736. *Formation of Tyrosine Melanin. Part IV.**

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For a study of the effect of alkyl substituents in the phenylalanine system on melanin formation we have prepared 1-*p*-hydroxybenzylethylamine and several hydroxyphenylalanines.

Continuing our work on the assumption that melanin results from the polymerised coupling at certain positions of the 5 : 6-dihydroxyindole system (Clemo and Duxbury, *J.*, 1950, 1795), we have synthesised new alkyl-substituted hydroxyphenylalanines and (by a modification of Woodruff and Conger's method, *J. Amer. Chem. Soc.*, 1938, **60**, 465) 1-*p*-hydroxybenzylethylamine hydrochloride.

2-Methyltyrosine was synthesised from the 2-*p*-methoxyphenylpropaldehyde sodium bisulphite compound. The latter, prepared from anethole essentially by Bougault's method (*Ann. Chim. Phys.*, 1902, **25**, 483), was converted into 5-(1-*p*-methoxyphenylethyl)-hydantoin which was hydrolysed by concentrated hydrochloric acid to 2-methyltyrosine.

5-Allyl-4-hydroxy-3-methoxybenzaldhyde (Claisen and Eisleb, *Annalen*, 1913, **401**, 79) was converted into the azlactone of α-benzamido-β-(4-acetoxy-5-allyl-3-methoxyphenyl)-acrylic acid, hydrolysed to α-benzamido-β-(4-acetoxy-5-allyl-3-methoxyphenyl)acrylic acid and then reduced to α-benzamido-β-(4-acetoxy-3-methoxy-5-*n*-propylphenyl)propionic acid, which on treatment with hydriodic acid and phosphorus yielded 3 : 4-dihydroxy-5-*n*-propylphenylalanine. 2 : 3-Dihydroxy-5-*n*-propylphenylalanine was synthesised similarly from 2-hydroxy-3-methoxy-5-*n*-propylbenzaldehyde, the hydrogenation stage being omitted.

2-Allyl-6-methoxy-*p*-cresol (OH = 1), on treatment with potassium hydroxide, yielded the propenylphenol. The latter on ozonisation and hydrolysis yielded 2-hydroxy-3-methoxy-5-methylbenzaldehyde. This formed the azlactone of α-benzamido-β-(2-acetoxy-3-methoxy-5-methylphenyl)acrylic acid, which was hydrolysed and reduced to 2 : 3-dihydroxy-5-methylphenylalanine.

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* Part III, *J.*, 1952, 3464.

Attempts to prepare 2 : 3-dihydroxy-5-methylphenylalanine from 3-ethoxy-2-hydroxy-5-methylphenylacetaldehyde and 2 : 3-dimethoxy-5-methylphenylacetaldehyde failed.

4 : 5-Dimethoxy-2-*n*-propylbenzyl chloride condensed with acetamidomalonic ester, and the product was hydrolysed and decarboxylated with alcoholic potassium hydroxide to form α-acetamido-β-(4 : 5-dimethoxy-2-*n*-propylphenyl)propionic acid which was converted into 4 : 5-dihydroxy-2-*n*-propylphenylalanine with hydriodic acid.

An attempt to synthesise 3 : 4-dihydroxy-2-methylphenylalanine from α-benzamido-β-(4-hydroxy-3-methoxy-2-methylphenyl)acrylic acid was unsuccessful. A method similar to that of Cromartie and Harley-Mason (*J.*, 1952, 1053) was, however, successful.

The action of tyrosinase on the above compounds will be reported later.

EXPERIMENTAL

DL-3 : 4-*Dihydroxy*-5-n-*propylphenylalanine*.—5-Allyl-4-hydroxy-3-methoxybenzaldehyde (3 g.), hippuric acid (3 g.), anhydrous sodium acetate (1·5 g.), and acetic anhydride (10 ml.) were heated on a water-bath for 45 minutes, then cooled, and, after the addition of water, warmed again for 15 minutes. The yellow product was filtered off, washed with hot water, and recrystallised from acetic acid.

