# Synthesis of Isopentenylated Chrysins

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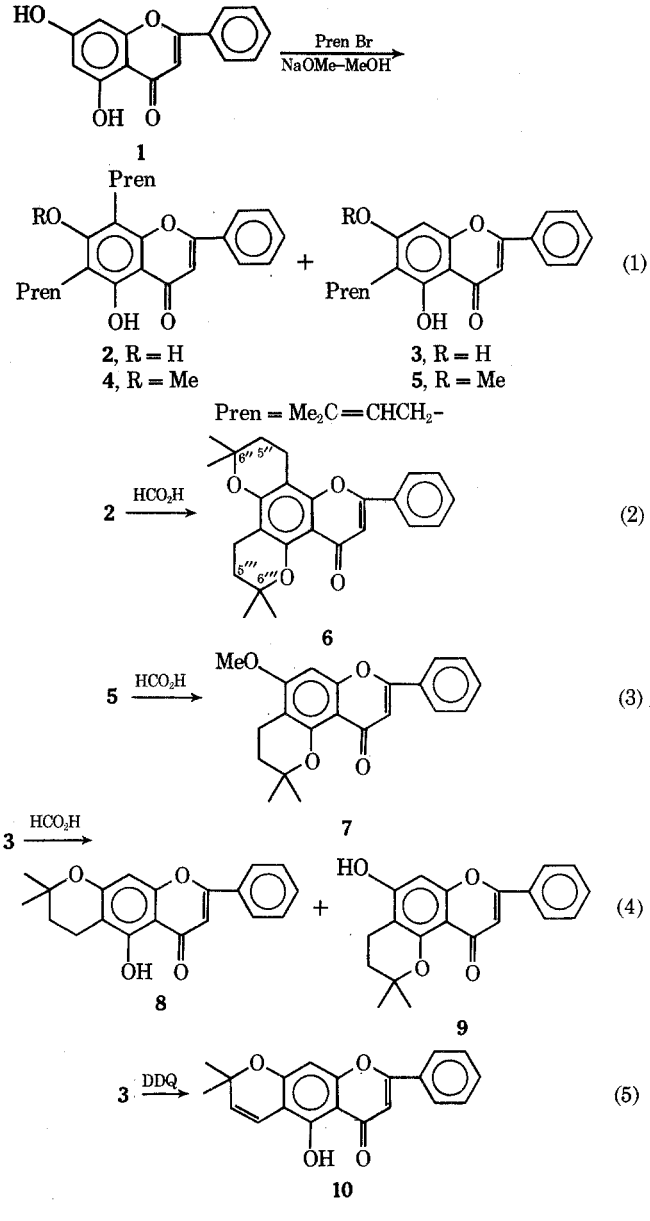
Chrysin (1) when heated with prenyl bromide in the presence of methanolic methoxide gives 6-prenyl (3) and 6,8-diprenyl (2) derivatives, but with 2-hydroxy-2-methyl-3-butene in the presence of boron trifluoride etherate affords, besides the above two compounds, the 8-prenyl derivative (11). Their structures have been established by nmr spectra of themselves, their acetates, and partial methyl ethers and by acid cyclization of the hydroxy compounds and their partial methyl ethers. Cyclodehydrogenation of the three prenyl compounds (3, 11, and 2) has been accomplished by DDQ in benzene; the first two formed chromenes 10 and 14, respectively, and the last one yielded 3-deoxy derivatives of sericetin (16) and isosericetin (15).

Thirteen isopentenylated flavones have been isolated from species of the two genera *Artocarpus* and *Morus* by Venkataraman, *et al.*[2] They are artocarpesin,[3] cycloartocarpesin,[4] oxydihydroartocarpesin,[4] artocarpin,[5] norartocarpin,[5] cycloartocarpin,[6] heterophyllin,[7] cycloheterophyllin,[7] chaplashin,[8] mulberrin,[9] mulberrochromene,[9] cyclomulberrin,[9] and cyclomulberrochromene.[9] They are either 5,7,2′,4′-tetra- or 5,7,2′,4′,5′-pentaoxygenated flavones having isopentenylation at either C-6 or C-8 or C-3 and C-6, or C-3, C-6, and C-8. The isopentenyl unit is either γ,γ-dimethylallyl (prenyl), 3-methyl-1-butenyl, a condensed 2,2-dimethylpyran ring, 2-(2-methyl-2-propenyl)-pyran, or exepine ring. Besides the above flavones, 8-prenylluteolin[10,11] and laceolatin A[12] have been isolated from other plant families. The last named compound is unique in having an unusual $C_5$ moiety, *viz.* a 3-hydroxy-3-methyl-1-butenyl unit in the 8 position. Although the constitutions of all the above 15 flavones have been established on the basis of their spectral data and degradation, none of them has been synthesized so far. As a model experiment, the simplest flavone, chrysin (1), has been subjected to nuclear prenylation under two different conditions in order to see which positions are affected. Further oxidative cyclization of the resulting *o*-prenyl phenols has been accomplished to get the corresponding chromenes.

