# Synthesis of Parvisoflavones A and B

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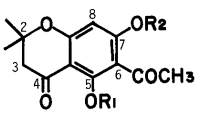
**Parvisoflavone B (2′,4′,5-trihydroxy-2″,2″-dimethylpyrano[5″,6″-*g*]isoflavone) (2) was synthesized by regioselective reduction of 7-[2,4-bis(benzyloxy)phenyl]-2,3-dihydro-5-methoxy-2,2-dimethyl-4*H*,6*H*-benzo[1,2-*b*:5,4-*b*′]dipyrano-4,6-dione (7) with sodium borohydride and dehydration of the resultant alcohol, followed by dealkylation with boron trichloride. Its angular isomer, parvisoflavone A (2′,4′,5-trihydroxy-2″,2″-dimethylpyrano[6″,5″-*h*]isoflavone) (1) was also synthesized from 3-[2,4-bis(benzyloxy)phenyl]-8,9-dihydro-5-methoxy-8,8-dimethyl-4*H*,10*H*-benzo[1,2-*b*:3,4-*b*′]-dipyran-4,10-dione (15) in a similar manner.**

**Keywords** pyranoisoflavone; parvisoflavone A; parvisoflavone B; pyronochalcone; pyronoisoflavone; regioselective reduction; sodium borohydride; dealkylation; boron trichloride

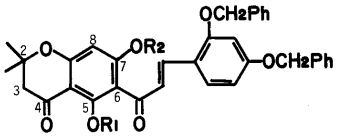
A mixture of parvisoflavones A and B was separated from the trunk wood of *Poecilanthe parviflora* and their structures were shown to be 2′,4′,5-trihydroxy-2″,2″-dimethylpyrano-[6″,5″-*h*]isoflavone {systematic name 5-hydroxy-3-(2,4-dihydroxyphenyl)-8,8-dimethyl-4*H*,8*H*-benzo[1,2-*b*:3,4-*b*′]-dipyran-4-one} (**1**) and 2′,4′,5-trihydroxy-2″,2″-dimethylpyrano[5″,6″-*g*]isoflavone {5-hydroxy-7-(2,4-dihydroxyphenyl)-2,2-dimethyl-2*H*,6*H*-benzo[1,2-*b*:5,4-*b*′]dipyran-6-one} (**2**) by spectroscopy[1] and synthesis[2] of their trimethyl ethers. Recently, parvisoflavone B was also isolated from the root of *Lupinus albus* by Tahara *et al.* and they reported that it exhibited high antifungal activity.[3] During the course of our synthetic studies of pyranoisoflavones, we have already found a more convenient method for synthesizing linear and angular pyranoisoflavones from the corresponding pyronochalcones.[4] We report here on the synthesis of parvisoflavones A (**1**) and B (**2**) from the corresponding pyronochalcones by application of this method and confirm the identities of the two natural isomers.

Condensation of 6-acetyl-7-hydroxy-5-methoxy-2,2-dimethyl-4-chromanone[4] (**3**) with 2,4-bis(benzyloxy)-benzaldehyde (**4**) afforded the chalcone (**5**), which was converted into the acetate (**6**). The oxidative rearrangement of **6** with thallium(III) nitrate trihydrate (TTN), followed by cyclization of the resultant compound with diluted hydrochloric acid under reflux afforded the linear pyronoisoflavone (**7**). Debenzylation of **7** with palladium on charcoal was accompanied with hydrogenation of the 2,3-carbon–carbon double bond and afforded an about 1:1 mixture of the corresponding 2′,4′-dihydroxypyronoisoflavone and 2′,4′-dihydroxypyronoisoflavanone. Therefore, the debenzylation of **7** was examined and it was found that a solution of boron trichloride[5] in dichloromethane was the most appropriate reagent: it cleaved simultaneously the two benzyloxy groups and the methoxy group at the $C_5$-position under the conditions of −65——70 °C for 15 min to give quantitatively 2′,4′,5-trihydroxypyronoisoflavone. Furthermore, 2′,4′-bis(benzyloxy)-5-methoxypyranoisoflavone (**9**) was also easily dealkylated to linear 2′,4′,5-trihydroxypyranoisoflavone (**2**) without influencing the acid-labile dimethylchromene ring under similar dealkylating conditions. Thus, parvisoflavone B (**2**) was easily synthesized by using this dealkylation in the following manner. Compound **7** was regioselectively reduced with sodium borohydride in tetrahydrofuran (THF)–water[4,6] to give the desired monoalcohol (**8**) in good yield. The alcohol **8** was dehydrated with *p*-toluenesulfonic acid monohydrate in toluene to give the linear pyranoisoflavone (**9**), which was converted into **2** as described above. Acetylation and methylation of **2** afforded the triacetate (**10**) and the trimethyl ether[1] (**11**), respectively.

