Synthesis of 4-Phenyl-2*H*-1-benzopyrans

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Sesamol and other phenols react with equimolar quantities of cinnamaldehyde and morpholine in methanol to yield epimeric 2-morpholinyl-4-phenylbenzopyran derivatives, which are useful intermediates for the synthesis of alcoholic neoflavanoid (4-phenylbenzopyran) compounds.

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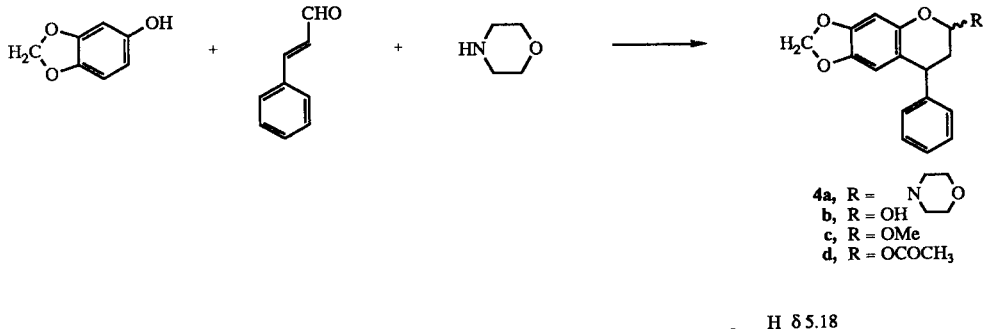
Aromatic aldehydes react with morpholine and sesamol (3,4-methylenedioxyphenol) to form Mannich bases of type 1 [1]. With ketonic reagents, *e.g.* 2-butanone, 2,4-pentanedione, or dimedone, these bases yield benzopyran derivatives, *e.g.* 2,3, some of which possess tubulin-binding, anti-mitotic and anti-tumor properties [2,3,4]. These preparative studies have now been extended to unsaturated aldehydes. It has been determined that similar condensations of phenols with morpholine and cinnamaldehyde give good yields of 2-morpholinyl-4-phenylbenzopyrans, which are useful intermediates for the synthesis of neoflavanoid (*i.e.* 4-phenylbenzopyran) derivatives.

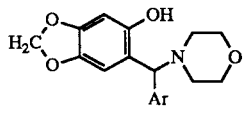
Thus, when equimolecular quantities of sesamol, morpholine and cinnamaldehyde were warmed in methanol, a crystalline product, $C_{20}H_{21}NO_4$, rapidly precipitated. TLC of this product indicated it to be a mixture of two isomers, identified as epimeric 2-morpholinyl-4-phenylbenzopyrans of structure **4a** on the basis of nmr spectra and hydrolysis reactions. In aqueous acetic acid the morpholinyl product was hydrolyzed to a crystalline alcohol, $C_{16}H_{14}O_4$, **4b**, which with acidified methanol formed a methyl ether, $C_{17}H_{16}O_4$, **4c**. Location of the methoxyl and phenyl groups at positions 2 and 4 respectively on the pyran ring of **4c** was clearly indicated by its ^{1}H nmr spectrum. The protons at positions 2 and 4 of the pyran ring appeared as double doublets at δ 5.10 and δ 4.08 respectively, coupled to the two protons of the methylene group (multiplet at δ 2.12- δ 2.47). The chemical shifts of these protons closely agree with those of the corresponding protons in **6**, a 4-phenylbenzopyran of unequivocal structure which had been previously synthesized by reaction of the quinone methide **5** with ethyl vinyl ether [5].

Confirmatory synthetic evidence that the cinnamaldehyde condensation products are 2-morpholinyl-4-phenylbenzopyrans, and not isomeric 4-morpholinyl-2-phenyl compounds, was obtained by reacting 3,5-dimethoxyphenol with morpholine and cinnamaldehyde. Hydrolysis of the product **7a** gave an alcohol **7b**, which formed a monoacetate **7c**. Analysis (tlc), of the purified acetate indicated it to be a single isomer. The ^{1}H nmr of the acetate (which fully supported a 2-acetoxyl-4-phenylbenzopyran structure) and its mp (142-143°) showed that it was not identical with either of the known [6] isomeric flavan acetates **8** (mp 96-98°) and **9** (mp 123-125°).

