NUCLEAR METHYLATION OF $\beta$-RESORCYLIC ALDEHYDE

BY T. R. SESHADRI AND V. VENKATESWARLU

(From the Department of Chemistry, Andhra University, Waltair)

Received August 5, 1941

Under conditions of methylation, certain poly-hydroxy phenyl derivatives exhibit a tendency to undergo substitution in the benzene nucleus. This phenomenon is known as nuclear methylation. Not only is the chemistry of this reaction interesting, but it has also useful applications in synthetic work. For instance, methyl orsellinate was found to be directly and conveniently methylated with the formation of methyl rhizonate (I). In a similar manner rhizonic aldehyde (II) has been prepared readily by the methylation of orcylic aldehyde. Early work of Perkin\(^5\) and of Herzig et al.\(^4\) on the methylation of $\beta$-resorcylic acid and ester (III) has been reviewed in the above-mentioned paper by Robinson and Shah.\(^1\) Their ideas have been confirmed by Jones and Robertson\(^5\) by careful comparison of some of the important products of methylation with substances obtained by definite methods of synthesis.

\[ \text{CH}_3 \text{O} / \text{CHO} / \text{COOCH}_3 \]
\[ \text{CH}_3 \text{OH} \]
\[ \text{(I)} \]

\[ \text{CH}_3 \]
\[ \text{CH}_3 \text{O} / \text{CHO} / \text{COOCH}_3 \]
\[ \text{CH}_3 \text{OH} \]
\[ \text{(II)} \]

\[ \text{CH}_3 \]
\[ \text{OCH}_3 \]
\[ \text{CH}_3 \text{O} / \text{CHO} / \text{COO(CH}_3)_2 \]
\[ \text{(IV)} \]

\[ \text{CH}_3 \text{OH} \]
\[ \text{CH}_3 \text{OH} \]
\[ \text{COOR} \]
\[ \text{COOR} \]
\[ \text{(III)} \]

Kaufler\(^6\) and Perkin\(^8\) found that nuclear ethylation is a much less facile process. Robinson and Shah,\(^1\) however, were able to effect nuclear ethylation of the methyl ester of resorcylic acid using large excess of the reagents. Nuclear methylation of resocetophenone was effected by Greger,\(^7\) Wechler\(^8\) and Crabtree and Robinson\(^9\) and nuclear ethylation was carried out by Robinson and Shah.\(^1\) The constitution of the products was drawn only
from analogy with the similar reaction with resorcylic acid and ester. The subject was subsequently reinvestigated by Rangaswami and Seshadri,\textsuperscript{10} who confirmed the structures by unequivocal synthesis and by preparation of derivatives. They employed for this purpose resacetophenone and \(\omega\)-methoxy-resacetophenone. An observation regarding nuclear methylation of a phloroglucinol derivative has been recently made by Hems and Todd.\textsuperscript{11} Using phloroisobutyrophenone, they found that the reaction took place even under very mild conditions by boiling the substance in acetone solution with methyl iodide and potassium carbonate; \(\text{bæckeol (IV)}\) was thus obtained. This may be taken as an instance of very facile nuclear methylation.