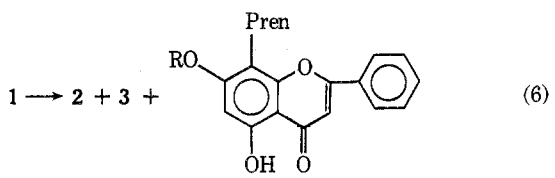
Chrysin[13] (1) when refluxed with prenyl bromide in the presence of methanolic methoxide gave two products separable by column chromatography (reaction 1). The first eluate analyzed for a diprenyl derivative and formed a monomethyl ether (nmr δ 3.80, s, 3 H, $OCH_3$) with 1 mol of dimethyl sulfate in the presence of potassium carbonate and acetone. The positive ferric reaction of both the hydroxy compound and the partial methyl ether indicated that both hydroxyl groups were free. This was confirmed by the formation of a diacetate (nmr δ 2.34, 2.45, 2 s, 6 H, $OCOCH_3$). Further, both prenyl units were found to be in the nuclear positions of ring A by the nmr signals of H-3 and the protons of intact side phenyl ring but not of ring A. The nmr spectra also showed the signals of two benzylic methylene groups, two methine protons, and four olefinic methyl groups (see Experimental Section). Hence the first prenylation product could be assigned formula 2 (5,7-dihydroxy-6,8-diprenylflavone) which was further confirmed by preparing its bisdihydropyran derivative (6) on heating with formic acid (reaction 2). The structure of 6 was confirmed by its nmr spectrum.

The second prenylation product also showed a positive ferric reaction and formed a diacetate [nmr δ 2.34, 2.46 (2 s, 6 H, $-OCOCH_3$)] and a 7-methyl ether [nmr δ 3.92 (s, 3 H, $OCH_3$)]. The nmr spectra of the diacetate and the 7-methyl ether show the presence of only one prenyl unit and one aromatic H of ring A. Hence, it could be either a 6-prenyl or a 8-prenyl derivative. The precise location of the prenyl unit was established by studying the cyclization of the hydroxy compound and its 7-methyl ether with formic acid. The latter gave 7 (reaction 3), which had a negative ferric reaction and exhibited two characteristic triplets of methylene protons in its nmr spectrum at δ 1.78 and 2.65 ($J$ = 7 Hz). The formation of a dihydropyran is possible only when the prenyl group is in the 6 position.



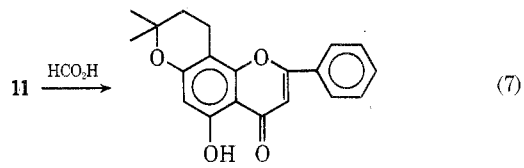
The same conclusion was reached on acid cyclization of the dihydroxy compound (3), which yielded two dihydropyrans (reaction 4). One dihydropyran derivative, mp 180°, which gave a positive ferric reaction and has two characteristic triplets of methylene protons in its nmr spectrum at $\delta$ 1.85 and 2.77 ($J$ = 7 Hz) was assigned structure 8. Since the other dihydropyran of mp 296° gave no ferric reaction and was isomeric with 8, it was assigned structure 9. Cyclodehydrogenation of 3 with DDQ provided further confirmation for its structure by yielding the 10 (reaction 5), which was identical in melting point with the chromene obtained by Hlubucek, *et al.*,[14] on heating chrysin with 3-chloro-2-methyl-1-butyne.

