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Synthetic studies in cinnamylated derivatives of resacetophenone and related compounds

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Abstract. Resacetophenone (1) reacts with cinnamyl bromide in the presence of K_2CO_3 and acetone to give its 4-O-cinnamyl derivative (2); whereas the same reaction in the presence of methanolic methoxide affords 3-C-cinnamyl-(6), 5-C-cinnamyl-(8) and 3,5-di-C-C-cinnamyl- (4) derivatives in the ratio of 36 : 1 : 15. Reaction of 1 with cinnamyl alcohol in boiling formic acid results in the formation of 8 in the largest amount followed by 6 and a new compound which is a mono-C-cinnamyl flavan (10 or 11). 6 was converted into the corresponding flavan (12), flavene (13) and 4-hydroxycoumarin (14).

On Claisen rearrangement yielded a mixture of three compounds, two of which were found to be the normal products viz. 3-(1-phenyl-allyl) resacetophenone (18) and its 5-isomer (19). The third but major compound was the further rearranged but uncyclised 3-(1-phenyl-1-propenyl) derivative (15) which forms the corresponding chalcone (21) when condensed with anisaldehyde in the presence of alkali.

Keywords. C- and O-cinnamylation; Claisen rearrangement; 1-phenyl-1-propenyl and 1-phenyl-allyl derivatives.

1. Introduction

Some natural polyphenols have a cinnamyl unit in its varied forms. Particularly two groups of natural compounds called neoflavonoids and cinnamylphenols (Gregson *et al* 1968) occurring in the species of Dalbergia and Machaerium may be mentioned. The introduction of a cinnamyl or its modified unit in a polyphenol can be brought about in two broad ways, involving direct cinnamylation or transformation of C- or O-cinnamyl residue. Nuclear cinnamylation is not only an important biochemical reaction which seems to render the timbers durable and resistant to attack by insects, fungi and larvae. Direct cinnamylation of polyphenols has been achieved earlier either with cinnamyl bromide in the presence of methanolic sodium methoxide or with cinnamyl alcohol in the presence of an acid. Thus 2-methyl-5, 7-dihydroxyisoflavone and 2-methyl-5,7-dihydroxychromone were studied by Jain and Gupta (1975a); alkaline conditions afforded 6-C-cinnamyl derivatives and acidic conditions made available 8-C-cinnamyl derivatives besides the di-C-C-cinnamyl derivatives in both the cases. O-Cinnamylation occurs with cinnamyl bromide in the presence of potassium carbonate and acetone and the resulting ethers have been rearranged successfully to give different variants of cinnamyl residue (Jain and Gupta 1974,

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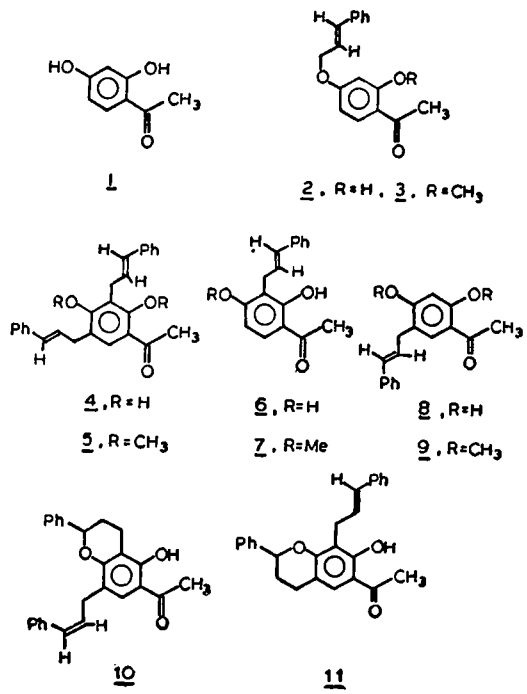
1975b, Jain *et al* 1977). In continuation of this work, cinnamylation of resacetophenone has been studied in detail using all these methods with a view to provide differently cinnamylated compounds which could in turn be used for the preparation of more elaborated polyphenols.