The *azlactone* of α-benzamido-β-(4-acetoxy-5-allyl-3-methoxyphenyl)acrylic acid was obtained as a yellow solid (4·5 g.), m. p. 153° (Found : C, 70·0; H, 5·1. $C_{22}H_{19}O_5N$ requires C, 70·0; H, 5·0%). The azlactone (4 g.), sodium hydroxide (1·8 g.), and 50% aqueous ethanol (60 ml.), were warmed on a water-bath for 15 minutes, water (120 ml.) was added to the deep red solution, and 20% hydrochloric acid added dropwise with stirring until the acid was precipitated. The α-*benzamido*-β-(4-*acetoxy*-5-*allyl*-3-*methoxyphenyl*)*acrylic acid* was recrystallised from 50% ethanol (charcoal) (yield, 2·0 g.), and had m. p. 207° (Found : C, 66·7; H, 5·1. $C_{22}H_{21}O_6N$ requires C, 66·8; H, 5·3%).

The acrylic acid (10 g.), acetic acid (100 ml.), and 5% palladium–charcoal (0·75 g.) were shaken under hydrogen (100 lb./sq. in.) for 12 hours. The acetic acid was distilled off, and the residue recrystallised from acetic acid, giving α-*benzamido*-β-(4-*acetoxy*-3-*methoxy*-5-n-*propylphenyl*)*propionic acid* (9·0 g.), m. p. 200° (Found: C, 65·8; H, 6·2. $C_{22}H_{25}O_6N$ requires C, 66·2; H, 6·3%).

This acid (5 g.), hydriodic acid (27 ml.; *d* 1·7), acetic anhydride (27 ml.), and red phosphorus (2·3 g.) were refluxed under a slow stream of hydrogen for 2 hours. Water was added, the phosphorus filtered off, the red filtrate extracted three times with ether, and the aqueous layer evaporated in a stream of hydrogen under reduced pressure. The semisolid hydriodide was dissolved in water (100 ml.), and passed down a column of De-acidite E (2 × 35 cm.), at 5 ml./min. The column was washed with water until the effluent was colourless. The resulting purple solution was decolorised with sulphur dioxide and evaporated to dryness over concentrated sulphuric acid *in vacuo*. The white residue was twice recrystallised from water containing a little sulphur dioxide (charcoal), yielding 3 : 4-*dihydroxy*-5-n-*propylphenylalanine* (1·0 g.), m. p. 278—280° (Found : C, 55·8; H, 7·5. $C_{12}H_{17}O_4N,H_2O$ requires C, 56·0; H, 7·4. Found, after drying in a vacuum over concentrated sulphuric acid : C, 60·8; H, 7·2. $C_{12}H_{17}O_4N$ requires C, 60·3; H, 7·1%). The amino-acid was soluble in water, gave a positive ninhydrin test and a blue-black colour with ferric chloride, and reduced silver nitrate solution.

DL-2 : 3-*Dihydroxy*-5-n-*propylphenylalanine*.—To a stirred mixture of dihydroeugenol (37 g.), ethanol (90 ml.), sodium hydroxide (75 g.), and water (157 ml.) at 80—90°, chloroform (39 ml.) was added during 1 hour and the resulting mixture heated for a further 2 hours, steam-distilled, and then saturated with sulphur dioxide. The mixture was shaken for 1 hour with sodium hydrogen sulphite (25 g.). The resulting semisolid mass was shaken with ether, centrifuged to separate the layers, and filtered. The solid bisulphite complex was washed with ether and decomposed with 10% sulphuric acid (30 ml.) on a water-bath. The brown oil so formed was extracted with ether and dried ($CaCl_2$), the solvent removed, and the 2-*hydroxy*-3-*methoxy*-5-n-*propylbenzaldehyde* distilled as a pale yellow oil, b. p. 115—120°/1 mm. (Found : C, 67·9; H, 7·1. $C_{11}H_{14}O_3$ requires C, 68·0; H, 7·2%).

The aldehyde (6 g.), hippuric acid (6 g.), anhydrous sodium acetate (3 g.), and acetic anhydride (15 ml.) gave, as in the previous case, the *azlactone* of α-benzamido-β-(2-acetoxy-3-methoxy-5-*n*-propylphenyl)acrylic acid as a yellow solid (9 g.), m. p. 150° (Found : C, 69·6; H, 5·4. $C_{22}H_{21}O_5N$ requires C, 69·6; H, 5·5%).

