

**Some phenolic derivatives of beta-phenylethylamine / by George Barger and Arthur James Ewins.**

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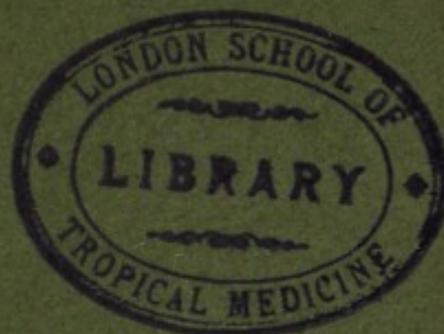
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SOME PHENOLIC DERIVATIVES  
OF  
 $\beta$ -PHENYLETHYLAMINE

BY  
GEORGE BARGER, M.A., D.SC.  
AND  
ARTHUR JAMES EWINS, B.SC.

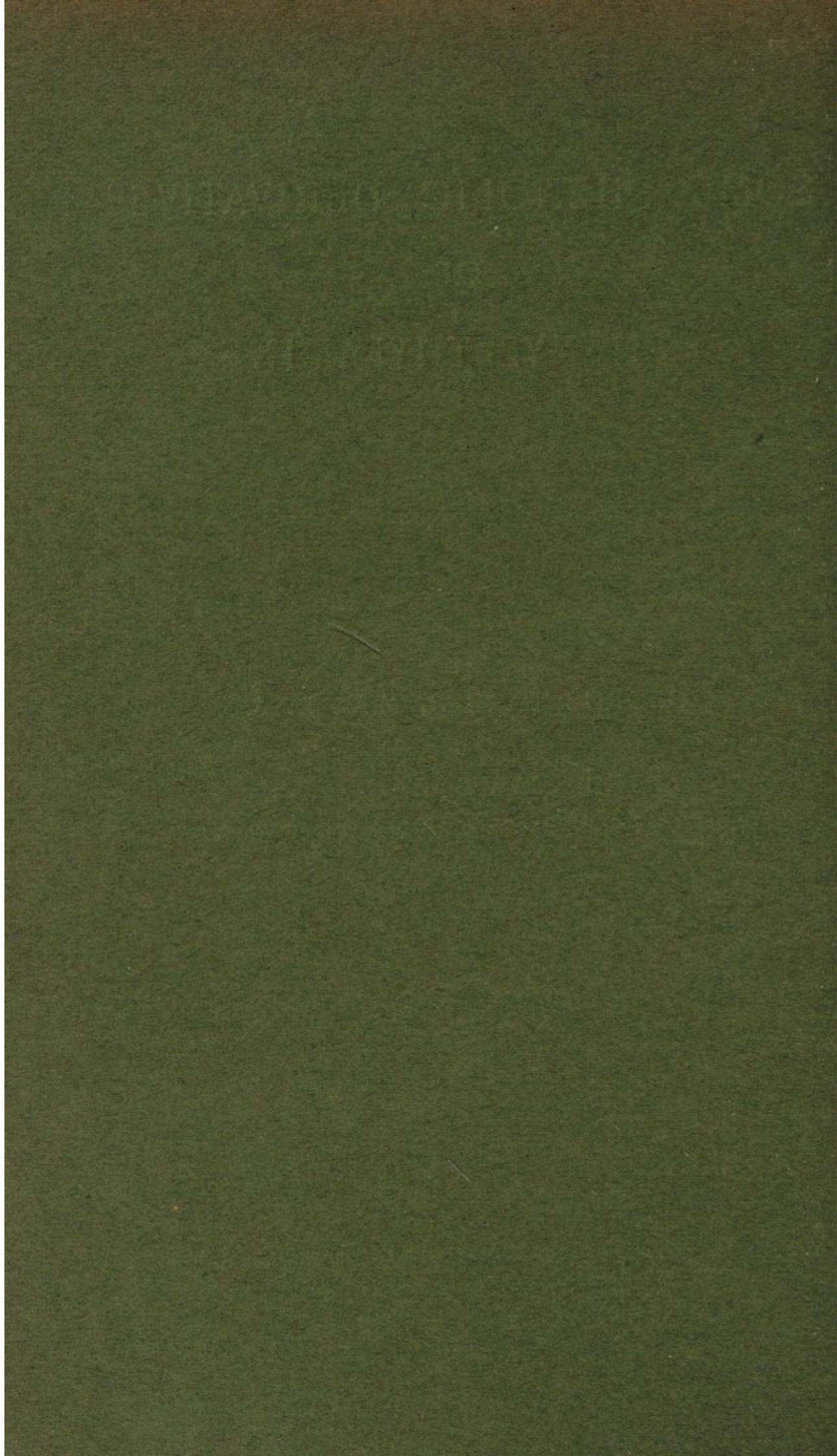
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From

