2-BENZYLRESORCINOL was required in connection with the work described
in the accompanying paper. As it was unknown, possible methods for its
synthesis were investigated. 2-Alkylresorcinols in general, can be prepared
by the method of Robinson and Shah,\(^1\) by nuclear alkylation of methyl
β-resorcyate to 4-O-alkyl-3-alkyl derivative, which on subsequent dealkyla-
tion, hydrolysis and decarboxylation would give 2-alkylresorcinol.

Methyl β-resorcyate, when treated with benzyl chloride in methanolic
potassium hydroxide gave methyl -2-hydroxy-3-benzyl-4-benzyloxybenzoate
\((\text{I, } R=\text{Me, } R_1=\text{CH}_2\text{Ph})\). It was debenzylated by concentrated hydro-
chloric acid to methyl -2:4-dihydroxy-3-benzylbenzoate \((\text{I, } R=\text{Me, } R_1=\text{H})\).
The latter was hydrolysed by alkali to 2:4-dihydroxy-3-benzylbenzoic acid
\((\text{I, } R=R_1=\text{H})\), which was then decarboxylated by heating with copper
in quinoline to get 2-benzylresorcinol \((\text{II})\).

\[
\begin{align*}
(\text{I}) & : CH_2\text{Ph} & (\text{II}) & : CH_2\text{Ph} & (\text{III}) & : \text{Ph} - CH_2 \\
& : OH & & : OH & & : CO \\
& & : OH & & : OH & & : Me \\
R_1 & : OCOR & R_1 & : OCOR & R_1 & : OCOR \\
\end{align*}
\]

For comparison it was also prepared by Clemmensen reduction of 2-benzoylresorcinol.\(^2\)

2-Benzyeresorcinol \((\text{II})\) was characterised by preparing its diacetyl,
dibenzoyl and dibromo derivatives. On condensation with phthalic anhydride
in presence of concentrated sulphuric acid, it gave a product which from
its properties, appears to be a homologue of fluorescein.

It easily underwent Pechmann condensation with ethyl acetoacetate in
presence of concentrated sulphuric acid to give 7-hydroxy-4-methyl-8-benzyl-
coumarin \((\text{III})\), which was also obtained by the Clemmensen reduction of
7-hydroxy-4-methyl-8-benzoyl coumarin. Attempts at nuclear benzylation of 7-hydroxy-4-methyl coumarin, to get the above compound, resulted in a failure and only 7-benzyloxy-4-methyl coumarin was formed.

**EXPERIMENTAL**

**Nuclear Benzylation of Methyl β-Resorcylate**: Methyl 2-Hydroxy-3-benzyl-4-benzyloxybenzoate \((I, R = \text{Me}, R_1 = \text{CH}_2\text{Ph})\)

To a methanolic solution of potassium hydroxide (8.4 g. in 50 c.c.), methyl β-resorcylate (8.4 g.) and benzyl chloride (19.0 g.) were added, and the mixture left overnight. Next day the reaction mixture was refluxed for 6 hours, methanol was distilled off and excess of benzyl chloride was removed by steam-distillation. The residue was extracted with ether and the ether extract washed with sodium hydroxide solution (10%). On removing the ether an oily product was obtained, which was washed with petroleum ether. The solid product, thus obtained was crystallised from alcohol when colourless needles of methyl 2-hydroxy-3-benzyl-4-benzyloxybenzoate \((I, R = \text{Me}, R_1 = \text{CH}_2\text{Ph})\) separated, m.p. 100-101 ° (1.2 g.) (Found: C, 76.2; H, 5.5. \(\text{C}_{12}\text{H}_{16}\text{O}_4\) requires C, 75.9; H, 5.7%). It is insoluble in alkali and gives a deep violet coloration with alcoholic ferric chloride.