The azlactone (4 g.), 50% ethanol (60 ml.), and sodium hydroxide (1·8 g.) gave, as in the previous case, *α-benzamido-β-(2-hydroxy-3-methoxy-5-*n*-propylphenyl)acrylic acid,* (3·4 g.), m. p. 202—203° (from 50% ethanol) (Found: C, 67·6; H, 6·0. $C_{20}H_{21}O_5N$ requires C, 67·6; H, 5·9%).

The acrylic acid (1 g.), hydriodic acid (7 ml.), acetic anhydride (7 ml.), and red phosphorus (0·7 g.) were refluxed under hydrogen for 1½ hours. The phosphorus was filtered off, the filtrate extracted three times with ether, and the aqueous layer evaporated under hydrogen. The dark residue was treated with charcoal in water (20 ml.) containing a little sulphur dioxide, and the resulting pale yellow solution was treated dropwise with aqueous ammonia (*d* 0·88) till the solid acid separated. The 2 : 3-*dihydroxy-5-*n*-propylphenylalanine* was filtered off, redissolved in a minimum amount of dilute hydrochloric acid, and treated with charcoal, and aqueous ammonia once more added until the acid (0·3 g.), m. p. 260°, separated (Found: C, 60·3; H, 7·1. $C_{12}H_{17}O_4N$ requires C, 60·25; H, 7·1%). The amino-acid is sparingly soluble in water, gives a positive ninhydrin test and a blue-black colour with ferric chloride, and reduces silver nitrate solution.

DL-2 : 3-*Dihydroxy-5-methylphenylalanine.*—Vanillin (60 g.), water (113 ml.), concentrated hydrochloric acid (263 ml.), toluene (150 ml.), ethanol (40 ml.), and zinc amalgam (180 g.) were refluxed for 48 hours. Concentrated hydrochloric acid (38 ml.) was added every 6 hours. The toluene layer was separated and the aqueous layer extracted twice with toluene. The toluene solution was dried ($MgSO_4$) and the solvent removed. 2-Methoxy-*p*-cresol (OH = 1) distilled as a colourless liquid (30 g.), b. p. 102—105°/15 mm. (Found: C, 69·6; H, 7·55. Calc. for $C_8H_{10}O_2$: C, 69·5; H, 7·25%).

2-Allyl-6-methoxy-*p*-cresol (OH = 1) (30 g.) (Kawai, *Ber.*, 1939, **72**, 376), ethanol (400 ml.), and potassium hydroxide (120 g.) were refluxed for 60 hours. The ethanol was distilled off, and sufficient water added to dissolve the residue. The resulting solution was acidified with hydrochloric acid (50%) and steam-distilled. 2-*Methoxy-6-propenyl-*p*-cresol* (OH = 1) recrystallised from ethanol–water as needles (16 g.), m. p. 60—62° (Found: C, 74·6; H, 8·0. $C_{11}H_{14}O_2$ requires C, 74·2; H, 7·8%). A solution of this (5 g.) in ethyl acetate (30 ml.) was cooled in ice–salt and ozonised (5%) until excess of ozone could be detected leaving the solution (potassium iodide–starch). The solvent was removed under reduced pressure at $<50°$ (care !). The resulting pale yellow, syrupy ozonide was treated with water (25 ml.) and steam-distilled, yielding 2-hydroxy-3-methoxy-5-methylbenzaldehyde as pale yellow needles (2·5 g.), m.p. 74—75° (Found: C, 64·8; H, 6·4. Calc. for $C_9H_{10}O_3$: C, 65·1; H, 6·0%).

The aldehyde (5 g.), hippuric acid (5 g.), anhydrous sodium acetate (2·5 g.), and acetic anhydride (10 ml.) were heated on a water-bath for 1 hour. Water (30 ml.) was added and the yellow product warmed, filtered off, washed with hot water, and recrystallised from acetic acid. The *azlactone* of α-benzamido-β-(2-acetoxy-3-methoxy-5-methylphenyl)acrylic acid was obtained as yellow needles (7·5 g.), m. p. 198—200° (Found: C, 68·7; H, 4·9. $C_{20}H_{17}O_5N$ requires C, 68·4; H, 4·8%).

The azlactone (5 g.), hydriodic acid (20 ml.), acetic anhydride (20 ml.), and red phosphorus (2·1 g.) were refluxed under hydrogen for 4 hours. Treatment as in the first case above yielded 2 : 3-*dihydroxy-5-methylphenylalanine* (1·0 g.), m. p. 278—280° (Found: C, 57·2; H, 6·2. $C_{10}H_{13}O_4N$ requires C, 56·9; H, 6·1%). The amino-acid possessed properties similar to those described previously.

