethyl formate. Also the benzyl ether of the corresponding acid (X) could not be dehydrated to a hydrindone derivative.

(IX.)





(X.)

Experimental.

7-Hydroxy-1'-ketoindeno(2' : 3' : 3 : 4)coumarin (IV, R = H).—Cold saturated alcoholic hydrogen chloride (100 c.c.) was gradually added, during ½ hour, to a well-cooled and agitated mixture of resorcinol (60 g.), alcohol (300 c.c.), and ethyl indanedionecarboxylate (20 g.; Wislicenus, *Ber.*, 1887, **20**, 593). Complete solution occurred after 20 minutes and the yellow product began to crystallise after 1 hour; it was collected after 12 hours, washed with alcohol and acetone, and dried (10·2 g., sufficiently pure for most purposes). The *indenocoumarin* is sparingly soluble in most organic solvents and crystallises from a large volume of aqueous acetone in orange-yellow needles, which do not melt at 340° (Found : C, 72·9; H, 3·4. $C_{16}H_8O_4$ requires C, 72·7; H, 3·1%). The solution in aqueous sodium carbonate is deep red and on the addition of 10 vols. of 10% aqueous potassium hydroxide the colour changes to intense pure blue in about 2 minutes. On acidification the unchanged substance is regenerated.

1'-Keto-7-methoxyindeno(2' : 3' : 3 : 4)coumarin (IV, R = Me).—The foregoing phenol cannot be conveniently methylated by means of methyl sulphate and alkali. Methyl iodide (50 c.c.) was added to a mixture of hydroxyketoindenocoumarin (7·5 g.), silver oxide (20 g.), and methyl alcohol (150 c.c.), and the mixture refluxed until a sample did not give a red colour on addition to aqueous sodium carbonate (15—30 minutes). After cooling, the solids were collected and extracted (Soxhlet) with acetone. The *methyl* ether separated during the extraction and was collected (7·0 g.); it crystallised from acetone in small, rectangular, orange-yellow plates, m. p. 270° (Found : C, 73·3; H, 3·7. $C_{17}H_{10}O_4$ requires C, 73·4; H, 3·6%). This methyl ether is somewhat more readily soluble in the usual organic solvents than the parent phenol; it is insoluble in aqueous alkalis. The solution in alcoholic sodium ethoxide is deep blue; on the addition of a little water this changes to red and on further dilution the yellow indenocoumarin separates. This formation of the lactone in alkaline solution is noteworthy.

When zinc dust was added in small portions to a boiling solution of ketomethoxyindenocoumarin (1 g.) in acetic acid (40 c.c.), a colourless liquid was obtained; this became yellow again on shaking with air. If the colourless solution was expeditiously filtered and added to water, the *dihydro*-derivative (V) was obtained as a colourless precipitate (yield, quantitative). The substance suffers rapid autoxidation in solvents in the presence of air; a quick crystallisation from alcohol afforded slightly yellowish needles, m. p. 185—187° after turning yellow and softening at 180° (Found : C, 72·6; H, 4·6. $C_{17}H_{12}O_4$ requires C, 72·8; H, 4·3%). Microscopic examination of a specimen crystallised from ethyl acetate disclosed a mixture of needles of the dihydro-derivative and yellow rectangular plates of the ketomethoxyindenocoumarin.

2'-Hydroxy-4'-methoxy-3-phenylindan-1-one (VI).—Sodium hydroxide (200 c.c. of 5%) was added to a mechanically stirred, boiling solution of ketomethoxyindenocoumarin (4 g.) in 50% alcohol (400 c.c.); the colour changed from red to intense violet. Under the same conditions zinc dust (about 50 g.) was added in small portions until the solution became colourless (about 1 hour). The filtered solution was acidified with hydrochloric acid, and the *product* isolated by means of ether. 3·2 G. crystallised on concentration of the extract to a small volume. The substance was thrice crystallised from alcohol and obtained in colourless rectangular prisms, m. p. 141·5° (Found : C, 75·7; H, 5·4. $C_{16}H_{14}O_3$ requires C, 75·6; H, 5·5%). The phenolic function is shown by the insolubility of the substance in aqueous sodium carbonate and the ready solubility to a colourless solution in aqueous sodium hydroxide.

The *semicarbazone*, prepared in cold aqueous alcoholic solution, crystallised from alcohol in small hexagonal plates, m. p. 213—214° (Found : C, 65·6; H, 5·6; N, 13·3. $C_{17}H_{17}O_3N_3$ requires C, 65·6; H, 5·5; N, 13·5%). An oxime was also prepared but not completely purified; m. p. 75—77° after precipitation from aqueous ammoniacal solution by means of acetic acid. The *methyl* ether, obtained by the action of methyl sulphate on a solution of the phenolic ketone in 20% aqueous sodium hydroxide, crystallised from alcohol in slender needles, m. p. 89° (Found : C, 75·7; H, 5·9. $C_{17}H_{16}O_3$ requires C, 76·1; H, 6·0%).

