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A STUDY OF NUCLEAR PRENYLATION OF 2,4-DIHYDROXY PHENYL BENZYL KETONE

SYNTHESES OF LINEAR AND ANGULAR 6″,6″-DIMETHYL PYRANO-ISOFLAVONES, AND THEIR 2-METHYL AND 2-PHENYL ANALOGUES

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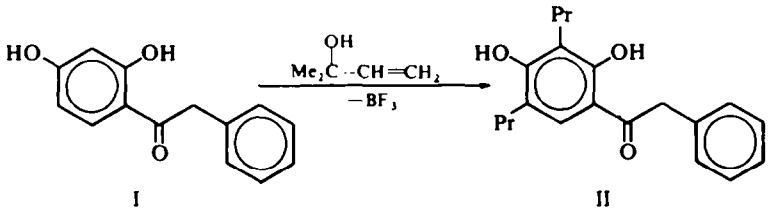
Abstract-- 2,4-Dihydroxyphenyl benzyl ketone (I) condenses with 2-methyl but-3-en-2-ol in the presence of boron trifluoride etherate to afford a mixture of 3-C-, 5-C- and 3,5-di C C-prenyl derivatives separable by chromatography. The above mixture without the 5-C-prenyl but with the 4-O-prenyl derivative results when ketone I is treated with prenyl bromide in the presence of methanolic potash. 3-C-(III a) and 5-C-(IV) prenyl derivatives undergo ready oxidative cyclization with DDQ to yield the corresponding pyrano derivatives VIII and XII respectively which form good starting materials for various isoflavone condensations. Thus both linear and angular 6″,6″-dimethyl pyrano-isoflavones and their 2-methyl and 2-phenyl analogues have been synthesized.

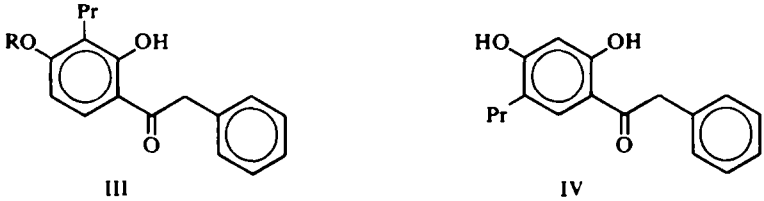
AMONG THE NATURALLY occurring isopentenylated isoflavones, a large number are 5,7-dioxygenated derivatives and the isopentenyl unit is present generally either in the 6 or 8 position but rarely in the side phenyl nucleus. Such compounds are readily obtainable in the laboratory by direct prenylation of 5,7-dihydroxyisoflavones and subsequent modification stages. For example, the 4′-methyl ethers of naturally occurring osajin and warangalone have been prepared earlier by direct prenylation of 5,7-dihydroxy-4′-methoxyisoflavone with prenyl bromide in the presence of methanolic $^{-}$OMe and subsequent oxidative cyclization of the resulting 6,8-di-CC prenyl derivative with DDQ.[1] However, there are also some examples of natural isopentenylated isoflavones which have 7- or 6,7-dioxygenation patterns. For example, jamaicin[2] and ichthynone[3,4] are present in *Piscidia erythyrina* and durmillone occurs in the seeds of *Milletia dura*.[5] Their syntheses may involve nuclear prenylation either at the isoflavone or the corresponding desoxy-benzoin stage. The latter alternative has now been explored and is found to be quite satisfactory for the syntheses of isopentenylated 7-hydroxyisoflavones.

