Constitution of Luteone and Parvisoflavones-A and -B and Synthesis of their Methyl Ethers and Related Isoflavones

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The reaction of 5,7-dihydroxy-2',4'-dimethoxyisoflavone (7) with 2-methylbut-3-en-2-ol in the presence of BF_3–ether affords the 6-(3-methylbut-2-enyl) derivative (13) and its 8-isomer (9). Partial methylation of 7-hydroxy in (13) yields luteone trimethyl ether (15) and subsequent acid cyclisation gives α-isoluteone trimethyl ether (17) derived from natural luteone (3). Cyclodehydrogenation of (13) with DDQ followed by methylation afforded the fully methylated ether (19) of parvisoflavone-B, and the same two steps with (9) yielded the fully methylated ether (21) of parvisoflavone-A.

Six isopentenylated 5,7,2',4'-tetraoxygenated isoflavones are known to occur in nature. Auriculatin was the first to be isolated from *Milletia auriculata*,[1] and assigned the structure 2',4',5-trihydroxy-10-(3-methylbut-2-enyl)-8,8-dimethylpyrano[3,2-*g*]isoflavone (1).† From the same plant, isoauriculatin was later isolated by the same workers.[2] Its earlier structure was revised to 2',5-dihydroxy-4'-(3-methylbut-2-enyloxy)-8,8-dimethylpyrano[3,2-*g*]isoflavone (2).[3] Fukui *et al.*[4] reported the occurrence of luteone from immature fruits of *Lupinus luteus* and assigned it the structure 2',4',5,7-tetrahydroxy-6-(3-methylbut-2-enyl)isoflavone (3) by degradation and spectroscopic studies. More recently, the same isoflavone has been found to be present in healthy leaves of *Lupinus albus* and eleven other species of *Lupinus* by Harborne *et al.*[5] This isoflavone had been reported to be fungitoxic,[4] and was therefore regarded as a prohibitin. Harborne *et al.*[5] also reported the isolation of another antifungal compound from *L. albus* and designated it as LA-I. Although its structure was not studied, it was considered to be related to luteone from its spectral behaviour. Gottlieb *et al.*[6] isolated a yellow crystalline material from the trunkwood of *Poecilanthe parviflora*, which on complete methylation separated into two compounds called trimethyl ethers of parvisoflavones-A and -B. However, the parent hydroxy isoflavones, *i.e.* parvisoflavones-A and -B could not be separated from each other. A study of the spectral data of the methyl ethers showed that parvisoflavone-A is 2',4',5-trihydroxy-8,8-dimethylpyrano[2,3-*h*]isoflavone (4) ‡ and parvisoflavone-B is the linear isomer (5). A distinction between the two isomers was made by use of ^{1}H n.m.r. spectroscopy. It should be noted that no synthetic evidence has been given in either case so far.

In view of the ill defined structures of the above natural compounds, it was considered necessary to synthesise some of their derivatives unambiguously. Obviously, all six compounds are derived in nature by nuclear 3-methylbut-2-enylation of 2',4',5,7-tetrahydroxyisoflavone. Hence this nuclear alkylation has now been studied in detail in the case of 5,7-dihydroxy-2',4'-dimethoxyisoflavone (7). This isoflavone (7) has been prepared by application of the general method of isoflavone synthesis devised by Bass.[7] It involves reaction of 2,4,6-trihydroxyphenyl 2,4-dimethoxybenzyl ketone (6) with methanesulphonyl chloride in the presence of DMF and BF_3–Et_2O. The structure of the product is in agreement with that of the synthetic compound reported earlier.[8]

