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AN ABNORMAL CLAISEN REARRANGEMENT OF
5-HYDROXY-7-CINNAMYLOXY-2-METHYLCHROMONE

A.C. JAIN* and R.K. GUPTA
Department of chemistry, Himachal Pradesh University,
The Manse, Simla -171001, India

The Claisen rearrangement of 5-hydroxy-7-cinnamyloxy-2-methyl chromone (2) has yielded 4',5'-dihydro-5-hydroxy-2,4'-dimethyl-5'-phenyl-furo (2',3':7,8) chromone (6) as established by its NMR spectrum and that of its acetate and methyl ether. The pathway of its formation presumably has structures 3 to 5.

The Claisen rearrangement of cinnamyl ethers of polyphenols is of current interest because it can afford different types of natural products such as cinnamyl phenols,[1] 3,3-diphenyl-1-propenes,[2] and related neoflavonoids.[2] In this connection, cinnamyl ethers of simple phenols like resorcinol and pyrogallol derivatives were first rearranged by Barnes et al.[3] and found to give p-cinnamylphenols and o-(1-phenylallyl) phenols. Both are symmetry - allowed products. However, more recently tocyl cinnamyl ether was found to give both the possible ortho cinnamyl phenols[4] which products are forbidden by the Woodward - Hoffmann's selection rules. This anamolous Claisen rearrangement was considered characteristic of 6-hydroxy chromene structure present in tocyl residue. We report here still another type of Claisen rearrangement with-5-hydroxy-7-cinnamyloxy-2-methylchromone(2).

5,7-Dihydroxy-2-methylchromone (1) when refluxed with one mole of cinnamylbromide in the presence of K_2CO_3 and acetone, yielded 7-cinnamyl ether (2); m.p. 121-22°; R_f 0.54 (Solvent);[5] violet ferric reaction; NMR[6] 2.35 (s, 3H, CH_3 in 2 position), 4.75 (d, J 5.5Hz, 2H, $-O-CH_2$), 6.00 (s, 1H, olefinic H 3), 6.36 (broad s, 1H, ArH 6), 6.36 - 6.58 (m, 2H, 1-CH=CH-),

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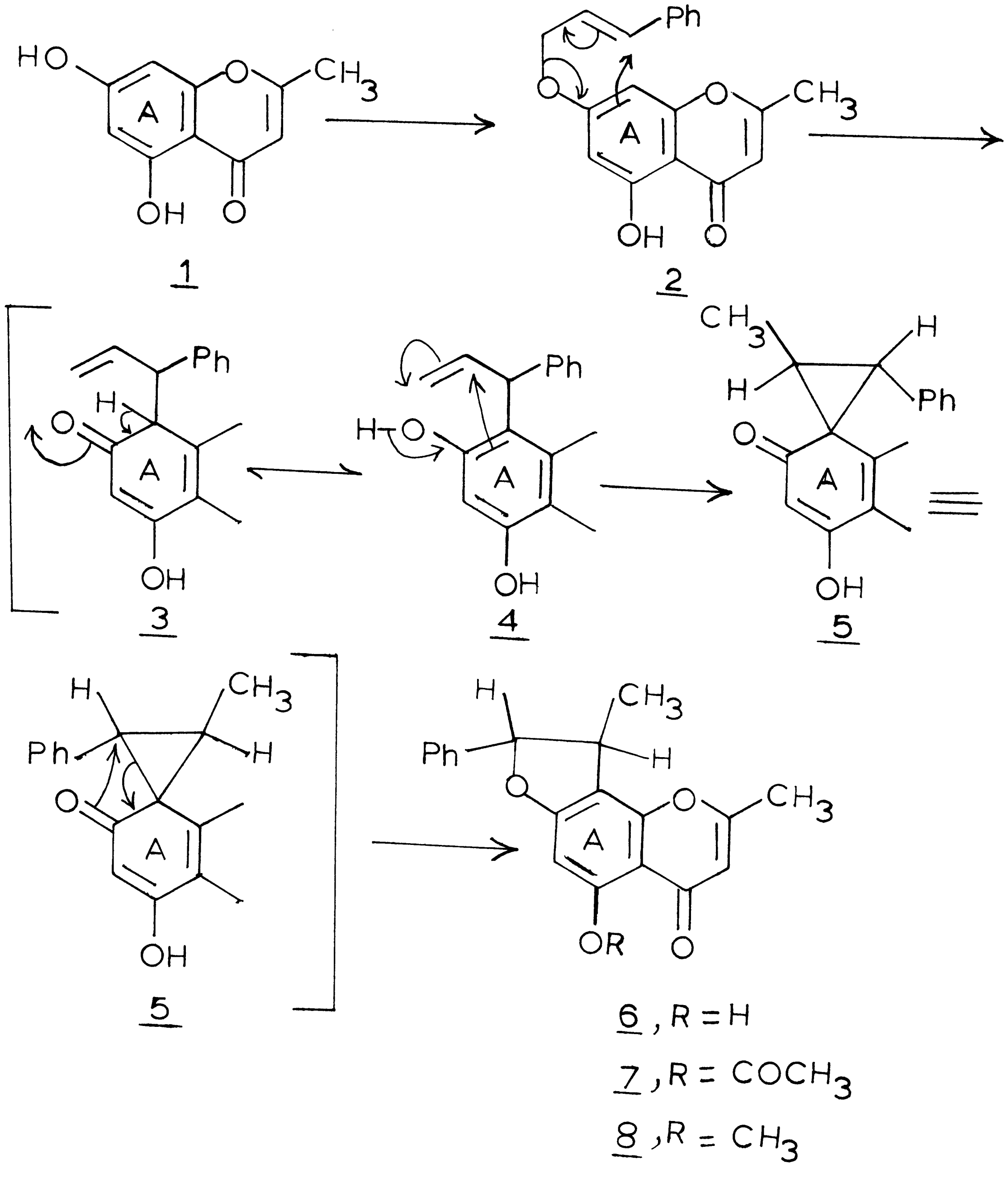
*To whom correspondence should be addressed.