2,4-Dihydroxyphenyl benzyl ketone (I) was first prenylated with 2-methyl-but-3-en-2-ol in the presence of BF_3 etherate according to the general procedure of Bohlmann and Kleine.[6] A mixture of three products was obtained which could be separated by column chromatography. The first mobile component obtained in nearly 7% yield was identified as 3,5-di-C,C-prenyl 2,4-dihydroxy-desoxybenzoin (II) on the basis of elemental analysis, solubility in Na_2CO_3 aq, positive Fe^{+3} reaction and NMR spectrum which showed resonance signals of one phenyl group and methylene protons, two acyclic C-prenyl units and only one aromatic proton in the

peri position as a low field singlet at δ 7·56 ppm. The next eluate isolated in about 18% yield was also soluble in Na_2CO_3aq and gave a positive Fe^{+3} reaction but had only one C-prenyl unit. This was assigned to the 3-position (formula IIIa) on the basis of NMR data which showed two *ortho* coupled protons as two doublets centred at δ 6·38 ppm and 7·68 ppm (J = 9 Hz). The third eluate isolated in approximately 23%, yield was found to be isomeric with the above 3-C-prenyl derivative (IIIa) and was, assigned the structure of 5-C-prenyl-2,4-dihydroxyphenyl benzyl ketone (IV). In confirmation the NMR spectrum showed aromatic singlets at δ 6·38 ppm and at δ 7·62 ppm. These results agree with those obtained for β-resacetophenone under identical conditions.[7]

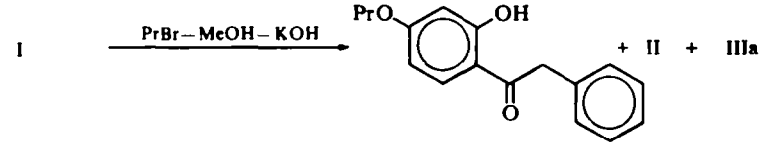


I II



III IV

a: R = H
b: R = Me



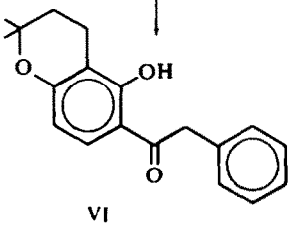
V

(Note: Pr in all formulae indicates the γ,γ-dimethyl allyl unit).

2,4-Dihydroxyphenyl benzyl ketone has also been prenylated with prenyl bromide in the presence of methanolic KOH. The major component of the mixture in this reaction was found to be the 3-C-prenyl derivative (IIIa) identical with the one obtained in the above experiment. The 3,5-di-C,C-prenyl compound (II) was formed in small amounts and could be only identified by TLC and the third product obtained again in small amount was identified as 2-hydroxy-4-prenyloxy-phenyl benzyl ketone (V) on the basis of its insolubility in Na_2CO_3 and of its NMR spectrum (methylene protons attached to oxygen doublet at δ 4·56 ppm (J = 7 Hz)). The structure was further confirmed by synthesis from 2,4-dihydroxyphenyl benzyl ketone (I) with one mole of prenyl bromide in the presence of K_2CO_3 and acetone.

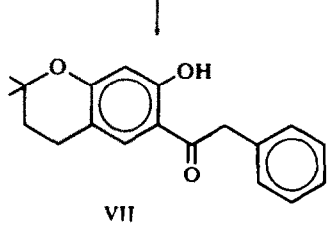
The above 3-C-prenyl derivative (IIIa) was converted into the 4-methyl ether (IIIb) and both the 3-C (IIIa) and 5-C-prenyl (IV) derivatives were cyclized with formic acid to give 2,2-dimethyl-6-phenacyl-5-hydroxy-(VI) and 7-hydroxy-(VII) chromans, the structures of which were supported by their NMR spectra (triplets centred at δ 1·82 ppm and δ 2·72 ppm corresponding respectively to the 3- and 4-methylene protons in compound VI and at δ 1·74 and δ 2·68 ppm in compound VII).