Other phenols, *viz.* resorcinol, pyrogallol and methoxy-



5 6



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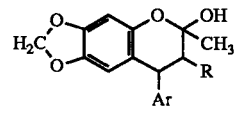
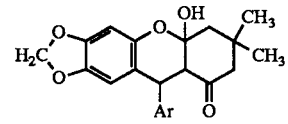


2 R = CH_3 or $COCH_3$



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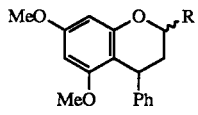

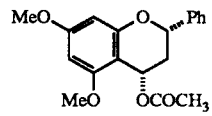

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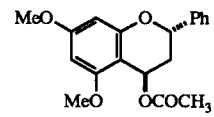

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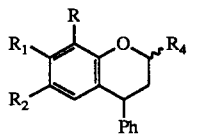
7a, R = N(morpholine)O
b, R = OH
c, R = $OCOCH_3$

quinol reacted similarly with morpholine and cinnamaldehyde to give good yields of 2-morpholinyl-4-phenylbenzopyrans, **10a-10c** respectively.

The 2-morpholinyl-4-phenylbenzopyrans do not react with phloroglucinol or with 2,4-pentanedione in either methanol or aqueous acetic acid solutions; in the latter solvent only hydrolysis to the previously described alcohols was observed. With the cyclic β-diketone, dimedone, however, the 2-morpholinyl compounds undergo rapid ring opening and reaction with two molecules of the β-diketone to form high yields of open chain products of type **11**. These compounds are readily dehydrated in acid media to cyclized products **12**. In one case, *viz*, **4a**, it was possible to isolate the crystalline intermediate monosubstituted dimedone product **13** by reaction with limited amounts of dimedone.

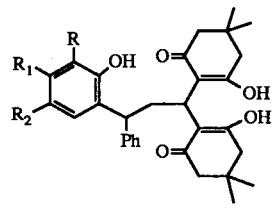


10a, R = R_2 = H, R_1 = OH, R_4 = N(morpholine)O

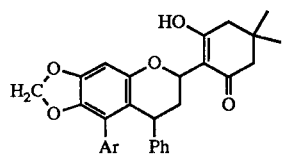
10b, R = R_1 = OH, R_2 = H, R_4 = N(morpholine)O

10c, R = H, R_1 = OMe, R_2 = OH, R_4 = N(morpholine)O

10d, R = H, R_1 = OMe, R_2 = R_4 = OH



11a, R = H, R_1R_2 = OCH_2O
11b, R = R_2 = H, R_1 = OH
11c, R = R_1 = OH, R_2 = H



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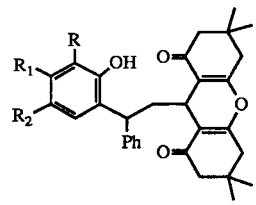

12a, R = H, R_1R_2 = OCH_2O
12b, R = R_2 = H, R_1 = OH
12c, R = R_1 = OH, R_2 = H

EXPERIMENTAL

The ^1H nmr spectra were determined in deuteriochloroform with TMS as the internal standard on a Varian EM-300 instrument. Microanalyses were performed in the Center's Structural Analysis Unit. Melting points were determined in unsealed capillaries and are uncorrected.

1-[7,8-Dihydro-8-phenyl-6*H*-1,3-dioxolo[4,5-*g*][1]benzopyran-6-yl]-morpholine **4a**.

A solution of 3,4-methylenedioxyphenol (6.9 g), morpholine (4.3 g) and cinnamaldehyde (6.6 g) in methanol (25 ml) was heated to boiling under reflux. Within 5 minutes a mass of colorless crystals separated. After 2 hours the mixture was cooled and the product was collected and washed well with methanol and Skellysolve F (11.1 g, mp 153-154°). Recrystallized from acetone-methanol, **4a** was obtained as colorless needles, mp 157°; tlc on silicic acid showed the presence of two stereoisomers in about equal amounts.

Anal. Calcd. for $C_{20}H_{21}NO_4$: C, 70.8; H, 6.2; N, 4.1; M^+ = 339.1468. Found: C, 70.8; H, 6.2; N, 4.1; M^+ = 339.1458.

7,8-Dihydro-8-phenyl-6*H*-1,3-dioxolo[4,5-*g*][1]benzopyran-6-ol **4b**.