2. Results and discussion

2.1. *Cinnamylation under alkaline conditions*

Resacetophenone (1) when reacted with one mole equiv. of cinnamylbromide in the presence of potassium carbonate and acetone yielded only its 4-cinnamyl ether (2) which showed in its NMR spectrum one doublet of one methylenoxy protons at δ 4·60, one multiplet of two olefinic protons at δ 6·25–6·45 and another of a phenyl group at δ 7·20–7·32 besides the resonance signals of the starting compound. On the other hand, when it was refluxed with cinnamylbromide in the presence of methanolic sodium methoxide, it gave a mixture of four products which could be separated by column chromatography. The first mobile fraction proved to be 4-O-cinnamyl resacetophenone (2) identical with the one prepared above. The next fraction was identified as 3,5-di-C-C-cinnamyl resacetophenone (4) as it formed dimethyl ether (5) showing two singlets of two $-OCH_3$ groups at δ 3·75 and 3·82. Further NMR spectra of both the hydroxy compound (4) and the methyl ether (5) showed only one aromatic hydrogen and two cinnamyl units. The next compound was established as 3-C-cinnamyl resacetophenone (6) by its NMR spectrum. Thus it shows resonance signals of only C-cinnamyl unit and of two *ortho* coupled aromatic protons at δ 6·39 and 7·50. Further it formed monomethyl ether (7) having chelated hydroxyl group.



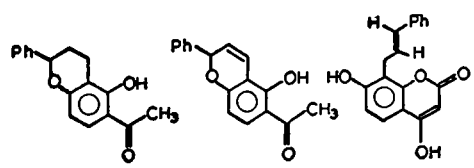
The last compound formed in the above cinnamylation reaction but in a very small amount proved to be 5-C-cinnamyl resacetophenone (8) by its NMR spectrum which shows resonance signals of one cinnamyl unit and two *p*-coupled aromatic protons at δ 6·25 and 7·46. 8 also formed a dimethyl ether. The formation of 8 albeit in small amounts is a reaction product which type is normally not formed under alkaline conditions of nuclear alkylation. But it cannot be ruled out, when di-alkyl derivatives have been isolated.

2.2. *Cinnamylation under acidic conditions*

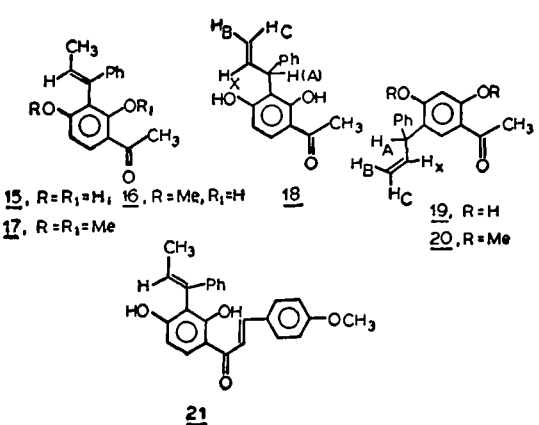
Resacetophenone when heated with cinnamyl alcohol in formic acid medium gave a mixture of three compounds. The compound formed in the largest amount was identified as 5-C-cinnamyl resacetophenone (8) by direct comparison with the sample prepared above. The second compound was similarly identified as 3-C-cinnamyl resacetophenone (6). The last minor compound proved to be 5-hydroxy-6-acetyl-8-cinnamyl flavan (10) or its isomer (11). Thus its NMR showed signals of one C-cinnamyl unit, one aromatic proton and five protons of ABMNX system (two protons appeared as a multiplet centred at δ 2·12, another two appeared as a triplet at δ 2·65 and the fifth proton resonated as a triplet at δ 6·22). A distinction between 10 and 11 is possible by a study of NOE on irradiating the aromatic proton, and this is under investigation.