**Debenzylation of Methyl 2-Hydroxy-3-benzyl-4-benzyloxybenzoate**: Methyl 2, 4-Dihydroxy-3-benzylbenzoate \((I, R = \text{Me}, R_1 = \text{H})\)

A mixture of methyl 2-hydroxy-3-benzyl-4-benzyloxybenzoate (4.0 g.) and concentrated hydrochloric acid (50 c.c.) in glacial acetic acid (100 c.c.) was refluxed for 2 hours. After removing acetic acid and benzyl alcohol by steam distillation, the product obtained was boiled in benzene with activated charcoal. On concentrating the benzene solution pale yellow rhombic crystals were obtained. On recrystallising from alcohol, colourless crystals of methyl 2, 4-dihydroxy-3-benzylbenzoate \((I, R = \text{Me}, R_1 = \text{H})\) were obtained, m.p. 129-130 ° (0.6 g.) (Found: C, 69.5; H, 5.4. \(\text{C}_{12}\text{H}_{16}\text{O}_4\) requires C, 69.8; H, 5.4%).

**Hydrolysis of Methyl 2, 4-Dihydroxy-3-benzylbenzoate**: Methyl 2, 4-Dihydroxy-3-benzyl benzoic Acid \((I, R = R_1 = \text{H})\)

Methyl 2, 4-dihydroxy-3-benzyl benzoate \((I, R = \text{Me}, R_1 = \text{H})\) (2.5 g.) was dissolved in sodium hydroxide solution (10%) and allowed to stand for 48 hours. The solid obtained on acidification was crystallised from
y-Substitution in the Resorcinol Nucleus—X

Dilute alcohol when 2:4-dihydroxy-3-benzylbenzoic acid (I, R = R₁ = H) separated in colourless needles, m.p. 84–85° (1·2 g.) (Found: C, 68·5; H, 4·8. C₁₄H₁₂O₄ requires C, 68·9; H, 4·9%).

Decarboxylation of 2:4-Dihydroxy-3-benzylbenzoic Acid (I, R = R₁ = H):

2-Benzylresorcinol (II)

To a solution of 2:4-dihydroxy-3-benzylbenzoic acid (I, R = R₁ = H) (0·1 g.) in quinoline (5 c.c.), copper powder (0·1 g.) was added and the mixture heated at 180° for 1 hour. Copper was filtered and washed with ether. The filtrate was treated with dilute hydrochloric acid and extracted with ether. The ether extract was washed with sodium bicarbonate and then with water and dried. 2-Benzylresorcinol was obtained on removal of the ether, and was found to be identical with the product described below.

Clemmensen Reduction of 2-Benzoylresorcinol:

2-Benzoylresorcinol (II) (10·0 g.) was mixed with zinc amalgam (prepared from zinc, 20·0 g., and mercuric chloride, 1·0 g.) and dilute hydrochloric acid (1:1; 25 c.c.) was added to it. The reaction mixture was heated on a steam-bath. At intervals of half an hour, more of dilute hydrochloric acid (1:1) was added and heating continued till the reaction mixture gave no coloration with alcoholic ferric chloride. The supernatant liquid was decanted and extracted with ether. On removal of ether it gave an oily product which when distilled under reduced pressure (230–40°/30 mm.) gave 2-benzylresorcinol, m.p. 82–84° (6·0 g.) (Found: C, 77·6; H, 5·7. C₁₃H₁₀O₂ requires C, 78·0; H, 6·0%).

Diacetyl derivative was prepared by acetic anhydride and pyridine method and was crystallised from rectified spirit, m.p. 79–80° (Found: C, 71·6; H, 5·5. C₁₃H₁₀O₄ requires C, 71·8; H, 5·6%).

Dibenzoyl derivative was prepared by benzyol chloride and pyridine method, and was crystallised from rectified spirit in small pale yellow needles, m.p. 138–39° (Found: C, 79·3; H, 5·3. C₁₇H₁₇O₄ requires C, 79·4; H, 4·9%).