When 5,7-dihydroxy-2',4'-dimethoxyisoflavone (7) was treated with 1-bromo 3-methylbut-2-ene in the presence of potassium carbonate and acetone, only the 7-(3-methylbut-2-enyloxy) derivative (8) was obtained as indicated by its n.m.r. spectrum which showed besides the resonance signals of the starting material those of a 3-methylbut-2-enyloxy group. On the other hand, when the isoflavone (7) was treated with 2-methylbut-3-en-2-ol in the presence of BF_3–Et_2O, a mixture of three compounds was formed. The major product was identified as 8-(3-methylbut-2-enyl) derivative (9) because it formed the trimethoxyisoflavone (10) and the tetramethoxyisoflavone (11), n.m.r. data (see Experimental section) of which provided the unambiguous evidence for the assigned structures. The location of 3-methylbut-2-enyl unit in position 8 was determined in two ways. Firstly the dihydroxy compound (9) gave only one dihydropyran derivative (12) by treatment with formic acid as shown by a characteristic pair of triplets at δ 1.87 and 2.52 for two adjacent methylene groups. Secondly the 7-methyl ether (10) did not undergo cyclisation.

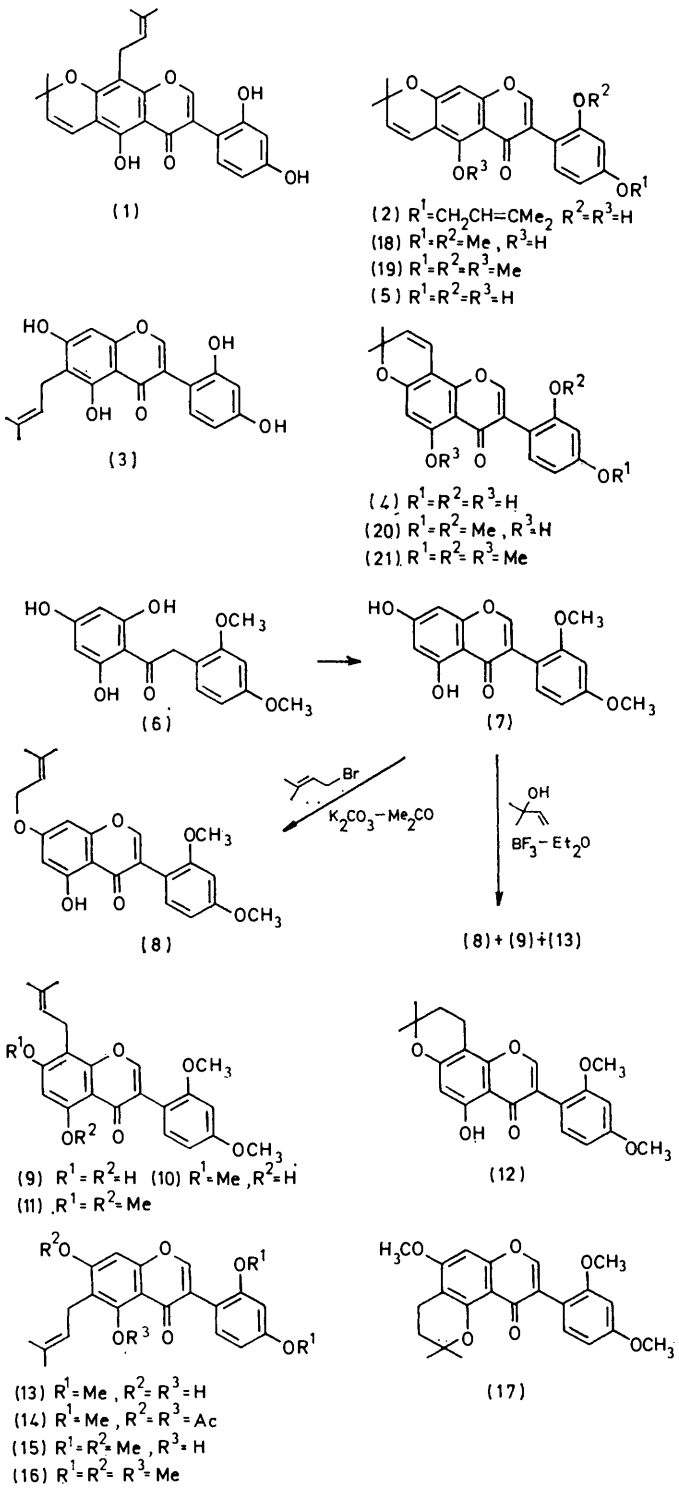
The second product of 3-methylbut-2-enylation was characterised as 6-(3-methylbut-2-enyl) derivative (13) on the basis of the formation of a diacetate (14) and the trimethoxyisoflavone (15). Again, n.m.r. data on these compounds (see Experimental section) assisted in assigning the structures. The latter unit was determined to be in the 6 position on the basis of the formic acid reaction of its monomethyl ether (15), when the dihydropyran derivative (17) was formed, the n.m.r. signals showing two triplets at δ 1.78 and 2.62 for two adjacent methylenes and a *gem*-dimethyl group at δ 1.41. The properties of the synthetic compounds (15) and (17) agree with those of the compounds derived from natural luteone by Fukui *et al.*[4] Hence the structure of luteone as (3) is established.