2.3. *Derivatives from 3-C-cinnamyl resacetophenone*

The above experiments indicated that the alkaline method is the best method for getting 3-C-cinnamyl-(6) and 3,5-di-C,C-cinnamyl-(4) derivatives and the acid



12 13 14



15, R=R₁=H; 16, R=Me, R₁=H
17, R=R₁=Me

18

19, R=H
20, R=Me

21

method is the best for 5-*C*-cinnamyl (8) derivative. As a model case, 3-C-cinnamyl resacetophenone (6) has been converted into various derivatives. Cyclisation with formic acid gave 5-hydroxy-6-acetyl flavan (12); whereas cyclodehydrogenation with DDQ yielded 5-hydroxy-6-acetyl flav-3-ene (13). The structures of both the products were supported by their NMR spectra. It may be noted that the flavene is unstable under acidic conditions because of the presence of a hydrogen atom in the 2-position. Further when 6 was heated with ethyl chloroformate in the presence of potassium carbonate and acetone, 4,7-dihydroxy-8-C-cinnamyl coumarin (14) was obtained as shown by its UV and NMR spectra.

2.4. *The Claisen rearrangement of 4-cinnamyl ether*

The Claisen rearrangement of 4-O-cinnamyl resacetophenone (2) was studied by heating it in *N*, *N*-dimethylaniline when a mixture of three products was isolated. The compound formed in the largest amount was identified as 2, 4-dihydroxy-3-(1-phenyl-1-propenyl) acetophenone (15). In accordance with this structure, it formed monomethyl ether (16) and a dimethyl ether (17) and the hydroxy compound showed resonance signals of two *ortho* coupled aromatic protons at δ 6·52 and 7·63 and one olefinic methyl as a doublet and an olefinic proton as a multiplet centred at δ 6·57. The other two products were characterised similarly as 3-(18) and 5-(19) (1-phenylallyl) derivatives of resacetophenone. These two products are the normal rearranged products in both the available positions, but the first major compound (15) being thermodynamically more stable is formed as a result of further allylic rearrangement of 18. As a model case, 3-(1-phenyl-1-propenyl) resacetophenone (15) has been converted into the corresponding chalcone (21) by condensation with anisaldehyde in the presence of alkali.

3. Experimental

All melting points are uncorrected. Unless stated otherwise, all UV data were recorded in MeOH; NMR spectra were determined in $CDCl_3$ using 80 MHz BS 487C spectrometer and TMS as an internal standard; the chemical shifts are reported in δ values; light petroleum ether used had the boiling range 60–80°; silica gel was used for column chromatography, R_f values are for TLC on silica gel-G using following solvent systems: (A) ethyl acetate: benzene (15:85), (B) ethyl acetate: benzene (1:9); 10% H_2SO_4 or 1% alcoholic $FeCl_3$ was used as spraying agent for development of the TLC plates.

3.1. 4-*O-Cinnamyl resacetophenone* (2)

An acetone solution of resacetophenone (1, 4 g) was refluxed with cinnamylbromide (5 ml) and anhydrous potassium carbonate (20 g) for 6 hr. Acetone was distilled, water added and the solid collected. (2) crystallised from benzene-light petroleum as colourless crystals (3·5 g), mp 110–11° (Found: C, 76·1; H, 5·8. $C_{17}H_{16}O_3$ requires C, 76·1; H, 5·9%); R_f 0·8 (solvent A); brown ferric reaction; λ_{max} 218, 252 and 270 nm (log ϵ 3·84, 4·32, 4·53); 60 MHz NMR: 2·40 (s, 3H, $-COCH_3$), 4·60 (d, J = 5 Hz

2H, OCH_2—CH =), 6·25–6·45 (m, 2H, CH_2—CH = CH), 6·45 (d, J_{ortho} = 10 Hz, 1H, H—5), 7·18 (d, J_{meta} = 3 Hz, 1H, H—3), 7·20–7·32 (m, 5H, C_6H_5) and 7·49 (d, J_{ortho} = 10 Hz, 1H, H—6).

3.2. *Nuclear cinnamylation of resacetophenone under alkaline conditions*

To a solution of resacetophenone (1, 6 g) in anhydrous methanol (150 ml) a methanolic solution of sodium methoxide (7 g Na/100 ml MeOH) was added. The resulting solution was cooled, treated with cinnamyl bromide (20 ml) in one lot and then refluxed for 10 hr. The solvent was distilled and the residue treated with ice, acidified with HCl (1:1) and extracted with ether. The ethereal extract was washed with water (2 × 200 ml), dried (Na_2SO_4) and evaporated. The residue on column chromatogrpahy and successive elution with benzene-light petroleum (1:9), benzene-light petroleum (1:4 followed by 1:1) gave four fractions A-D.

