Synthesis of coumarins by transfer of C\textsubscript{3}-unit of cinnamic acids to phenols using polyphosphoric acid

J Bhattacharjee & S K Paknikar*
Department of Chemistry, Goa University, Bambolim, 403 005, Goa
Received 12 August 1988; accepted 30 January 1989

The reaction of cinnamic acid derivatives with different phenols in the presence of polyphosphoric acid gives coumarins in a single step, which involves transfer of the C\textsubscript{3}-unit of cinnamic acids to the phenols used. A plausible mechanism is proposed.

Because of our interest in the reactions of aromatic acids with phenols in the presence of PPA\textsuperscript{1}, our attention was drawn to the recent publication of Talapatra and coworkers who reported the formation of 7-methoxycoumarin (1) upon heating \(p\)-methoxycinnamic acid (2) and resorcinol monomethyl ether with PPA\textsuperscript{2}. The novel mechanism (Scheme 1) proposed by these authors finds a close analogy to the suggested mechanism of biosynthetic conversion of 2 into 1 by oxidative cyclisation\textsuperscript{3}. Though attractive, further evidence in support of the proposed mechanism appeared essential. In this communication we wish to report some interesting observations made during a study of the reactions of certain cinnamic acid derivatives with various phenols in the presence of PPA.

The results which are summarised in Table 1 clearly show that the aromatic ring of cinnamic acid gets eliminated under the experimental conditions used and leads to the formation of coumarin derivatives. The reaction of resorcinol monomethyl ether with ferulic acid and 3,4-dimethoxycinnamic acid (entries 1 and 2, Table 1) substantiate this claim as 7-methoxycoumarin (1) was the end product in each case.

The most likely mechanism which would account for all the observations made during the present and the previous studies\textsuperscript{2} is given in Scheme 2. That 4-aryl-3,4-dihydrocoumarins are intermediates in the above transformation finds support from the actual isolation of 6-chloro-4-(4'-methoxyphenyl)-3,4-dihydrocoumarin (3) (entry 5, Table 1). In fact isolation of 7-hydroxy-4-(4'-methoxyphenyl)-3,4-dihydrocoumarin (4) and its methyl ether from the reaction of 2 in the presence of PPA with resorcinol and resorcinol monomethyl ether respectively was reported by Talapatra \textit{et al.}\textsuperscript{2} under slightly different experimental conditions and can be taken as a further support to the present mechanism (Scheme 2). Reaction of 4 with PPA should afford 1. Attempts to isolate 4 following the reaction conditions of Talapatra \textit{et al.}\textsuperscript{2} however, resulted in the isolation of 1.

It should be pointed out that further treatment of compound 3 with PPA at 70° for 6 hr resulted in the recovery of the starting material. Presumably the intermediate carbocation 5 is not formed under these experimental conditions as the position of the chlorine atom is not favourable to assist its stabilisation in contrast to the methoxy substituent at C-7.
Table 1 — Reactions of cinnamic acid derivative with various phenols

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Phenol</th>
<th>Cinnamic acid</th>
<th>Product</th>
<th>m.p. (°C)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Resorcinol monomethyl ether</td>
<td>4-Hydroxy-3-methoxy</td>
<td>1</td>
<td>118^2</td>
<td>40</td>
</tr>
<tr>
<td>2</td>
<td>Resorcinol monomethyl ether</td>
<td>3,4-Dimethoxy</td>
<td>1</td>
<td>118</td>
<td>37</td>
</tr>
<tr>
<td>3</td>
<td>α-Naphthol</td>
<td>p-Methoxy</td>
<td>6</td>
<td>(140)^4</td>
<td>42</td>
</tr>
<tr>
<td>4</td>
<td>β-Naphthol</td>
<td>-Do-</td>
<td>7</td>
<td>(118)^4</td>
<td>35</td>
</tr>
<tr>
<td>5</td>
<td>p-Chlorophenol</td>
<td>-Do-</td>
<td>3</td>
<td>(118)^4</td>
<td>37</td>
</tr>
</tbody>
</table>

All known coumarins were characterised by their spectral data and physical constants. PMR of 3 (CDCl₃, 80 MHz; δ 3.0(d,2HJ = 7.5 Hz), 3.85(s,3H), 4.28(t,1HJ = 7.5 Hz) & 6.8-7.5(m,7Hz).
In conclusion, this work provides a convenient synthesis of coumarins by transfer of the C3-unit of cinnamic acids to the phenols used under acidic conditions. Though the yields are somewhat lower as compared to those reported in other recently reported coumarin syntheses, the simplicity and one-pot operation would be in favour of the present synthesis. Investigations which are currently in progress are expected to clarify the scope and utility of the present method.

We thank the CSIR, New Delhi for the award a senior research fellowship (to JB) and the UGC, New Delhi for a National Fellowship (to SKP). We are grateful to the Director, NIO, Goa for providing facilities (to JB).

References