The following is an account of past work relating to the nuclear methylation of \(\beta\)-resorcylic aldehyde. Tiemann and Parrisius\textsuperscript{12} obtained a compound (A) melting at 62–63\(^\circ\) by two methods: (i) by the action of chloroform and alkali on mono-methyl resorcinol, and (ii) by the methylation of \(\beta\)-resorcylic aldehyde with methyl iodide and alcoholic potash. They assigned to it the structure of 2-hydroxy-4-methoxy-benzaldehyde and this has been shown to be wrong by subsequent work. Claisen and Eisleb\textsuperscript{13} showed that by employing methyl iodide and potassium carbonate for the methylation of \(\beta\)-resorcylic aldehyde, two compounds could be isolated: (i) melting at 62–63\(^\circ\) and identical with (A) and (ii) melting at 41–42\(^\circ\) (B). The mixture of these two products could be separated by taking advantage of their difference in volatility with steam under different conditions; compound (A) distilled over from a faintly alkaline solution and subsequently after rendering the solution acid, compound (B) could be distilled. The above work was confirmed by OTT and Nauen\textsuperscript{14} who further showed that methylation of \(\beta\)-resorcylic aldehyde with methyl iodide and alcoholic potash gave compound (A) along with a small quantity of (B), whereas when dimethyl sulphate or methyl bromide and aqueous potash were employed, compound (B) was exclusively formed. The constitution of compound (B) was established by them as 4-0-methyl-resorcylic aldehyde from careful elementary analysis and comparison with a sample obtained from natural products (\textit{e.g.}, from the root of chlorocodon from Natal isolated by Goulding and Pelly).\textsuperscript{15} It is now known to occur widely in the following plants: (i) \textit{Decalepis Hamiltonii} (Srinivasa Rao and Sesha Iyengar\textsuperscript{16}); (ii) \textit{Periploca Gracea} (Solacolin, Mavrodin and Hermann\textsuperscript{17}); (iii) \textit{Hemidesmus indicus} (Dutta, Ghosh and Chopra\textsuperscript{18}). Compound (A) was subsequently taken to be nuclear methylated homologue of (B) and it was assumed to have the structure of 2-hydroxy-3-methyl-4-methoxy-benzaldehyde; this assumption was based on analogy with similar resorcinol derivatives. Its formation in small amounts in the experiments of Tiemann and Parrisius\textsuperscript{12} using chloroform, alkali and mono-methyl resorcinol was
difficult to explain. OTT and Nauen\textsuperscript{14} were of the opinion that the mono-
methyl resorcinol employed by these authors probably contained 2-methyl-
resorcinol. But the explanation does not seem to be satisfactory and the
original observations may require revision.

\begin{center}
\begin{tikzpicture}
  \node at (0,0) {\includegraphics[width=0.5\textwidth]{diagram1}};
\end{tikzpicture}
\end{center}

The methods employed by previous workers for effecting nuclear methy-
lolation of $\beta$-resorcylic aldehyde have not yielded satisfactory results and the
constitution of the product has not been established by independent
synthesis. OTT and Nauen\textsuperscript{14} treated a solution of $\beta$-resorcylic aldehyde and
methyl iodide in methyl alcohol with finely powdered potassium hydroxide
during the course of 12 days. They obtained compound (A) in low yields
and it had to be separated from a small quantity of 4-O-methyl-resorcylic-
aldehyde. A rapid and convenient procedure has now been worked out and
under these conditions (see experimental part) only one product, compound
(A) melting at 64–65°C, is obtained. The constitution of this compound, as
2-hydroxy-3-methyl-4-methoxy-benzaldehyde has been established by two
independent methods: (i) it has been synthesised, starting from 2-methyl-
resorcinol (V) according to the method of Jones nd Robertson\textsuperscript{5} and the
synthetic product compared with the sample obtained by methylation of
$\beta$-resorcylic aldehyde. The two are identical.

\begin{center}
\begin{tikzpicture}
  \node at (0,0) {\includegraphics[width=0.5\textwidth]{diagram2}};
\end{tikzpicture}
\end{center}

(ii) Compound (A) was condensed with diethyl malonate using piperidine
as the condensing agent. The coumarin-3-carboxylic ester (VII) thereby
obtained was hydrolysed and the product (VIII) decarboxylated. The final
coumarin (IX) thus obtained was found to be 8-methyl-7-methoxy-coumarin,
by comparison with a sample obtained independently by synthesis as given
below. 2-Methyl-resorcinol (V) was condensed with malic acid to form
8-methyl-7-hydroxy-coumarin (X). The same compound was also obtained
by the reduction of 8-aldehydo-7-hydroxy-coumarin (XI) (Spaeth\textsuperscript{18}) with
hydrogen using palladium charcoal as catalyst. It readily underwent
methylation with methyl iodide and potassium carbonate to yield 8-methyl-7-methoxy-coumarin (IX). Thus it is clear that the nuclear position involved in the methylation of β-resorcylic aldehyde is position 3, and that of the two hydroxyl groups, only that present at 4 undergoes ether formation.