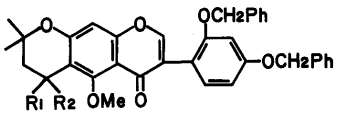
The isomeric angular pyranoisoflavone (**1**) was synthesized in a similar manner: the angular pyronoisoflavone (**15**) was derived from the acetate (**14**) of the corresponding chalcone (**13**), which was prepared from 6-acetyl-5-hydroxy-7-methoxy-2,2-dimethyl-4-chromanone[4] (**12**) and **4**. The angular 2′,4′,5-trihydroxypyranoisoflavone (parvisoflavone A) (**1**) was synthesized from **15** *via* the corresponding monoalcohol (**16**) and pyranoisoflavone (**17**). However, the cleavage of the $C_5$-methoxy group in **17** was more difficult than that in the linear pyranoisoflavone (**9**) because there is no substituent at the $C_6$-position adjacent to the 5-



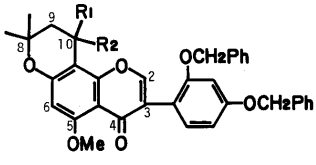
3 : $R_1$=Me, $R_2$=H
12 : $R_1$=H, $R_2$=Me



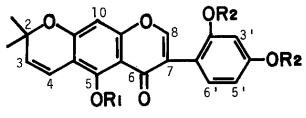
5 : $R_1$=Me, $R_2$=H
6 : $R_1$=Me, $R_2$=Ac
13 : $R_1$=H, $R_2$=Me
14 : $R_1$=Ac, $R_2$=Me



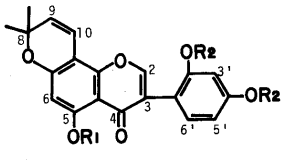
7 : $R_1$, $R_2$=O
8 : $R_1$=H, $R_2$=OH



15 : $R_1$, $R_2$=O
16 : $R_1$=H, $R_2$=OH



2 : $R_1$=$R_2$=H
9 : $R_1$=Me, $R_2$=$PhCH_2$
10 : $R_1$=$R_2$=Ac
11 : $R_1$=$R_2$=Me



1 : $R_1$=$R_2$=H
17 : $R_1$=Me, $R_2$=$PhCH_2$
18 : $R_1$=$R_2$=Ac
19 : $R_1$=$R_2$=Me

TABLE I. $^1$H-NMR ($CDCl_3$) Spectral Data for Parvisoflavones A (**1**), B (**2**), and Their Derivatives (**10**, **11**, **18**, and **19**)[a]