IIIa



VI

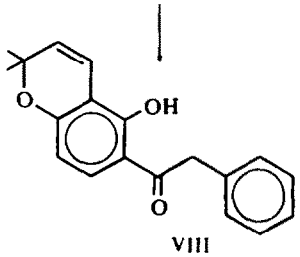
IV



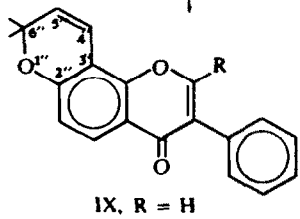
VII

In order to synthesize linear and angular 6″,6″-dimethyl pyranoisoflavones, 3-C-prenyl-(IIIa) and 5-C-prenyl-(IV)-2,4-dihydroxyphenyl benzyl ketones were subjected to oxidative cyclization with DDQ[8] when 2,2-dimethyl-6-phenacyl-5-hydroxy (VIII) and 7-hydroxy-(XII) chromenes were obtained in good yield. These chromenes were purified by column chromatography and subsequently characterized by their NMR spectra (two characteristic doublets of two protons in the 3 and 4 positions at about δ 5·60 ppm and δ 6·35 ppm. These chromenes (VIII and XII) were subsequently converted into the corresponding isoflavones (IX and XIII respectively) by condensation with ethyl formate in the presence of sodium and into the 2-methyl isoflavones (X and XIV respectively) by refluxing in the presence of NaOAc and Ac_2O.

IIIa

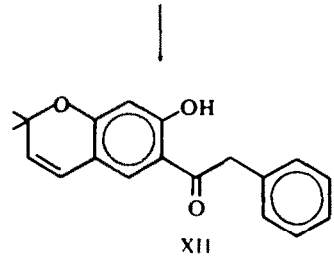


VIII

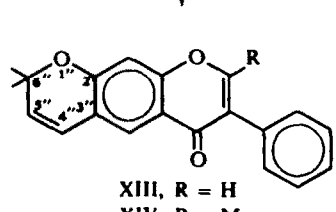


IX, R = H
X, R = Me
XI, R = Ph

IV



XII



XIII, R = H
XIV, R = Me

5-Hydroxychromene (VIII) has also been condensed with benzoic anhydride in the presence of K_2CO_3 and acetone according to the procedure of Jain *et al.*,[9] affording the corresponding 2-phenyl isoflavone (XI) in good yield. NMR spectra of all these linear and angular pyranoisoflavones are recorded in the experimental part. The characteristic two doublets of the two protons of the pyrano nucleus were discerned in each case in the region of δ 5·60 ppm and δ 6·95 ppm (J = 9–10 Hz). Thus it may be concluded that the above method of prenylation at the desoxybenzoin stage can be used for the syntheses of both linear and angular pyranoisoflavones having a 7-oxygenation pattern in the A ring.

EXPERIMENTAL

Unless otherwise stated, all m.ps are uncorrected: UV spectra were taken in EtOH (figures in parenthesis are log ε values); light petroleum b.p. 60–80°, silica gel was used for column chromatography; and TLC was carried out on silica gel G plates using one of the following systems: (A) benzene: (B) toluene·ethyl formate:formic acid (5:4:1), detection either by 3% alcoholic $FeCl_3$ or 10% dil H_2SO_4.