\[
\begin{align*}
\text{(VII)} & \quad \rightarrow \\
\text{(VIII)} & \\
\text{(X)} & \quad \rightarrow \\
\text{(IX)} & \\
\text{(XI)} & \quad \rightarrow \\
\text{(V)} &
\end{align*}
\]

In the examples of nuclear methylation discussed in the previous pages, it should be noted that they come under the category of polyhydroxy carbonyl compounds. The same characteristics of the reactions are observed throughout. Nuclear position 3 with respect to the carbonyl group is the reactive one. Regarding the hydroxyl groups, one of these ortho to the carbonyl group is left unmethylated. It is well known that all these hydroxy-carbonyl compounds are chelated and this chelation has a tendency to cause fixation of the benzene double bonds as shown in (XII).

\[
\begin{align*}
\text{(XII)} & \\
(R = H, \text{CH}_3 \text{ or OCH}_3)
\end{align*}
\]

The existence of chelation may account for the non-methylation of the ortho-hydroxyl group and it may also explain the high reactivity of position 3.
From a study of the nuclear methylation of resacetophenone, Crabtree and Robinson have advanced the following regarding the mechanism of the reaction. These authors indicated that the nuclear methylation of resacetophenone is a reaction of the alkali metal derivatives of the original ketone itself (not of paeanol, the mono-methyl ether) and that it is favoured by an excess of alkali. They found that 4-O-methyl-resacetophenone does not undergo nuclear methylation under the above conditions.

The analogy between the above nuclear methylation and the C-alkylation of ethyl-aceto-acetate seems to be obvious. In both cases the primary cause of the reaction is the existence of an anionoid carbon atom. In the presence of sodium (or potassium) alkoxide the following (E) and (K) may be said to be in equilibrium when ethyl-aceto-acetate is involved.

\[
\begin{array}{c}
\text{CH}_3\text{C}=\text{CH}\cdots\text{C}=\text{OEt} \\
\text{O} \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \q
It has been the practice to view C- alkylation of ethyl-aceto-acetate as involving addition of methyl iodide at the double bond of the enol. This does not seem to be tenable since there is no positive proof of such addition and since there is no other example where methyl iodide has been proved to add on to the double bonds. On the other hand, all its reactions seem to be characterised by the ready elimination of iodide ions after attack at the unstable anionoid carbon. In this connection it may be mentioned that acid chlorides react with the sodium derivative of ethyl-aceto-acetate similarly to form C-acyl derivatives whereas when the free compound itself is employed in the presence of pyridine O-acyl derivatives are formed. The latter is obviously simple ester formation in which the enol takes part and the keto-isomer is unreactive (X). The reaction with the metal derivative is again due to attack on the anionoid carbon (Y). Definite cases of addition of acyl chlorides to double bonds are not known.

\[
\begin{align*}
\text{(X)} & \quad \text{CH}_3-C-CH_2-C-\text{OEt} \xrightarrow{\text{OH}} \text{CH}_3-C-\text{C}=\text{CH}\text{C}-\text{OEt} \\
\text{(Y)} & \quad \text{CH}_3-C-C=\text{CH}\text{C}-\text{OEt} \rightarrow \left[\text{CH}_3-C-\text{C}=\text{CH}\text{C}-\text{OEt}\right] \rightarrow \text{CH}_3-C-\text{C}=\text{CH}\text{C}-\text{OEt}
\end{align*}
\]

**Experimental**

_Nuclear methylation of β-resorcylic aldehyde: 2-hydroxy-3-methyl-4-methoxy-benzaldehyde (A)._—To a solution of caustic potash (7.5 g., 4.5 mols.) in anhydrous methyl alcohol (40 c.c.) β-resorcylic aldehyde (5 g.) was added. The solid dissolved slowly to form a clear solution which was deep brown in colour. On cooling it in a freezing mixture, it set into a solid mass. Enough methyl alcohol was therefore added to obtain a clear solution again at this low temperature and then the mixture was treated with excess of ice-cold methyl iodide (30 c.c., 7 mols.) in one lot.
Nuclear Methylation of β-Resorcylic Aldehyde