| Compound | Me×2 | $C_{3''}$-H | $C_{4''}$-H | $C_6$-H | $C_8$-H | $C_{3'}$-H | $C_{5'}$-H | $C_{6'}$-H | $C_2$-H | OH or Ac | OMe |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **2**[b] | 1.42 s | 5.70 d | 6.55 d | | 6.37 s | 6.33 s | 6.25 d′ | 6.93 d′ | 8.09 s | 9.20 s, 9.29 s, 13.22 s | |
| Natural[c] | 1.48 s | 5.79 d | 6.69 d | | 6.41 s | 6.49 s | 6.45 d′ | 7.13 d′ | 8.17 s | 13.2 s | |
| **10** | 1.46 s | 5.66 d | 6.40 d | | 6.62 s | 6.98 s | 6.95 d′ | 7.20 d′ | 7.61 s | 2.12 s (3H), 2.25 s (3H) 2.37 s (3H) | |
| **11** | 1.45 s | 5.66 d | 6.71 d | | 6.56 s | 6.51 d″ | 6.51 d′,d″ | 7.20 d′ | 7.69 s | | 3.73 s (3H), 3.79 s (3H) 3.86 s (3H) |
| Natural[1] | 1.52 s | 5.72 d | 6.78 d | | 6.62 s | 6.57 s | 6.57 d′ | 7.27 d′ | 7.74 s | | 3.80 s (3H), 3.90 s (3H) 3.94 s (3H) |
| **1**[b] | 1.43 s | 5.70 d | 6.62 d | 6.19 s | | 6.33 s | 6.26 d′ | 6.96 d′ | 8.18 s | 9.23 s, 9.32 s, 13.01 s | |
| **18** | 1.47 s | 5.62 d | 6.68 d | 6.43 s | | 7.00 s | 6.97 d′ | 7.20 d′ | 7.68 s | 2.13 s (3H), 2.26 s (3H) 2.33 s (3H) | |
| **19** | 1.45 s | 5.48 d | 6.63 d | 6.22 s | | 6.47 s | 6.43 d′ | 7.13 d′ | 7.65 s | | 3.68 s (3H), 3.75 s (3H) 3.84 s (3H) |
| Natural[1] | 1.50 s | 5.60 d | 6.75 d | 6.23 s | | 6.55 s | 6.55 d′ | 7.25 d′ | 7.75 s | | 3.77 s (3H), 3.88 s (3H) 3.95 s (3H) |

*a*) s, singlet; d, doublet ($J$=10 Hz); d′, doublet ($J$=9 Hz); d″, doublet ($J$=2 Hz). *b*) Measured in DMSO-$d_6$. *c*) Lit. 3*a*: measured in acetone-$d_6$.

TABLE II. UV Spectral Data for Parvisoflavones A (**1**), B (**2**), and Their Derivatives (**10**, **11**, **18**, and **19**)[a]

| Linear form | | | | Angular form | | | |
|---|---|---|---|---|---|---|---|
| Compound | $\lambda_{max}$ nm (log ε) | | | Compound | $\lambda_{max}$ nm (log ε) | | |
| **2** | 284 (4.61) | 347 sh (3.60) | | **1** | 270 (4.64) | 307 i (3.88) | 349 (3.53) |
| ($AlCl_3$) | 284 (4.61) | 347 sh (3.61) | | ($AlCl_3$) | 284 (4.64) | 316 i (3.83) | 408 (3.52) |
| **10** | 265 (4.59) | 294 i (3.93) | 336 (3.88) | **18** | 258 (4.61) | 307 (3.76) | 315 (3.73) |
| **11** | 268 (4.59) | 325 (3.84) | | **19** | 266 (4.62) | 299 i (3.86) | 332 (3.69) |
| Natural[1] | 267 (4.65) | | | Natural[1] | 263 (4.56) | | |

*a*) sh, shoulder; i, inflection point.

methoxy group,[7] and a small amount of 2′,4′-dihydroxy-5-methoxypyranoisoflavone was isolated as a by-product.

The proton nuclear magnetic resonance ($^1$H-NMR) and ultraviolet (UV) spectral data for the synthetic pyranoisoflavones **1** and **2** and their derivatives (**10**, **11**, **18**, and **19**) are summarized in Tables I and II. On the basis of these results, the structures of parvisoflavones A and B were confirmed to be 2′,4′,5-trihydroxy-2″,2″-dimethylpyrano-[6″,5″-*h*]isoflavone and 2′,4′,5-trihydroxy-2″,2″-dimethylpyrano[5″,6″-*g*]isoflavone, respectively.

## Experimental

All the melting points are uncorrected. The UV spectra were taken in ethanol on a Hitachi 124 spectrophotometer. The $^1$H-NMR spectra were measured with a Hitachi R-20 spectrometer (60 MHz), using tetramethylsilane as an internal standard ($\delta$, ppm). Column chromatography and thin-layer chromatography were carried out on Kieselgel 60 (70—230 mesh) and with Kieselgel 60 F-254 (Merck).