Cyclodehydrogenation of 5,7-dihydroxy-2',4'-dimeth-

† Systematic name 3-(2,4-dihydroxyphenyl)-5-hydroxy-10-(3-methylbut-2-enyl)-8,8-dimethyl-4*H*,8*H*-benzo[1,2-*b*:5,4-*b*']-dipyran-4-one.

‡ Systematically named 8-(2,4-dihydroxyphenyl)-6-hydroxy-3,3-dimethyl-3*H*,7*H*-benzo[1,2-*b*:3,4-*b*']dipyran-7-one.

oxy-6-(3-methylbut-2-enyl)isoflavone (13) with DDQ yielded the linear 2,2-dimethylpyran derivative (18)



identified by its n.m.r. spectrum which showed a deshielded aromatic proton at the 8 position at δ 6.50 and two characteristic doublets at δ 5.80 and 6.75 (two adjacent vinylic protons) and a *gem*-dimethyl group at δ 1.48. The pyranoisoflavone (18) on methylation with dimethyl sulphate in the presence of potassium carbonate and acetone yielded (19) which was found to be identical (m.p. and u.v. spectrum) with parvisoflavone-B trimethyl ether and hence the structure given to parvisoflavone-B by Gottlieb *et al.*[6] is correct.

When 5,7-dihydroxy-2′,4′-dimethoxy-8-(3-methylbut-2-enyl)isoflavone (9) was cyclohydrogenated with DDQ, the corresponding angular 2,2-dimethylpyran derivative (20) was formed. In accord with this structure, it showed a shielded aromatic proton in ring A at δ 6.25 and two adjacent vinylic protons of the pyran ring at δ 5.56 and 6.66. Further methylation of (20) with excess of dimethyl sulphate in the presence of potassium carbonate, and acetone afforded (21) identical with the permethyl ether of parvisoflavone-A. Hence the structure of parvisoflavone-A is also unambiguously proven to be (4).

EXPERIMENTAL

All m.p.s reported are uncorrected. Unless stated otherwise, u.v. data were recorded for MeOH solutions and n.m.r. spectra were taken on an 80 MHz instrument. Light petroleum had b.p. 60—80°. Silica gel was used for column chromatography and silica gel G for t.l.c. R_F Values refer to t.l.c. using the solvent system benzene–ethyl acetate (9 : 1); t.l.c. plates were sprayed with 10% H_2SO_4–1% alcoholic $FeCl_3$.

5,7-Dihydroxy-2′,4′-dimethoxyisoflavone (7).—To a stirred and cooled solution of 2,4-dimethoxybenzyl 2,4,6-trihydroxyphenyl ketone (6) (2 g) in DMF (20 ml) was added BF_3–Et_2O (3.5 cm³) dropwise during 0.5 h. The temperature was then raised to 60° and methanesulphonyl chloride (2.3 cm³) in DMF (5 cm³) added in one lot. The mixture was heated on a water-bath for 90 min, cooled, and added to ice-cold water (250 cm³). The solid thus obtained was crystallised from methanol to give the isoflavone (7) as crystals (1.75 g), m.p. 218—219° (lit.,[8] 219—220°); R_F 0.42; green Fe^{III} reaction (Found: C, 64.8; H, 4.9. Calc. for $C_{17}H_{14}O_6$: C, 64.9; H, 5.0%); δ[$(CD_3)_2CO$] 3.78 and 3.84 (6 H, 2s, 2 CH_3O), 6.32 (1 H, 2d, *J* 9 and 3 Hz, H-5′), 6.54 (1 H, d, *J* 3 Hz, H-3′), 6.55 (2 H, d, *J* 3 Hz, H-6,-8), 7.59 (1 H, d, *J* 9 Hz, H-6′), and 7.80 (1 H, s, H-2).