THE WELLCOME PHYSIOLOGICAL RESEARCH LABORATORIES  
BROCKWELL HALL  
HERNE HILL  
LONDON, S.E.



CCXXXVII.—*Some Phenolic Derivatives of  $\beta$ -Phenylethylamine.*

By GEORGE BARGER AND ARTHUR JAMES EWINS.

*p*-HYDROXY- $\beta$ -PHENYLETHYLAMINE,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2$ , which is formed by the action of micro-organisms from tyrosine and from proteins containing tyrosine, has been shown to have a pronounced physiological activity (Barger and Walpole, *J. Physiol.*, 1909, 38, 343); it is, for instance, one of the active constituents of ergot extracts (Barger, *Trans.*, 1909, 95, 1123).

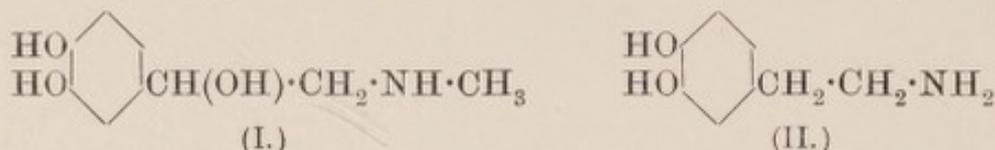
Since the effect of this base on the vascular system and on certain organs is essentially similar to that of adrenaline (Dale and Dixon, *J.*

*Physiol.*, 1909, **39**, 25), to which *p*-hydroxy- $\beta$ -phenylethylamine is also chemically related, an examination of a considerable number of similarly constituted amines was undertaken by Dale in order to trace as far as possible the connexion between physiological activity and chemical structure within the limits of this group (Barger and Dale, *J. Physiol.*, 1910, **41**, 19).

The present paper deals with the synthesis of some of these amines. They were chosen for the following reasons:

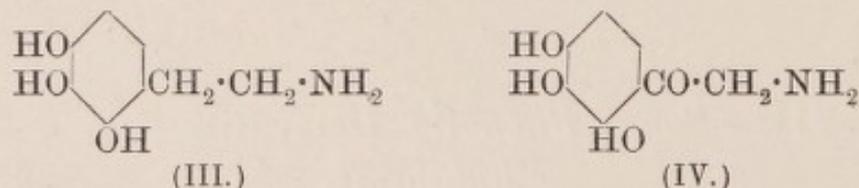
(1) Since the bactericidal action of phenol is greatly enhanced by the introduction of a methyl group into the benzene ring (yielding cresol), we prepared 3-methyl-4-hydroxy- $\beta$ -phenylethylamine. The pressor action of this base was found, however, to be only about one half as great as that of the parent substance.

(2) One of the differences between *p*-hydroxy- $\beta$ -phenylethylamine and adrenaline (I) is that the former substance has only a single



phenolic hydroxyl group as compared with two in the latter substance. We therefore prepared 3:4-dihydroxy- $\beta$ -phenylethylamine (II), which was found to be scarcely more active than the monophenolic amine although its *N*-methyl derivative, obtained by Pyman from an oxidation product of laudanosine (this vol., p. 268), approximates much more closely to adrenaline.

