

Communications

Synthesis of coumarins by transfer of C₃-unit of cinnamic acids to phenols using polyphosphoric acid

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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 C₃-unit of cinnamic acids to the phenols used. A plausible mechanism is proposed.

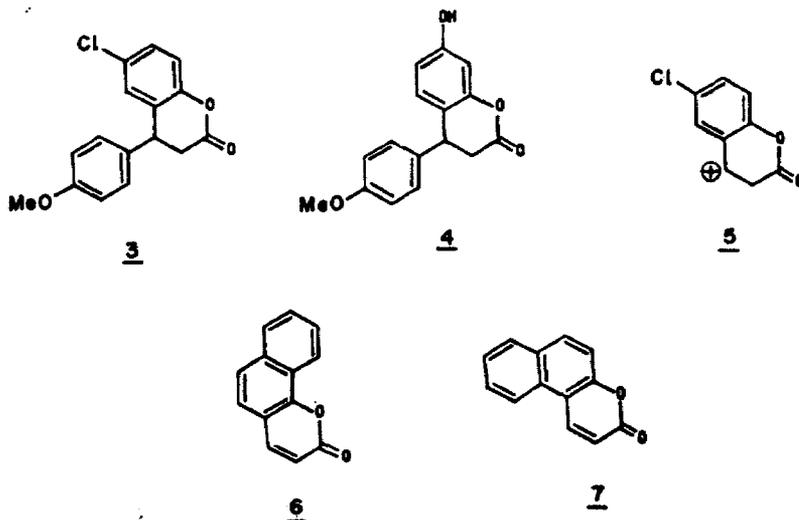
Because of our interest in the reactions of aromatic acids with phenols in the presence of PPA¹, our attention was drawn to the recent publication of Talapatra and coworkers who reported the formation of 7-methoxycoumarin (**1**) upon heating *p*-methoxycinnamic acid (**2**) and resorcinol monomethyl ether with PPA². 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 cyclisation³. 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.

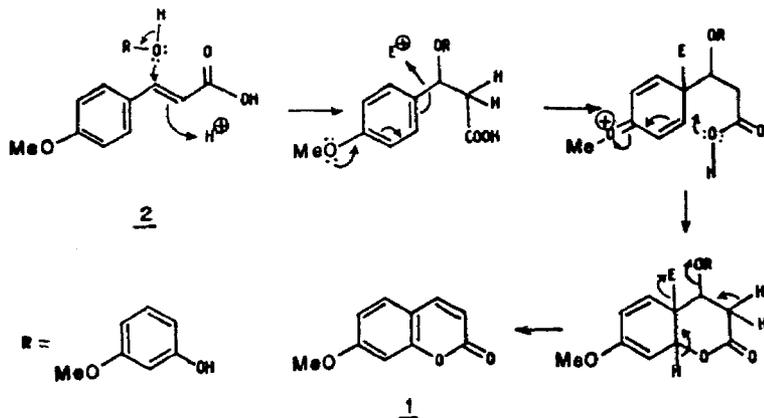
The results which are summarised in Table 1 clearly show that the aromatic ring of cinnamic acid gets el-

minated 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.

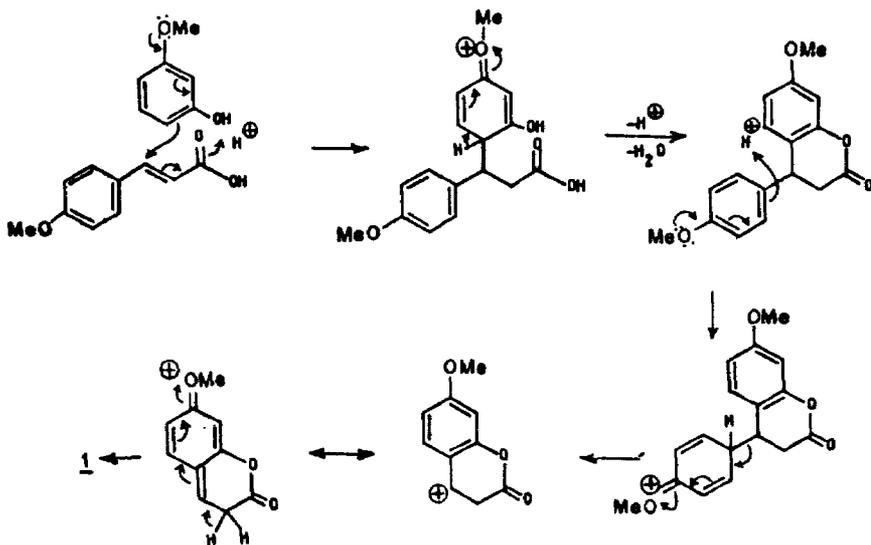
The most likely mechanism which would account for all the observations made during the present and the previous studies² is given in Scheme 2. That 4-aryl-3,4-dihydrocoumarins are intermediates in the above transformation finds support from the actual isolation of 6-chloro-4-(4'-methoxyphenyl)-3,4-dihydrocoumarin (**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 *et al.*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 *et al.*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.





Scheme - 1



Scheme - 2

Table 1—Reactions of cinnamic acid derivative with various phenols
[Reaction temp. = 70°C; reaction time: 1 hr for entry 2 and 4 hr for the rest]

Sl. No.	Phenol	Cinnamic acid	Product	m.p. (°C)	Yield (%)
1	Resocinol mono-methyl ether	4-Hydroxy-3-methoxy	1	(118) ² (118) ²	40
2	Resocinol mono-methyl ether	3,4-Dimethoxy	1	118	37
3	α -Naphthol	<i>p</i> -Methoxy	6	(140) ⁴ (141) ⁴	42
4	β -Naphthol	-Do-	7	(118) ⁴ (118) ⁴	35
5	<i>p</i> -Chlorophenol	-Do-	3	130	37

All known coumarins were characterised by their spectral data and physical constants. PMR of 3 (CDCl₃, 80 MHz): δ 3.0(d, 2H, J = 7.5 Hz), 3.85(s, 3H), 4.28(t, 1H, J = 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^{5,6}, 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.

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