5-Hydroxy-2′,4′-dimethoxy-7-(3-methylbut-2-enyloxy)isoflavone (8).—To an acetone solution of isoflavone (7) (100 mg) was added 1-bromo-3-methylbut-2-ene (0.05 cm³) and potassium carbonate (0.5 g). The mixture was refluxed for 4 h. Acetone was removed by distillation, water added, and the precipitated solid collected. It crystallised from benzene–light petroleum yielding the *isoflavone* (8) as creamy crystals (65 mg), m.p. 129—130°; green Fe^{III} reaction; R_F 0.7 (Found: C, 69.3; H, 5.7. $C_{22}H_{22}O_6$ requires C, 69.1; H, 5.8%); $\lambda_{max.}$ 256 (log ε 4.45) and 302 nm (3.98); δ($CDCl_3$) 1.77 and 1.82 (6 H, 2s, Me_2C=), 3.77 and 3.85 (6 H, 2s, 2 CH_3O), 4.55 (2 H, d, *J* 7 Hz, OCH_2), 5.37—5.55 (1 H, m, CH=), 6.37 (1 H, d, *J* 3 Hz, H-3′), 6.45 (1 H, dd, *J* 10 and 3 Hz, H-5′), 6.47 (1 H, d, *J* 3 Hz, H-8), 6.57 (1 H, d, *J* 3 Hz, H-6), 7.20 (1 H, d, *J* 10 Hz, H-6′), and 7.78 (1 H, s, H-2).

Nuclear 3-Methylbut-2-enylation of 5-7-Dihydroxy-2′,4′-dimethoxyisoflavone (7).—To an ice-cold solution of the isoflavone (7) (3 g) in dioxan (150 cm³) was added BF_3–Et_2O (3 cm³) followed by 2-methylbut-3-en-2-ol (2 cm³) in dioxan (35 cm³). The resulting mixture was stirred for 10 h

and left for 24 h at room temperature. It was diluted with moist ether and the ether extract washed with water (200 $cm^3 \times 3$), dried (Na_2SO_4), distilled, and the residue subjected to column chromatography. The column was eluted successively with light petroleum–benzene (9 : 1, 1 : 1, and 1 : 3) to give three fractions A—C.

Fraction A. This was crystallised from benzene–light petroleum to give the isoflavone (8) (30 mg), m.p. and mixed m.p. with the sample prepared above 129—130°; R_F 0.7.

Fraction B. This was crystallised from benzene–light petroleum to afford *5,7-dihydroxy-2′,4′-dimethoxy-6-(3-methylbut-2-enyl)isoflavone* (13) as crystals (250 mg), m.p. 190—192° (Found: C, 69.2; H, 6.1. $C_{22}H_{22}O_6$ requires C, 69.1; H, 5.8%); green Fe^{III} reaction; R_F 0.55; $\lambda_{max.}$ 259 (log ε 4.45) and 288 nm (4.69); δ[$(CD_3)_2CO$] 1.65 and 1.77 (6 H, 2s, Me_2C=), 3.35 (2 H, d, *J* 8 Hz, $ArCH_2CH$=), 3.76 and 3.82 (6 H, 2s, 2 CH_3O), 5.25 (1 H, t, *J* 6.5 Hz, CH=), 6.50 (1 H, d, *J* 3 Hz, H-3), 6.52 (1 H, dd, *J* 10 and 3 Hz, H-5′), 6.56 (1 H, s, H-8), 7.19 (1 H, d, *J* 10 Hz, H-6′), and 7.87 (1 H, s, H-2).

