D(−)-pantoyl lactone (2.60 g, 20 mmol), obtained in the above reaction, was mixed with freshly distilled β-alanine ethyl ester (2.80 g, 24 mmol) in 20 mL of benzene and heated under reflux for 6 h. After the solvent was evaporated, the residue was submitted to column chromatography on silica. The unreacted pantoyl lactone was recovered (0.52 g, 20%) from the *n*-hexane–benzene eluate, and ethyl D(+)-pantothenate (3.80 g, 77%) was obtained from the ether eluate. Ethyl D(+)-pantothenate: colorless liquid; $[\alpha]^{18}_D$ +42.20° (*c* 2.18, absolute EtOH). Anal. Calcd for $C_{11}H_{21}O_5N$: C, 53.43; H, 8.56; N, 5.66. Found: C, 53.39; H, 8.69; N, 5.47.

The previously reported maximum rotation of this compound by Güssner et al. was $[\alpha]^{15}_D$ +36.8° (*c* 4.68, absolute EtOH). This lower value could be due to a partial racemization during distillation at high temperature.

Acknowledgment. The authors are grateful to Dr. S. Iriuchijima of Sagami Chemical Research Center for his helpful discussions.

Registry No.—Ethyl D(+)-pantothenate, 10527-68-1; BPPM, 61478-28-2; $[Rh(cycloocta\text{-}1,5\text{-}diene)Cl]_2$, 12092-47-6; ketopantoyl lactone, 13031-04-4; D(−)-pantoyl lactone, 599-04-2; BPPM–rhodium(I) complex, 66787-44-8; ethyl β-alaninate, 924-73-2.

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Synthesis of Pomiferin, Auriculasin, and Related Compounds

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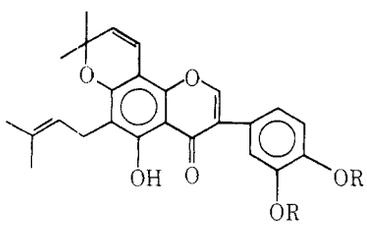
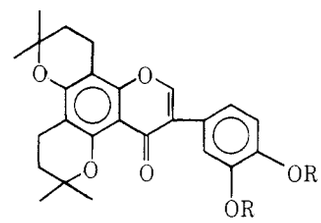
Nuclear prenylation of 3′,4′-di-*O*-methylorobol (**4**) with prenyl bromide under alkaline conditions has yielded its 7-*O*-prenyl (**8**), 6-*C*-prenyl (**12**), and 6,8-di-*C*,*C*-prenyl (**9**) derivatives. Acetylation, partial methylation, and cyclization with formic acid of **12** and **9** separately and their NMR spectra established their structures. Cyclodehydrogenation of **9** with DDQ gave di-*O*-methyl derivatives (**6** and **18**) of pomiferin and auriculasin, respectively. Pomiferin (**1**) and auriculasin (**5**) themselves were synthesized by nuclear prenylation of orobol (**19**), giving the 6-*C*-prenyl (**21**) and the 6,8-di-*C*,*C*-prenyl (**20**) derivatives. Cyclodehydrogenation of 6,8-di-*C*,*C*-prenylorobol (**20**) afforded both the isomers (**1** and **5**). Cyclodehydrogenations of **21** and **12** yielded 6″,6″-dimethylpyrano[2″,3″:7,6]orobol (**22**) and its dimethyl ether (**16**), respectively.

Pomiferin was isolated from the fruit of the osaje orange tree, *Maclura pomifera* Raf., along with osajin (Dr. D. Dreyer, Western Regional Research Laboratory, Berkeley, states that both osajin and pomiferin are present in almost equal amounts in the fruit), and assigned the structure of 5,3′4′-trihydroxy-6-*C*-prenyl-6″,6″-dimethylpyrano[2″,3″:7,8]isoflavone (**1**) by Wolfrom et al.[1,2] using mostly the chemical

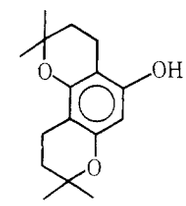


1, R = H (pomiferin)
6, R = Me

methods of degradation and color reactions. The only synthetic evidence given so far has been the synthesis of its derivative, dihydroisopomiferin (**2**), formed in two stages. Wolfrom et al.[2] synthesized dihydroisopomiferin (**2**) from bis(dihydropyrano)phloroglucinol (**3**) by Hoesch reaction with 3,4-dimethoxybenzyl cyanide, followed successively by isoflavone condensation with ethyl formate in the presence of sodium and demethylation with HI, whereas Raizada et al.[3]