The contents were then well shaken for about half an hour, the flask being immersed in freezing mixture and kept well-stoppered. Subsequently it was allowed to assume laboratory temperature slowly and to stand overnight. Next morning, crystals of potassium iodide had separated at the bottom and a clear solution was found above. The mixture was gently boiled under reflux for 8 hours, cooled and poured into ice-water and left overnight. As much of the alcohol as possible was then removed by distillation under reduced pressure and the highly coloured residue was subjected to steam-distillation. A colourless oil came over and soon solidified. When recrystallised from methyl alcohol it was obtained as colourless elongated rectangular plates melting at 64-65°. [Found: C, 64.9; H, 6.2; C₉H₁₀O₃ requires C, 65.1; H, 6.0.] The yield of the pure product was 1.5 g. It does not undergo condensation with acetic anhydride and sodium acetate under the conditions of Perkin's reaction.

2:4-Dihydroxy-3-methyl-benzaldehyde (VI): was made according to the method of Jones and Robertson with the modification that zinc cyanide was used in the place of hydrogen cyanide.

A solution of 2-methyl resorcinol (2 g.) and zinc cyanide (5 g.) in anhydrous ether (40 c.c.) was cooled in ice and saturated with hydrogen chloride. The aldimine hydrochloride began to separate after thirty minutes. The current of the gas was, however, continued for 4 hours, at the end of which the solid was separated, washed with more ether and decomposed with water (35 c.c.) by heating on a boiling water-bath. The aldehyde separated out from water in colourless rhombic prisms melting at 150° with slight sintering at 137°. The yield of the product was 1.6 g.

The above dihydroxy-aldehyde (VI) was methylated using excess of methyl iodide and potassium carbonate in boiling acetone solution. Almost quantitative yield of the 4-methyl ether was obtained and it crystallised from dilute alcohol in plates melting at 64-65°. It was found to be identical with the sample obtained from the nuclear methylation of β-resorcylic aldehyde.

Ethyl-7-methoxy-8-methyl-coumarin-3-carboxylate (VII).—The nuclear methylation product (A) (1 g., 1 mol.) was mixed with diethyl malonate (1.4 g., 1.4 mol.) and cooled in ice. Piperidine (10-15 drops) was then added. (Cooling was found necessary as otherwise heat was developed causing considerable resinification.) The mixture was allowed to stand overnight and to attain room temperature slowly. The resulting solid was treated with dilute hydrochloric acid, filtered and recrystallised from alcohol. It came out as colourless thin rectangular plates melting at 159-60°. In neutral alcoholic solution it emitted a violet fluorescence and in concentrated
sulphuric acid the fluorescence was green. [Found: C, 64·3; H, 5·5; 
C_{14}H_{14}O_{5} requires C, 64·1; H, 5·3%.] Yield 1·5 g.

7-Methoxy-8-methyl-coumarin-3-carboxylic acid (VIII).—The above ester
(1 g.) was treated with excess of alcoholic potash (20 c.c. of alcohol containing
3 g. of potassium hydroxide) and allowed to stand for 3 days. The clear
solution was then diluted with water and acidified with dilute hydrochloric
acid. The precipitated solid was filtered and purified by dissolution in aqueous
sodium carbonate and reprecipitation. When finally crystallised from
alcohol it came out as light yellow needles and rectangular plates melting
at 211–212°. It resembled the ester very closely in the nature of its fluores-
cence. [Found: C, 61·4; H, 4·6; C_{12}H_{10}O_{5} requires C, 61·6; H, 4·3%.

7-Methoxy-8-methyl-coumarin (IX).—The above carboxylic acid (0·5 g.)
was heated with quinoline (20 c.c.) and copper bronze (1 g.) for 4
hour at 150–60° in an oil-bath. After cooling, the mixture was treated with excess
of ether and the solution quickly filtered. Ether was then distilled off; the
residue was treated with excess of dilute hydrochloric acid and the mixture
was repeatedly shaken with ether. The ether extract was washed free from
acid with aqueous sodium bicarbonate and then water and finally evaporated.
The resulting solid was extracted with petroleum ether, whereby some resin
was left behind. The petroleum extract was evaporated and the solid residue
crystallised from alcohol. Colourless rectangular prisms and plates were
thus obtained melting at 122–23°. The substance gave a weak violet fluores-
cence in alcohol and a bluish green fluorescence in concentrated sulphuric
acid. It was found to be identical with the sample of 7-methoxy-8-methyl-
coumarin prepared from 2-methyl-resorcinol as given below. [Found: C,
69·7; H, 5·5; C_{11}H_{10}O_{3} requires C, 69·5; H, 5·3%.