The morpholinyl compound **4a** (2.5 g) was heated to boiling with acetic acid (12 ml) and water (15 ml). It rapidly dissolved to give a yellow solution which on cooling deposited colorless crystals. Recrystallized from acetone-methanol **4b** was obtained as colorless needles, mp 136-137° (1.7 g, 86%), consisting of an 80:20 mixture of stereoisomers; ^1H nmr (major stereoisomer): δ 2.14 (m, CH_2), 4.22 (dd, J = 6, 11 Hz, CH), 5.60 (dd, J = 3, 3 Hz, CH), 5.83 (m, OCH_2O), 6.21 (ArH), 6.51 (ArH), 7.40 (m, 5 ArH); ^1H nmr (minor stereoisomer): δ 2.43 (m, CH_2), 4.12 (m, CH), 5.46 (dd, J = 3, 9 Hz, CH), 5.83 (m, OCH_2O), 6.15 (ArH), 7.40 (m, 5 ArH).

Anal. Calcd. for $C_{16}H_{14}O_4$: C, 71.1; H, 5.2; M^+ = 270.0892. Found: C, 71.3; H, 5.2; M^+ = 270.0893.

A solution of **4b** in methanol containing one drop of concentrated hydrochloric acid was concentrated and cooled. Colorless crystals separated. Recrystallized from methanol the methyl ether **4c** was obtained as colorless, glistening prisms, mp 127-128°; tlc and ^1H nmr spectra showed this purified product was a single stereoisomer; ^1H nmr: δ 2.12 and 2.47 (m, CH_2), 3.57 (OCH_3), 4.08 (dd, J = 6, 11 Hz, CH), 5.10 (dd, J = 3, 9 Hz, CH), 5.84 (OCH_2O), 6.16 (ArH), 6.46 (ArH), 7.26 (5 ArH).

Anal. Calcd. for $C_{17}H_{16}O_4$: C, 71.8; H, 5.7; M^+ = 284.1048. Found: C, 71.6; H, 5.6; M^+ = 284.1050.

Warmed briefly with acetic anhydride and a drop of pyridine **4b** formed an acetate. This crystallized from methanol to give **4d** as colorless glistening needles, mp 154°; ^{1}H nmr indicated this product was a single isomer; ^{1}H nmr: δ 2.12 ($COCH_3$), 2.24 (m, CH_2), 4.16 (dd, J = 6, 11.5 Hz, CH), 5.84 (d, J = 1 Hz and 5.86, d, J = 1 Hz, OCH_2O), 6.17 (ArH), 6.47 (ArH), 6.51 (dd, J = 2, 3 Hz, CH), 7.28 (m, 5 ArH).

Anal. Calcd. for $C_{18}H_{16}O_5$: C, 69.2; H, 5.2; M^+ = 312.0997. Found: C, 69.2; H, 5.15; M^+ = 312.0992.

Reaction of **4a** with 5,5-Dimethyl-1,3-cyclohexanedione.

(a) A solution of **4a** (0.34 g) and 5,5-dimethyl-1,3-cyclohexanedione (dimedone) (0.70 g, 5 molar equivalents) in methanol (4 ml) was heated to boiling for 5 minutes and diluted with water. The solid product was collected and recrystallized from methanol to give **11a** as colorless needles, mp 177-178° (0.42 g); ^{1}H nmr: δ 1.01 (CH_3), 1.02 (CH_3), 1.08 (CH_3), 1.10 (CH_3), 2.24 (m, 4 CH_2), 2.67 (t, J = 8 Hz, CH_2), 3.48 (2 OH), 3.98 (t, J = 8 Hz, CH), 4.13 (t, J = 8 Hz, CH), 5.82 (d, J = 1 Hz) and 5.85, d, J = 1 Hz, OCH_2O), 6.32 (ArH), 6.57 (ArH), 7.23 (m, 5 ArH). The same product was obtained by warming **4a** with excess of 5,5-dimethyl-1,3-cyclohexanedione in aqueous acetic acid.

Anal. Calcd. for $C_{32}H_{36}O_7$: C, 72.2; H, 6.8, M^+ = 532.2461. Found: C, 72.2; H, 6.7; M^+ = 532.2450.

(b) Compound **4a** (0.34 g) was heated with 5,5-dimethyl-1,3-cyclohexanedione (0.28 g, 2 molar equivalents) in methanol for 10 minutes and diluted with water. Analysis (tlc) indicated the product to be a mixture of **11a** and a second, higher R_F component. A solution of the crude product in wet methanol deposited the higher R_F component on standing (0.16 g). Recrystallized from acetone **13** separated as colorless needles, mp 181-182°; ^{1}H nmr: δ 1.01 (CH_3), 1.11 (CH_3), 2.23 (m, 3 CH_2), 4.24 (dd, J = 6, 12 Hz, CH), 5.37 (dd, J = 1, 13 Hz, CH), 5.87 (OCH_2O), 6.22 (ArH), 6.44 (ArH), 7.25 (m, 5 ArH).