Nuclear prenylation of 2,4-dihydroxyphenyl benzyl ketone. (A) *With 2-methyl-but-3-en-2-ol.* To an ice-cooled solution of 2,4-dihydroxyphenyl benzyl ketone (6 g) in dry dioxane (30 ml) was slowly added $BF_3 \cdot Et_2O$ (2·5 ml) followed by 2-methyl-but-3-en-2-ol (6·8 ml) in dioxane (20 ml) in one lot. The resulting mixture was shaken for 4 hr at room temp, diluted with moist ether (300 ml), washed with ice-cold 1% Na_2CO_3 aq and finally with water. The alkaline solution gave unchanged 2,4-dihydroxyphenyl benzyl ketone (1·5 g). The ethereal extract was dried and examined by TLC (solvent A) when it showed a number of compounds. It was therefore subjected to column chromatography. The column was eluted successively with light petroleum, light petroleum·benzene (1:1) and benzene when three fractions were obtained. *Fraction* A crystallized from light petroleum yielding 3,5-di-C,C-prenyl 2,4-dihydroxyphenyl benzyl ketone (II) as yellow plates (0·6 g), m.p. 103°: bluish green ferric reaction: R_f 0·78 (solvent A): λ_{max} (MeOH) 289·91 nm (4·06): $\lambda_{infl.}$ 320–335 nm (3·72): NMR ($CDCl_3$): δ 1·74 and 1·84 (2 s, 12H of two $(C\underline{H}_3)_2C=$ groups), 3·28 and 3·47 (2d, J = 8 Hz, 4H of two Ar—$C\underline{H}_2$— groups), 4·22 (1s, 2H of —CO—$C\underline{H}_2$-Ar), 5·35 (1t, J = 7·5 Hz, 2H of two —$C\underline{H}$= groups of two C-prenyl units), 7·56 (1s, 1 aromatic H in 6 position) and 7·36 ppm (1s, 5H of Ph group) (Found: C, 78·9; H, 7·6. $C_{24}H_{28}O_3$ requires: C, 79·1; H, 7·7%). *Fraction* B crystallized from benzene–light petroleum mixture and afforded 3-C-prenyl-2,4-dihydroxyphenyl benzyl ketone (IIIa) as white silky plates (1·4 g), m.p. 107°: reddish brown ferric reaction: R_f 0·43 (solvent A): λ_{max} 290 nm (4·21): NMR ($CDCl_3$): δ 1·74 and 1·83 (2s, 6H of $(C\underline{H}_3)_2C=$ group), 3·45 (1d, J = 7·5 Hz, 2H of —$C\underline{H}_2$-in prenyl unit), 4·22 (1s, 2H of —$COC\underline{H}_2$— group), 5·32 (t, J = 7 Hz, 1H of —$C\underline{H}$= group of C-prenyl unit), 6·38 and 7·68 (2d, J = 9 Hz, 2 aromatic H at 5 and 6 positions) and 7·32 ppm (1s, 5H of Ph) (Found: C, 77·1; H, 6·8. $C_{19}H_{20}O_3$ requires: C, 77·0; H, 6·8%). *Fraction* C crystallized from benzene–light petroleum mixture giving 5-C-prenyl-2,4-dihydroxyphenyl benzyl ketone (IV) as white plates (1·8 g): m.p. 106–108°; R_f 0·1 (solvent A): violet ferric reaction: λ_{max} 235, 285 and 330 nm (3·92, 3·97 and 3·78 respectively): NMR ($CDCl_3$): δ 1·72 and 1·82 (2s, 6H of $(C\underline{H}_3)_2C=$ group), 3·27 (1d, J = 8 Hz, 2H of —$C\underline{H}_2$— of prenyl unit), 4·22 (1s, 2H of —CO —$C\underline{H}_2$—), 5·33 (1t, J = 6·5 Hz, 1H of —$C\underline{H}$= of prenyl unit), 6·38 (1s, 1 aromatic H in 3 position), 7·62 (1s, 1 aromatic H at 6 position) and 7·32 ppm (1s, 5H of Ph) (Found: C, 77·2: H, 7·2. $C_{19}H_{20}O_3$ requires: C, 77·0: H, 6·8%).

(B) *With prenyl bromide.* 2,4-Dihydroxyphenyl benzyl ketone (3 g) was dissolved in absolute methanolic KOH (3·6 g) in 15 ml) and the solution cooled and treated with PrBr (4·2 ml) slowly while shaking. After keeping the mixture for 20 hr at room temp it was diluted with ice-cold water, acidified and extracted with ether. The ethereal solution was extracted successively with 7% Na_2CO_3 aq (solution A), 1% KOH (solution B) leaving a neutral fraction in ether (solution C). Solution A gave an acidification unreacted 2,4-dihydroxyphenyl benzyl ketone (0·7 g). Solution B on acidification gave a solid which proved to be by TLC a mixture of the unchanged compound and one new compound and was purified by column chromatography. Elution with benzene–light petroleum (1·3) yielded the new compound which on crystallization from benzene–light petroleum formed shining plates of 3-C-prenyl 2,4-dihydroxyphenyl benzyl ketone (IIIa, 0·8 g), m.p. and m.m.p. with an authentic sample 107°; reddish brown ferric reaction: R_f 0·43 (solvent A).