(3) Since in several cases the introduction of a second phenolic hydroxyl group greatly increases the physiological activity of bases of this type, we wished to trace the effect of introducing yet another phenolic hydroxyl group, and for this purpose prepared 2:3:4-trihydroxy- $\beta$ -phenylethylamine (III) and  $\omega$ -aminogallacetophenone (IV).



Both these bases were somewhat less active than the corresponding dihydroxy-bases (namely, 3:4-dihydroxy- $\beta$ -phenylethylamine and  $\omega$ -aminoacetylcatechol).

The close chemical relationship of the bases (I), (II), (III), and (IV) is further illustrated by the fact that they all give the colour reactions hitherto described as characteristic for adrenaline (I) (Ewins, *J. Physiol.*, 1910, **40**, 317).

The synthesis of 4-hydroxy- $\beta$ -*m*-tolylethylamine started with *m*-tolylacetonitrile, and was completely analogous to that of *p*-hydroxy- $\beta$ -

phenylethylamine from phenylacetonitrile (Barger, Trans., 1909, 95, 1123).

3:4-Dihydroxy- $\beta$ -phenylethylamine was obtained from its dimethyl ether, and has already been described by Mannich (*Ber.*, 1910, 43, 196).

The production of the pyrogallol bases (III and IV) at first gave considerable difficulty. The 2:3:4-trihydroxybenzaldehyde required for (III) had to be prepared with anhydrous hydrogen cyanide according to Gattermann's method. It was found impossible to obtain 2:3:4-trimethoxy- $\beta$ -phenylethylamine from 2:3:4-trimethoxyphenylpropionamide by Hofmann's reaction, although this method was employed in preparing the corresponding dimethoxy-base. We therefore had to use Curtius's method, starting from 2:3:4-trimethoxyphenylpropionylhydrazide.

In the case of  $\omega$ -aminogallacetophenone (IV) we found it quite impossible to isolate a pure substance when  $\omega$ -chlorogallacetophenone was acted on by ammonia, although this method is employed technically in the case of  $\omega$ -chloroacetylcatechol; the substance is destroyed too readily in alkaline solution. We therefore had recourse to an indirect method;  $\omega$ -chlorogallacetophenone reacts readily with sodium azide, and from the  $\omega$ -triazogallacetophenone,  $C_6H_2(OH)_3 \cdot CO \cdot CH_2 \cdot N_3$ , thus produced the required amine is obtainable by reduction.

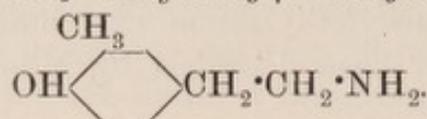
In the course of our work on this subject we have also prepared  $\beta$ -phenylethylmethylamine,  $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot NH \cdot CH_3$ , of which adrenaline is the trihydroxy-derivative. Two methods for preparing this base will be mentioned, although it is not a phenolic amine, and was recently prepared by Johnson and Guest (*Amer. Chem. J.*, 1909, 42, 340) according to a third method (methylation of benzenesulphonylphenylethylamine and subsequent hydrolysis).

#### EXPERIMENTAL.

##### *$\beta$ -Phenylethylmethylamine*, $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot NH \cdot CH_3$ .

As the direct methylation of  $\beta$ -phenylethylamine yields a quaternary iodide, we condensed methylamine (in 33 per cent. aqueous solution) with phenylacetaldehyde by means of sodium hydroxide, and reduced the crude condensation product, which separated out, with sodium and alcohol. The base was isolated as the oxalate.

A second, and more convenient, method consists in acting on  $\alpha$ -chloro- $\beta$ -phenylethane,  $C_6H_5 \cdot CH_2 \cdot CH_2Cl$  (Barger, Trans., 1909, 95, 2194), with an excess of a 33 per cent. alcoholic solution of methylamine at  $100^\circ$  for several hours. The base thus obtained was distilled (b. p.  $205^\circ$ ), and its hydrochloride was analysed. (Found, Cl = 20.7. Calc., Cl = 20.4 per cent.)