Fraction A crystallised from benzene-light petroleum mixture to give 2 as colourless crystals (250 mg), identical with the authentic sample prepared above in mp and TLC.

Fraction B crystallised from benzene-light petroleum mixture to yield 3,5-di-C-cinnamyl resacetophenone (4) as light yellow needles (750 mg), mp 168–69° (Found: C, 81·1; H, 6·4. $C_{26}H_{24}O_3$ requires C, 81·2; H, 6·2%); R_f 0·75 (solvent B); brown ferric reaction; λ_{max} 280 and 330 nm (log ϵ 4·32 and 3·90 respectively); NMR: 2·50. (s, 3H, $COCH_3$), 3·46 (d, J = 5 Hz, 2H, Ar—CH_2—CH=), 3·58 (d, J = 5 Hz, 2H, Ar—CH_2—CH =), 6·25–6·45 (m, 4H, 2ArCH$_2$—CH = CH—), 7·17–7·30 (m, 10H, $2C_6H_5$) and 7·40 (s, 1H, H-6).

Fraction C crystallised from benzene-light petroleum mixture to afford 3-C-cinnamyl resacetophenone (6) as colourless crystals (1·8 g); mp 147–48° (Found: C, 76·2; H, 5·8. $C_{17}H_{16}O_3$ requires C, 76·1; H, 5·9%); R_f 0·7 (solvent B); dark brown ferric reaction; λ_{max} 220, 252 and 320 nm (log ϵ 3·42, 4·25 and 3·95 respectively); NMR: 2·52 (s 3H, —$COCH_3$), 3·60 (d, J = 5 Hz, 2H, Ar—CH_2—CH=), 6·39 (d, J_{ortho} = 10 Hz, 1H, H-5), 6·25–6·50 (m, 2H, CH_2—CH=CH—). 7·12–7·32 (m, 5H, C_6H_5) and 7·50 (d, J_{ortho} = 10 Hz, 1H, H-6).

Fraction D crystallised from ethyl acetate-petroleum ether to give (8) as colourless crystals (50 mg), m p 135–36° (Found: C, 75·9; H, 6·0. $C_{17}H_{16}O_3$ requires C, 76·1; H, 5·9%); R_f 0·55 (solvent B); brown ferric reaction; λ_{max} 208 and 325 nm (log ϵ 4·52 and 3·92 respectively); NMR: 2·45 (s, 3H, —$COCH_3$), 3·56 (d, J = 5 Hz, 2H, Ar-CH_2-CH=), 6·12–6·50 (m, 2H, CH_2—CH=CH—), 6·25 (s, 1H, H-3), 7·0–7·77 (m, 5H, C_6H_5) and 7·46 (br s, 1H, H-6).

3.2.1. 2-*Methoxy*-4-*cinnamyloxy acetophenone* (3)

A mixture of 4-O-cinnamylresacetophenone (2, 100 mg), dimethyl sulphate (0·14 ml) and anhydrous potassium carbonate (0·5 g) in dry acetone was refluxed for 8 hr. Acetone was distilled and water added to the residue. The solid thus obtained was crystallised from methanol when 3 was obtained as colourless crystals (80 mg), mp 65–66° (Found: C, 76·4; H, 6·2. $C_{18}H_{18}O_3$ requires C, 76·6; H, 6·4%); R_f 0·58 (solvent B); λ_{max} 207, 252 (log ϵ 4·25 and 3·55 respectively); NMR: 2·59 (s, 3H,

—$COCH_3$), 3·92 (s, 3H, CH_3O—), 4·68 (d, J=5 Hz, 2H, OCH_2—CH=), 6·25–6·75 (m, 2H, CH_2—CH=CH—), 6·62 (dd, J_{ortho} =9 Hz, J_{meta} =3 Hz, 1H, H-5), 7·29 (d, J=3 Hz, 1H, H-3), 7·19–7·57 (m, 5H, C_6H_5) and 7·88 (dd, J_{ortho} = 9 Hz, J_{meta} = 3 Hz, 1H, H-6).