Solution C was also a mixture and was purified by column chromatography. Elution with light petroleum

alone and then with benzene–light petroleum mixture (1:3) afforded the following two fractions. Fraction A (1 g) could not be crystallized but it was found to contain mainly 3,5-di-C-prenyl-2,4-dihydroxyphenyl benzyl ketone (II) when compared on TLC with the sample prepared in the previous experiment. Fraction B afforded 4-prenyloxy-2-hydroxyphenyl benzyl ketone (V) as a colourless solid (0·2 g), m.p. and m.m.p. with the sample described below 53°; red ferric reaction; R_f 0·68 (solvent A).

4-Prenyloxy-2-hydroxyphenyl benzyl ketone (V). A solution of 2,4-dihydroxyphenyl benzyl ketone (0·75 g) in acetone (10 ml) was refluxed with PrBr (0·4 ml) and anhyd K_2CO_3 (2 g) for 2 hr. The product crystallized from light petroleum as colourless needles (0·7 g), m.p. 53°; red ferric reaction; R_f 0·68 (solvent A); λ_{max} 280 and 315 nm (4·25 and 3·99 respectively); NMR ($CDCl_3$): δ 1·74 and 1·78 (2s, 6H of one $(C\underline{H}_3)_2C-$ group), 4·56 (1d, g = 7 Hz, 2H of $-(C\underline{H}_2O-$ Ar group), 4·19 (s, 2H of $-CO-C\underline{H}_2-$), 5·53 (1t, J = 6·5 Hz, 1H of $-C\underline{H}=$ of prenyl unit), 6·49 (q, J = 2 Hz, 1 aromatic H at 5 position), 6·55 (1d, J = 3 Hz, 1 aromatic H at 3 position), 7·78 (1d, J = 9·5 Hz, 1 aromatic H at 6 position) and 7·33 ppm (1s, 5H of Ph). (Found: C, 77·0; H, 6·8. $C_{19}H_{20}O_4$ requires: C, 77·0; H, 6·8%.)

3-C-Prenyl-4-methoxy2-hydroxyphenyl benzyl ketone (IIIb). A solution of 3-C-prenyl-2,4-dihydroxyphenyl benzyl ketone (IIIa, 0·3 g) in acetone (10 ml) was refluxed with dimethyl sulphate (0·1 ml) and dry K_2CO_3 (2 g) for 3 hr. Acetone was distilled, water added and the whole solution extracted with ether. The ethereal residue gave a solid (0·25 g) which after purification by column chromatography and crystallization from light petroleum yielded 3-C-prenyl-4-methoxy-2-hydroxyphenyl benzyl ketone (IIIb) as colourless crystals (0·2 g), m.p. 67–68°; brown ferric reaction; R_f 0·8 (solvent A); λ_{max} 290 nm (3·98); NMR ($CDCl_3$): δ 1·68 and 1·82 (2s, of $(C\underline{H}_3)_2C=$ group), 3·41 (1d, J = 7·5 Hz, 2H of $-C\underline{H}_2-$of prenyl unit), 3·88 (1s, 3H of one $-OC\underline{H}_3$), 4·22 (1s, 2H of $-CO-C\underline{H}_2-$), 5·27 (1t, J = 7·5 Hz, 1H of $-C\underline{H}=$ of prenyl unit), 6·49 and 7·78 (2d, J = 10 Hz, 2 aromatic H in 5 and 6 positions) and 7·30 ppm (1s, 5H of Ph). (Found: C, 77·5 H, 7·2. $C_{20}H_{22}O_3$ requires: C, 77·4; H, 7·1%.)