Condensation of the phenolic ketone with ethyl formate and powdered sodium afforded a small quantity of a red substance, very sparingly soluble in alcohol. After washing with hot alcohol this had m. p. 184—185° and appeared to have the composition of a hydroxymethylene derivative (Found : C, 72·2; H, 4·7. $C_{17}H_{14}O_4$ requires C, 72·3; H, 5·0%). The quantity obtained was insufficient to enable us to make a more complete investigation.

2-Hydroxy-4 : 3' : 4'-trimethoxybenzophenone.—Powdered aluminium chloride (16 g.) was added to a mixture of veratroyl chloride (16 g.), resorcinol dimethyl ether (11 g.), and carbon disulphide (25 c.c.). After the reaction had subsided, the mixture was refluxed for 1 hour. The *product* was crystallised from alcohol (yield, 14·0 g.); m. p. 140—141° (Found : C, 66·8; H, 5·5; MeO, 32·0. $C_{16}H_{16}O_5$ requires C, 66·6; H, 5·6; 3MeO, 32·3%). The phenolic hydroxyl

(strong ferric reaction) remained unaffected when the substance was treated with chloroacetic acid or β-chloropropionic acid in alkaline solution or with ethyl diazoacetate; in all cases a variety of conditions was tried.

Ethyl Veratroylacetate.—By a slight modification of Claisen's method for the preparation of ethyl benzoylacetate, veratroyl chloride (40 g.) afforded 35 g. of the ester. Mitter and Paul (*loc. cit.*) obtained it as an oil; our product crystallised, m. p. 37·5—39·5°, after being washed with a little chilled alcohol. The ferric reaction in alcoholic solution is brown-red and appears only in the course of a few seconds; hence the solid is the keto-modification (Found: C, 61·8; H, 6·5. Calc. for $C_{18}H_{16}O_5$: C, 61·9; H, 6·4%).

7-Hydroxy-4-veratrylcoumarin.—The method of Mitter and Paul (*loc. cit.*) gives a poor yield. Under the following conditions the yield is 90%. An ice-cooled mixture of ethyl veratroylacetate (2·5 g.), resorcinol (5·5 g.), and alcohol (25 c.c.) was saturated with hydrogen chloride and kept for 20 hours. The product obtained on the addition of water was crystallised from alcohol (yield, 2·7 g.); m. p. 233—235° (Found: C, 68·7; H, 4·9. Calc. for $C_{17}H_{14}O_5$: C, 68·4; H, 4·7%).

7-Methoxy-4-veratrylcoumarin.—Methyl sulphate (60 c.c.) was added to a stirred solution of hydroxyveratrylcoumarin (10 g.) in aqueous potassium hydroxide (500 c.c. of 1%). Any excess of methyl sulphate was destroyed by the addition of small quantities of concentrated potash. The yield of recrystallised product was 7·4 g., and 0·5 g. was obtained from the mother-liquors. This coumarin derivative occurs in two forms: long thin prisms, m. p. 151—153°, and short stout prisms, m. p. 161—163°. The latter form is the more sparingly soluble and has been previously described by Mitter and Paul (*loc. cit.*). The more fusible variety, not mentioned by these authors, crystallises from hot concentrated alcoholic solutions (Found in material of m. p. 151—153°: C, 69·3; H, 5·2. $C_{18}H_{16}O_5$ requires C, 69·2; H, 5·2%).

7-Methoxy-4-veratryldihydrocoumarin.—A solution of sodium ethoxide (0·5 g. of sodium) in alcohol (25 c.c.) was added to a boiling one of 7-methoxy-4-veratrylcoumarin (2 g.) in alcohol (25 c.c.); a sodium salt soon separated from the yellow liquid. Water (25 c.c.) was added, and reduction effected by means of sodium amalgam (80 g. of 3%). The acid was liberated and isolated by extraction with ethyl acetate (A). The residue after evaporation of the dried extract was heated in a vacuum at 120°, and an alcoholic solution of the product allowed to evaporate at the room temperature. Crystals separated and these were purified by solution in ethyl acetate and slow evaporation; finally the *product* was washed with a little cold alcohol; m. p. 82—83° (Found: C, 68·6; H, 5·8. $C_{18}H_{18}O_5$ requires C, 68·8; H, 5·8%).

Ethyl β-Veratryl-β-(2-hydroxy-4-methoxyphenyl)propionate (IX).—The residue (A) above was refluxed for 2½ hours with alcohol (100 c.c.) and sulphuric acid (0·5 c.c.). The resulting *ester* was isolated by means of ether and crystallised in contact with a little alcohol; it was recrystallised from aqueous alcohol, m. p. 113—115° (yield, 1·65 g.) (Found: C, 66·8; H, 6·6. $C_{20}H_{24}O_6$ requires C, 66·6; H, 6·7%).