In the second method of prenylation, treatment of chrysin with 2-hydroxy-2-methyl-3-butene, in the presence of boron trifluoride etherate, gave three compounds which were separated by column chromatography (reaction 6). The first eluate was 2 and the second eluate 3. The third eluate was a new monoprenyl derivative, which gave a positive ferric reaction and formed a diacetate [nmr $\delta$ 2.36, 2.40 (2 s, 6 H, $-OCOCH_3$)] and a partial methyl ether [nmr $\delta$ 3.99 (s, 3 H, $-OCH_3$)], still showing a positive ferric reaction. Hence both of the hydroxyls were free. The nmr spectra of both the diacetate and the partial methyl ether showed the presence of one prenyl unit in ring A. Thus these were signals of protons of the intact phenyl ring, a proton in position 3, one aromatic proton of ring A, one benzylic methylene, one methine, and two methyl groups at the unsaturated center (see Experimental Section). Since the prenyl in the product was different from 3, it was assumed to be 8-prenyl chrysin (11). This was established as follows. While the partial methyl ether 12 did not undergo any cyclization with formic acid, the dihydroxy compound 11 could be cyclized to afford 5-hydroxy-6″,6″-dimethyl-4″,5″-dihydropyrano[2″,3″:7,8]flavone (13) (reaction 7) as shown by a positive ferric reaction and the characteristic two nmr triplets at $\delta$ 1.88 and 2.80 ppm ($J$ = 7 Hz). Further 11 gave the angular chromene, 5-hydroxy-6″,6″-dimethylpyrano[2″,3″:7,8]flavone (14) on treatment with DDQ, identical with the one obtained by Hlubucek, *et al.*,[14] (reaction 8).




(6)

11, R = H
12, R = Me




(7)

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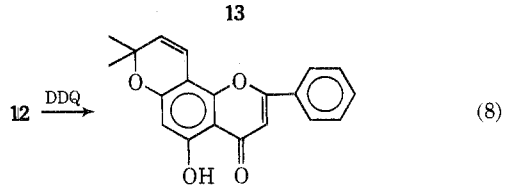


(8)

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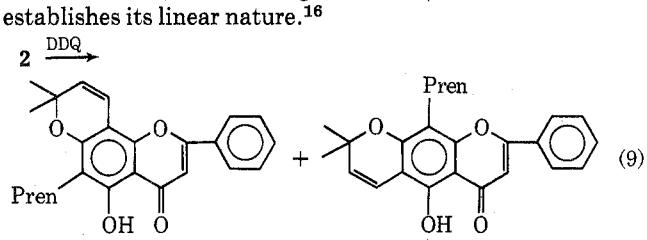
The above results indicate that only the 6 and 8 positions are affected by prenylation of chrysin and that the 3 position remains unaffected. Hence flavones having prenyl groups in ring A can be synthesized in this manner and those having a prenyl group in position 3 by using some active substrate like a 1,3 diketone.

Mulberrochromene[9] has free prenyl unit and a fused pyran system in the ring A of flavonoids. An analogous example in the flavonol series is sericetin which was isolated from the roots of *Mundulea sericea*[15] and identified as 8-prenyl-6″,6″-dimethylpyrano[2″,3″:7,6]galangin. It is therefore likely that analogous derivatives of chrysin may also be isolated from nature. In view of this possibility, cyclodehydrogenation of 6,8-diprenylchrysin with DDQ has been studied (reaction 9). A mixture of two isomeric products was obtained which was separated first by column chromatography and then by fractional crystallization. The major product, mp 156°, was identified as the angular chromene, 5-hydroxy-6-prenyl-6″,6″-dimethylpyrano[2″,3″:7,8]flavone [3-deoxyisosericetin (15)] on the basis of its nmr and mass spectra. Thus the nmr spectrum showed signals of one prenyl unit, a condensed 2,2-dimethylpyran unit, a proton in 3 position, and a phenyl group (see Experimental Section). The mass spectrum showed characteristic (M − 56) mass fragments at $m/e$ 332 (63%) which establishes its angular nature.[16] The minor products, mp 166°, was therefore the linear isomer[16] (3-deoxysericetin). The structure was confirmed by nmr and mass spectra. The mass spectrum showed the characteristic (M − 55) fragment at $m/e$ 333 (73%), which establishes its linear nature.[16]




(9)

15 16

## Experimental Section[17]

**Nuclear Prenylation of Chrysin (1) Using Prenyl Bromide.** To a solution of chrysin[13] (4 g) in anhydrous methanol (125 ml) was added a methanolic solution of sodium methoxide, *i.e.* 5.6 g of Na/60 ml of methanol. The mixture was cooled, treated with prenyl bromide (7.6 ml) in one lot, and refluxed for 3 hr. After removal of the solvent, the mixture was treated with ice and acidified in cold with dilute HCl. The solid product was examined on tlc using solvent system B which showed the presence of two compounds. It was therefore subjected to column chromatography and the column eluted successively with (1) light petroleum–benzene (8:2) and (2) benzene, giving the following fractions A and B.

