

It has also been reported²² that the R_f values of the metal ions after being complexed with ligands present in solvent have not been found to be appreciably different from the R_f values obtained by spotting the prepared complexes. Hence a similar behaviour may be expected in solvent system 2. Halide anions have been shown to influence the composition of the divalent metal ion complexes with neutral monodentate ligands¹⁷⁻²⁰. A similar effect of anions on the composition may be expected during the partition of the metal ions leading to differences in the R_f values in solvent systems 4 and 6. Further work in extracting and characterising the actual species formed during the chromatographic separation is in progress.

The present investigation indicates that separation of metal ions could be achieved by the use of solvent systems containing neutral monodentate ligands and halide anions.

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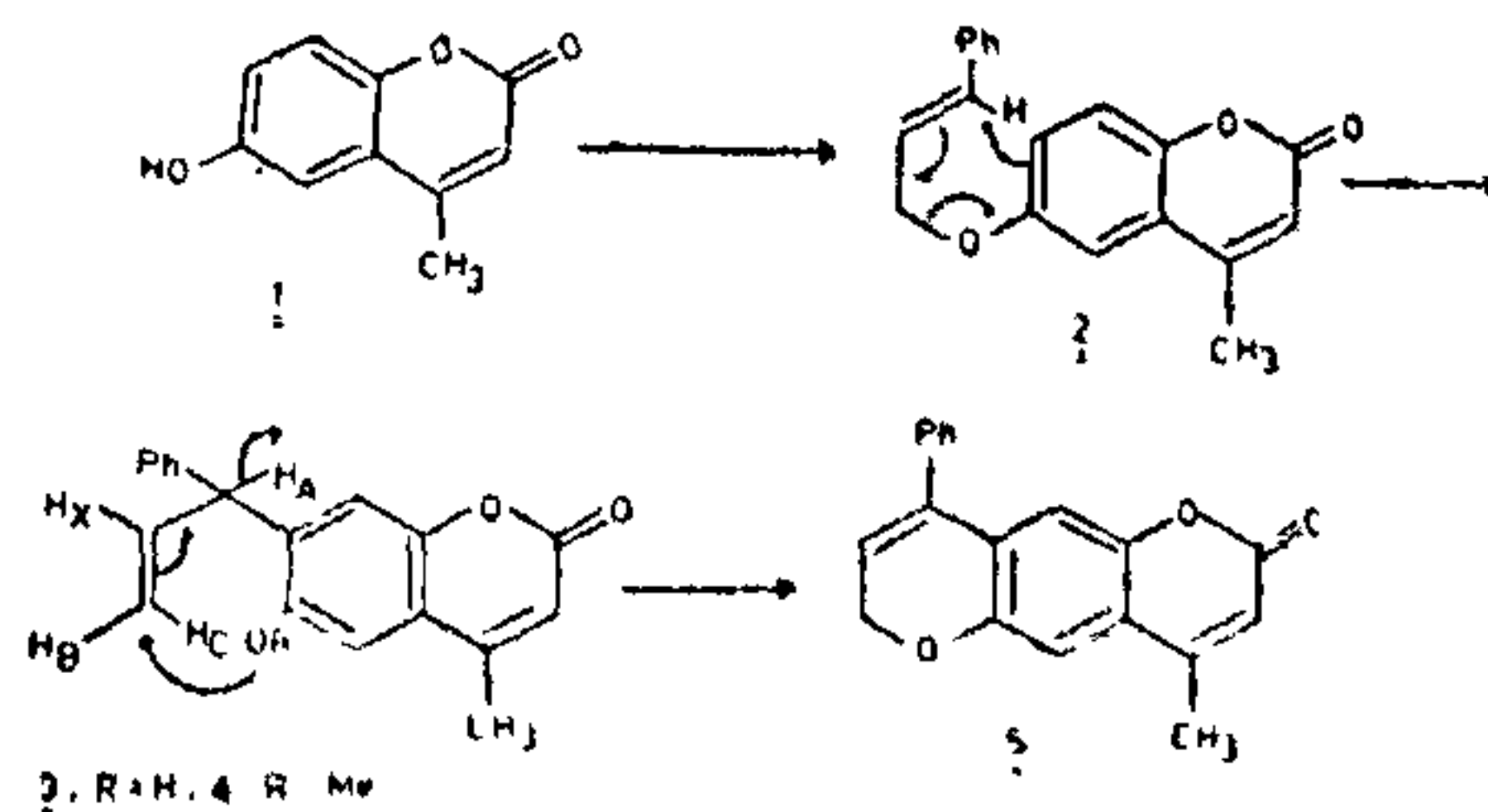
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A NOVEL PRODUCT IN THE CLAISEN REARRANGEMENT OF 6-CINNAMYLOXY-4-METHYL COUMARIN