DL-4 : 5-*Dihydroxy-2-*n*-propylphenylalanine.*—4 : 5-Dimethoxy-2-*n*-propylbenzyl chloride (5·0 g.) (Mr. R. W. Temple, unpublished work), acetamidomalonic ester (4·8 g.), ethanol (35 ml.), and sodium (0·5 g.) were refluxed for 6 hours. Sodium chloride was filtered off and the solvent removed under reduced pressure. The residual pale yellow oil was treated with 20% ethanolic sodium hydroxide (25 ml.), heated under reflux for 1 hour, cooled, and acidified with 3N-hydrochloric acid. The precipitate was filtered off, boiled an hour with N-hydrochloric acid, cooled, and filtered off. α-*Acetamido-β-(4 : 5-dimethoxy-2-*n*-propylphenyl)propionic acid,* recrystallised from water, had m. p. 165—166° (3·0 g.) (Found: C, 62·3; H, 7·5. $C_{16}H_{23}O_5N$ requires C, 62·1; H, 7·4%). The acid (3·5 g.), hydriodic acid (20 ml.), acetic anhydride (20 ml.), and red phosphorus (2 g.) were refluxed under hydrogen for 3 hours and then treated with water (25 ml.), evaporated to dryness in a stream of hydrogen under reduced pressure, and worked up as above, yielding 4 : 5-*dihydroxy-2-*n*-propylphenylalanine* (2·0 g.), m. p. 260—261° (Found: C, 58·3; H, 7·4. $C_{12}H_{17}O_4N,\frac{1}{2}H_2O$ requires C, 58·1; H, 7·3%). The amino-acid gives the usual reactions with ninhydrin, ferric chloride, and silver nitrate.

3-*Ethoxy-2-hydroxy-5-methylphenylacetaldehyde.*—*O*-Ethylvanillin (20 g.), water (37 ml.), concentrated hydrochloric acid (87 ml.), toluene (50 ml.), ethanol (40 ml.), and zinc amalgam (60 g.), by treatment as in the analogous case above, afforded 2-*ethoxy-*p*-cresol* (OH = 1) as a colourless liquid (12 g.), b. p. 105—108°/15 mm., m. p. 34° (Found : C, 70·9; H, 8·0. $C_9H_{12}O_2$ requires C, 71·05; H, 7·9%).

This phenol (30 g.), allyl bromide (27 g.), acetone (55 ml.), and anhydrous potassium carbonate (37 g.) were refluxed for 12 hours. Sufficient water was added to dissolve the carbonate, and the mixture was extracted three times with ether. The ethereal layer was washed with N-sodium hydroxide and then water, dried ($CaCl_2$), and evaporated. The pale yellow residual oil was heated at 210—230° until boiling ceased. The resulting dark liquid was distilled, yielding 2-*allyl*-6-*ethoxy*-p-*cresol* (OH = 1), a colourless liquid, rapidly becoming green in air (26 g.), b. p. 132—134°/15 mm. (Found : C, 75·3; H, 8·7. $C_{12}H_{16}O_2$ requires C, 75·0; H, 8·3%).

The above (9·3 g.), methanol (50 ml.), anhydrous potassium carbonate (3·3 g.), and benzyl chloride (6·9 g.) were refluxed for 24 hours. Methanol and excess of benzyl chloride were removed, sufficient water was added to dissolve the carbonate, and the aqueous solution extracted with ether. The ethereal extract was washed with aqueous sodium hydroxide and then water, dried ($CaCl_2$), and evaporated. 1-*Allyl*-2-*benzyloxy*-3-*ethoxy*-5-*methylbenzene* was obtained as a colourless liquid (9·0 g.), b. p. 195—197°/15 mm. (Found : C, 80·8; H, 8·0. $C_{19}H_{22}O_2$ requires C, 80·85; H, 7·8%). *Ethyl* 2-*allyl*-6-*ethoxy*-4-*methylbenzoate* was obtained as a colourless liquid, b. p. 153—155°/15 mm. (Found : C, 68·5; H, 7·6. $C_{15}H_{20}O_4$ requires C, 68·2; H, 7·6%). 1-*Allyl*-3-*ethoxy*-2-*methoxy*-5-*methylbenzene* was obtained as a colourless liquid, b. p. 128—130°/15 mm. (Found : C, 75·7; H, 9·2. $C_{13}H_{18}O_2$ requires C, 75·7; H, 8·7%).