**Fraction A** was crystallized from the benzene–light petroleum mixture yielding 5,7-dihydroxy-6,8-di-*CC*-prenylflavone (2) as shining yellow needles (1 g): mp 196°; soluble in aqueous $Na_2CO_3$; intense green ferric reaction; $R_f$ 0.42 (solvent A); nmr $\delta$ 1,80, 1.84 [2 d, 12, $J$ = 4 and 1.5 Hz, $(CH_3)_2C=$], 3.47, 3.65 (2 d, 4, $J$ = 6 Hz, $ArCH_2$), 5.36 (broad m, 2, $-CH=$), 6.72 (s, 1 H in position 3), 7.58 (m, 3 H in positions 3′, 4′, and 5′), and 7.96 (m, 2 H in positions 2′ and 6′).

*Anal.* Calcd for $C_{25}H_{26}O_4$: C, 76.9; H, 6.7. Found: C, 76.9; H, 6.8.

The diacetate, prepared from 2 by the acetic anhydride–pyridine method, was crystallized from ethyl acetate–light petroleum mixture as colorless needles: mp 176°; $R_f$ 0.50 (solvent D); negative ferric reaction; nmr $\delta$ 1.72, 1.74 [2 s, 12, $(CH_3)_2C=$], 2.34, 2.45 (2 s, 6, $OCOCH_3$), 3.29, 3.57 (2 d, 4, $J$ = 6 Hz, $CH_2$), 5.18 (m, 2, $-CH=$), 6.68 (s, 1 H in position 3), 7.51 (m, 3 H in positions 3′, 4′, and 5′) and 7.85 (m, 2 H in positions 2′ and 6′).

*Anal.* Calcd for $C_{29}H_{30}O_6$: C, 73.4; H, 6.3. Found: C, 73.4; H, 6.4.

**Fraction B** was crystallized from the ethyl acetate–light petroleum mixture to give 5,7-dihydroxy-6-prenylflavone (3) as yellow plates [0.5 g): mp 216°; $R_f$ 0.69 (solvent C); soluble in aqueous $Na_2CO_3$; green ferric reaction.

*Anal.* Calcd for $C_{20}H_{18}O_4$: C, 74.5; H, 5.6. Found: C, 74.5; H, 6.0.

The diacetate prepared from **3** by the acetic anhydride–pyridine method was crystallized from methanol as shining needles: mp 116°; $R_f$ 0.41 (solvent D); negative ferric reaction; nmr $\delta$ 1.69, 1.74 [2 s, 6, $(CH_3)_2C=$], 2.34, 2.46 (2 s, 6, $-OCOCH_3$), 3.30 (d, 2, $J$ = 6 Hz, $ArCH_2$), 5.03 (m, 1, $-CH=$), 6.68 (s, 1 H in position 3), 7.36 (s, 1 H in position 8), 7.54 (m, 3 H in positions 3′, 4′, and 5′), and 7.86 (m, 2 H in positions 2′ and 6′).

*Anal.* Calcd for $C_{24}H_{22}O_6$: C, 70.9; H, 5.5. Found: C, 70.9; H, 5.6.

**5-Hydroxy-7-methoxy-6,8-diprenylflavone (4).** A solution of 5,7-dihydroxy-6,8-diprenylflavone (**2**, 100 mg) in acetone (20 ml) was refluxed with dimethyl sulfate (0.03 ml) and $K_2CO_3$ (500 mg) for 3 hr. Acetone was distilled off and water added to the residue. The solid thus obtained was purified by column chromatography and crystallized from the ethyl acetate–light petroleum mixture; 5-hydroxy-7-methoxy-6,8-diprenylflavone (**4**) was obtained as long yellow needles (80 mg): mp 128°; $R_f$ 0.80 (solvent B); intense green ferric reaction; nmr $\delta$ 1.70, 1.83 [2 s, 12, $(CH_3)_2C=$], 3.43, 3.60 (2 d, 4, $J$ = 6 Hz, $ArCH_2$), 3.80 (s, 3, $OCH_3$), 5.29 (m, 2, $-CH=$), 6.70 (s, 1 H in position 3), 7.57 (m, 3 H in positions 3′, 4′, and 5′) and 7.94 (m, 2 H in positions 2′ and 6′).

*Anal.* Calcd for $C_{26}H_{28}O_4$: C, 77.2; H, 7.0. Found: C, 76.8; H, 7.2.