**7-Hydroxy-5-methoxy-2,2-dimethyl-6-[1-oxo-3-(2,4-bis(benzyloxy)-phenyl)-2-propenyl]-4-chromanone (5)** A mixture of 6-acetyl-7-hydroxy-5-methoxy-2,2-dimethyl-4-chromanone[4] (**3**) (9.80 g) and 2,4-bis(benzyloxy)benzaldehyde (**4**) (14.17 g) was refluxed with stirring in the presence of KOH (6.2 g) in EtOH (400 ml) for 7 h. The reaction mixture was concentrated to *ca.* 200 ml under reduced pressure and then poured into ice-cold water and acidified with HCl. The separated precipitates were recrystallized from EtOAc–petroleum ether to give **5** (18.22 g, 81%) as yellow prisms: mp 162—164 °C. $^1$H-NMR ($CDCl_3$) $\delta$: 1.44 (6H, s, $CH_3$×2), 2.66 (2H, s, $COCH_2$), 3.77 (3H, s, $OCH_3$), 5.00 and 5.09 (each 2H, s, $C_6H_5C\underline{H}_2$), 6.20 (1H, s, $C_8$-H), 6.40—6.70 (2H, m, $C_3$-H and $C_5$-H), 7.68 (1H, d, $J$=9 Hz, $C_6$-H), 7.78 and 8.26 (each 1H, d, $J$=16 Hz, CH=), 13.74 (1H, s, OH). *Anal.* Calcd for $C_{35}H_{32}O_7$: C, 74.45; H, 5.71. Found: C, 74.59; H, 5.51.

**The Acetate (6)** Compound **5** (16.8 g) was converted into the acetate (**6**) as pale yellow needles by treatment with acetic anhydride–pyridine at 120 °C, mp 142—143 °C (MeOH–EtOAc). *Anal.* Calcd for $C_{37}H_{34}O_8$: C, 73.25; H, 5.66. Found: C, 73.42; H, 5.65.

**7-[2,4-Bis(benzyloxy)phenyl]-2,3-dihydro-5-methoxy-2,2-dimethyl-4*H*,6*H*-benzo[1,2-*b*:5,4-*b*′]dipyran-4,6-dione (7)** A mixture of **6** (7.0 g) and TTN (8 g) was stirred in MeOH (850 ml) and 1,2-dichloroethane (150 ml) at 35—38 °C for 6 h, then 10% HCl (80 ml) was added, and the mixture was refluxed for a further 3 h. After removal of the precipitates by filtration, the filtrate was concentrated to *ca.* 400 ml under reduced pressure and poured into a large amount of water to give precipitates. The separated precipitates were recrystallized from MeOH–EtOAc to give **7** (3.57 g, 55%) as pale yellow needles, mp 169—171 °C. $^1$H-NMR ($CDCl_3$) $\delta$: 1.46 (6H, s, $CH_3$×2), 2.71 (2H, s, $COCH_2$), 3.97 (3H, s, $OCH_3$), 5.01 and 5.03 (each 2H, s, $C_6H_5C\underline{H}_2$), 6.60 (1H, d, $J$=9 Hz, $C_{5'}$-H), 7.22 (1H, d, $J$=9 Hz, $C_{6'}$-H), 6.64 (1H, s, $C_{3'}$-H), 6.67 (1H, s, $C_{10}$-H), 7.28 and 7.36 (each 5H, s, $C_6\underline{H}_5CH_2$), 7.69 (1H, s, $C_8$-H). *Anal.* Calcd for $C_{35}H_{30}O_7$: C, 74.72; H, 5.38. Found: C, 74.54; H, 5.23.