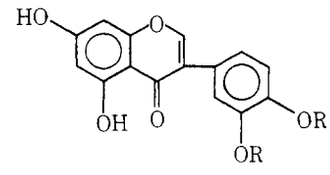


2, R = H (dihydroisopomiferin)
11, R = Me



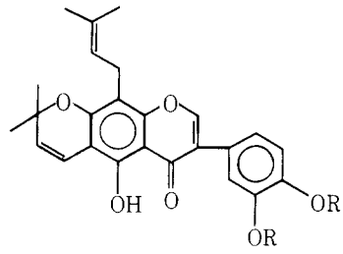
3

synthesized **2** from 3′,4′-di-*O*-methylorobol (**4**) by reacting it with prenyl bromide in the presence of zinc chloride and benzene. Auriculasin recently isolated from *Milletia auriculata* (Leguminosae) has been assigned the isomeric structure **5** by Minhaj et al.[4] on the basis of its special data and those on its trimethyl ether and triacetate. We now report the synthesis



4, R = Me
19, R = H

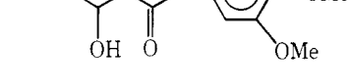
0022-3263/78/1943-3446$01.00/0



5, R = H (auriculasin)
18, R = Me

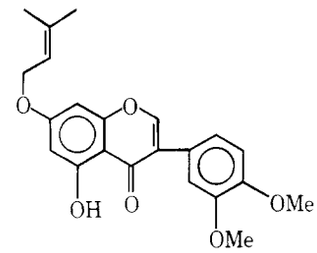
of both the natural compounds **1** and **5** and their 3′,4′-dimethyl ethers **6** and **18**, respectively.

The synthesis of 3′,4′-dimethyl ethers (**6** and **18**) starts with the preparation of orobol 3′,4′-dimethyl ether (**4**) which has been accomplished by Bass's general method of isoflavone synthesis.[5] It involves heating 2,4,6-trihydroxyphenyl 3,4-dimethoxybenzyl ketone (**7**) with methanesulfonyl chloride



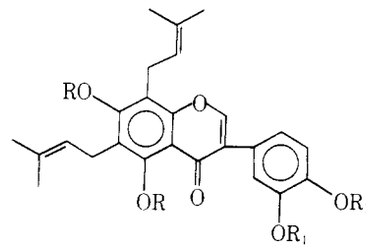
7

in the presence of boron trifluoride etherate and DMF. Orobol 3′,4′-dimethyl ether (**4**), when refluxed with prenyl bromide in the presence of K_2CO_3 and acetone, yielded its 7-prenyl ether (**8**) as shown by its NMR spectrum.[6] Thus, it showed



8

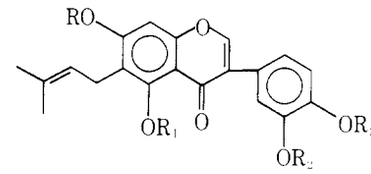
besides the signals of the starting compound, a doublet of OCH_2 at 4.53, two singlets of an olefinic *gem*-dimethyl group at 1.75 and 1.82, and a triplet of one methine hydrogen at 5.42 ppm. On the other hand, when orobol dimethyl ether (**4**) was reacted with prenyl bromide in the presence of methanolic sodium methoxide, a mixture of three compounds was isolated. The product formed in the largest yield was identified as the 6,8-di-*C*,*C*-prenyl derivative (**9**). Thus, it formed a diacetate (**10**) (NMR 2.23, 2.41 ppm (2 s)). Further, both the hydroxy compound (**9**) and its diacetate (**10**) showed no signal



9, R = H; R_1 = Me
10, R = Ac; R_1 = Me
20, R = R_1 = H

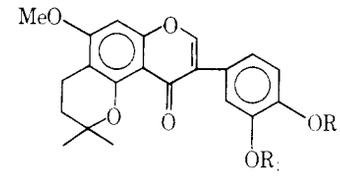
for aromatic protons of the condensed benzene ring but instead showed signals of two *C*-prenyl groups. The structure of di-*C*,*C*-prenylisoflavone (**9**) was finally supported by treatment with HCOOH when dihydroisopomiferin dimethyl ether (**11**) was obtained in agreement with the earlier description.[2,3] Further NMR spectra showed the expected two triplets of four protons each at 2.58 and 2.78 ppm.