Treatment with acetic anhydride–pyridine, followed by crystallisation from benzene–light petroleum gave *5,7-diacetoxy-2′,4′-dimethoxy-6-(3-methylbut-2-enyl)isoflavone* (14) as flakes, m.p. 145—146° (Found: C, 66.8; H, 5.8. $C_{26}H_{26}O_8$ requires C, 66.9; H, 5.6%); R_F 0.6; δ($CDCl_3$) 1.67 (6 H, s, Me_2C=), 2.32 and 2.37 (6 H, 2s, 2 CH_3CO_2), 3.22 (2 H, d, *J* 8 Hz, $ArCH_2$), 3.75 and 3.85 (6 H, 2s, 2 CH_3O), 5.07—5.37 (1 H, m, CH=), 6.50 (1 H, d, *J* 3 Hz, H-3′), 6.90 (1 H, dd, *J* 10 and 3 Hz, H-5′), 7.01 (1 H, s, H-8), 7.30 (1 H, d, *J* 10 Hz, H-6′), and 7.82 (1 H, s, H-2).

Fraction C. This was crystallised from benzene to yield *5,7-dihydroxy-2′,4′-dimethoxy-8-(3-methylbut-2-enyl)-isoflavone* (9) as crystals (400 mg), m.p. 200—202° (Found: C, 68.9; H, 5.7. $C_{22}H_{22}O_6$ requires C, 69.1; H, 5.8%); green Fe^{III} reaction; R_F 0.5; $\lambda_{max.}$ 266 (log ε 4.62) and 290 nm (4.29); δ[$(CD_3)_2CO$] 1.70 and 1.82 (6 H, 2s, Me_2C=), 3.40 (2 H, d, *J* 8 Hz, $ArCH_2$), 3.77 and 3.84 (6 H, 2s, 2 CH_3O), 5.07—5.40 (1 H, m, CH=), 6.37 (1 H, d, *J* 3 Hz, H-3′), 6.42 (1 H, dd, *J* 10 and 3 Hz, H-5′), 6.57 (1 H, s, H-6), 7.22 (1 H, d, *J* 10 Hz, H-6′), and 7.87 (1 H, s, H-2).

5-Hydroxy-2′,4′,7-trimethoxy-6-(3-methylbut-2-enyl)isoflavone (15).—To an acetone solution of isoflavone (13) (200 mg) was added dimethyl sulphate (0.14 cm^3) and potassium carbonate (1 g) and the mixture was refluxed for 3 h. The solvent was removed and water added. The solid thus obtained was crystallised from dilute methanol yielding the isoflavone (15) as crystals (150 mg), m.p. 134—135° (lit.,[4] 136—137°) (Found: C, 69.6, H, 6.3. Calc. for $C_{23}H_{24}O_6$: C, 69.7; H, 6.1%); R_F 0.8; $\lambda_{max.}$ 263 (log ε 4.42) and 287 nm (4.20); δ($CDCl_3$) 1.67 and 1.77 (6 H, 2s, Me_2C=), 3.37 (2 H, d, *J* 8 Hz, $ArCH_2$), 3.85 (9 H, s, 3 CH_3O), 5.19 (1 H, t, *J* 8 Hz, CH=), 6.33 (1 H, d, *J* 3 Hz, H-3′), 6.56 (1 H, s, H-8), 6.75—7.12 (2 H, m, H-5′ and -6′) and 7.82 (1 H, s, H-2). These properties are in agreement with those of luteone trimethyl ether.