2-Allyl-3-ethoxy-*p*-cresol (6 g.), in ethyl acetate (50 ml.), cooled in acetone–solid carbon dioxide, was ozonised (5%) until excess of ozone could be detected. After 20 minutes palladium–charcoal (0·5 g.) was added and the mixture shaken with hydrogen until no further uptake could be detected. The catalyst was filtered off, the filtrate shaken with aqueous sodium hydrogen carbonate and then water, and dried ($CaCl_2$). The solvent was removed and the residue cooled. The semisolid mass was filtered off and the 2-*hydroxy*-3-*ethoxy*-5-*methylphenylacetaldehyde* recrystallised from ether; it (2·5 g.) had m. p. 95—96° (Found : C, 68·2; H, 7·7. $C_{11}H_{14}O_3$ requires C, 68·0; H, 7·2%).

2-*Ethoxy*-6-*propenyl*-p-*cresol* (OH = 1).—The allylphenol (30 g.), ethanol (400 ml.), and potassium hydroxide (120 g.) were refluxed for 48 hours. The ethanol was distilled off, sufficient water to dissolve the residue added, and the solution acidified with 50% hydrochloric acid and steam-distilled. 2-*Ethoxy*-6-*propenyl*-p-*cresol* crystallised from ethanol–water as needles (15 g.), m. p. 73—74° (Found : C, 75·0; H, 8·6. $C_{12}H_{16}O_2$ requires C, 75·0; H, 8·3%).

2 : 3-*Dimethoxy*-5-*methylphenylacetaldehyde*.—2-Allyl-6-methoxy-*p*-cresol (Kawai, *loc. cit.*) (29 g.), methanol (64 ml.), and methyl sulphate (27 ml.) were stirred in ice–salt. Sodium hydroxide (23 g.) in water (58 ml.) was slowly added. After 30 minutes the mixture was extracted with ether, washed with 10% aqueous sodium hydroxide and then water, dried (Na_2SO_4), and evaporated. 1-*Allyl*-2 : 3-*dimethoxy*-5-*methylbenzene* was distilled, as a colourless liquid (25 g.), b. p. 120—124°/14 mm. (Found : C, 74·8; H, 8·5. $C_{12}H_{16}O_2$ requires C, 75·0; H, 8·3%).

A solution of the above (5 g.) in ethyl acetate (30 ml.), was ozonised (5%) and worked up as in the previous case. Final distillation (care !) gave 2 : 3-*dimethoxy*-5-*methylphenylacetaldehyde* as a pale yellow liquid (2·0 g.), b. p. 115—120°/1 mm. (Found : C, 68·55; H, 7·4. $C_{11}H_{14}O_3$ requires C, 68·0; H, 7·2%). The p-*nitrophenylhydrazone* had m. p. 170° (Found : C, 62·1; H, 6·2. $C_{17}H_{19}O_4N_3$ requires C, 62·0; H, 5·8%).

DL-2-*Methyltyrosine*.—Finely powdered iodine (40 g.) was added in small portions, during ½ hour, to a stirred mixture of anethole (25 g.), ether (100 ml.) saturated with water, and freshly prepared yellow mercuric oxide (40 g.). After each addition the orange colour was permitted to return before more iodine was added. The mixture was warmed for 10 minutes, left overnight, and filtered. The filtrate was shaken with sodium hydrogen sulphite solution (*d* 1·34), and the resulting semisolid mass was kept for 2 hours and filtered. The bisulphite compound of 2-*p*-methoxyphenylpropaldehyde was recrystallised from water (yield, 14 g.). The compound (2·0 g.), ammonium carbonate (2·4 g.), potassium cyanide (0·52 g.), and aqueous ethanol (12 ml.) were heated in a sealed tube for 4 hours at 100°. The contents were then diluted with water (8 ml.), and the resulting mixture heated for 20 minutes at 105—110° to decompose the excess of ammonium carbonate. The solid was then filtered off, after cooling, and washed with a little water. The 5-(1-p-*methoxyphenylethyl*)*hydantoin*, recrystallised from ethanol (yield, 0·9 g.), had m. p. 203—205° (Found : C, 61·2; H, 6·2. $C_{12}H_{14}O_3N_2$ requires C, 61·5; H, 6·0%).