The second product of the above prenylation reaction was identified as the 6-*C*-prenyl derivative (**12**) on the basis of formation of its diacetate (**13**) (NMR 2.33, 2.40 ppm (2 s)) and a monomethyl ether (**14**) (NMR 3.87, 3.89 ppm (2 s, three methoxy groups)). Further the NMR spectra of all these



12, R = R_1 = H; R_2 = Me
13, R = R_1 = Ac; R_2 = Me
14, R = R_2 = Me; R_1 = H
21, R = R_1 = R_2 = H

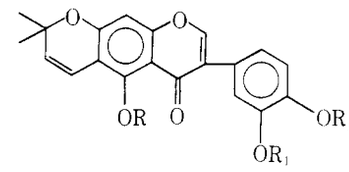
compounds, viz. **12**, **13** and **14**, showed the presence of only one *C*-prenyl unit and one aromatic proton of the ring A (NMR 6.49, 6.87, and 6.36 ppm (s), respectively). The orientation of the *C*-prenyl unit in the 6 position was established by acid cyclization of **14** to give the dihydropyrano derivative (**15**)



15, R_1 = Me

which showed a negative ferric reaction and two triplets at 1.81 and 2.67 ppm in its NMR spectrum. Had this been the 8-*C*-prenyl isomer, it would not have yielded the 2,2-dimethyl dihydropyrano derivative. The third minor product of the above C-prenylation reaction was identified as 7-prenyloxy-3′,4′-dimethoxy-5-hydroxyisoflavone (**8**).

The above *C*-prenyl derivatives **9** and **12** were separately cyclodehydrogenated with DDQ. The latter (**12**) gave 2,2-dimethylpyrano derivative having the structure 5-hydroxy-3′,4′-dimethoxy-6″,6″-dimethylpyrano[2″,3″:7,6]isoflavone (**16**). In accordance with this structure, it formed a monoacetate (**17**: NMR 2.30 ppm (1 s, 3 H)) and both compounds (**16** and **17**) showed two characteristic doublets at about 5.5



16, R = H; R_1 = Me
17, R = Ac; R_1 = Me
22, R = R_1 = H
23, R = R_1 = Ac

and 6.6 ppm of the pyran ring and a deshielded aromatic hydrogen as a singlet at 6.26 ppm. But 6,8-di-*C*,*C*-prenyl-3′,4′-di-*O*-methylorobol (**9**) on cyclodehydrogenation with DDQ gave two products. The major product was found identical with pomiferin dimethyl ether (**6**). The angular pyrano structure was proved by its mass spectrum which showed a mass ion peak at 392 having the *m/e* value of $(M - 56)^+$ characteristic of an *o*-prenylphenol.[7] The minor product was identified as a linear pyrano isomer, viz., auriculasin dimethyl ether (**18**), by its mass spectrum showing the mass ion peak at 393 having an *m/e* value of $(M - 55)^+$.

In order to synthesise pomiferin (**1**) and auriculasin (**5**) themselves, orobol (**19**) prepared from di-*O*-methylorobol (**4**) by heating with HI was subjected to nuclear prenylation as

in an earlier case. Here, a mixture of two products was obtained. The major product was identified as 6,8-di-*C*,*C*-prenylorobol (**20**) by its NMR spectrum. The second product was characterized as 6-*C*-prenylorobol (**21**) because it gave a trimethyl ether (**14**) identical with the one described above.

Cyclodehydrogenation of **21** with DDQ provided 5,3′,4′-trihydroxy-6″,6″-dimethylpyrano[2″,3″:7,6]isoflavone (**22**). Its structure was supported by the formation of its triacetate (**23**) and NMR spectra of both **22** and **23**.

When 6,8-di-*C*,*C*-prenylorobol (**20**) was refluxed with DDQ in benzene, a mixture of two 2,2-dimethylpyrano derivatives (**1** and **5**) was obtained. The structures of both of these derivatives were established by preparing their dimethyl ethers with 2 mol of dimethyl sulfate. The dimethyl ether of the major chromene (**1**) was found identical with **6** and that of the minor chromene identical with **18**. Further, the compound **1** was found identical in all respects with the natural sample of pomiferin,[1] and the compound **5** with auriculasin. Hence the constitutions of pomiferin and auriculasin are established by their total syntheses.

Experimental Section

General. All melting points are uncorrected. Unless stated otherwise, UV data were taken in MeOH; figures before parentheses represent λ_{max} in nanometers and those written in parentheses log ϵ values; IR spectra were recorded in Nujol mull; NMR spectra were run on a 80 MHz machine in $CDCl_3$ with Me_4Si as an internal standard; chemical shifts are expressed in parts per million (ppm) downfield from Me_4Si; R_f values refer to TLC carried out on plates coated with silica gel "G", and these plates were either developed with 10% aqueous sulfuric acid or with 3% alcoholic ferric chloride; column chromatography was done on silica gel; one of the following solvent systems was used for TLC: (A) benzene, (B) benzene–ethyl acetate (9:1), (C) benzene–ethyl acetate (17:3), and (D) toluene–ethyl formate–formic acid (5:4:1).