2,2-Dimethyl-6-phenacyl-5-hydroxychroman (VI). 3-C-Prenyl-2,4-dihydroxyphenyl benzyl ketone (0·3 g) was heated with HCOOH (20 ml) on a steam bath for 5 hr and the product poured over ice and extracted with ether. The ether solution was cautiously washed with $NaHCO_3$ aq and the ethereal residue crystallized from light petroleum when 2,2-dimethyl-6-phenacyl-5-hydroxychroman (VI) was obtained as a colourless solid (0·25 g), m.p. 84–86°, reddish brown ferric reaction; R_f 0·61 (solvent A); λ 235 and 290 nm (4·02 and 4·31 respectively); NMR ($CDCl_3$): δ 1·37 (1s, 6H of $(C\underline{H}_3)_2C<$), 1·82 and 2·72 (2t, J = 7 Hz, 4H of two $-C\underline{H}_2-$), 4·24 (1s, 2H of $-CO-C\underline{H}_2-$Ph), 6·44 and 7·70 (2d, J = 9·5 Hz; 2 aromatic H at 8 and 7 positions respectively) and 7·37 ppm (1s, 5H of Ph). (Found: C, 77·1; H, 6·8. $C_{19}H_{20}O_3$ requires: C, 77·0; H, 6·8%.)

2,2-Dimethyl-6-phenacyl-7-hydroxychroman (VII). 5-C-Prenyl-2,4-dihydroxyphenyl benzyl ketone (0·35 g) was heated with HCOOH (30 ml) for 4 hr and the product (after work up as above) crystallized from light petroleum to give 2,2-dimethyl-6-phenacyl-7-hydroxychroman (0·3 g), m.p. 112°; R_f 0·55 (solvent A); λ_{max} 235, 285 and 325 nm (3·92, 4·15 and 3·86 respectively); NMR ($CDCl_3$): 1·31 (1s, 6H of $(C\underline{H}_3)_2C<$), 1·74 and 2·68 (2t, J = 6·5 Hz, 4H of two $-C\underline{H}_2-$ groups in 3 and 4 positions), 4·13 (1s, 2H of $-CO-C\underline{H}_2-$Ph), 6·30 and 7·53 (2s, two aromatic H in 8 and 5 positions) and 7·25 ppm (1s, 5H of Ph). (Found: C, 77·2; H, 7·0. $C_{19}H_{20}O_3$ requires: C, 77·0; H, 6·8%.)

2,2-Dimethyl-6-phenacyl-5-hydroxychromene (VIII). 3-C-Prenyl-2,4-dihydroxyphenyl benzyl ketone (111a, 0·2 g) was refluxed with DDQ (0·2 g) in dry benzene (10 ml). Hydroquinone was filtered and the filtrate evaporated and subjected to column chromatography. Elution with benzene–light petroleum mixture (1:9) gave a solid which crystallized from MeOH to give 2,2-dimethyl-6-phenacyl-5-hydroxychromene (VIII) as yellow crystals (0·15 g), m.p. 62°; violet ferric reaction; R_f 0·61 (solvent A); NMR ($CDCl_3$): δ 1·47 (1s, 6H of $(C\underline{H}_3)_2C<$), 4·23 (1s, 2H of $CO-C\underline{H}_2-$Ph), 5·61 and 6·40 (2d, J = 9·5 Hz, 2 olefinic H in 3 and 4 positions respectively), 6·80 and 7·72 (2d, J = 10 Hz, 2 aromatic H in 8 and 7 positions respectively) and 7·35 ppm (1s, 5H of Ph). (Found: C, 77·5; H, 6·1. $C_{19}H_{18}O_3$ requires: C, 77·5; H, 6·3%.)

2,2-Dimethyl-6-phenacyl-7-hydroxychromene (XII). To a solution of 5-C-prenyl-2,4-dihydroxyphenyl benzene–light petroleum mixture (1:9) gave 2,2-dimethyl-6-phenacyl-7-hydroxychromene (XII) as colourless 10 min, when colourless hydroquinone separated. It was filtered hot and the residue washed with warm benzene. The filtrate was evaporated and the residue subjected to column chromatography. Elution with benzene–light petroleum mixture (1:9) gave 2,2-dimethyl-6-phenacyl-7-hydroxychromene (XII) as colourless crystals (0·18 g) from EtOH as yellow needles, m.p. 80–81°; green ferric reaction; R_f 0·68 (solvent A); λ_{max} 235, 260 and 350 nm (4·27, 4·47 and 3·81 respectively); NMR ($CDCl_3$): δ 1·43 (1s, 6H of $(C\underline{H}_3)_2C<$), 4·20 (1s, 2H of $CO-C\underline{H}_2-$Ph), 5·62 and 6·35 (2d, J = 10 Hz, 2 olefinic H in 3 and 4 positions respectively),