DURING the Claisen rearrangement, 6-cinnamyloxy-4-methyl coumarin (2) forms the normal rearranged product, viz., 4-methyl-6-hydroxy-7-(1-phenyl-allyl) coumarin (3) and its oxidatively cyclised neoflavene (5). The latter type of product has been noted for the first time in this reaction.

The Claisen rearrangement of cinnamyl ethers of polyphenols could be a method alternative to direct C-cinnamylation method for the preparation of cinnamylated polyphenols or their modified forms^{1,2}. While studying this rearrangement in various cinnamyloxy coumarins, a novel product has been observed in one case, i.e., 6-cinnamyloxy-4-methyl coumarin (2).



6-Hydroxy-4-methyl coumarin³ (1) when refluxed with one mole of cinnamyl bromide in the presence of K_2CO_3 and acetone yielded 6-cinnamyl ether (2), m.p., 145-46; R_f 0.35 (solvent)⁴; UV (nm)⁵, 218, 254 and 320 (4.53, 4.57 and 4.46 respectively); NMR⁶, 2.34 (s, 3H, CH_3 in 4 position), 4.67 (d, J = 6 Hz, 2H, CH_2O), 6.20 (s, 1H, H-3), 6.39-6.82 (m, 2H, $H_2C-CH-CH Ph$), 7.05 (d, J = 9 Hz, 1H, H-8), 7.30 (d, J = 9 Hz, 1H, H-7), 7.05-7.35 (m, 5H, C_6H_5) and 7.37 ppm (d, J = 3 Hz, 1H, H-5). When

2 was refluxed with *N,N*-dimethylaniline a mixture of two products was obtained. One compound crystallised from benzene-light petroleum mixture to afford 4-methyl-4'-phenyl-6' (H)-pyrano (2', 3': 6, 7) coumarin (**5**) as light yellow crystalline product, m.p., 119–20°; R_f 0.45; UV (nm), 226, 280 and 344 (3.92, 3.42 and 3.40 respectively); NMR, 2.43 (s, 3H, CH_3 in 4 position), 4.73 (d, $J = 5$ Hz, 2H, O- CH_2 -CH=), 6.28 (s, 1H, *H*-3), 6.75–7.03 (m, 1H, - CH_2 -CH=), 7.08 (d, $J = 1.5$ Hz, *H*-8), 7.28 (d, $J = 1.5$ Hz, *H*-5) and 7.20–7.45 ppm (m, 5H, C_6H_5). The second product crystallised from ethyl acetate-light petroleum mixture as colourless crystals to yield 4-methyl-6-hydroxy-7 (1-phenyl allyl) coumarin (**3**); m.p., 242–43°; R_f 0.38; UV (nm), 225, 245 and 330 (4.24, 4.19 and 3.87); NMR, 2.40 (s, 3H, CH_3 in 4 position), 4.80–5.01 (m, 1H, *H*-A), 5.04–5.30 (m, 1H, *H*-C), 5.30–5.52 (m, 1H, *H*-B), 5.94–6.32 (m, 1H, *H*-X), 6.25 (s, 1H, *H*-3), 6.90 (s, 1H, *H*-8), 7.1 (s, 1H, *H*-5), and 7.12–7.30 ppm (m, 5H, C_6H_5). This formed methyl ether (**4**), m.p., 180–81°; R_f 0.49; UV (nm), 228 and 250 (4.01 and 3.82 respectively); NMR, 2.42 (s, 3H, CH_3 in 4 position), 3.84 (s, 3H, CH_3O), 4.80–5.0 (m, 1H, *H*-A), 5.04–5.28 (m, 1H, *H*-C), 5.29–5.52 (m, 1H, *H*-B), 5.93–6.33 (m, 1H, *H*-X), 6.25 (s, 1H, *H*-3), 6.91 (s, 1H, *H*-8), 7.01 (s, 1H, *H*-5) and 7.28 ppm (br s, 5H, C_6H_5).