3′,4′-Di-*o*-methylorobol (4). To a well-stirred and ice-cooled solution of 2,4,6-trihydroxyphenyl 3,4-dimethyloxybenzyl ketone (**7**) (4 g) in DMF (35 mL) was added boron trifluoride etherate (7 mL) dropwise during the course of 30 min. The temperature was raised to 60 °C and then methanesulfonyl chloride (4.5 mL) in DMF (10 mL) was added in one lot. The resulting mixture was heated for 90 min on a water bath, cooled, and then added to ice-cold water (500 mL). The solid was collected and crystallized from a pyridine–water mixture when **4** separated as colorless crystals (3.6 g): mp 253–254 °C; R_f 0.46 (solvent B); intense green ferric reaction; IR 3380, 1640 cm^{-1}; UV 262 (3.97).

Anal. Calcd for $C_{17}H_{14}O_6$: C, 64.9; H, 5.0. Found: C, 65.0; H, 5.1.

5-Hydroxy-7-prenyloxy-3′,4′-dimethoxyisoflavone (8). A solution of the isoflavone **4** (100 mg) in acetone (20 mL) was refluxed with prenyl bromide (0.05 mL) and K_2CO_3 (1 g) for 3 h. Acetone was distilled off and water added to the residue. The solid thus obtained crystallized from MeOH yielding **8** as colorless needles (90 mg): mp 127–128 °C; R_f 0.55 (solvent A); green ferric reaction; IR 3450 and 1650 cm^{-1}; UV λ_{max} 255 (4.14); NMR 1.75, 1.82 (6 H, 2 s, $(CH_3)_2C$=), 3.90 (6 H, s, $2CH_3O$), 4.53 (2 H, d, J = 7 Hz, OCH_2), 5.42 (1 H, t, J = 6.5 Hz, $ArCH_2CH$=), 6.35, 6.98 (2 H, 2 d, J = 3 Hz, H-6 and -8, respectively), 6.82–7.02 (3 H, m, H-2′, -5′, and -6′), and 7.80 (1 H, s, H-2).

Anal. Calcd for $C_{22}H_{22}O_6$: C, 69.1; H, 5.9. Found: C, 68.9; H, 6.0.

Nuclear Prenylation of 3′,4′-Di-*O*-methylorobol (4). To a solution of **4** (4 g) in anhydrous MeOH (150 mL) was added a methanolic solution of sodium methoxide (5 g of Na/60 mL of MeOH). The mixture was cooled, treated with prenyl bromide (6 mL) in one lot, and refluxed for 4 h. After removal of the solvent, the mixture was treated with ice and acidified in cold dilute HCl. The solid product was examined by TLC using the solvent system B which showed the presence of four main compounds. It was therefore subjected to column chromatography and the column eluted successively with (1) benzene–light petroleum (1:9), (2) benzene–light petroleum (1:4), (3) benzene–light petroleum (1:1), and (4) benzene–ethyl acetate (9:1) when four fractions, A–D, were obtained.

Fraction A crystallized from a benzene–light petroleum mixture to yield **6,8-di-*C*,*C*-prenyl-3′,4′-dimethoxy-5,7-dihydroxyisoflavone (9)** as colorless crystals (0.73 g): mp 124–125 °C; R_f 0.65 (solvent B); green ferric reaction; IR 3340, 1630, 1680 cm^{-1}; UV λ_{max} 210, 240 (3.80 and 4.10, respectively); 90 MHz NMR 1.77, 1.85 (12 H, 2 s, $2(CH_3)_2C$=), 3.48 (4 H, d, J = 7 Hz, $2ArCH_2CH$=), 3.90 (6 H, s, $2CH_3O$), 5.10–5.40 (2 H, m, $2ArCH_2CH$=), 6.90–7.30 (3 H, m, H-2′, -5′, and -6′), and 7.92 (1 H, s, H-2).

Anal. Calcd for $C_{27}H_{30}O_6$: C, 72.0; H, 6.7. Found: C, 72.0; H, 7.1.

The diacetate (**10**) prepared from **9** by the acetic anhydride–pyridine method crystallized from a benzene–light petroleum mixture as colorless flakes: mp 114–115 °C; R_f 0.35 (solvent B); IR 1750 and 1640 cm^{-1}; UV λ_{max} 206 and 254 (4.02 and 4.32, respectively); NMR 1.72, 1.84 (12 H, 2 s, $2(CH_3)_2C$=), 2.23, 2.41 (6 H, 2 s, $2CH_3CO_2$), 3.28, 3.47 (4 H, 2 d, J = 7 Hz, $2ArCH_2$), 3.87, 3.94 (6 H, 2 s, CH_3O), 4.80–5.20 (2 H, m, 2XCH=), 6.80–7.12 (3 H, m, H-2′, -5′, and -6′), and 7.87 (1 H, s, H-2).

Anal. Calcd for $C_{31}H_{34}O_8$: C, 69.7; H, 6.4. Found: C, 70.0; H, 6.8.

Fraction B was crystallized from MeOH when **5-hydroxy-7-prenyloxy-3′,4′-dimethoxyisoflavone (8)** formed colorless crystals (0.15 g); mp and mmp with the sample prepared above 127–128 °C.