Dibromo derivative was prepared by bromination (3 mols. of bromine) in carbon disulphide and was crystallised from dilute alcohol, colourless plates, m.p. 127–28° (Found: Br, 44·8. C₁₇H₁₇O₂Br₂ requires Br, 44·7%).

Pechmann Condensation of 2-Benzylresorcinol with Ethyl Acetoacetate:

7-Hydroxy-4-methyl-8-benzylcoumarin (III)

2-Benzylresorcinol (1·0 g.) was dissolved in ethyl acetoacetate (1·2 g.), concentrated sulphuric acid (4 c.c.) was added to it and kept overnight,
The next day it was poured on crushed ice and the solid obtained was crystallised from dilute alcohol when 7-hydroxy-4-methyl-8-benzylcoumarin (III) separated, m.p. 238° (0.8 g.) (Found: C, 76.9; H, 5.1. C_{12}H_{14}O_{3} requires C, 76.7; H, 5.3%). It dissolves in alkali giving strong blue fluorescence.

**Clemmensen Reduction of 7-Hydroxy-4-methyl-8-benzylcoumarin:**

7-Hydroxy-4-methyl-8-benzylcoumarin (III) was reduced to 7-hydroxy-4-methyl-8-benzoylcoumarin from (10.0 g. zinc) in hydrochloric acid (1:1; 40 c.c.) were heated on a steam-bath, extra hydrochloric being added at intervals and heating continued till a drop of the reaction mixture gave no coloration with alcoholic ferric chloride. At the end of the reaction, the supernatant liquid was decanted when hot. On cooling crystals of 7-hydroxy-4-methyl-8-benzylcoumarin (III) were deposited, recrystallised from dilute alcohol, m.p. and mixed m.p. 238° (2.1 g.).

**Attempted Nuclear Benzylation of 7-Hydroxy-4-methylcoumarin**

A mixture of 7-hydroxy-4-methylcoumarin (5.9 g.), anhydrous potassium carbonate (6.3 g.) and benzyl chloride (12.6 g.) in dry acetone (25 c.c.) was kept overnight. The next day, it was refluxed for 6 hours. Excess of acetone and benzyl chloride were removed. The residue was washed with dilute sodium hydroxide (1 N) and the insoluble product after washing with water was collected and crystallised from rectified spirit, colourless needles, m.p. 118-20° (3 g.). It was identified as 7-benzyloxy-4-methylcoumarin. Bridge, Crodes, Cubin and Robertson give m.p. 117-5°.

**Benzylation of Methyl 2-Resorcylic Acid:**

Methyl 2-hydroxy-4-benzyloxybenzoate was obtained by refluxing a mixture of methyl 2-resorcylic acid (4.2 g.), benzyl chloride (12.6 g.) and anhydrous potassium carbonate (6.3 g.) in dry acetone (25 c.c.) for 8 hours. Acetone was distilled off and benzyl chloride was removed by steam distillation. The product obtained was crystallised from rectified spirit, when methyl 2-hydroxy-4-benzyloxybenzoate separated in colourless needles, m.p. 102-04° (4.1 g.) (Found: C, 69.6; H, 5.5. C_{15}H_{14}O_{4} requires C, 69.8; H, 5.4%).

**Summary**

Two syntheses of 2-benzylresorcinol are described. Methyl 2-resorcylic acid on nuclear benzylation gave methyl 2-hydroxy-3-benzyl-4-benzyloxybenzoate which on successive debenzylation, hydrolysis and decarboxylation gave
2-benzylresorcinol. It has also been prepared by the Clemmensen's reduction of 2-benzoylresorcinol. 2-Benzylresorcinol on Pechmann condensation with ethyl acetoacetate gave 7-hydroxy-4-methyl-8-benzylcoumarin. The latter was also obtained by Clemmensen's reduction of 7-hydroxy-4-methyl-8-benzoyl coumarin.

REFERENCES