**2′,4′-Bis(benzyloxy)-5-methoxy-2″,2″-dimethylpyrano[5″,6″-*g*]isoflavone (9)** Compound **7** (4.0 g) in THF (240 ml) was stirred, with gradual addition of an aqueous solution (60 ml) of $NaBH_4$ (1.08 g), at 5—10 °C for 30 min, and then $Me_2CO$ (5 ml) was added to the reaction mixture. The whole was diluted with water and the organic solvent was removed under reduced pressure. The residue was neutralized with HCl, and extracted with EtOAc. The extract was washed with water, dried ($Na_2SO_4$), and evaporated under reduced pressure to give the crude monoalcohol **8** (3.98 g) as a colorless paste: mp 140—142 °C (colorless needles from $Me_2CO$–$Et_2O$). $^1$H-NMR ($CDCl_3$) $\delta$: 1.38 and 1.43 (each 3H, s, $CH_3$), 2.07 (2H, d, $J$=6 Hz, $C\underline{H}_2CHOH$), 3.45 (1H, br, $CH_2CHO\underline{H}$), 3.88 (3H, s, $OCH_3$), 4.98 (4H, s, $C_6H_5C\underline{H}_2$×2), 5.02 (1H, t, $J$=6 Hz, $CH_2C\underline{H}OH$), 6.4—6.7 (3H, m, $C_{10}$-H, $C_{3'}$-H and $C_{5'}$-H), 7.0—7.4 (11H, m, $C_{6'}$-H and $C_6\underline{H}_5CH_2$×2), 7.67 (1H, s, $C_8$-H). *Anal.* Calcd for $C_{35}H_{32}O_7$: C, 74.45; H, 5.71. Found: C, 74.27; H, 5.68.

Crude **8** (3.98 g) was stirred in toluene (80 ml) in the presence of $TsOH \cdot H_2O$ (70 mg) at 110 °C for 20 min. The resulting compound was recrystallized from MeOH to give **9** (2.75 g, 71% based on **7**) as colorless needles, mp 124—126 °C. UV $\lambda_{max}^{EtOH}$ nm (log ε): 268 (4.60), 325 (3.87). $^1$H-NMR ($CDCl_3$) $\delta$: 1.43 (6H, s, $CH_3$×2), 3.78 (3H, s, $OCH_3$), 4.98 (4H, s, $C_6H_5C\underline{H}_2$×2), 5.60 (1H, d, $J$=10 Hz, $C_{3''}$-H), 6.64 (1H, d, $J$=10 Hz, $C_{4''}$-H), 6.48 (1H, s, $C_8$-H), 6.53 (1H, d, $J$=9 Hz, $C_{5'}$-H), 7.16 (1H, d, $J$=9 Hz, $C_{6'}$-H), 6.60 (1H, s, $C_{3'}$-H), 7.20 and 7.28 (each 5H, s, $C_6\underline{H}_5CH_2$),

7.63 (1H, s, $C_2$-H). *Anal.* Calcd for $C_{35}H_{30}O_6$: C, 76.90; H, 5.53. Found: C, 76.86; H, 5.35.

**2′,4′,5-Trihydroxy-2″,2″-dimethylpyrano[5″,6″-*g*]isoflavone (Parvisoflavone B) (2)** A solution of $BCl_3$–$CH_2Cl_2$ (7 ml) [$BCl_3$ (25 g) had been dissolved in $CH_2Cl_2$ (48 ml)] was added to compound **9** (500 mg) in $CH_2Cl_2$ (12 ml) at −65——70°C. The reaction mixture was stirred at that temperature for 15 min, then water was added, and the solvent was removed at below 40 °C under reduced pressure to give a precipitate. The separated precipitate was extracted with EtOAc, washed with aqueous $NaHCO_3$ and water, and dried ($Na_2SO_4$). The resulting compound was chromatographed over a silica-gel column with $CHCl_3$–$Me_2CO$ (5 : 1) to give **2** (250 mg, 78%) as yellow needles, mp 188.5—189.5 °C ($CHCl_3$). *Anal.* Calcd for $C_{20}H_{16}O_6$: C, 68.18; H, 4.58. Found: C, 68.01; H, 4.29.

**The Triacetate (10)** Compound **2** was converted into the acetate (**10**) as colorless needles by treatment with acetic anhydride–pyridine at 120 °C, mp 184—185 °C (MeOH). *Anal.* Calcd for $C_{26}H_{22}O_9$: C, 65.27; H, 4.64. Found: C, 65.16; H, 4.56.

**The Trimethyl Ether (11)** A mixture of **2**, dimethyl sulfate, and $K_2CO_3$ was refluxed with stirring in $Me_2CO$ for 6 h. The resulting compound was recrystallized from MeOH–$H_2O$ to give **11** as colorless needles, mp 150—151 °C. *Anal.* Calcd for $C_{23}H_{22}O_6$: C, 70.04; H, 5.62. Found: C, 69.80: H, 5.51.