3.2.2. 2,4-*Dimethoxy*-3,5-*di*-C, C-*cinnamylacetophenone* (5)

An acetone solution of 3,5-di-C, C-cinnamyl resacetophenone (100 mg), potassium carbonate (1·0 g) and dimethyl sulphate (0·3 ml) was refluxed for 10 hr. The product crystallised from methanol to give 5 as colourless needles (85mg), mp 150–51° (Found: C, 81·5; H, 6·7. $C_{28}H_{28}O_3$ requires C, 81·6; H, 6·8%); R_f 0·70 (solvent B); λ_{max} 210 and 260 nm (log ϵ 4·33 and 3·92 respectively); NMR: 2·62 (s, 3H, —$COCH_3$), 3·06 (d, J=5 Hz, 2H, Ar-CH_2—CH=), 3·20 (d, J=5 Hz, 2H, Ar-CH_2—CH=), 3·75, 3·82(2s, 6H, $2CH_3O$), 6·25–6·50 (m, 4H, 2 CH_2—CH=CH), 7·12–7·38 (m, 10H, 2 C_6H_5), and 7·55 (s, 1H, H-6).

3.2.3. 4-*Methoxy*-3-C-*cinnamyl*-2-*hydroxyacetophenone* (7)

3-C-cinnamylresacetophenone (6,100 mg) and dimethyl sulphate (0·14 ml) were refluxed together in dry acetone in the presence of anhydrous potassium carbonate (500 mg) for 4 hr. The product when crystallised from aqueous methanol yielded 7 as white crystals (70 mg), mp 168–69° (Found: C, 76·7; H, 6·5. $C_{18}H_{18}O_3$ requires C, 76·6; H, 6·4%); R_f 0·78 (solvent B); λ_{max} 220 and 245 nm (log ϵ 4·48 and 3·68 respectively); NMR: 2·42 (s, 3H, —$COCH_3$), 3·53 (d, J=5 Hz, 2H, Ar-CH_2—CH=), 3·85 (s, 3H, CH_3O—), 6.38 (d, J=10 Hz, 1H, H-5), 6·25–6·48 (m, 2H, CH=CH), 7·00–7·37 (m, 5H, C_6H_5) and 7·87 (d, J=10 Hz, 1H, H-6).

3.2.4. 2,4-*Dimethoxy*-5-C-*cinnamylacetophenone* (9)

An acetone solution of 5-C-cinnamyl resacetopheone (8, 50 mg) was refluxed with dimethyl sulphate (0·14 ml) and anhydrous potassium carbonate (0·5 g) for 10 hr. The product crystallised from methanol to give 9 as colourless crystals (65 mg), mp 65–66° (Found: C, 77·0; H, 6·8. $C_{19}H_{20}O_3$ requires C, 77·2; H, 7·0%); R_f 0·72 (solvent B); NMR: 2·53 (s, 3H, —$COCH_3$), 3·43 (d, J=5 Hz, 2H, Ar—CH_2—CH=), 3·87 (s, 6H, 2 CH_3O—), 6·13–6·37 (m, 3H, CH_2—CH=CH and H-3), 7·07–7·37 (m, 5H, C_6H_5) and 7·64 (d, J=1·5 Hz, 1H, H-6).

3.2.5. 5-*Hydroxy*-6-*acetyl*-*flavan* (12)

3-C-cinnamylresacetophenone (6, 50 mg) was heated with formic acid (8 ml) for 3 hr. The product crystallised from ethyl acetate to yield 12 as white flakes (30 mg), mp 181–82° (Found: C, 76·2; H, 7·6. $C_{17}H_{16}O_3$ requires C, 76·1; H, 7·4%); R_f 0·72 (solvent A); NMR: 2·0–2·25 (m, 2H, 2H-3), 2·49 (s, 3H, —$COCH_3$), 2·75 (t, J = 6·5 Hz, 2H, 2H-4), 6·30–6·45 (m, 1H, H-2), 6·39 (d, J=9 Hz, 1H, H-8), 7·07–7·37 (m, 5H, C_6H_5) and 7·43 (d, J_{ortho}=9 Hz, 1H, H-7).