The formation of (**3**) can be explained by a normal Claisen rearrangement with favoured migration to the 7-position rather than the 5-position, whereas that of (**5**) can be explained as a result of subsequent oxidative cyclisation to give a six-membered ring. The type of neoflavene ring present in **5** has never been noted earlier in the Claisen rearrangement but is present in some naturally occurring neoflavonoids⁷.

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4. R_f refers to t.l.c. carried out on silica gel-G plate using ethyl acetate: benzene (1:9) as the solvent.
5. UV data were recorded in methanol; figures before parenthesis represent λ_{max} values, whereas those in parenthesis are $\log \epsilon$ values.

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STUDIES ON THE MAJOR ACIDIC POLYSACCHARIDE FROM THE SEED MUCILAGE OF *OCIMUM CANUM*

IN continuation of our studies concerning the structure-function relationship in polysaccharides^{1,2}, we wish to report the isolation, and the physico-chemical characterization of the major acidic polysaccharide from the seed mucilage of *Ocimum canum*.

The acid-soluble portion of the mucilage of *O. canum*¹ obtained in improved yield (40%), by ethanol-sodium acetate precipitation, on DEAE-cellulose fractionation by stepwise elution successively with water, 0.05, 0.1, 0.2, 0.3, 0.4 and 0.5N sodium hydroxide gave one major and four minor acidic fractions. The nature and composition of these fractions are given in Table I. The compositions of these fractions were determined by the g.l.c. analysis, on 3% SE-52, of the trimethylsilyl ethers of the sugars present in the acid hydrolyzates of the respective fractions.

The major acidic fraction obtained in 55% yield was further purified by repeated DEAE-cellulose chromatography. Ultracentrifugal analysis of 0.4% solution of the polysaccharide in 0.1M sodium acetate-acetic acid buffer, pH 4.8, indicated a single sharp peak (sedimentation coefficient 11.1S). However free boundary electrophoresis of 1.0% solution of the polysaccharide in 0.05M sodium tetraborate, pH 9.26, indicated a trace amount of impurity having lower mobility than the major polysaccharide (electrophoretic mobility $-1.8 \times 10^{-4} \text{ cm}^2 \text{ sec}^{-1} \text{ volt}^{-1}$). The impurity was found to be strongly associated with the polysaccharide and attempts at further purification using sephadex G₂₀₀ were unsuccessful, and it was found to be excluded through the column indicating its high molecular weight. The molecular weight as determined by light scattering technique was 3.03×10^6 . The polysaccharide had an intrinsic viscosity of 22.6 dl/g and an uronic acid content of 34% as determined by the carbazole-sulfuric acid method³.

Hydrolysis of the polysaccharide with 0.5M sulfuric acid, separation of the resulting sugars into neutral and acidic portions using Amberlite IR-120 (H^+) and Amberlite IRA-400 (CO_3^{2-}), and g.l.c. analysis⁴ of the neutral sugars as their alditol acetates on 3% ECNSS-M indicated the presence of xylose, arabinose, rhamnose and galactose in the molar ratio 9.7: 6.0: 7.7: 1.1. Paper chromatographic examination of the acidic sugars using 4: 1: 5 *n*-butanol, acetic acid, water (upper