5-Hydroxy-2′,4′,7-trimethoxy-8-(3-methylbut-2-enyl)isoflavone (10).—An acetone solution of isoflavone (9) (100 mg) was refluxed with dimethyl sulphate (0.07 cm^3) and potassium carbonate (0.5 g) for 4 h. The product crystallised from methanol as crystals yielding the *isoflavone* (10) (70 mg), m.p. 153—154° (Found: C, 69.5; H, 6.3. $C_{23}H_{24}O_6$ requires C, 69.7; H, 6.1%); green Fe^{III} reaction; R_F 0.75; $\lambda_{max.}$ 267 (log ε 4.64) and 293 nm (4.23); δ($CDCl_3$) 1.67 and 1.78 (6 H, 2s, Me_2C=), 3.46 (2 H, d, *J* 7 Hz, $ArCH_2$), 3.79, 3.80, and 3.87 (9 H, 3s, 3 CH_3O), 5.08—5.37 (1 H, m, CH=), 6.36 (1 H, d, *J* 3 Hz, H-3′), 6.43 (1 H, dd, *J* 10 and 3 Hz, H-5′), 7.00 (1 H, s, H-6), 7.24 (1 H, d, *J* 10 Hz, H-6′), and 7.75 (1 H, s, H-2).

2′,4′,5,7-Tetramethoxy-8-(3-methylbut-2-enyl)isoflavone (11).—An acetone solution of the isoflavone (9) (100 mg) and dimethyl sulphate (0.15 cm^3) was refluxed in the presence of anhydrous potassium carbonate (0.5 g) for 12 h. The product crystallised from methanol to yield the completely methylated *isoflavone* (11) as needles (80 mg), m.p. 180—181° (Found: C, 70.6, H, 6.7. $C_{24}H_{26}O_6$ requires C, 70.2; H, 6.4%); R_F 0.70; $\lambda_{max.}$ 264 nm (log ε 4.65); δ($CDCl_3$) 1.67 (6 H, s, Me_2C=), 3.25 (2 H, d, *J* 7 Hz, $ArCH_2$), 3.75, 3.77, 3.85, and 3.90 (12 H, 4s, 4 CH_3O), 5.12—5.37 (1 H, m, CH=), 6.40 (1 H, d, *J* 3 Hz, H-3′), 6.30—6.54 (1 H, m, H-5′), 7.01 (1 H, s, H-6), 7.27 (1 H, d, *J* 10 Hz, H-6′), and 7.67 (1 H, s, H-2).

2′,4′,9-Trimethoxy-6,6-dimethyl-7,8-dihydropyrano[2,3-f]-*isoflavone* (17).—Isoflavone (15) (50 mg) was heated with formic acid (15 cm^3) for 3 h. The product was crystallised from benzene–light petroleum when the isoflavone (17) was obtained as crystals (30 mg), m.p. 185—187° (lit.,[4] 186—187°) (Found: 70.0; H, 5.9. Calc. for $C_{23}H_{24}O_6$: C, 69.7; H, 6.1%); R_F 0.38; $\lambda_{max.}$ 264 (log ε 4.40) and 292 nm (4.05); δ($CDCl_3$) 1.40 and 1.41 (6 H, 2s, Me_2C=), 1.78 (2 H, t, *J* 6.5 Hz, $ArCH_2$), 2.62 (2 H, t, *J* 6.5 Hz, $ArCH_2$), 3.85 (9 H, s, 3 CH_3O), 6.31 (1 H, s, H-10), 6.80—7.05 (2 H, m, H-5′, and -3′), 7.23 (1 H, d, *J* 9 Hz, H-6′), and 7.65 (1 H, s, H-2). These properties agree with those of the methyl ether of α-isoluteone trimethyl ether.[4]

5-Hydroxy-2′,4′-dimethoxy-8,8-dimethyl-9,10-dihydropyrano[2,3-h]*isoflavone* (12).—Isoflavone (9) (50 mg) was heated with formic acid (15 cm^3) for 3 h. The product crystallised from benzene–light petroleum yielding the *isoflavone* (12) as crystals (35 mg), m.p. 180—181° (Found: C, 69.1; H, 6.05. $C_{22}H_{22}O_6$ requires C, 69.1; H, 5.8%); R_F 0.8; $\lambda_{max.}$ 258 (log ε 4.48) and 288 nm (4.19); δ($CDCl_3$) 1.38 (6 H, s, Me_2C=), 1.87 (2 H, t, *J* 7 Hz, $ArCH_2$), 2.52 (2 H, t, *J* 7 Hz, $ArCH_2$), 3.78 and 3.84 (6 H, 2s, 2 CH_3O), 6.25 (1 H, s, H-6), 6.45—6.65 (2 H, m, H-3′ and -5′), 7.32 (1 H, d, *J* 10 Hz, H-6′), and 7.87 (1 H, s, H-2).