3.2.6. 5-*Hydroxy*-6-*acetyl*-3-*flavene* (13)

A benzene solution of 3-C-cinnamylresacetophenone (6, 100 mg) was refluxed with DDQ (60 mg) for 18 hr. The mixture was filtered while hot and the filtrate evaporated. The residue was dried and subjected to column chromatography. Elution with benzene-light petroleum (1:1) gave an yellow solid which on crystallisation from benzene-light petroleum mixture gave 13 as yellow needles (40 mg), mp 116–117° (Found: C, 76·8; H, 5·3. $C_{17}H_{14}O_3$ requires C, 76·7; H, 5·2%); R_f 0·58 (solvent A); brown ferric reaction; λ_{max} 218 and 252 nm (log ϵ 4·52 and 3·97 respectively); NMR: 2·50 (s, 3H, —$COCH_3$), 5·60–6·00 (m, 2H, H-3 and 4), 6·37 (d, J=9 Hz, 1H, H-8), 6·92 (d, J=14 Hz, 1H, H—2), 7·20–7·55 (m, 5H, C_6H_5) and 7·56 (d, J=9 Hz, 1H, H–7).

3.2.7. 4, 7-*Dihydroxy*-8-*C*-*cinnamylcoumarin* (14)

A mixture of 3-C-cinnamylresacetophenone (6, 100 mg), ethyl chloroformate (0·12 ml), anhydrous potassium carbonate (0·5 g) and acetone was refluxed for 3 hr. Acetone was distilled and 4% aqueous sodium carbonate (100 ml) added to the residue. The whole mixture was refluxed for 1 hr, cooled and acidified and the solid crystallised from methanol when 14 was obtained as colourless needles (30 mg), mp 136–37° (Found: C, 77·6; H, 5·2. $C_{18}H_{14}O_3$ requires C, 77·7; H, 5·0%); R_f 0·65 (solvent A); λ_{max} 235, 287 and 343 nm (log ϵ 4·65, 4·19 and 4·27 respectively); NMR (CD_3COCD_3): 3·56 (d, J=4 Hz, 2H, Ar—CH_2—CH=), 6·36–6·50 (m, 2H, CH_2—CH=CH), 6·42 (d, J=10 Hz, 1H, H-6), 7·07–7·37 (m, 6H, C_6H_5 and H-3) and 7·48 (d, J=10 Hz, 1H, H-5).

3.3. *Nuclear cinnamylation of resacetophenone under acidic conditions*

A solution of resacetophenone (1, 5 g) in aq. formic acid (20 ml HCOOH and 5 ml water) was refluxed with cinnamyl alcohol (5 g) for 30 min. The mixture was cooled, diluted with water and the solid collected. This on column chromatography and successive elution with (1) benzene: light petroleum (1:9), (2) benzene:light petroleum (2:8) and (3) benzene:light petroleum (1:1) and benzene alone gave four fractions A, B, C and D.

Fraction A crystallised from benzene-light petroleum mixture to afford 5-hydroxy-6-acetyl-8-cinnamylflavan (10) or its isomer (11) as cream coloured crystals (0·6 g), mp 158–59° (Found: C, 80·9; H, 6·4. $C_{26}H_{24}O_3$ requires C, 81·2; H, 6·2%); R_f 0·9 (solvent A); brown ferric reaction; λ_{max} 254 nm (log ϵ 4·12); NMR (Acetone-d_6): 2·01–2·24 (m, 2H, 2H 3), 2·55 (s, 3H, $COCH_3$), 2·65 (t, J=6·5 Hz, 2H, 2H-4), 3·50 (d, J=4 Hz, 2H, Ar—CH_2—CH=), 6·22 (t, J=6·5 Hz, 1H, H-2), 6·25–6·50 (m, 2H, —CH_2—CH=CH—), 7·17–7·48 (m, 10H, 2 C_6H_5) and 7·67 (s, 1H, H-7).

Fraction B crystallised from benzene-light petroleum mixture to afford 3-C-cinnamyl resacetophenone (6) as colourless crystals (0·9 g) identical in all respects with the sample prepared earlier.