The hydantoin (0·5 g.) and concentrated hydrochloric acid (5 ml.) were heated in a sealed tube for 4½ hours at 155—160°, then cooled, water (12 ml.) was added, and the mixture filtered. The pH of the boiling solution was adjusted to 6 with ammonium hydroxide (*d* 0·88), treated with charcoal, and filtered. The resulting solution was reduced to 5—10 ml. *in vacuo* and the acid filtered off. DL-2-*Methyltyrosine*, recrystallised from water (charcoal), had m. p. 263—265° (0·25 g.) (Found : C, 61·4; H, 6·9. $C_{10}H_{13}O_3N$ requires C, 61·5; H, 6·7%).

DL-1-p-*Hydroxybenzylethylamine Hydrochloride*.—Sodium amalgam (4%; 200 g.) was added during ½ hour to a stirred mixture of *p*-methoxy-α-methylcinnamic acid (12 g.), and 10% sodium hydroxide solution (50 ml.). The solution was then warmed on a water-bath until reaction had ceased, filtered, and acidified with 3N-hydrochloric acid. The yellow oil was extracted with chloroform, the extract dried ($MgSO_4$), and the solvent removed. Thionyl chloride (10 ml.) was added to the resulting yellow oil, and the mixture refluxed for 3 hours. Excess of thionyl chloride was removed *in vacuo*, the residue poured into aqueous ammonia (*d* 0·88), and after 1 hour the solid was filtered off. α-p-*Methoxybenzylpropionamide*, recrystallised from aqueous alcohol, had m. p. 126° (9 g.) (Found : C, 67·8; H, 7·7. $C_{11}H_{15}O_2N$ requires C, 68·4; H, 7·8%).

The amide (6·0 g.) was added to an ice-cold solution of bromine (6·0 g.) in 10% potassium hydroxide solution (90 ml.), the mixture shaken for about 20 minutes and then filtered, and the filtrate heated at 70—80° for 90 minutes. Sodium hydroxide (5·0 g.) was then added, the mixture heated at 80° for 2 hours, cooled, and extracted with ether. The extract was dried ($MgSO_4$), filtered, and treated with hydrogen chloride. 1-*p*-Methoxybenzylethylamine hydrochloride was filtered off and recrystallised from ether–ethanol (5·0 g.), m. p. 204° (Found : C, 59·6; H, 7·9. Calc. for $C_{10}H_{16}ONCl$: C, 59·8; H, 8·2%).

Bougault's method (*loc. cit.*) gave a material which, on treatment with ether, solidified and from ethanol–ether afforded 1-*p*-hydroxybenzylethylamine hydrochloride (0·7 g.), m. p. 169—170° (Found : C, 57·6; H, 7·7. Calc. for $C_9H_{14}ONCl$: C, 57·6; H, 7·5%).

α-*Benzamido*-β-(4-*hydroxy*-3-*methoxy*-2-*methylphenyl*)*acrylic Acid*.—4-Hydroxy-3-methoxy-2-methylbenzaldehyde (5 g.), anhydrous sodium acetate (3 g.), hippuric acid (6 g.), and acetic anhydride (20 ml.) yielded, as in previous cases, the *azlactone* of α-benzamido-β-(4-acetoxy-3-methoxy-2-methylphenyl)acrylic acid as yellow needles (5 g.) (dried at 120—130°), m. p. 153—155° (Found : C, 68·3; H, 4·7. $C_{20}H_{17}O_5N$ requires C, 68·3; H, 4·8%).

The azlactone (5 g.), sodium hydroxide (2·0 g.), and 50% aqueous ethanol (60 ml.) were warmed on a water-bath for 15 minutes, affording, as above, α-*benzamido*-β-(4-*hydroxy*-3-*methoxy*-2-*methylphenyl*)*acrylic acid* (1 g.), m. p. 270—271° (from acetic acid) (Found : C, 66·0; H, 4·9. $C_{18}H_{17}O_5N$ requires C, 66·1; H, 5·2%).

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