**5-Hydroxy-7-methoxy-2,2-dimethyl-6-[1-oxo-3-(2,4-bis(benzyloxy)-phenyl)-2-propenyl]-4-chromanone (13)** A mixture of 6-acetyl-5-hydroxy-7-methoxy-2,2-dimethyl-4-chromanone[4] (**12**) (5.10 g) and **4** (7.26 g) was refluxed with stirring in the presence of piperidine (1.8 ml) in EtOH (200 ml) for 10 h. The resulting compound was recrystallized from MeOH–$Me_2CO$ to give **13** (6.67 g, 61%) as yellow needles, mp 165—167 °C. $^1$H-NMR ($CDCl_3$) $\delta$: 1.45 (6H, s, $CH_3 \times 2$), 2.67 (2H, s, $COCH_2$), 3.67 (3H, s, $OCH_3$), 5.02 (4H, s, $C_6H_5C\underline{H}_2 \times 2$), 5.92 (1H, s, $C_8$-H), 6.40—6.70 (2H, m, $C_3$-H and $C_5$-H), 6.95 and 7.80 (each 1H, d, $J$=16 Hz, CH=), 7.26 and 7.30 (each 5H, s, $C_6\underline{H}_5CH_2$), 7.46 (1H, d, $J$=9 Hz, $C_6$-H), 12.30 (1H, s, OH). *Anal.* Calcd for $C_{35}H_{32}O_7$: C, 74.45; H, 5.71. Found: C, 74.51; H, 5.71.

**The Acetate (14)** mp 127—128 °C, pale yellow needles (MeOH). *Anal.* Calcd for $C_{37}H_{34}O_8$: C, 73.25; H, 5.66. Found: C, 73.11; H, 5.63.

**3-[2,4-Bis(benzyloxy)phenyl]-8,9-dihydro-5-methoxy-8,8-dimethyl-4*H*,10*H*-benzo[1,2-*b*:3,4-*b*′]dipyran-4,10-dione (15)** A mixture of **14** (4.70 g) and TTN (5.13 g) was stirred in MeOH (700 ml) and 1,2-dichloroethane (100 ml) at 35—38 °C for 10 h, and then cyclized with diluted HCl. The resulting compound was recrystallized from EtOAc–petroleum ether to give **15** (2.66 g, 61%) as colorless needles, mp 155—156 °C. $^1$H-NMR ($CDCl_3$) $\delta$: 1.47 (6H, s, $CH_3 \times 2$), 2.70 (2H, s, $COCH_2$), 3.90 (3H, s, $OCH_3$), 4.99 (4H, s, $C_6H_5C\underline{H}_2 \times 2$), 6.25 (1H, s, $C_6$-H), 6.40—6.75 (2H, m, $C_3$′-H and $C_5$′-H), 7.18 (1H, d, $J$=9 Hz, $C_6$′-H), 7.22 and 7.31 (each 5H, s, $C_6\underline{H}_5CH_2$), 7.87 (1H, s, $C_2$-H). *Anal.* Calcd for $C_{35}H_{30}O_7$: C, 74.72; H, 5.38. Found: C, 74.49; H, 5.27.

**2′,4′-Bis(benzyloxy)-5-methoxy-2″,2″-dimethylpyrano[6″,5″-*h*]isoflavone (17)** The selective reduction of **15** (350 mg) with $NaBH_4$ (100 mg) at 5—10 °C for 25 min gave the crude monoalcohol **16** (347 mg) as a colorless paste, mp 167—168.5 °C (colorless prisms from $Me_2CO$–$Et_2O$). $^1$H-NMR ($CDCl_3$) $\delta$: 1.36 and 1.44 (each 3H, s, $CH_3$), 1.85—2.15 (2H, m, $C\underline{H}_2CHOH$), 3.01 (1H, br, $CH_2CHO\underline{H}$), 3.79 (3H, s, $OCH_3$), 4.93 (4H, s, $C_6H_5C\underline{H}_2 \times 2$), 4.80—5.10 (1H, m, $CH_2C\underline{H}OH$), 6.19 (1H, s, $C_6$-H), 6.49 (1H, d, $J$=9 Hz, $C_5$′-H), 7.18 (1H, d, $J$=9 Hz, $C_6$′-H), 6.58 (1H, s, $C_3$′-H), 7.19 and 7.28 (each 5H, s, $C_6\underline{H}_5CH_2$), 7.63 (1H, s, $C_2$-H). *Anal.* Calcd for $C_{35}H_{32}O_7$: C, 74.45; H, 5.71. Found: C, 74.35; H, 5.78.