Preparation of 4-Hydroxy- $\beta$ -m-tolylethylamine,

*p*-Nitro-*m*-tolylacetonitrile,  $\text{NO}_2 \langle \text{C}_6\text{H}_4 \rangle \text{CH}_2 \cdot \text{CN}$ .—Ten grams of *m*-tolylacetonitrile (Señkowski, *Monatsh.*, 1888, 9, 854) were dropped into 40 c.c. of nitric acid (D 1.5) at a temperature below  $-5^\circ$ . The acid solution was then poured into water and extracted with ether. After washing with sodium carbonate, drying, and distilling, a fraction boiling at  $201\text{--}205^\circ/22$  mm. was collected, which solidified, and on crystallisation from ether and light petroleum melted at  $52^\circ$ . The yield was 80 per cent. of the theoretical:

0.1584 gave 0.3554  $\text{CO}_2$  and 0.0665  $\text{H}_2\text{O}$ . C = 61.2; H = 4.6.

$\text{C}_9\text{H}_8\text{O}_2\text{N}_2$  requires C = 61.4; H = 4.5 per cent.

*p*-Amino-*m*-tolylacetonitrile,  $\text{NH}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{CH}_2 \cdot \text{CN}$ .—*p*-Nitro-*m*-tolylacetonitrile (19 grams) was dissolved in alcohol (240 c.c.), tin-foil (25 grams), and then gradually concentrated hydrochloric acid (120 c.c.) was added. The temperature was at first kept below  $60^\circ$ , finally being raised to  $100^\circ$ . After extraction with ether, the base was distilled, and 8.5 grams (60 per cent.) boiling at  $175\text{--}185^\circ/20$  mm. were obtained. On crystallisation from benzene, the substance melted at  $87^\circ$ :

0.1552 gave 0.4204  $\text{CO}_2$  and 0.0902  $\text{H}_2\text{O}$ . C = 73.9; H = 6.5.

$\text{C}_9\text{H}_{10}\text{N}_2$  requires C = 74.0; H = 6.8 per cent.

The *hydrochloride*, prepared by adding alcoholic hydrogen chloride to the ethereal solution of the base, melts at  $247\text{--}248^\circ$ :

0.2082 gave 0.1620  $\text{AgCl}$ . Cl = 19.3.

$\text{C}_9\text{H}_{10}\text{N}_2 \cdot \text{HCl}$  requires Cl = 19.4 per cent.

The *oxalate* melts at  $164\text{--}165^\circ$ :

0.1884 gave 24 c.c.  $\text{N}_2$  (moist) at  $20^\circ$  and 768 mm. N = 14.7.

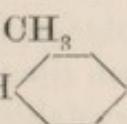
$(\text{C}_9\text{H}_{10}\text{N}_2)_2 \cdot \text{H}_2\text{C}_2\text{O}_4$  requires N = 14.7 per cent.

*p*-Hydroxy-*m*-tolylacetonitrile,  $\text{OH} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{CH}_2 \cdot \text{CN}$ .—3.9 Grams of sodium nitrite dissolved in a little water were slowly added to a boiling solution of 8.5 grams of the amino-compound dissolved in 200 c.c. of dilute sulphuric acid (210 c.c. of water and 17 c.c. of concentrated sulphuric acid). On extracting the acid solution with ether, 2.5 grams (30 per cent.) of a substance were obtained, which distilled at  $162\text{--}164^\circ/2$  mm. and crystallised in the receiver. It crystallises from benzene in leaflets melting at  $84^\circ$ :

0.1526 gave 0.4093  $\text{CO}_2$  and 0.0807  $\text{H}_2\text{O}$ .  $\text{C} = 73.1$ ;  $\text{H} = 5.9$ .

0.1718 ,, 14.2 c.c.  $\text{N}_2$  (moist) at  $22^\circ$  and 760 mm.  $\text{N} = 9.4$ .

$\text{C}_9\text{H}_9\text{ON}$  requires  $\text{C} = 73.5$ ;  $\text{H} = 6.1$ ;  $\text{N} = 9.5$  per cent.