**6″,6″,6‴,6‴-Tetramethyl-4″,5″:4‴,5‴-bis(dihydropyrano)[2″,3″:7,8;2‴,3‴:5,6]flavone (6).** A solution of **2** (300 mg) in formic acid (20 ml) was heated on a steam bath for 2 hr and then poured over ice. The solid thus obtained was purified by column chromatography. Elution with benzene gave **6**, which was crystallized from benzene–light petroleum mixture as yellow prisms (100 mg): mp 186°; $R_f$ 0.40 (solvent C); negative ferric reaction; nmr $\delta$ 1.38, 1.43 [2 s, 12, $(CH_3)_2C<$], 1.86 (m, 4, $-CH_2-$), 2.64, 2.96 (2 t, 4, $J$ = 6 Hz, $-CH_2-$), 6.64 (s, 1 H in position 3), 7.47 (m, 3 H in positions 3′, 4′, and 5′) and 7.88 (m, 2 H in positions 2′ and 6′).

*Anal.* Calcd for $C_{25}H_{26}O_4$: C, 76.9; H, 6.7. Found: C, 77.3; H, 7.2.

**5-Hydroxy-7-methoxy-6-prenylflavone (5).** A solution of **3** (100 mg) in acetone (18 ml) was refluxed with dimethyl sulfate (0.025 ml) and $K_2CO_3$ (500 mg) for 3 hr. The product was crystallized from ethyl acetate–light petroleum mixture to afford **5** (70 mg) as glistening light yellow crystals: mp 162–63°; $R_f$ 0.80 (solvent C); green ferric reaction; nmr $\delta$ 1.70, 1.83 [2 s, 6, $(CH_3)_2C=$], 3.39 (d, 2, $J$ = 6 Hz, $ArCH_2$), 3.92 (s, 3, $OCH_3$), 5.29 (m, 1, $-CH=$), 6.52 (s, 1 H in position 3), 6.68 (s, 1 H in position 8), 7.57 (m, 3 H in positions 3′, 4′, and 5′), and 7.90 (m, 2 H in positions 2′ and 6′).

*Anal.* Calcd for $C_{21}H_{20}O_4$: C, 75.0; H, 6.0 Found: C, 75.4; H, 6.3.

**7-Methoxy-6″,6″-dimethyl-4″,5″-dihydropyrano[2″,3″:5,6]flavone (7).** **5** upon treatment with formic acid gave **7** which was crystallized from methanol as light yellow needles: mp 250°; $R_f$ 0.50 (solvent D); negative ferric reaction; nmr $\delta$ 1.42 [s, 6, $(CH_3)_2C<$], 1.78, 2.65 (2 t, 4, $J$ = 7 Hz, $-CH_2-$), 3.90 (s, 3, $OCH_3$), 6.47 (s, 1 H in position 8), 6.58 (s, 1 H in position 3), 7.47 (m, 3 H in 3′, 4′, and 5′ positions), and 7.82 (m, 2 H in positions 2′ and 6′).

*Anal.* Calcd for $C_{21}H_{20}O_4$: C, 75.0; H, 6.0. Found: C, 74.5; H, 6.5.

**Reaction of 5,7-Dihydroxy-6-prenylflavone (3) with formic acid.** A solution of **3** (400 mg) in formic acid (30 ml) was kept at room temperature for 1 hr, water added and the whole mixture extracted with $CHCl_3$. The product in $CHCl_3$ showed two spots on tlc, one showing positive ferric reaction and the other negative. It was separated by column chromatography. Elution with benzene–light petroleum (1:1) gave 5-hydroxy-6″,6″-dimethyl-4″,5″-dihydropyrano[2″,3″:7,6]flavone (**8**), which was crystallized from methanol as yellow needles (200 mg): mp 180°; $R_f$ 0.78 (solvent C); bluish green ferric reaction; nmr $\delta$ 1.39 [s, 6, $(CH_3)_2C<$], 1.85, 2.77 (2 t, 4, $J$ = 7 Hz, $-CH_2-$), 6.47 (s, 1 H in position 8), 6.66 (s, 1 H in position 3), 7.54 (m, 3 H in positions 3′, 4′, and 5′), and 7.91 (m, 2 H in positions 2′ and 6′).

*Anal.* Calcd for $C_{20}H_{18}O_4$: C, 74.5; H, 5.6. Found: C, 74.8; H, 6.0.