β-Veratryl-β-(2-benzyloxy-4-methoxyphenyl)propionic Acid (X).—A mixture of the foregoing ester (3·6 g.), benzyl chloride (5·2 g.), potassium carbonate (5·6 g.), potassium iodide (0·5 g.), and acetone (10 c.c.) was refluxed for 7 hours. Potassium hydroxide (20 g.) in 50% alcohol (120 c.c.) was then introduced, and the mixture boiled for 2 hours; during the second hour alcohol was allowed to evaporate. Water was added, and the solution shaken with ether; when the aqueous layer was cautiously acidified in the presence of a little sulphur dioxide, the *acid* soon separated in a crystalline condition (yield, quantitative). The substance may be purified by conversion into its sparingly soluble sodium salt and by crystallisation from aqueous alcohol or ethyl acetate–light petroleum. The crystals, m. p. 95°, contain approximately $1H_2O$; after drying at 50° in a high vacuum the m. p. was 104—105° (Found in anhydrous material: C, 71·2; H, 6·4. $C_{25}H_{26}O_6$ requires C, 71·1; H, 6·2%). Attempts to effect ring-closure of this acid were made in several ways, but in most cases there was evidence of hydrolysis of the benzyloxy-group and no hydrindone derivative could be isolated.

As shown above, our objective has meanwhile been reached along other lines, so this route has been abandoned.

ω-Veratroylresacetophenone 4-Veratrate (VII).—The constitution of this substance has been confirmed by hydrolysis. It was boiled with dilute aqueous sodium hydroxide for a few minutes and the resulting solution was extracted with ether. Acetoveratrone was thus isolated, m. p. 48° alone or mixed with an authentic specimen.

7-Veratroyloxy-3′: 4′-dimethoxyflavone.—A solution of ω-veratroylresacetophenone 4-veratrate (1 g.) in acetic acid (15 c.c.) was saturated with hydrogen chloride. After 1 hour the orange-yellow oxonium salt was collected, washed with acetic acid, decomposed by stirring

into water, collected, and dried. After recrystallising twice from acetic acid, it formed colourless microscopic prisms, m. p. 219° (Found in material dried at 100° in a vacuum over sodium hydroxide : C, 67·3; H, 4·7. $C_{26}H_{22}O_8$ requires C, 67·6; H, 4·7%). The solution in a mixture of chloroform and alcohol shows a marked blue fluorescence.

9-Keto-7-veratroyloxy-4′ : 5′-dimethoxybrazylium Zincichloride (related to VIII).—ω-Veratroylresacetophenone 4-veratrate (0·5 g.) was added to a mixture of acetic anhydride (1 c.c.) and powdered anhydrous zinc chloride (0·5 g.). Complete solution occurred in about 5 minutes with production of an intense orange-red colour. After 12 hours the solution was saturated with hydrogen chloride, and after a further 24 hours the crystalline material was collected on a porous tile. It separated from boiling acetic acid (20 c.c.), containing a little hydrogen chloride, in bright red, minute, prismatic needles [Found : C, 55·7; H, 4·4; Cl, 10·3; Zn—residue of ZnO, 6·3. $(C_{28}H_{23}O_8)_2ZnCl_4$ requires C, 56·9; H, 3·9; Cl, 12·0; Zn, 5·5%].

The Stannichloride (related to VIII).—A freshly prepared 10% solution of stannic chloride in acetic anhydride (12 c.c.) was added to ω-veratroylresacetophenone 4-veratrate (2 g.) with instantaneous production of a brilliant red solution. The *stannichloride* began to separate in about 2 hours, and after about 12 hours was collected, washed with acetic acid and then benzene, and dried (yield, 2·5 g.). It formed microscopic, purplish-red crystals [Found : C, 48·1; H, 3·6; Cl, 19·3; Sn as residue, 10·9. $(C_{28}H_{23}O_8)_2SnCl_6,2HCl$ requires C, 48·7; H, 3·5; Cl, 20·6; Sn, 8·6%]. The compound may be crystallised with difficulty and in small quantity from acetic acid containing a little stannic chloride. When it is boiled with water, a tin-containing ochre-yellow powder is produced; when heated with dilute hydrochloric acid, it gives a tin-free black powder, which shows signs of being converted into an oxonium salt on treatment with hydrogen chloride in acetic acid.