7-Hydroxy-8-methyl-coumarin (X): Method I.—An intimate mixture of
2-methyl-resorcinol (1 g., 1 mol.), malic acid (1·2 g., 1 mol.), and concen-
trated sulphuric acid (2·5 c.c.) was heated in an oil-bath maintained at 120°
until effervescence ceased (1½ hours). After cooling, the product was poured
with stirring into excess of crushed ice and left overnight. The solid was then
filtered and extracted with ether. By this treatment, a small quantity of
insoluble resin was removed. After distilling off the solvent the residue was
recrystallised from alcohol, when colourless triangular prisms melting at
231–232° were obtained. The substance gave a pale blue fluorescence in neutral
alcoholic solution and it was bright bluish in alkaline solution. In concen-
trated sulphuric acid the colour of the fluorescence was bluish green. [Found:
C, 72·6; H, 4·4; C_{10}H_{8}O_{3} requires C, 72·7; H, 4·6%.]
Method II: Reduction of 7-hydroxy-coumarin-8-aldehyde (XI).—A solution of the aldehyde in glacial acetic acid was treated with palladium charcoal and shaken in an atmosphere of hydrogen till two molecular proportions of the gas were absorbed. The solution was then filtered and the solvent removed as far as possible by distillation under reduced pressure. The residue was then treated with water, the acetic acid remaining behind was neutralised with sodium carbonate and the mixture repeatedly extracted with ether. The ether solution was then shaken with saturated sodium bisulphite to remove any unreduced aldehyde and subsequently washed with water. After distilling off the solvent the residue was recrystallised from alcohol whereby 8-methyl-7-hydroxy coumarin was obtained melting at 231–32°. A mixture of this specimen with the one made from 2-methyl-resorcinol melted at the same temperature. [Found: C, 72·5; H, 4·5; C_{10}H_{8}O_{3} requires C, 72·7; H, 4·6%.

7-Methoxy-8-methyl-coumarin (IX).—The above hydroxy coumarin (1 g.) was dissolved in anhydrous acetone (20 c.c.), excess of methyl iodide (2 c.c.) and potassium carbonate (2 g.) added and the mixture gently boiled under reflux for 20 hours. After filtering, the clear solution was distilled in order to recover the solvent, the solid residue was taken up in ether and washed with dilute sodium hydroxide in order to remove unmethylated hydroxy compound. After final washing with water, it was evaporated and the residue crystallised from alcohol. Colourless rectangular prisms and plates melting at 122–23° were obtained. This sample was found to be identical with the one prepared from the nuclear methylation product of β-resorcylic aldehyde. [Found: C, 69·4; H, 5·6; C_{11}H_{16}O_{3} requires C, 69·5; H, 5·3%.

Summary

A survey of past work on the nuclear methylation and ethylation of resorcinol and phloroglucinol derivatives is given and a mechanism for this reaction suggested. The nuclear methylation of β-resorcylic aldehyde has now been carried out giving rise to a good yield of the product (A). Its constitution as 4-methoxy-3-methyl-2-hydroxy benzaldehyde has been established in two ways: (i) A sample of 4-methoxy-3-methyl-2-hydroxy benzaldehyde was prepared according to the synthetic method of Jones and Robertson and compared with (A). (ii) The corresponding coumarin was prepared from (A) and was identified as 7-methoxy-8-methyl coumarin by comparison with the compound obtained by independent synthesis, starting from 2-methyl-resorcinol and passing through 7-hydroxy-8-methyl-coumarin as an intermediate stage. The same coumarin was also prepared by the reduction of umbelliferone-8-aldehyde and subsequent methylation.
REFERENCES

3. Perkin ..  *J. C. S.*, 1895, 990.
5. Jones and Robertson ..  *J. C. S.*, 1932, 1689.
12. Tiemann and Parrissius ..  *Ber.*, 1880, 13, 2366.