5-Hydroxy-2′,4′-dimethoxy-8,8-dimethylpyrano[3,2-g]*isoflavone* (18).—To benzene solution of isoflavone (13) (100 mg) was added DDQ (60 mg) and the mixture was refluxed for 2 h. The solution was filtered while hot and the filtrate evaporated to dryness. The residue was subjected to column chromatography. Elution with benzene–light petroleum (1 : 4) yielded (18) as light yellow *needles* (75 mg), m.p. 164—165° (Found: C, 69.6; H, 5.4. $C_{22}H_{20}O_6$ requires C, 69.4; H, 5.3%); green Fe^{III} reaction; R_F 0.78; $\lambda_{max.}$ 265 (log ε 4.64) and 308 nm (3.80); δ($CDCl_3$) 1.48 (6 H, s, Me_2C=), 3.75 and 3.87 (6 H, 2s, 2 CH_3O), 5.80 (1 H, d, *J* 10 Hz, H-7), 6.50 (1 H, s, H-10), 6.75 (1 H, d, *J* 10 Hz, H-6), 7.20 (1 H, dd, *J* 10 and 3 Hz, H-5′), 7.18 (1 H, d, *J* 3 Hz, H-3′), 7.32 (1 H, d, *J* 10 Hz, H-6′), and 7.16 (1 H, s, H-2).

2′,4′,5-Trimethoxy-8,8-dimethylpyrano[3,2-g]*isoflavone* (*Tri*-O-*methylparvisoflavone*-B) (19).—An acetone solution of isoflavone (18) (10 mg) was refluxed with dimethyl sulphate (0.01 cm^3) and potassium carbonate (50 mg) for 12 h. The product crystallised from methanol to give (19) as crystals (8 mg), m.p. 147—148° (lit.,[6] 149—151°); R_F 0.5. These properties agree with those of the trimethyl ether of parvisoflavone-B.

5-Hydroxy-2′,4′-dimethoxy-8,8-dimethylpyrano[2,3-h]*isoflavone* (20).—A benzene solution of isoflavone (9) (100 mg)

was refluxed with DDQ (60 mg) for 2 h. The product was purified by column chromatography when (20) was obtained as light yellow *crystals* (60 mg), m.p. 171—172° (Found: C, 69.1; H, 5.5. $C_{22}H_{20}O_6$ requires C, 69.4; H, 5.3%); greenish Fe^{III} reaction; R_F 0.8; $\lambda_{max.}$ 255 (log ε 4.52), 266 (4.58), and 305 nm (3.91); δ($CDCl_3$) 1.41 (6 H, s, Me_2C=), 3.86 and 3.87 (6 H, 2s, 2 CH_3O), 5.56 (1 H, d, *J* 10 Hz, H-9), 6.25 (1 H, s, H-6), 6.66 (1 H, d, *J* 10 Hz, H-10), 7.09 (1 H, dd, *J* 10 and 3 Hz, H-5′), 7.07 (1 H, d, *J* 3 Hz, H-3′), 7.20 (1 H, d, *J* 10 Hz, H-6′), and 7.87 (1 H, s, H-2).

2′,4′,5-*Trimethoxy*-8,8-*dimethylpyrano*[2,3-h]*isoflavone* (*Tri*-O-*methylparvisoflavone*-A) (21).—An acetone solution of isoflavone (20) (10 mg) was refluxed with dimethyl sulphate (0.01 cm^3) in the presence of potassium carbonate (50 mg) until the Fe^{III} reaction was negative. The product crystallised from methanol to give (21) as crystals (9 mg) m.p. 164—165° (lit.,[6] 166—168°); R_F 0.58. These properties agree with those of tri-*O*-methylparvisoflavone-A.

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