4-Hydroxy- $\beta$ -*m*-tolylethylamine,  $\text{OH}$    $\text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_2$ .—0.9 Gram of *p*-hydroxy-*m*-tolylacetonitrile yielded, on reduction with 4 grams of sodium in boiling alcoholic solution, 0.62 gram of a crude hydrochloride, which was crystallised by adding ether to its concentrated solution in alcohol. From this the free base was obtained; it crystallised from xylene, and, after sublimation in a vacuum, melted at  $132$ — $133^\circ$ :

0.1290 gave 0.3364  $\text{CO}_2$  and 0.0910  $\text{H}_2\text{O}$ .  $\text{C} = 71.2$ ;  $\text{H} = 7.9$ .

$\text{C}_9\text{H}_{13}\text{ON}$  requires  $\text{C} = 71.5$ ;  $\text{H} = 8.6$  per cent.

The hydrochloride was also analysed:

0.1226 gave 0.0956  $\text{AgCl}$ .  $\text{Cl} = 19.3$ .

$\text{C}_9\text{H}_{13}\text{ON} \cdot \text{HCl}$  requires  $\text{Cl} = 19.0$  per cent.

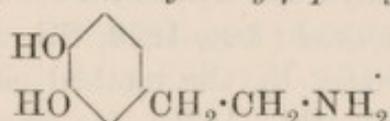
The *dibenzoyl* derivative crystallised from dilute alcohol in long, thin needles, melting at  $130$ — $131^\circ$ .

The quaternary iodide,  $\text{OH} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NMe}_3\text{I}$ , was obtained by boiling the base with a little methyl alcohol and a large excess of methyl iodide. It melts at  $231$ — $232^\circ$ , and closely resembles hordenine methiodide in solubility and other properties.

4-Hydroxy- $\beta$ -*m*-tolylethylamine resembles *p*-hydroxy- $\beta$ -phenylethylamine in behaviour and derivatives.

The physiological action of the former base is about one-half of the latter. Both bases give Millon's reaction, but it is significant that, unlike *p*-hydroxy- $\beta$ -phenylethylamine, the tolyl compound does not give Mörner's reaction (green coloration after heating with sulphuric acid and formaldehyde). It would appear that substitution in the phenolic ring prevents this reaction from taking place.

*Preparation of 3:4-Dihydroxy- $\beta$ -phenylethylamine,*



3:4-Dimethoxy- $\beta$ -phenylethylamine was prepared from vanillin according to the method described in detail by Pictet and Finkelstein (*Ber.*, 1909, 42, 1979), and 5.2 grams of the amine boiling at  $164$ — $166^\circ/13$  mm. were obtained from 20.5 grams of homoveratric acid.

The amine was hydrolysed by heating with ten parts of concentrated hydrochloric acid to  $170^\circ$  for two hours. The hydrochloride so obtained crystallised from 90 per cent. alcohol in glistening, almost colourless

plates, melting and decomposing at 240—241°. Yield, 45 per cent. of the theoretical. (Found, C = 50.6; H = 6.2. Calc., C = 50.7; H = 6.2 per cent.)

The *hydrobromide* was obtained by heating the dimethoxy-amine to 130° for two hours with ten times its weight of concentrated aqueous hydrobromic acid. The crystalline hydrobromide was obtained quite pure in the same manner as that employed in the preparation of the hydrochloride. The salt crystallises in plates, melting at 212°:

0.1212 gave 0.0984 AgBr. Br = 34.5.

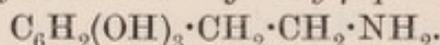
$C_8H_{12}O_2NBr$  requires Br = 34.2 per cent.

The aqueous solution of the salts of 3:4-dihydroxy- $\beta$ -phenylethylamine gave an intense green coloration with ferric chloride.

The quaternary chloride,  $C_6H_3(OH)_2 \cdot CH_2 \cdot CH_2 \cdot NMe_3Cl$ , was prepared in order to compare its action with that of hordenine methiodide,  $OH \cdot C_6H_4 \cdot CH_2 \cdot CH_2 \cdot NMe_3I$ . The action of the two substances is very similar, like that of nicotine, and unlike that of adrenaline.