6·40 and 7·49 (2s, 2 aromatic H at 8 and 5 positions respectively) and 7·35 ppm (1s, 5H of Ph). (Found: C, 77·8; H, 6·4. $C_{19}H_{18}O_3$ requires: C, 77·5; H, 6·2%).

6'', 6''-*Dimethyl pyrano* (3'', 2''; 6,7,)*isoflavone* (XIII). An ice-cold solution of the above chromene (XII) (0·2 g) in dry ethyl formate (10 ml) was added to a freshly prepared powdered suspension of Na (0·2 g) in ethyl formate (20 ml) slowly, while shaking during 2 hr. The mixture was left over-night in an ice chest, treated with ice-cold water, extracted with ether and the ethereal solution dried over Na_2SO_4. The ethereal residue was refluxed with Ac_2O for 1 hr and poured over ice. The solid after crystallization from MeOH yielded 6'', 6''-dimethylpyrano (3'', 2'' : 6,7)isoflavone (XIII) as a colourless solid (0·1 g), m.p. 168°: R_f 0·80 (solvent B): λ_{max} 225 and 265 nm (4·31 and 4·58); NMR ($CDCl_3$): δ 1·48 (1s, 6H of $>C(C\underline{H}_3)_2$), 5·63 and 6·46 (2d, J = 10 Hz, 2 olefinic H in 5'' and 4'' positions), 6·78 (1s, 1 aromatic H at position 8), 7·88 (1s, 2 aromatic H at 2 and 5 positions) and 7·45 ppm (1s, 5H of Ph). (Found: C, 78·8; H, 5·8. $C_{20}H_{16}O_3$ requires: C, 78·9; H, 5·3%).

2,6'',6''-*Trimethyl pyrano* (3'',2'' : 6,7) *isoflavone* (XIV). The chromene (XII) (120 mg) was refluxed with Ac_2O (1 ml) and fused NaOAc (130 mg) in an oil bath at 170–80° for 12 hr. and the resulting mixture poured over ice. The solid (120 mg) was collected and crystallized from EtOAc-light petroleum when 2,6'',6''-trimethyl pyrano (3'',2'' :6,7) isoflavone (XIV) separated as yellow crystals (0·1 g), m.p. 216–18°: R_f 0·75 (solvent B): NMR ($CDCl_3$): δ 1·49 (1s, 6H of $>C(C\underline{H}_3)_2$), 2·29 (1s, 3H of Me at 2 position), 5·78 and 6·54 (2d, J = 10 Hz, 2 olefinic H in 5'' and 4'' positions), 6·82 and 7·89 (2s, 2 aromatic H in 8 and 5 positions respectively) and 7·49 ppm (1s, 5H of Ph) (Found: C, 79·6; H, 6·0. $C_{21}H_{18}O_3$ requires: C, 79·2; H, 5·7%).

6'',6''-*Dimethyl pyrano* (2'', 3'' :7,8) *isoflavone* (IX). The chromene (VIII) (130 mg) was condensed with ethyl formate (10 ml) in the presence of powdered Na (130 mg) as described earlier. 6'',6''-Dimethyl pyrano (2'',3'' :7,8) isoflavone (IX) crystallized from EtOAc-light petroleum as white crystals (0·1 g), m.p. 179–80°: R_f 0·61 (solvent B); NMR ($CDCl_3$); δ 1·52 (1s, 6H of $>C(CH_3)_2$, 5·78 and 6·87 (2d, J = 10 Hz, 2 olefinic H in 5'' and 4'' positions respectively), 6·92 and 8·15 (2d, J = 9 Hz, 2H at 6 and 5 positions respectively, 8·03 (1s, 1H at 2 position) and 7·50 (1s, 5H of Ph). (Found: C, 78·5; H, 5·4. $C_{20}H_{16}O_3$ requires: C, 78·9; H, 5·3%).