Fraction C was crystallized from ethyl acetate–light petroleum mixture to give 6-*C*-prenyl-3′,4′-dimethoxy-5,7-dihydroxyisoflavone (**12**) as colorless crystals (0.25 g): mp 209–210 °C; R_f 0.58 (solvent A); IR 1620 and 3300 cm^{-1}; UV λ_{max} 218 and 254 (4.18 and 4.09, respectively); NMR 1.65, 1.78 (6 H, 2 s, $(CH_3)_2C$=), 3.40 (2 H, d, J = 7 Hz, $ArCH_2CH$=), 3.69 (6 H, s, $2CH_3O$), 5.06–5.32 (1 H, m, CH=), 6.49 (1 H, s, H-8), 6.85–7.26 (3 H, m, H-2′, -5′, and -6′), and 7.97 (1 H, s, H-2).

Anal. Calcd for $C_{22}H_{22}O_6$: C, 69.1; H, 5.8. Found: C, 69.2; H, 6.1.

The diacetate (**13**) prepared from **12** by the acetic anhydride–pyridine method crystallized from benzene as colorless needles: mp 184–185 °C; R_f 0.45 (solvent C); IR 1630 and 1745 cm^{-1}; NMR 1.64, 1.80 (6 H, 2 s, $(CH_3)_2C$=), 2.33, 2.40 (6 H, 2 s, $2CH_3CO_2$), 3.25 (2 H, d, J = 7 Hz, $ArCH_2$), 3.88 (6 H, s, $2CH_3O$), 4.82–5.12 (1 H, m, ArCH=), 6.87 (1 H, s, H-8), 6.90–7.20 (3 H, m, H-2′, -5′, and -6′), and 7.82 (1 H, s, H-2).

Anal. Calcd for $C_{26}H_{26}O_8$: C, 66.9; H, 5.6. Found: C, 66.8; H, 5.9.

Fraction D on crystallization from an acetone–MeOH mixture afforded the starting material **4**, 2.3 g.

Dihydroisopomiferin 3′,4′-Dimethyl Ether (11). The isoflavone **9** (200 mg) was heated with formic acid (25 mL) on a boiling water bath for 2 h and then left overnight at room temperature. The product was poured into ice-cold water (250 mL) and the solid was collected and subjected to column chromatography. Elution with a benzene–light petroleum mixture (1:4) gave **11** which crystallized from MeOH–acetone mixture as colorless needles: mp 213–214 °C (lit.[2] mp 207.5–209 °C); R_f 0.50 (solvent B); IR 1635 cm^{-1}; NMR 1.34, 1.37 (12 H, 2 s, $(CH_3)_2C$<), 1.78, 1.87 (4 H, 2 t, J = 6 Hz, $2ArCH_2CH_2$), 2.58, 2.78 (4 H, 2 t, J = 6 Hz, $2ArCH_2$), 3.81, 3.84 (6 H, 2 s, $2CH_3O$), 6.80–7.20 (3 H, m, H-2′, -5′, and -6′), and 7.72 (1 H, s, H-2).

Anal. Calcd for $C_{27}H_{30}O_6$: C, 72.0; H, 6.7. Found: C, 72.0; H, 6.9.

6-*C*-Prenyl-5-hydroxy-7,3′,4′-trimethoxyisoflavone (14). An acetone solution of the isoflavone **12** (200 mg) was refluxed with dimethyl sulfate (0.14 mL) in the presence of ignited K_2CO_3 (1 g) for 3 h. The solvent was removed and the residue treated with water (100 mL). The solid was collected and crystallized from MeOH when **14** separated as colorless plates (160 mg): mp 134–135 °C; R_f 0.60 (solvent B); green ferric reaction; IR 3250 and 1620 cm^{-1}; UV 216 and 280 (3.83 and 4.05, respectively); NMR 1.65, 1.78 (6 H, 2 s, $(CH_3)_2C$=), 3.35 (2 H, d, J = 7 Hz, $ArCH_2CH$=), 3.87, 3.89 (9 H, 2 s, $3CH_3O$), 5.19 (1 H, t, J = 6.5 Hz, $ArCH_2CH$=), 6.36 (1 H, s, H-8), 6.88–7.01 (3 H, m, H-2′, -5′, and -6′), and 7.81 (1 H, s, H-2).

Anal. Calcd for $C_{23}H_{24}O_6$: C, 69.7; H, 6.1. Found: C, 70.0; H, 5.9.