3:4-Dihydroxy- $\beta$ -phenylethyltrimethylammonium chloride was obtained from 3:4-dimethoxy- $\beta$ -phenylethylamine. The quaternary iodide obtained by treating the latter base with methyl iodide was transformed into the chloride by digestion with silver chloride, and was then hydrolysed by concentrated hydrochloric acid at 170°. On removal of the latter, the residue crystallised from alcohol and ether, and melted at 201°.

*Preparation of 2:3:4-Trihydroxy- $\beta$ -phenylethylamine,*



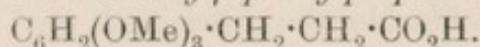
2:3:4-Trimethoxybenzaldehyde,  $C_6H_2(OMe)_3 \cdot CHO$ .—This aldehyde does not appear to have been described before, although F. Mauthner (*Ber.*, 1909, **42**, 188) has stated that it can be obtained from 2:3:4-trimethoxyphenylglyoxylic acid by the action of aniline. The methylation of 2:3:4-trihydroxybenzaldehyde, which was prepared from pyrogallol and anhydrous hydrocyanic acid according to Gattermann and Kœbner's method (*Ber.*, 1899, **32**, 281), was carried out in an atmosphere of hydrogen by the method employed by Perkin and Robinson (*Trans.*, 1907, **91**, 1079) for the preparation of veratraldehyde from vanillin. Twenty-five grams of 2:3:4-trihydroxybenzaldehyde were dissolved in 80 c.c. of methyl alcohol, and to this solution was added 24 grams of sodium hydroxide dissolved in the minimum quantity of water. The solution became very dark brown in colour. Eighty grams of methyl sulphate were then added, and when the vigorous reaction had nearly subsided, a further 66 grams in small quantities alternately with small quantities of sodium hydroxide were added at such a rate that a vigorous reaction was maintained.

The mixture was kept for half an hour, and then poured into 500 c.c. of water. An oil separated, which was extracted by means of ether, and, after drying and removal of the solvent, the residue was distilled. 18.5 Grams of a colourless liquid, boiling at 168—170°/12 mm., were thus obtained. The distillate solidified after some time to a crystalline mass of long, thin needles, melting at 30° :

0.1840 gave 0.4126 CO<sub>2</sub> and 0.1020 H<sub>2</sub>O. C = 61.1 ; H = 6.2.

C<sub>10</sub>H<sub>12</sub>O<sub>4</sub> requires C = 61.2 ; H = 6.1 per cent.

*2 : 3 : 4-Trimethoxy- $\beta$ -phenylpropionic Acid,*

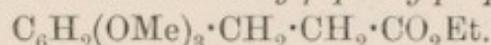


Twenty grams of 2 : 3 : 4-trimethoxybenzaldehyde were dissolved in 35 grams of ethyl acetate, and the solution added to 3.3 grams of finely divided sodium contained in a large flask provided with a reflux condenser. A vigorous reaction ensued. The product was kept for one hour, and then a solution of 14 grams of sodium hydroxide in methyl alcohol was added. After the reaction had ceased, 250 c.c. of water were added. The alcohol was then removed by evaporation on a water-bath, water being added from time to time to avoid undue concentration. The alkaline solution was then reduced by the addition of 500 grams of 2½ per cent. sodium amalgam in small portions, concentrated hydrochloric acid being added from time to time to neutralise the excess of sodium hydroxide formed in the reaction. The resulting solution was filtered, and acidified with hydrochloric acid. A yellow oil separated, which slowly crystallised. The acid was purified by distillation under diminished pressure (it boils at 200—203°/2 mm.) and subsequent crystallisation from ether and light petroleum, from which it separated in clusters of prisms, melting at 76°. Yield, 50 per cent. of the theoretical :

0.2150 gave 0.4722 CO<sub>2</sub> and 0.1282 H<sub>2</sub>O. C = 59.9 ; H = 6.6.

C<sub>12</sub>H<sub>16</sub>O<sub>5</sub> requires C = 60.0 ; H = 6.7 per cent.