Further elution with benzene–ethyl acetate (7:3) gave a compound which was crystallized from ethyl acetate to give 7-hydroxy-6″,6″-dimethyl-4″,5″-dihydropyrano[2″,3″:5,6]flavone (**9**) as yellow hexagonal plates (50 mg): mp 296°; $R_f$ 0.36 (solvent D); negative ferric reaction.

*Anal.* Calcd for $C_{20}H_{18}O_4$: C, 74.5; H, 5.6. Found: C, 74.9; H, 5.2.

**5-Hydroxy-6″,6″-dimethylpyrano[2″,3″:7,6]flavone (10).** **3** (100 mg) was dissolved in dry benzene (20 ml), and the solution was refluxed for 35 min; colorless hydroquinone separated out. It was filtered and purified by column chromatography. When the column was eluted with benzene–light petroleum (5:95) and the eluate crystallized from methanol, **10** was obtained as pale yellow needles: mp 188° (lit.[14] mp 187–188°); $R_f$ 0.56 (solvent B); bluish green ferric reaction; nmr $\delta$ 1.47 (s, 6, $(CH_3)_2C=$), 5.60, 6.71 (2d, 2, $J$ = 10 Hz, two olefinic H of pyran ring), 6.50 (s, 1 H in position 8), 6.60 (s, 1 H in position 3), 7.50 (m, 3 H in positions 3′, 4′, and 5′), and 7.90 (m, 2 H in positions 2′ and 6′).

*Anal.* Calcd for $C_{20}H_{16}O_4$: C, 75.0; H, 5.0. Found: C, 75.1; H, 5.0.

**Nuclear Prenylation of Chrysin (1) using 2-Hydroxy-2-methyl-3-butene.** To a stirred solution of chyrsin (6 g) in dry dioxane (140 ml) was added gradually boron trifluoride etherate (3.5 ml) at room temperature during a course of 30 min, and the solution acquired a pink-red color. To this was added a solution of 2-hydroxy-2-methyl-3-butene (3 ml) in dry dioxane (20 ml), and the whole solution was stirred for 4 hr and kept at room temperature overnight. After dilution with moist ether (300 ml), the ethereal solution was washed with water (6 × 100 ml), whereby the color of the solution discharged. It was then extracted with 1% aqueous $Na_2CO_3$ (3 × 100 ml) to remove unreacted chrysin (3 g); the remaining ethereal solution on examination by tlc (solvent B) showed the presence of three compounds. Hence it was subjected to column chromatography and column eluted successively with (1) benzene–light petroleum (2:8), (2) benzene, and (3) benzene–ethyl acetate (9:1) giving the following three distinct fractions A, B, and C.

**Fraction A** was crystallized from the benzene–light petroleum mixture affording **2** (240 mg), identical in melting point, mixture melting point, and $R_f$ with the sample prepared earlier.

**Fraction B** was crystallized from the ethyl acetate–light petroleum mixture yielding **3** (480 mg), identical in melting point, mixture melting point, and $R_f$ with the sample prepared earlier.

**Fraction C** was crystallized from benzene to give **11** (1 g) as yellow needles: mp 206°; soluble in aqueous $Na_2CO_3$; intense green ferric reaction; $R_f$ 0.60 (solvent C).

*Anal.* Calcd for $C_{20}H_{18}O_4$: C, 74.5; H, 5.6. Found: C, 75.0; H, 5.7.

The diacetate prepared from **11** by acetic anhydride–pyridine method was crystallized from methanol as colorless needles: mp 173°; $R_f$ 0.40 (solvent C); negative ferric reaction; nmr $\delta$ 1.72 (1 broad s, 6, $(CH_3)_2C=$), 2.36, 2.40 (2 s, 6, $OCOCH_3$), 3.60 (d, 2, $J$ = 7 Hz, $ArCH_2$), 5.22 (m, 1, $-CH=$), 6.98 (s, 1 H in position 3), 7.30 (s, 1 H in position 6), 7.53 (m, 3 H in positions 3′, 4′, and 5′), and 7.95 (m, 2 H in positions 2′ and 6′).

*Anal.* Calcd for $C_{24}H_{22}O_6$: C, 70.9; H, 5.5 Found: C, 70.7; H, 5.9.

**5-Hydroxy-7-methoxy-8-prenylflavone (12).** It was prepared from **11** as the 6-prenyl isomer and was crystallized from ethyl acetate–light petroleum mixture. It formed glistening yellow crystals: mp 156°; $R_f$ 0.87 (solvent C); intense green ferric reaction; nmr $\delta$ 1.72, 1.82 (2 broad s, 6, $(CH_3)_2C=$), 3.43 (d, 2, $J$ = 7 Hz, $ArCH_2$), 3.99 (s, 3, $OCH_3$), 5.24 (m, 1, $-CH=$), 6.60 (s, 1 H in position 3), 7.35 (s, 1 H in position 6), 7.49 (m, 3 H in positions 3′, 4′, and 5′), and 7.99 (m, 2 H in positions 2′ and 6′).