The Ferrichloride (VIII).—ω-Veratroylresacetophenone 4-veratrate (0·5 g.) was added to a solution of anhydrous ferric chloride (0·25 g.) in acetic anhydride (3 c.c.). After 12 hours the dark brownish-red solution had become a pasty crystalline mass, which, after being pressed on porous earthenware, left a mass of rather dark purplish-red, microscopic crystals. When these were warmed with a little acetic anhydride, a dark solution was obtained, but almost immediately the *ferrichloride* crystallised in bright red, microscopic needles. The substance was collected, washed with acetic acid, then with benzene, and dried for ½ hour at 100° (Found, in two different specimens : C, 49·5, 49·6; H, 3·5, 3·9; Fe, 10·2, 7·8; Cl, 18·1. $C_{28}H_{23}O_8FeCl_4$ requires C, 49·1; H, 3·4; Fe, 8·2; Cl, 20·7%).

Oxidation to m-*Hemipinic Acid.*—Powdered potassium permanganate (7 g.) was added in small quantities at a time to a solution of the stannichloride (1·5 g.) in pyridine (20 c.c.) and water (20 c.c.). The mixture was shaken and warmed; towards the end of the oxidation more water was added and the mixture heated more strongly. Sulphur dioxide was then passed in excess, the hot solution extracted thrice with ethyl acetate, and the extracts dried with sodium sulphate and distilled, leaving a mainly crystalline residue. This was found to be incompletely oxidised, so it was again treated with warm aqueous potassium permanganate and a little sodium hydroxide, and the acidic product again collected as before. The crystalline residue was boiled twice with water (the filtrate, after treatment with charcoal and evaporation to a small bulk, deposited veratric acid in fine needles, m. p. and mixed m. p. with an authentic specimen, 179°), the remaining solid dissolved in an aqueous solution of ethylamine, the solution evaporated to dryness, and the residue distilled. The yellowish crystalline material separated from alcohol, in which it was very sparingly soluble, in very fine prisms, m. p. 225—226° (Found : C, 61·1; H, 5·7. Calc. for $C_{12}H_{13}O_4N$: C, 61·3; H, 5·6%). A genuine specimen of *m*-hemipinethylimide had m. p. 227°, and a mixed m. p. of the two specimens was 225—226°. The specimens were indistinguishable in their crystalline form, and both exhibited the same weak bluish-green fluorescence in alcoholic solution.

Pæanol.—Methyl sulphate (96 g.; 1·1 mols.) was added during 2 hours at room temperature to a stirred solution of crude resacetophenone (105 g.) in water (300 c.c.) containing sodium hydroxide (30·5 g.; 1·1 mols.) and methyl alcohol (200 c.c.). The mixture was slowly heated on the steam-bath for a further 2 hours with continuous stirring, most of the alcohol being allowed to distil during the last hour. The mixture was made faintly alkaline to litmus by the addition of a little sodium hydroxide and cooled in ice, and the solid pæanol collected, washed thoroughly with water, dried, and distilled; b. p. 154°/ 20 mm. (yield, about 60 g.).

O-*Veratroylpæanol.*—A mixture of pæanol (26·5 g.), veratroyl chloride (32 g.) and pyridine (50 c.c.) was heated on the water-bath for ½ hour, and poured into dilute hydrochloric acid. The colourless crystalline product was collected, washed with dilute hydrochloric acid, then

water, stirred into a large volume of cold alcohol, collected, and dried at 100° (yield, 34 g.). This *product* is sufficiently pure for the succeeding step. For analysis it was crystallised first from benzene–alcohol, then ethyl acetate, and finally acetone; it formed minute colourless needles, m. p. 158—159° (Found : C, 65·3; H, 5·5. $C_{18}H_{18}O_6$ requires C, 65·4; H, 5·5%).

ω-*Veratroylpæanol*.—Sodamide (5 g.) was finely powdered under a little toluene and transferred with the help of more toluene (in all, 100 c.c.) to a flask containing *O*-veratroylpæanol (10 g.). The yellow sodium salt of ω-veratroylpæanol began to appear at once in the cold, and increased rapidly in amount when the flask was heated on the water-bath for 4 hours with frequent shaking, ammonia being abundantly evolved. The yellow solid (containing some unchanged sodamide !) was collected, washed with hot benzene, dried on the water-bath, and stirred cautiously into cold water; the solution was acidified with hydrochloric acid, and the yellow solid collected, washed, and dried on the water-bath (yield, 7 g.). It separated from about 5 times its weight of benzene in pale yellow, extremely fine prisms, m. p. 162—163° (Found : C, 65·4; H, 5·7. $C_{18}H_{18}O_6$ requires C, 65·4; H, 5·5%).

When treated in acetic anhydride with zinc chloride, stannic chloride, or ferric chloride, this *compound* gives brilliant red solutions exactly resembling those given by ω-veratroylresacetophenone 4-veratrate, but the pyrylium salts do not separate on standing. Unlike the diveratroyl compound, ω-veratroylpæanol is not converted into a flavone derivative by treatment with hydrogen chloride in acetic acid; no oxonium salt separates, and the substance is recovered unchanged by pouring into water.

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