6″,6″-Dimethyl-7,3′,4′-trimethoxy-4″,5″-dihydropyrano[2″,3″:5,6]isoflavone (15). The isoflavone **14** (100 mg) was heated with formic acid (10 mL) for 3 h. The product crystallized from a benzene–light petroleum mixture to afford **15** as colorless crystals (60 mg): mp 185–86 °C; R_f 0.36 (solvent B); IR 1575 and 1640 cm^{-1}; NMR 1.40 (6 H, s, $(CH_3)_2C$<), 1.81, 2.65 (4 H, 2 t, J = 7 Hz, $ArCH_2CH_2$), 3.88 (9 H, s, $3CH_3O$), 6.37 (1 H, s, H-8), 6.65–7.27 (3 H, m, H-2′, -5′, and -6′), and 7.72 (1 H, s, H-2).

Anal. Calcd for $C_{23}H_{24}O_6$: C, 69.7; H, 6.1. Found: C, 70.0; H, 5.8.

6″,6″-Dimethyl-5-hydroxy-3′,4′-dimethoxypyrano[2″,3″:7,6]isoflavone (16). To a solution of the isoflavone **12** (150 mg) in freshly distilled dry benzene (30 mL) was added DDQ (90 mg) and the resulting mixture refluxed for 2 h on a boiling water bath when colorless hydroquinone separated out. It was filtered while hot and the filtrate evaporated to dryness. The residue on column chromatography and elution with benzene–light petroleum mixture (1:3) yielded **16** (80 mg) as light yellow needles: mp 136 °C; light green ferric reaction; R_f 0.55 (solvent B); IR 1620 cm^{-1}; UV 208 and 276 (4.03 and 4.07, respectively); 60 MHz NMR 1.42, 1.66 (6 H, 2 s, $(CH_3)_2C$<), 3.86 (6 H, s, $2CH_3O$), 5.53, 6.63 (2 H, 2 d, J = 10 Hz, ArCH=CH), 6.36 (1 H, s, H-8), 6.92–7.22 (3 H, m, H-2′, -5′, and -6′), and 7.84 (1 H, s, H-2).

Anal. Calcd for $C_{22}H_{20}O_6$: C, 69.4; H, 5.3. Found: C, 69.6; H, 5.4.

The monoacetate of **17** prepared from **16** by the acetic anhydride–sodium acetate method crystallized from MeOH as white flakes: mp 185–186 °C; R_f 0.45 (solvent B); 220 MHz NMR 1.40, 1.45 (6 H, 2 s, $(CH_3)_2C<$), 2.30 (3 H, s, CH_3CO_2), 3.80 (6 H, s, $2CH_3O$), 5.55, 6.76 (2 H, 2 d, J = 10 Hz, ArCH=CH), 6.40 (1 H, s, H-8), 6.76–7.00 (3 H, m, H-2′, -5′, and -6′), and 7.74 (1 H, s, H-2).

Anal. Calcd for $C_{24}H_{22}O_7$: C, 68.2; H, 5.3. Found: C, 68.2; H, 5.2.

Pomiferin 3′,4′-Dimethyl Ether (6) and Auriculasin 3′,4′-Dimethyl Ether (18). A solution of the isoflavone **9** (300 mg) and DDQ (150 mg) in benzene (25 mL) was refluxed for 30 min. The product on column chromatography and elution with benzene–light petroleum mixture (1:4) gave a solid which again proved to be a mixture by TLC. This on fractional crystallization from ethyl acetate–light petroleum mixture gave a solid (mother liquor A) which recrystallized from MeOH to afford **6** as light yellow neeldes (120 mg): mp 130–131 °C (lit.[2] mp 132 °C); R_f 0.70 (solvent B); green ferric reaction; IR 3360, 1630 cm^{-1}; UV 224 and 278 (4.18 and 4.28, respectively); NMR 1.50 (6 H, s, $(CH_3)_2C<$), 1.70, 1.82 (6 H, 2 s, $(CH_3)_2C=$), 3.38 (2 H, d, J = 8 Hz, $ArCH_2CH=$), 3.90 (6 H, s, $2CH_3O$), 5.23 (1 H, t, J = 7 Hz, $ArCH_2CH=$), 5.53, 6.66 (2 H, 2 d, J = 10 Hz, ArCH=CH), 6.87–7.15 (3 H, m, H-2′, -5′, and -6′), and 7.82 (1 H, s, H-2); MS 448 (M^+), 433 395, 392 $(M - 56)^+$, 377, 215, 181, 152, 97.

Anal. Calcd for $C_{27}H_{28}O_6$: C, 72.3; H, 6.3. Found: C, 72.0; H, 6.6.