Fraction C crystallised from ethyl acetate-petroleum ether to afford 5-C-cinnamyl

resacetophenone (8) as colourless crystals (1·4 g) identical in all respects with the sample prepared earlier.

Fraction D crystallised from methanol to give starting compound viz. resacetopheone (0·9 g).

3.4. *The Claisen rearrangement of* 4-*O*-*cinnamylresacetopheone* (2)

The ketone (2, 3 g) was refluxed in *N*, *N*-dimethylaniline (40 ml) for 6 hr. The mixture was treated with excess of HCl (1:1) and the solid on column chromatography and successive elution with (1) benzene: light petroleum (20:80), (2) benzene: petroleum ether (1:1) gave three fractions A – C.

Fraction A crystallised from benzene-light petroleum yielding 2,4-dihydroxy-3-(1-phenyl-allyl) acetophenone (18) as white solid (100 mg) mp 140–42° (Found: C, 75·9; H, 6·1. $C_{17}H_{16}O_3$ requires, C, 76·1; H, 5·9%); R_f 0·83 (solvent A); λ_{max} 224, 252 and 319 nm (log ϵ 4·01, 4·21 and 4·18 respectively); 60 MHz NMR: 2·56 (s, 3H, —$COCH_3$), 4·98 (t, J=1·5 Hz, 1H, H—A), 5·25 (d, J=1·5 Hz, 1H, H—C), 5·40–5·61 (m, 1H, H—B) 6·20–6·23 (m, 1H, H—X), 6·36 (d, J=9Hz, 1H, H-5), 7·21–7·35 (m, 5H, C_6H_5) and 7·58 (d, J=9 Hz, 1H, H-6).

Fraction B crystallised from benzene-light petroleum to yield 2, 4-dihydroxy-3-(1-phenyl-1-propenyl) acetophenone (15) as colourless light needles (1 g), mp 147–48° (Found : C, 76·3; H, 5·9. $C_{17}H_{16}O_3$ requires C, 76·1; H, 5·9%); R_f 0·75 (solvent A); λ_{max} 218, 246 and 325 nm (log ϵ 3·92, 4·35 and 4·01 respectively); 60 MHz NMR: 1·69 (d, J=7 Hz, 3H, CH_3—CH=), 2·53 (s, 3H, —$COCH_3$), 6·52 (d, J=9 Hz, 1H, H-5), 6·52–6·62 (m, 1H, CH_3—CH=), 7·11–7·31 (m, 5H, C_6H_5) and 7·63 (d, J=9 Hz, 1H, H-6).

Fraction C crystallised from benzene to afford 2,4-dihydroxy-5-(1-phenyl-allyl) acetophenone (19) as colourless crystals, mp 122–23° (Found: C, 76·2; H, 6·2. $C_{17}H_{16}O_3$ requires C, 76·1; H, 5·9%); R_f 0·75 (solvent A); brown ferric reaction; λ_{max} 226, 254 and 309 nm (log ϵ 3·84, 4·02 and 3·92 respectively); 60 MHz NMR: 2·43 (s, 3H, —$COCH_3$), 4·77 (d, J=2 Hz, 1H, H—A), 5·00–5·10 (m, 1H, H—C), 5·26–5·34 (m, 1H, H—B), 6·00–6·29 (m, 1H, H—X), 6·38 (s, 1H, H-3), 7·17–7·28 (m, 5H, C_6H_5) and 7·36 (s, 1H, H-6).

3.4.1. 2-*Hydroxy*-4-*methoxy*-3-(1-*phenyl*-1-*propenyl*) *acetophenone* (16)

An acetone solution of the acetophenone (15, 100 mg) was refluxed with dimethyl sulphate (0·15 ml) and K_2CO_3 (0·5 g) for 4 hr. The product crystallised from methanol to yield 16 as colourless crystals (75 mg), mp 115–16° (Found: C, 76·5; H, 6·4. $C_{18}H_{18}O_3$ requires C, 76·6; H, 6·4%); R_f 0·85 (solvent A); λ_{max} 230 and 282 nm (log ϵ 3·42 and 3·92 respectively); 60 MHz NMR: 1·62 (d, J=7 Hz, 3H, CH_3—CH=), 2·59 (s, 3H, —$COCH_3$), 3·78 (s, 3H, CH_3O—), 6·31 (d, J=10Hz, 1H, H-5) 6·30–6·60 (m, 1H, CH_3—CH=), 7·08–7·25 (m, 5H, C_6H_5) and 7·75 (d, J=10 Hz, 1H, H-6).