*Ethyl 2 : 3 : 4-Trimethoxy- $\beta$ -phenylpropionate,*



The acid obtained as above was converted into the corresponding ethyl ester by dissolving in five times its weight of 5 per cent. alcoholic hydrogen chloride and boiling under reflux for six hours. The alcohol and hydrochloric acid were evaporated off, and the residue was distilled. The ester boils at 200—201°/20 mm. Yield, 70 per cent. of the theoretical :

0.2074 gave 0.4797 CO<sub>2</sub> and 0.1390 H<sub>2</sub>O. C = 63.1 ; H = 7.4.

C<sub>14</sub>H<sub>20</sub>O<sub>5</sub> requires C = 62.7 ; H = 7.4 per cent.

2 : 3 : 4-Trimethoxy- $\beta$ -phenylpropionylhydrazide Hydrochloride,  
 $C_6H_2(OMe)_3 \cdot CH_2 \cdot CH_2 \cdot CO \cdot NH \cdot NH_2, HCl$ .

Two grams of the above ester were gradually added to 0.6 gram of boiling hydrazine hydrate. Solution was complete at the end of one hour, and the solution was boiled under reflux for several hours longer. The excess of hydrazine was removed by evaporation in a vacuum over sulphuric acid. The syrupy residue could not be crystallised, but on dissolving in alcohol and adding a little alcoholic hydrogen chloride a crystalline precipitate separated, which was increased by the addition of ether. The hydrochloride thus obtained was recrystallised from 98 per cent. alcohol, separating in the form of hexagonal plates, which melted at  $155^\circ$ :

0.1679 gave 0.3020  $CO_2$  and 0.0947  $H_2O$ .  $C = 49.0$ ;  $H = 6.3$ .

$C_{12}H_{19}O_4N_2Cl$  requires  $C = 48.8$ ;  $H = 6.5$  per cent.

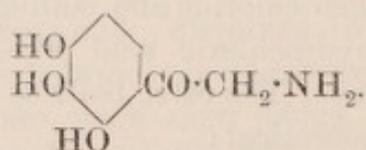
The solution of this salt readily reduced ammoniacal silver in the cold, and Fehling's solution on boiling.

2 : 3 : 4-Trihydroxy- $\beta$ -phenylethylamine Hydrochloride,  
 $C_6H_2(OH)_3 \cdot CH_2 \cdot CH_2 \cdot NH_2, HCl$ .

The hydrazide obtained as described above was diazotised at  $0^\circ$ . The crude azide, obtained by extraction with ether, was converted into the corresponding urethane derivative by boiling in absolute alcoholic solution for twelve hours under reflux. The alcohol was then distilled off, and the residue hydrolysed by heating in a sealed tube with concentrated hydrochloric acid to  $170-180^\circ$  for three hours. The very dark-coloured contents of the tube were evaporated to dryness, dissolved in a little water, boiled with animal charcoal, filtered, and the solution evaporated nearly to dryness. From the dark brown syrupy product, crystals slowly separated. These were pressed on a plate, and recrystallised from absolute alcohol by addition of ether. The crystals, which melted at  $162-163^\circ$ , were still dark brown in colour. The aqueous solution gives with ferric chloride a deep purple-brown coloration, which rapidly fades:

0.1000 gave 0.0700  $AgCl$ .  $Cl = 17.32$ .

$C_8H_{11}O_3NCl$  requires  $Cl = 17.35$  per cent.

Preparation of  $\omega$ -Aminogallacetophenone, 

$\omega$ -Triazogallacetophenone,  $C_6H_2(OH)_3 \cdot CO \cdot CH_2 \cdot N_3$ .—Seven grams of  $\omega$ -chlorogallacetophenone, prepared according to Nencki's method

(*J. Russ. Phys. Chem. Soc.*, 1883, 25, 182), were dissolved in 50 c.c. of hot water, and a hot solution of 2.5 grams of sodium azide in a little water added. On cooling, a crystalline solid separated. This was collected and recrystallised from xylene, when rhomb-shaped plates, melting at  $155^{\circ}$ , were obtained. Yield, 50 per cent. of the theoretical :

0.2460 gave 44.2 c.c.  $N_2$  (moist) at  $19^{\circ}$  and 758 mm.  $N = 20.7$ .