The mother liquor A after evaporation yielded a viscous mass which after crystallization twice from MeOH gave **18** as shining yellow needles (40 mg): mp 98–99 °C; R_f 0.62 (solvent B); green ferric reaction; IR 1645 cm^{-1}, UV 218 and 274 (4.25 and 4.34, respectively); 100 MHz NMR 1.44, 1.48 (6 H, 2 s, $(CH_3)_2C<$), 1.68, 1.80 (6 H, 2 s, $(CH_3)_2C=$), 3.36 (2 H, d, J = 7.5 Hz, $ArCH_2CH=$), 3.90 (6 H, s, $2CH_3O$), 5.16–5.32 (1 H, m, $ArCH_2CH=$), 5.56, 6.70 (2 H, 2 d, J = 10 Hz, ArCH=CH), 6.83–7.18 (3 H, m, H-2′, -5′, and -6′), and 7.84 (1 H, s, H-2); MS 448 (M^+), 433, 405, 393 $(M - 55)^+$, 377, 365, 351, 338, 215, 181, 162, 118, 91.

Anal. Calcd for $C_{27}H_{28}O_6$: C, 72.3; H, 6.3. Found: C, 72.0; H, 6.1.

Orobol (19) was prepared by demethylation of **4** with HI and identified by converting it into its acetate which crystallized from MeOH as white flakes: mp 160–161 °C (lit.[8] mp 163 °C); R_f 0.54 (solvent B); NMR 2.26, 2.30, and 2.38 (12 H, 3 s, $4CH_3CO_2$), 6.87 (1 H, d, J = 3 Hz, H-6), 7.14 (1 H, d, J = 3 Hz, H-8), 7.18–7.38 (3 H, m, H-2′, -5′, and -6′), and 7.92 (1 H, s, H-2).

Nuclear Prenylation of Orobol (19). To a solution of orobol **19** (2 g) in anhydrous MeOH (100 mL) was added a methanolic solution of sodium methoxide (2.1 g of Na/25 mL of MeOH). This mixture was cooled and treated with prenyl bromide (2.6 mL) in one lot and then refluxed for 2 h. The product on column chromatography and successive elution with (1) benzene–light petroleum (1:4), (2) benzene alone, and (3) ethyl acetate–benzene (1:9) gave three fractions A to C.

Fraction A crystallized from a benzene–light petroleum mixture to yield **5,7,3′,4′-tetrahydroxy-6,8-di-*C,C*-prenylisoflavone (20)** as colorless crystals (120 mg): mp 156–157 °C; R_f 0.46 (solvent D); green ferric reaction; NMR 1.48, 1.75, 1.82 (12 H, 3 s, $2(CH_3)_2C=$), 3.25–3.50 (4 H, m, $2ArCH_2CH=$), 5.00–5.37 (2 H, m, $2ArCH_2CH=$), 6.58–7.06 (3 H, m, H-2′, -5′, and -6′), and 8.01 (1 H, s, H-2).

Anal. Calcd for $C_{25}H_{26}O_6$: C, 71.1; H, 6.2. Found: C, 70.8; H, 6.0.

Fraction B on crystallization from benzene–light petroleum mixture afforded **6-*C*-prenylorobol (21)** as white flakes (90 mg): mp 243–244 °C; R_f 0.30 (solvent D); IR 1655, 1620 cm^{-1}; NMR (CD_3COCD_3) 1.65, 1.78 (6 H, 2 s, $(CH_3)_2C=$), 3.42 (2 H, d, J = 7 Hz, $ArCH_2CH=$), 5.08–5.32 (1 H, m, $ArCH_2CH=$), 6.33 (1 H, s, H-8), 6.75–7.21 (3 H, m, H-2′, -5′, and -6′), and 7.95 (1 H, s, H-2).

Anal. Calcd for $C_{20}H_{18}O_6$: C, 67.8; H, 5.2. Found: C, 67.5; H, 5.3.

An acetone solution of **21** (60 mg) was treated with dimethyl sulfate (0.035 mL) and anhydrous K_2CO_3 (1 g) for 4 h. The product crystallized from MeOH yielding **14** as colorless needles (40 mg); mp and mmp with the synthetic sample prepared above 134–135 °C.

Fraction C proved to be the starting compound.

6″,6″,6‴,6‴-Tetramethyl-4″,5″,4‴,5‴-tetrahydro-3′,4′-dihydroxybis(pyrano[2″,3″:7,8::2‴,3‴:5,6]isoflavone[dihydroisopomiferin]) (2). The isoflavone **20** (100 mg) was heated with formic acid (15 mL) for 2 h. The product crystallized from benzene–light petroleum mixture yielding **2** as colorless crystals (50 mg): mp 262–263 °C (lit.[2] mp 264.5–265 °C); R_f 0.61 (solvent C); NMR 1.25, 1.35 (12 H, 2 s, $2(CH_3)_2C<$), 1.62–1.85 (4 H, m, $2ArCH_2CH_2$), 2.58–2.86 (4 H, m, $2ArCH_2CH$), 6.81–7.20 (3 H, m, H-2′, -5′, and -6′), and 7.82 (1 H, s, H-2).