2,6'',6''-*Trimethyl pyrano* (2'',3'' :7,8) *isoflavone* (X). The above chromene (VIII) (150 mg) was refluxed with Ac_2O (0·5 ml) and fused NaOAc (125 mg) for 12 hr at 170–80°. 2,6'',6''-Trimethyl pyrano (2'',3'' :7,8) isoflavone (X) crystallized from EtOAc-light petroleum as a white solid (150 mg), m.p. 140–41°: R_f 0·67 (solvent B): NMR ($CDCl_3$): δ 1·51 (1s, 6H of $>C(C\underline{H}_3)_2$), 2·30 (1s, 3H of Me in 2 position), 5·78 and 6·89 J = 9·5 Hz, 2 olefinic H at 5'' and 4'' positions respectively), 6·89 and 8·07 (2d, J = 9·5 Hz, 2H in 6 and 5 positions respectively) and 7·40 ppm (1s, 5H of Ph). (Found: C, 78·8; H, 6·3. $C_{21}H_{18}O_3$ requires: C, 79·2; H, 5·7%).

2,3-*Diphenyl* 6'',6''-*dimethyl pyrano* (2'',3'' :7,8) *chromone* (XI). The chromene (VIII) (150 mg) was refluxed with benzoic anhydride (290 mg), anhyd. K_2CO_3 (0·7 g) and acetone (15 ml) for 10 hr. Acetone was distilled and the residue treated with water when a colourless solid (200 mg) separated. 2,3-Diphenyl 6'',6''-dimethyl pyrano (2'',3'' :7,8) chromone (XI) crystallized from EtOAc-light petroleum as fine needles (150 mg), m.p. 198–99°: R_f 0·70 (solvent B): λ_{max} 235, 255 and 320 nm (4·57, 4·50 and 3·91 respectively): NMR ($CDCl_3$): δ 1·53 (1s, 6H of $>C(CH_3)_2$), 5·78 and 6·95 (2d, J = 10 Hz, of 2 olefinic H in 5'' and 4'' positions in pyrano ring), 6·95 and 8·18 (2d, J = 10 Hz, 2 aromatic H at 6 and 5 positions respectively) and 7·41 ppm (1m, 10H of two Ph units in 2 and 3 positions). (Found: C, 82·3; H, 5·5. $C_{26}H_{20}O_3$ requires: C, 82·1; H, 5·3%).

REFERENCES

1. A. C. Jain, P. Lal and T. R. Seshadri, *Tetrahedron* **26**, 1977 (1970)
2. O. A. Stamm, H. Schmid and J. Buchi, *Helv. Chim. Acta* **41**, 2006 (1958)
3. J. S. P. Schwarz, A. I. Cohen, W. D. Ollis, E. A. Kachzka and L. M. Jackman, *Tetrahedron* **20**, 1317 (1964)
4. S. F. Dyke, W. D. Ollis, M. Sainsbury and J. S. P. Schwarz, *Ibid.* **20**, 1331 (1964)
5. W. D. Ollis, C. A. Rhodes and I. O. Sutherland, *Ibid.* **23**, 4741 (1967)
6. F. Bohlman and K. M. Kleine, *Chem. Ber.* **99**, 885 (1966)
7. A. C. Jain, P. Lal and T. R. Seshadri, *Tetrahedron* **26**, 2631 (1970)
8. G. Cardillo, R. Cricchio and L. Merlini, *Ibid.* **24**, 4825 (1968)
9. S. K. Grover, A. C. Jain, S. K. Mathur and T. R. Seshadri, *Indian J. Chem.* **1**, 382 (1963)