Dehydration of crude **16** (347 mg) with TsOH·$H_2O$ (10 mg) gave **17** (260 mg, 76% based on **15**) as colorless needles, mp 151—152 °C. UV $\lambda_{max}^{EtOH}$ nm (log $\varepsilon$): 265 (4.67), 299i (3.90), 332 (3.68). $^1$H-NMR ($CDCl_3$) $\delta$: 1.44 (6H, s, $CH_3 \times 2$), 3.84 (3H, s, $OCH_3$), 4.95 (4H, s, $C_6H_5C\underline{H}_2 \times 2$), 5.43 (1H, d, $J$=10 Hz, $C_3$″-H), 6.60 (1H, d, $J$=10 Hz, $C_4$″-H), 6.20 (1H, s, $C_6$-H), 6.52 (1H, d, $J$=9 Hz, $C_5$′-H), 7.10 (1H, d, $J$=9 Hz, $C_6$′-H), 6.56 (1H, s, $C_3$′-H), 7.18 and 7.25 (each 5H, s, $C_6\underline{H}_5CH_2$),7.63 (1H, s, $C_2$-H). *Anal.* Calcd for $C_{35}H_{30}O_6$: C, 76.90; H, 5.53. Found: C, 76.80; H, 5.58.

**2′,4′,5-Trihydroxy-2″,2″-dimethylpyrano[6″,5″-*h*]isoflavone (Parvisoflavone A) (1)** Compound **17** (220 mg) in $CH_2Cl_2$ (9 ml) was stirred with $BCl_3$–$CH_2Cl_2$ (5.5 ml) at −65——70 °C for 15 min. The resulting compound was chromatographed over a silica-gel column with $CHCl_3$–$Me_2CO$ (5 : 1) to give **1** (105 mg, 73%) and 2′,4′-dihydroxy-5-methoxypyranoisoflavone (5 mg, 4%).

Parvisoflavone A (**1**): Pale yellow prisms, mp 236—238 °C ($CHCl_3$). *Anal.* Calcd for $C_{20}H_{16}O_6$: C, 68.18; H, 4.58. Found: C, 68.00; H, 4.60.

2′,4′-Dihydroxy-5-methoxypyranoisoflavone: Colorless prisms, mp 245—247 °C ($CHCl_3$). $^1$H-NMR (DMSO) $\delta$: 1.44 (6H, s, $CH_3 \times 2$), 3.78 (3H, s, $OCH_3$), 5.68 (1H, d, $J$=10 Hz, $C_3$″-H), 6.1—6.5 (3H, m, $C_3$′-, $C_5$′- and $C_6$-H), 6.63 (1H, d, $J$=10 Hz, $C_4$″-H), 6.88 (1H, d, $J$=9 Hz, $C_6$′-H), 7.92 (1H, s, $C_2$-H), 9.10 and 9.21 (each 1H, s, OH). *Anal.* Calcd for $C_{21}H_{18}O_6$: C, 68.84; H, 4.95. Found: C, 69.13; H, 4.70.

**The Triacetate (18)** Colorless needles, mp 152—154 °C (MeOH). *Anal.* Calcd for $C_{26}H_{22}O_9$: C, 65.27; H, 4.64. Found: C, 65.10; H, 4.51.

**The Trimethyl Ether (19)** Colorless needles, mp 165—167 °C (MeOH–$H_2O$). *Anal.* Calcd for $C_{23}H_{22}O_6$: C, 70.04; H, 5.62. Found: C, 69.79; H, 5.70.

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