Anal. Calcd for $C_{25}H_{26}O_6$: C, 71.1; H, 6.2. Found: C, 70.9; H, 6.0.

6″,6″-Dimethyl-5,3′,4′-trihydroxypyrano[2″,3″:7,6]isoflavone (22). To a solution of **21** (100 mg) in benzene (30 mL) was added DDQ (50 mg) and the resulting solution refluxed for 30 min. The product on column chromatography and elution with benzene–light petroleum (1:1) yielded **22** as light yellow needles (20 mg): mp 166–167 °C; R_f 0.66 (solvent C); light brown ferric reaction; NMR 1.48 (6 H, s, $(CH_3)_2C<$), 5.58, 6.61 (2 H, 2d, J = 10 Hz, ArCH=CH), 6.25 (1 H, s, H-8), 7.25–7.53 (3 H, m, H-2′, -5′, and -6′), and 7.81 (1 H, s, H-2).

Anal. Calcd for $C_{20}H_{16}O_6$: C, 68.2; H, 4.5. Found: C, 68.1; H, 4.6.

The triacetate **(23)** prepared from **22** by the acetic anhydride–pyridine method crystallized from MeOH as colorless crystals: mp 151–152 °C; R_f 0.40 (solvent D); NMR 1.47 (6 H, s, $(CH_3)_2C<$), 2.42 (9 H, s, $3CH_3CO_2$), 5.59, 6.68 (2 H, 2 d, J = 10 Hz, ArCH=CH), 6.27 (1 H, s, H-8), 6.85–7.21 (3 H, m, H-2′, -5′, and -6′), and 7.67 (1 H, s, H-2).

Anal. Calcd for $C_{26}H_{22}O_9$: C, 61.9; H, 4.6. Found: C, 61.4; H, 4.8.

Pomiferin (1) and Auriculasin (5). A solution of **20** (150 mg) and DDQ (70 mg) in dry benzene (30 mL) was refluxed for 10 min. The product on column chromatogrphy and elution with benzene–light petroleum mixture (1:9) gave a solid which again proved to be a mixture on TLC. This on fractional crystallization from ethyl acetate–light petroleum mixture yielded a solid (mother liquor A) which when crystallized from MeOH afforded pomiferin (1) as pale yellow crystals (50 mg): mp and mmp with the natural sample 198–199 °C (lit.[2] mp 200.5 °C); R_f 0.58 (solvent A); green ferric reaction; UV 280 and 310 (4.40 and 4.51, respectively); NMR 1.50 (6 H, s, $(CH_3)_2C$), 1.70, 1.83 (6 H, 2 s, $(CH_3)_2C=$), 3.38 (2 H, d, J = 8 Hz, $ArCH_2CH=$), 5.25 (1 H, t, J = 6.5 Hz, $ArCH_2CH=$), 5.62, 6.72 (2 H, 2 d, J = 10 Hz, ArCH=CH), 6.93–7.26 (3 H, m, H-2′, -5′, and -6′), and 7.90 (1 H, s, H-2). The IR spectrum was superimposable on that of natural sample.

Anal. Calcd for $C_{25}H_{24}O_6$: C, 71.4; H, 5.7. Found: C, 71.3; H, 5.5.

The identity of the synthetic pomiferin was further established by converting it (50 mg) into its dimethyl ether (**6**) by refluxing with dimethyl sulfate (0.025 mL), dry K_2CO_3 (1 g), and acetone (30 mL) for 2 h; mp and mmp with the sample described above were 132 °C.

The mother liquor A on evaporation yielded a semisolid mass which crystallized from benzene yielding auriculasin (**5**) as pale yellow needles (20 mg): mp 174–176 °C; green ferric reaction; R_f 0.55 (solvent A); UV λ_{max} 240, 310 (4.40 and 4.52); NMR (with 90 MHz machine) 1.86 (6 H, s, $(CH_3)_2C<$), 1.90 (6 H, s, $(CH_3)_2C=$), 3.52 (2 H, d, J = 7 Hz, $ArCH_2CH=$), 5.20–5.31 (1 H, m, $ArCH_2CH=$), 5.45, 6.41 (2 H, 2 d, J = 10 Hz, ArCH=CH), 6.99–7.37 (3 H, m, H-2′, -5′, -6′), and 7.96 (1 H, s, H-2). These properties agree closely with those described for natural compound.[4]

Anal. Calcd for $C_{25}H_{24}O_6$: C, 71.4; H, 5.7. Found: C, 71.3; H, 5.4.

Its identity was established by converting it (50 mg) into its dimethyl ether (**18**) by refluxing with dimethyl sulfate (0.025 mL), K_2CO_3 (1 g), and acetone (10 ml) for 2 h; mp and mmp with the sample prepared above were 98–99 °C.

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