*Anal.* Calcd for $C_{21}H_{20}O_4$: C, 75.0; H, 6.0. Found: C, 75.2; H, 6.4.

It was recovered unchanged when heated with formic acid.

**5-Hydroxy-6″,6″-dimethyl-4″,5″-dihydropyrano[2″,3″:7,8]flavone (13).** **11** upon treatment with formic acid and subsequent crystallization of the product from ethyl acetate–light petroleum mixture gave **13** as light yellow needles: mp 210°; $R_f$ 0.74 (solvent C); light green ferric reaction; nmr $\delta$ 1.37 [s, 6, $(CH_3)_2C<$], 1.88, 2.80 (2 t, 4, $J$ = 7 Hz, $-CH_2-$), 6.70 (s, 1 H in position 3), 7.36 (s, 1 H in position 6), 7.59 (m, 3 H in positions 3′, 4′, and 5′), and 7.86 (m, 2 H in positions 2′ and 6′).

*Anal.* Calcd for $C_{20}H_{18}O_4$: C, 74.5; H, 5.6. Found: C, 74.2; H, 6.0.

**5-Hydroxy-6″,6″-dimethylpyrano[2″,3″:7,8]flavone (14).** **11** (100 mg) was refluxed with DDQ (70 mg) in dry benzene (20 ml) for 35 min and the product purified by column chromatography. Elution with benzene–light petroleum (9:1) gave angular chromene **14** (60 mg) which was crystallized from ethyl acetate–light petroleum mixture as yellow prisms: mp 178° (lit.[14] mp 176–177°); $R_f$ 0.50 (solvent B); intense green ferric reaction; nmr $\delta$ 1.49 [s, 6, $(CH_3)_2C=$], 5.65, 6.76 (2 d, 2, $J$ = 10 Hz, two olefinic H of pyran ring), 6.48 (s, 1 H in position 3), 7.45 (s, 1 H in position 6), 7.56 (m, 3 H in positions 3′, 4′, and 5′), and 7.96 (m, 2 H in positions 2′ and 6′).

*Anal.* Calcd for $C_{20}H_{16}O_4$: C, 75.0; H, 5.0. Found: C, 75.0; H, 5.0.

**3-Deoxysericetin (16) and 3-Deoxyisosericetin (15).** To a solution of **2** (500 mg) in dry benzene (40 ml) was added DDQ (300 mg) and the whole solution refluxed for 1 hr. It was filtered while hot, benzene distilled off, and the residue subjected to column chromatography. Elution with benzene–light petroleum (2:8) gave a solid which again proved to be a mixture. Fractional crystallization with light petroleum (mother liquor A) yielded the sparingly soluble solid which on recrystallization from ethyl acetate–light petroleum mixture afforded 5-hydroxy-6-prenyl-6″,6″-dimethylpyrano[2″,3″:7,8]flavone [3-deoxyisosericetin (**15**)] (120 mg): mp 156°; $R_f$ 0.78 (solvent A); light green ferric reaction; nmr $\delta$ 1.50 [s, 6, $(CH_3)_2C<$], 1.70, 1.83 [2 broad s, 6, $(CH_3)_2C=$], 3.41 (d, 2, $J$ = 7 Hz, $ArCH_2$), 5.33 (m, 1, $-CH=$), 5.67 6.88 (2 d, 2, $J$ = 10 Hz, two olefinic H of pyran ring), 6.70 (s, 1 H in position 3), 7.59 (m, 3 H in positions 3′, 4′, and 5′) and 7.93 (m, 2 H in positions 2′ and 6′); mass spectrum (70 eV) *m/e* (rel intensity) 388 (85), 373 (100), 345 (57), 332 (63), 317 (11), 215 (17), 165 (11), 105 (11), 77 (10).

*Anal.* Calcd for $C_{25}H_{24}O_4$: C, 77.3; H, 6.2. Found: C, 76.8; H, 5.9.