3.4.2. 2, 4-*Dimethoxy*-3-(1-*phenyl*-1-*propenyl*) *acetophenone* (17)

A mixture of the acetophenone (15, 100 mg), dimethyl sulphate (0·3 ml) and anhydrous potassium carbonate (1·0 g) was refluxed for 8 hr. The product crystallised from methanol to yield 17 as colourless shining crystals (65 mg), mp 55–56° (Found: C, 77·1; H, 6·8. $C_{19}H_{20}O_3$ requires C, 77·0; H, 6·7%); R_f 0·8 (solvent A); λ_{max} 281 nm (log ϵ 4·24); NMR 1·64 (d, J=7 Hz, 3H, CH_3—CH=), 2·56 (s, 3H, —$COCH_3$), 3·59, 3·76 (2s, 6H, 2 CH_3O), 6·30–6·43 (m, 1H, CH_3—CH=), 6·51 (d, J=9 Hz, 1H, H-5), 7·31–7·34 (m, 5H, C_6H_5—) and 7·66 (d, J=9 Hz, 1H, H-6).

3.4.3. 2,4-*Dimethoxy*-5-(1-*phenyl-allyl*) *acetophenone* (20)

An acetone solution of the acetophenone (19, 100 mg) was refluxed with dimethyl sulphate (0·3 ml) and potassium carbonate (1·0 g) for 10 hr. The product crystallised from methanol to give 20 as colourless needles (73 mg), mp 85–86° (Found: C, 76·9; H, 6·7. $C_{19}H_{20}O_3$ requires C, 77·0; H, 6·7%); R_f 0·74 (solvent A); λ_{max} 254 and 298 nm (log ϵ 4·12 and 4·07 respectively); NMR: 2·55 (s, 3H, —$COCH_3$), 3·80, 3·89 (2s, 6H, $2CH_3O$), 4·80 (t, J=1·5 Hz, 1H, H—A), 5·00 (t, J=1·5 Hz, 1H, H—C), 5·13–5·25 (m, 1H, H—B), 6·39 (s, 1H, H-3), 6·27–6·55 (m, 1H, H—X), 7·12–7·30 (m, 5H, C_6H_5) and 7·68 (s, 1H, H-6).

3.4.4. 2',4'-*Dihydroxy*-4-*methoxy*-3-(1-*phenyl*-1-*propenyl*) *chalcone* (21)

To a solution of 2,4-dihydroxy-3-(1-phenyl-1-propenyl) acetophenone (15, 100 mg) in ethanol (1·5 ml) was added anisaldehyde (0·08 ml) and aqueous potassium hydroxide (1 g/1 ml, 0·13 ml). The whole mixture was heated at 65° for 10 hr and then kept at room temp. for 24 hr. It was diluted with water, extracted with petroleum ether and the aqueous layer acidified with dilute HCl. The resulting yellow solid was crystallised from ethanol when (21) formed yellow crystals (30 mg), mp 145–46° (Found: C, 77·6; H, 5·8. $C_{25}H_{22}O_4$ requires C, 77·7; H, 5·7%); R_f 0·7 (solvent A); λ_{max} 238 and 300 nm (log ϵ 4·17 and 3·90 respectively); NMR: 1·72 (d, J=7 Hz, 3H, CH_3—CH=), 3·82 (s, 3H, CH_3O), 6·70 (q, J= 7 Hz, 1H, =CH—CH_3), 6·91 (d, J = 10 Hz, 2H, H-3, 5), 7·31–7·37 (m, 5H, C_6H_5), 7·53 (d, J=9·5 Hz, 1H, H-5'), 7·56 (d, J=10 Hz, 2H, H-2, 6), 7·62 (d, J=9·5 Hz, 1H, H-6') and 7·65–7·74 (m, 2H, CH=CH, α, β).

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