Anal. Calcd. for $C_{24}H_{24}O_5$: C, 73.45; H, 6.2; M^+ = 392.1624. Found: C, 73.6; H, 6.35; M^+ = 392.1630.

The bis-cyclohexanedione product **11a** (0.5 g) was dissolved in boiling acetic acid containing a drop of 10% aqueous hydrochloric acid. Crystals separated on cooling. Water was added and the product was collected and recrystallized from acetone-methanol. The cyclized product **12a** separated as slightly yellow needles, mp 215-217° (0.30 g); ^{1}H nmr: δ 0.99 (CH_3), 1.03 (CH_3), 1.06 (CH_3), 1.12 (CH_3), 2.16 (m, 5 CH_2, OH), 3.87 (t, J = 6 Hz, CH), 4.21 (t, J = 6 Hz, CH), 5.79 (d, J = 1 Hz and 5.86, J = 1 Hz, OCH_2O), 6.36 (ArH), 6.63 (ArH), 7.19 (m, 5 ArH).

Anal. Calcd. for $C_{32}H_{34}O_6$: C, 74.7; H, 6.7; M^+ = 514.2355. Found: C, 74.6; H, 6.7; M^+ = 514.2358.

Warmed with acetic anhydride and pyridine **12a** formed a monoacetate, which crystallized from methanol as colorless needles, mp 157-158°; ^{1}H nmr: δ 1.01 (CH_3), 1.03 (CH_3), 1.06 (CH_3), 1.13 (CH_3), 2.17 (m, 5 CH_2), 2.23 ($COCH_3$), 3.90 (t, J = 6 Hz, CH), 3.96 (t, J = 6 Hz, CH), 5.90 (d, J = 1 Hz and 5.94 J = 1 Hz, OCH_2O), 6.50 (ArH), 6.93 (ArH), 7.17 (m, 5 ArH).

Anal. Calcd. for $C_{34}H_{36}O_7$: C, 73.4; H, 6.5; M^+ = 556.2461. Found: C, 73.6; H, 6.5; M^+ = 556.2440.

Compound **12a** was methylated by refluxing it (0.15 g) with dimethyl sulfate (0.1 ml), potassium carbonate (0.6 g) and acetone (5 ml) for an hour. The mixture was concentrated and diluted with water. The solid product was crystallized from methanol to give the *O*-methyl derivative as glistening, colorless needles, mp 194-195°; ^{1}H nmr: δ 1.00 (CH_3), 1.04 (CH_3), 1.08 (CH_3), 1.10 (CH_3), 2.19 m (5 CH_2), 3.70 (OCH_3), 3.93 (t, J = 6 Hz, CH), 4.32 (t, J = 6 Hz, CH), 5.78 (d, J = 1 Hz and 5.86, d, J = 1 Hz, OCH_2O), 6.43 (ArH), 6.67 (ArH), 7.18 (m, 5 ArH).

Anal. Calcd. for $C_{33}H_{36}O_6$: C, 75.0; H, 6.9; M^+ = 528.2512. Found: C, 74.9; H, 6.9; M^+ = 528.2515.

1-(3,4-Dihydro-5,7-dimethoxy-4-phenyl-2*H*-1-benzopyran-2-yl)-morpholine **7a**.

A solution of 2,4-dimethoxyphenol (1.54 g), morpholine (0.87 g) and cinnamaldehyde (1.32 g) in methanol (5 ml) was refluxed for 30 minutes and cooled. The crystalline product (2.2 g) was recrystallized from acetone-methanol to give **7a** as colorless needles, mp 170-171°.

Anal. Calcd. for $C_{21}H_{25}NO_4$: C, 71.0; H, 7.1; N, 3.9. Found: C, 70.9; H, 7.0; N, 3.9.

3,4-Dihydro-5,7-dimethoxy-4-phenyl-2*H*-1-benzopyran-2-ol **7b**.

A solution of **7a** (0.5 g) in acetic acid (4 ml) and water (3 ml) was heated to boiling for 3 minutes and allowed to cool. The crystalline product was collected and recrystallized from methanol to give **7b** as colorless needles, mp 141-142°; ^{1}H nmr (major isomer): δ 2.16 (m, CH_2), 3.56 (OCH_3), 3.79 (OCH_3), 4.32 (dd, J = 4, 6 Hz CH), 5.24 (m, CH), 6.07 (d, J = 2 Hz, ArH), 6.15 (d, J = 2 Hz, ArH), 7.21 (m, 5 ArH).