$C_8H_7O_4N_3$  requires  $N = 20.1$  per cent.

*$\omega$ -Aminogallacetophenone Hydrochloride,*

$C_8H_2(OH)_3 \cdot CO \cdot CH_2 \cdot NH_2, HCl$ .

—Five grams of  $\omega$ -triazogallacetophenone were dissolved in absolute alcohol. Ten grams of tin-foil were then placed in the liquid, and 60 c.c. of concentrated hydrochloric acid added in small portions. As reduction proceeded, the hydrochloride of the base separated out in small, rectangular plates. The yield was 1.2 grams, or 25 per cent. of the theoretical

For analysis, the salt was recrystallised from alcohol and ether, when it melted at  $259-260^{\circ}$  :

0.1916 gave 10.8 c.c.  $N_2$  (moist) at  $17^{\circ}$  and 754 mm.

0.1275 ,, 0.0838 AgCl.  $Cl = 16.2$  ;  $N = 6.5$ .

$C_8H_{10}O_4NCl$  requires  $N = 6.4$  ;  $Cl = 16.1$  per cent.

The salt is readily soluble in water ; its aqueous solution darkens on keeping, and with very dilute ferric chloride solution gives a dirty green coloration, which rapidly changes to a brownish-yellow.

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(1) The first series of tests was conducted in 1918 and 1919, and consisted of 50 separate tests, each of which was conducted in a different field. The results of these tests were reported in the annual report of the Department of Agriculture for 1919.

0-1518 gave 10.5 on 2 (total of 11 and 12) and 0-1519 gave 10.5 on 2 (total of 11 and 12).

0-1520 gave 10.5 on 2 (total of 11 and 12) and 0-1521 gave 10.5 on 2 (total of 11 and 12).

0-1522 gave 10.5 on 2 (total of 11 and 12) and 0-1523 gave 10.5 on 2 (total of 11 and 12).

0-1524 gave 10.5 on 2 (total of 11 and 12) and 0-1525 gave 10.5 on 2 (total of 11 and 12).

0-1526 gave 10.5 on 2 (total of 11 and 12) and 0-1527 gave 10.5 on 2 (total of 11 and 12).

0-1528 gave 10.5 on 2 (total of 11 and 12) and 0-1529 gave 10.5 on 2 (total of 11 and 12).

0-1530 gave 10.5 on 2 (total of 11 and 12) and 0-1531 gave 10.5 on 2 (total of 11 and 12).

0-1532 gave 10.5 on 2 (total of 11 and 12) and 0-1533 gave 10.5 on 2 (total of 11 and 12).

0-1534 gave 10.5 on 2 (total of 11 and 12) and 0-1535 gave 10.5 on 2 (total of 11 and 12).

0-1536 gave 10.5 on 2 (total of 11 and 12) and 0-1537 gave 10.5 on 2 (total of 11 and 12).

0-1538 gave 10.5 on 2 (total of 11 and 12) and 0-1539 gave 10.5 on 2 (total of 11 and 12).

0-1540 gave 10.5 on 2 (total of 11 and 12) and 0-1541 gave 10.5 on 2 (total of 11 and 12).

0-1542 gave 10.5 on 2 (total of 11 and 12) and 0-1543 gave 10.5 on 2 (total of 11 and 12).

0-1544 gave 10.5 on 2 (total of 11 and 12) and 0-1545 gave 10.5 on 2 (total of 11 and 12).

0-1546 gave 10.5 on 2 (total of 11 and 12) and 0-1547 gave 10.5 on 2 (total of 11 and 12).

0-1548 gave 10.5 on 2 (total of 11 and 12) and 0-1549 gave 10.5 on 2 (total of 11 and 12).

0-1550 gave 10.5 on 2 (total of 11 and 12) and 0-1551 gave 10.5 on 2 (total of 11 and 12).