The mother liquor A yielded a solid which after crystallization twice from methanol yielded 5-hydroxy-8-prenyl-6″,6″-dimethylpyrano[2″,3″:7,6]flavone [3-deoxysericetin (**16**)] (80 mg) as pale yellow needles: mp 166°; $R_f$ 0.74 (solvent A); intense green ferric reaction; nmr $\delta$ 1.50 [s, 6, $(CH_3)_2C<$], 1.72, 1.79 [2d, 6, $J$ = 2 Hz, $(CH_3)_2C=$], 3.56 (d, 2, $J$ = 7 Hz, $ArCH_2$), 5.26 (m, 1, $-CH=$), 5.66, 6.81 (2 d, 2, $J$ = 10 Hz, two olefinic H of pyran ring), 6.71 (s, 1 H in position 3), 7.59 (m, 3 H in positions 3′, 4′, and 5′), and 7.96 (m, 2 H in positions 2′ and 6′); mass spectrum (70 eV) *m/e* (rel intensity) 388 (82), 373 (100), 345 (68), 333 (73), 215 (28), 165 (14), 105 (27), 85 (36), 77 (22), 71 (55), 55 (46).

*Anal.* Calcd for $C_{25}H_{24}O_4$: C, 77.3; H, 6.2. Found: C, 76.8; H, 5.9.

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**Registry No.**—**1**, 480-40-0; **2**, 50678-89-2; **2** diacetate, 50678-90-5; **3**, 50678-91-6; **3** diacetate, 50678-92-7; **4**, 50678-93-8; **5**, 50678-94-9; **6**, 50678-95-0; **7**, 50678-96-1; **8**, 50830-97-2; **9**, 50678-97-2; **10**, 34187-26-3; **11**, 34125-75-2; **11** diacetate, 50678-98-3; **12**, 50678-99-4; **13**, 50679-00-0; **14**, 34187-25-2; **15**, 50679-01-1; **16**, 50679-02-2; prenyl bromide, 870-63-3; 2-hydroxy-2-methyl-3-butene, 115-18-4.

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(17) All melting points were taken on Buchi melting point apparatus and are uncorrected. Tlc was carried out on plates coated with silica gel supplied by NCL, Poona. Spraying reagent was generally 10% aqueous sulfuric acid, but 10% alcoholic ferric chloride was also used for such compounds which gave positive ferric reaction. Tlc was carried out using one of the following solvent systems: (A) benzene, (B) benzene–ethyl acetate (9:1), (C) benzene–ethyl acetate (75:25), (D) benzene–ethyl acetate (1:1). Column chromatography was carried out using silica gel supplied by NCL, Poona. Nuclear magnetic resonance spectra were determined in $CDCl_3$ using 60 MHz spectrophotometer. Chemical shifts are expressed in parts per million (ppm) downfield from tetramethylsilane as internal standard. Mass spectra were determined on samples introduced through the heated inlet system using MS 72 spectrometer, 70 eV ionizing voltage, 900 × 10 trap current, and 2.0 kV accelerating voltage.

# 1,8 Interactions in Naphthalene Derivatives. An X-Ray Structure Determination and Nuclear Magnetic Resonance Studies of 1,8-Di(bromomethyl)naphthalene[1]

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The conformation of 1,8-di(bromomethyl)naphthalene has been determined in the crystalline state and it has been found that the molecule has essentially twofold symmetry about the C-9–C-10 bond with the bromines located above and below the plane of the ring. The carbon–bromine bonds are inclined toward one another about 10° from planes perpendicular to the naphthalene ring which contain the C-1–C-11 and C-8–C12 bonds. This conformation has formally nonbonded H···Br distances of 2.85 Å which are substantially less than the sum of the van der Waals radii and could well indicate some degree of electrostatic binding. The strain in the molecule is largely relieved both by in-plane and out-of-plane bending of the C-1–C-11 and the C-8–C-12 bonds as well as some skeletal distortion of the ring. Low-temperature proton nmr studies of 1,8-di(bromomethyl)naphthalene and some related compounds showed no evidence of barriers to rotation about the C-1–C-11 and C-8–C-12 bonds large enough to be detectable.

Alkyl or aryl substituents at the 1,8 positions (the peri positions) of naphthalene are in close proximity to one another and provide many interesting opportunities for study of conformations and barriers to rotation about the extracyclic bonds, C-1–C-11 and C-8–C-12.[3,4] Relatively few other simple molecules have the special feature of having the substituents close to one another and attached to a relatively rigid framework by essentially parallel bonds. Because of the importance of knowing just what conformations are, in fact, favored for molecules of this type, we have determined the structure of 1,8-di(bromomethyl)naphthalene (1) by X-ray diffraction. On the as-