Anal. Calcd. for $C_{17}H_{18}O_4$: C, 71.3; H, 6.3. Found: C, 71.5; H, 6.4. Calcd. for $C_{17}H_{16}O_3$ (*i.e.* $C_{17}H_{18}O_4$-H_2O): M^+ = 268.1099. Found: M^+ = 268.1106.

A solution of **7b** (0.05 g) in acetic anhydride (0.5 ml) pyridine (1.0 ml) was warmed on a steam-bath for 3 minutes and diluted with water. The solid product crystallized from methanol to give the acetate **7c** as colorless needles, mp 142-143°; tlc and ^{1}H nmr spectrum indicated this purified product was a single isomer; ^{1}H nmr: δ 2.11 ($COCH_3$), 2.26 (m, CH_2), 3.52 (OCH_3), 3.78 (OCH_3), 4.30 (dd, J = 4, 6 Hz, CH), 6.09 (d, J = 2 Hz, ArH), 6.18 (d, J = 2 Hz, ArH), 6.21 (dd, J = 4, 12 Hz, CH), 7.20 (m, 5 ArH).

Anal. Calcd. for $C_{19}H_{20}O_5$: C, 69.5; H, 6.1; M^+ = 328.1310. Found: C, 69.6; H, 6.2; M^+ = 328.1316.

1-(3,4-Dihydro-7-hydroxy-4-phenyl-2*H*-1-benzopyran-2-yl)morpholine **10a**.

A solution of resorcinol (5.5 g), morpholine (4.3 g) and cinnamaldehyde (6.6 g) in methanol (20 ml) was warmed for an hour. A crystalline mass separated. After cooling the crystalline product was collected (13.7 g). Recrystallized from acetone-methanol and from benzene-Skellysolve F, **10a** was obtained as colorless needles, mp 164-165°.

Anal. Calcd. for $C_{19}H_{21}NO_3$: C, 73.3; H, 6.8; N, 4.5. Found: C, 73.3; H, 6.9; N, 4.3.

Compound **10a** (2 g) was heated with dimedone (2 g) in 50% aqueous acetic acid (12 ml) for 10 minutes and diluted with water. The solid product was recrystallized from acetone-methanol to give **11b** as solvated colorless needles, mp 148-149° (2.4 g); from acetone-benzene **11b** crystallizes as hard, colorless needles, mp 185-186°; ^{1}H nmr: δ 1.02 (2 CH_3), 1.05 (CH_3), 1.07 (CH_3), 2.26 (m, 4 CH_2), 2.62 (m, and 2.83, m, CH_2), 3.92 (dd, J = 6, 8 Hz, CH), 4.14 (dd, J = 6, 8 Hz, CH), 6.28 (d, J = 3 Hz, ArH), 6.37 (dd, J = 3, 8 Hz, ArH), 6.93 (d, J = 8 Hz, ArH), 7.27 (m, 5 ArH). The same product was obtained by reaction of **10a** with dimedone in methanol.

Anal. Calcd. for $C_{31}H_{36}O_6$: C, 73.8; H, 7.2; M^+ = 504.2512. Found: C, 74.2; H, 7.2; M^+ = 504.2505.

Compound **11b** (1.0 g) was dissolved by warming for 15 seconds in acetic acid (2 ml) containing a drop of concentrated hydrochloric acid. Water (0.5 ml) was added, and the crystals which separated were recrystallized from acetone-methanol to give the cyclized product **12b** as colorless, soft needles, mp 276-277° (0.85 g).

Anal. Calcd. for $C_{31}H_{34}O_5$: C, 76.5; H, 7.0; M^+ = 486.2406. Found: C, 76.5; H, 7.1; M^+ = 486.2425.

Warmed with acetic anhydride and pyridine the cyclized product **12b** formed a diacetate. This crystallized from methanol as colorless, brittle needles, mp 128-129°; ^{1}H nmr: δ 1.03 (CH_3), 1.06 (CH_3), 1.08 (CH_3), 1.09 (CH_3), 2.08 (m, 4 CH_2), 2.24 ($COCH_3$), 2.26 ($COCH_3$), 2.44 (m, CH_2), 3.94 (dd, J = 3, 5 Hz, CH), 4.06 (dd, J = 4, 6 Hz, CH), 6.84 (d, J = 2 Hz, ArH), 6.93 (dd, J = 2, 8 Hz, ArH), 7.14 (m, 5 ArH), 7.49 (d, J = 8 Hz, ArH).