6.65 (d, J 1Hz, 1H, ArH 8), 7.35 (d, J 1.5Hz, 5H, C_6H_5) and 13.00,(s, 1H chelated OH) (Found: C, 73.7; H, 5.2. $C_{19}H_{16}O_4$ requires C, 74.0; H, 5.2%). This cinnamyl ether (2) was heated *in vacuo* at 240-60° for 5 hours and the product purified by column chromatography when one crystalline product (A) was obtained, m.p. 161-62°; R_f 0.55 (Solvent);[5] green ferric reaction. Elemental analysis (Found: C, 73.8; H, 5.0. $C_{19}H_{16}O_4$ requires C, 74.0; H,



5.2%) showed it to be an isomeric compound. Since it formed only monoacetate (NMR 2.29, s, 3H, $OCOCH_3$; m.p. 135-36°) and a monomethyl ether (NMR 3.95, s, 3H, OCH_3 ; m.p. 156-57°), 7-hydroxyl is obviously engaged. NMR spectra of the product A, its acetate, and methyl ether indicated the presence of condensed 2-phenyl-3-methyl-2,3-dihydrofuro unit, besides one aromatic proton, one methyl group in the 2-position and one olefinic hydrogen in the 3-position (see Table 1). Thus there is a characteristic doublet of a methyl group round 1.55, a multiplet and a doublet of two protons round 3.65 and 5.35 and a singlet of one phenyl group at about 7.40. The orientation of the dihydrofuro ring is established as angular one because the aromatic signal at 6.32 in the hydroxy compound (A) and 6.38 in its methyl ether undergo a downfield shift to 6.62 in the acetate. Hence the structure of the Claisen rearrangement product (A) is 4',5'-dihydro-5-hydroxy-2,4'-dimethyl-5'-phenyl-furo(2',3': 7,8)chromone (6) and consequently acetate is (7) and methyl ether is (8). The stereochemistry of the dihydrofuro moiety is difficult to be decided on the basis of vicinal coupling constant of two protons which is known to be the same for both the cis- and trans-isomers.[7]

The Claisen product (6) is abnormal and its formation can be rationalised as follows. In the first step the normal Claisen rearrangement product namely 5,7-dihydroxy-2-methyl-8-(1-phenylallyl)chromone (4) is formed which undergoes further thermal rearrangement via the cyclic intermediate (5) to give the final product (6). The formation of the product (6) is interesting because two natural products obtusafuran[7] and melanoxin[8] have such a condensed dihydrofuro system.

Table 1

Compound	$2\text{-}CH_3$	3-H	6-H	4'H	5'H	$4'CH_3$	$5'C_6H_5$	5-OH or $5\text{-}OCH_3$ or $5\text{-}OCOCH_3$
(6)	2.35(s)	6.00(s)	6.32(s)	3.62(m)	5.32(d*)	1.57(d*)	7.38(s)	13.10(s)
(7)	2.42(s)	6.00(s)	6.62(s)	3.74(m)	5.42(d*)	1.60(d*)	7.42(s)	2.29(s)
(8)	2.24(s)	5.96(s)	6.38(s)	3.62(m)	5.32(d*)	1.56(d*)	7.32(s)	3.95(s)

*J values in all cases are 7Hz.

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5. TLC was carried out on Silica gel G chromoplates using benzene: ethyl acetate mixture (9:1) as the Solvent. TLC plates were sprayed with 1% alcoholic $FeCl_3$ or 10% aq. H_2SO_4.
6. NMR spectra were recorded with a 60 MHZ NMR spectrophotometer in $CDCl_3$ and chemical shifts are expressed in δ values.
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