Anal. Calcd. for $C_{35}H_{38}O_7$: C, 73.7; H, 6.7. Found: C, 73.7; H, 6.7. Calcd. for $C_{35}H_{38}O_7 \cdot H^+$: M^+ = 571.2635. Found: M^+ = 571.2635.

1-(3,4-Dihydro-7,8-dihydroxy-4-phenyl-2*H*-1-benzopyran-2-yl)morpholine **10b**.

A solution of pyrogallol (6.3 g) morpholine (4.3 g) and cinnamaldehyde (6.6 g) in methanol (20 ml) was warmed for 30 minutes and cooled. The crystalline product was recrystallized from acetone-methanol to give **10b** as colorless needles, mp 169-170° (8.8 g).

Anal. Calcd. for $C_{19}H_{21}NO_4$: C, 69.7; H, 6.5; N, 4.3. Found: C, 69.7; H, 6.4; N, 4.3.

Compound **10b** (0.5 g) was warmed with dimedone (1.0 g) in methanol (10 ml) for 15 minutes and diluted with water. The gummy product was washed with warm water and crystallized from methanol to give the bis-dimedone adduct **11c** as colorless needles, mp 147-148° (0.6 g); ^{1}H nmr: δ 0.99 (2 CH_3), 1.06 (CH_3), 1.07 (CH_3), 2.27 (m, 4 CH_2, 30H), 2.27 (m, CH_2), 4.02 (dd, J = 4, 6 Hz, CH), 4.12 (dd, J = 4, 7 Hz, CH), 6.37 (d, J = 8 Hz, ArH), 6.53 (d, J = 8 Hz, ArH), 7.22 (m, 5 ArH).

Anal. Calcd. for $C_{31}H_{36}O_7$: C, 71.5; H, 7.0; M^+ = 520.2461. Found: C, 71.5; H, 7.0; M^+ = 520.2433.

Warmed with acetic acid containing a drop of concentrated hydrochloric acid **11c** cyclized to form **12c**. This product crystallized from acetone-methanol as colorless needles, mp 260°; ^{1}H nmr: δ 1.00 (2 CH_3), 1.06 (CH_3), 1.09 (CH_3), 2.20 (m, 5 CH_2), 2.89 (3 OH's, H_2O), 3.87 (dd, J = 3, 5 Hz, CH), 4.23 (dd, J = 7, 9 Hz, CH), 6.30 (d, J = 8 Hz, ArH), 6.57 (d, J = 8 Hz, ArH), 7.14 (m, 5 ArH).

Anal. Calcd. for $C_{31}H_{34}O_6$: C, 74.1; H, 6.8; M^+ = 502.2355. Found: C, 73.9; H, 6.8; meas. M^+ = 502.2258.

1-(3,4-Dihydro-6-hydroxy-7-methoxy-4-phenyl-2*H*-1-benzopyran-2-yl)morpholine **10c**.

A solution of methoxyhydroquinone (6.9 g), morpholine (4.3 g) and cinnamaldehyde (6.6 g) in methanol (40 ml) was heated on a steam-bath. Colored crystals rapidly separated, and after one hour the product was collected (11.3 g) and recrystallized from acetone-methanol; **10c** was obtained as colorless needles, mp 235-236°.

Anal. Calcd. for $C_{20}H_{23}NO_4$: C, 70.4; H, 6.8; N, 4.1. Found: C, 70.4; H, 6.9; N, 4.1.

3,4-Dihydro-2,6-dihydroxy-7-methoxy-4-phenyl-2*H*-1-benzopyran **10d**.

Compound **10c** (5.7 g) was heated to boiling with acetic acid (15 ml) and water (15 ml) until a clear, yellow solution resulted (30 seconds). Water (15 ml) was slowly added and the solution was allowed to cool, causing cream-colored crystals to separate (4.4 g). Recrystallized from aqueous methanol **10d** was obtained as colorless needles, mp 149-150°; ^{1}H nmr (major isomer): δ 2.19 (m, CH_2), 3.17 (OH), 3.83 (OCH_3), 4.23 (dd, J = 4, 10 Hz, CH), 5.16 (OH), 5.63 (t, J = 4 Hz, CH), 6.34 (ArH), 7.27 (m, 5 ArH).

Anal. Calcd. for $C_{16}H_{16}O_4$: C, 70.6; H, 5.9; M^+ = 272.1049. Found: C, 70.8; H, 6.0; M^+ = 272.1037.

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