A New Synthesis of Pongachalcone I, Glabrachromene, Mixtecacin, Candidin, Atalantoflavone Dimethylether, Racemoflavone Dimethylether, and Dihydropyranoaurones, and Their Analogues

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A NEW SYNTHESIS OF PONGACHALCONE I, GLABRACHROMENE, MIXTECACIN, CANDIDIN, ATALANTOFLAVONE DIMETHYLETHER, RACEMOFLAVONE DIMETHYLETHER, AND DIHYDRO-PYRANOAURONES, AND THEIR ANALOGUES

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ABSTRACT.—Treatment of substituted *o*-hydroxychalcones **1–3** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone [DDQ] afforded a mixture of chromenochalcones **4–6** (pongachalcone I [**5a**], glabrachromene [**5d**]), aurones **7–9** and flavones **10–12**. A new and convenient synthesis of candidin [**17a**], atalantoflavone dimethylether [**17b**], racemoflavone dimethylether [**17d**], mixtecacin [**20a**], and their derivatives via the corresponding unknown dihydropyranoflavanones **13–15** has also been described.

Pyranoflavonoids which possess interesting pharmacological properties (1–3) are known to occur mainly in the plant family Leguminosae. The naturally occurring flavonoids pongachalcone I, glabrachromene, candidin, and mixtecacin isolated from *Pongamia glabra* (4–6), *Tephrosia candida* (7), *Tephrosia bracteolata* (8), *Tephrosia praecans* (9), and *Tephrosia woodii* (10) have a 2,2-dimethyl-2*H*-pyrano moiety as a part of their structure. Several methods have been developed (11–17) for synthesis of these flavonoids in the literature. However in these approaches the yields of the flavonoids were not appreciable. Herein we report a facile method for deriving the flavonoids mentioned in the title from dihydropyranochalcones **1–3**, which were prepared by Friedel-Crafts acylation of hydroxychromans (18).

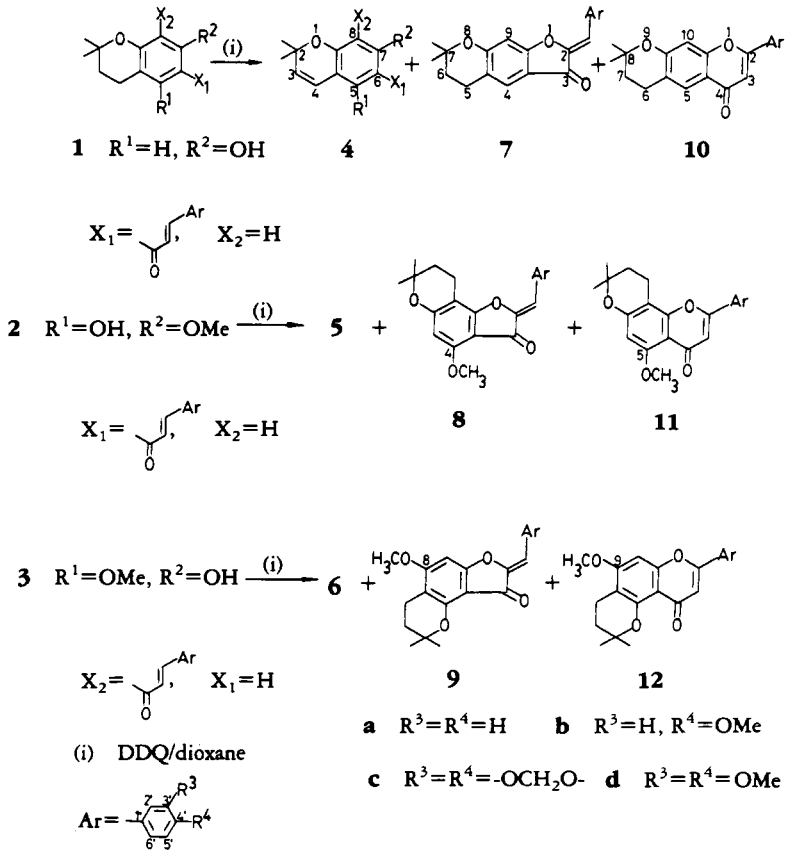
RESULTS AND DISCUSSION

7-Hydroxy-6-cinnamoyl-2,2-dimethylchroman [**1a**] was treated with DDQ in boiling dioxane for 15 h. Three products, **4a**, **7a**, and **10a**, were identified. Compound **4a**, obtained from petroleum ether elution of a Si gel column, showed absorption at 1630 cm^{-1} in its ir spectrum indicating the presence of an α,β-unsaturated carbonyl group. The coupled doublets at δ 5.70 and 6.38 ppm ($J = 10$ Hz) in its ^{1}H-nmr spectrum are due to H-3 and H-4 of the pyran ring. Further, proton doublets at 7.73 and 8.00 ppm ($J = 16$ Hz) and the one-proton singlet at 13.60 ppm closely resembled those of chalcone **1a** (19), in addition to the *gem*-dimethyl and aromatic protons, and were assigned to H-α, H-β, and 7-OH, respectively. These data indicate the structure 7-hydroxy-6-cinnamoyl-2,2-dimethylchromene for **4a**. The identity of **4a** was further established by preparing it by condensation of 6-acetyl-7-hydroxy-2,2-dimethylchromene with benzaldehyde and comparing the analytical and spectral data (mp, undepressed mixed mp, co-tlc, and superimposable ir and nmr spectra). Further elution of the column with 4% EtOAc/petroleum ether provided **7a**, mp 196–197°. Absorptions at 1685 and 1630 cm^{-1} in its ir spectrum were ascribed to lactone carbonyl and C=C stretching vibrations. In the ^{1}H-nmr ($CDCl_3$) spectrum, in addition to a six-proton singlet at δ 1.34 ppm (CMe_2), two-proton triplets at δ 1.90 and 2.85 ppm (-CH_2-CH_2-) of the pyran ring, and a seven-proton multiplet at δ 7.30–7.90 ppm (aromatic H), the single proton singlet at δ 6.45 ppm was assigned to a benzylidene proton (=HC-). Both **4a** and **7a** were $C_{20}H_{18}O_3$ by elemental analyses (**4a**: C 78.41, H 5.95; **7a**: C 78.43, H 5.90) and mass spectra (*m/z* 306.36). These data confirmed structure **7a** to be 2-benzylidene-7,7-dimethyl-5,6-dihydropyrano[3,2-*f*]benzofuran-3-one. The third compound, **10a**, mp 145–146° [lit. (11) mp 146°] was obtained in 30%

yield and identified as 8,8-dimethyl-2-phenyl-6,7-dihydro-4*H*,8*H*-benzo[1,2-*b*:5,4-*b'*]dipyran-4-one.

Extension of this reaction technique to chalcones **1b–1d** gave rise to the corresponding chromenochalcones **4b–4d**, dihydropyranoaurones **7b–7d**, and dihydropyranoflavones **10b–10d**, respectively (Scheme 1). The pyranoflavones **10a–10d** were compared with authentic samples prepared (20) from 6-acetyl-7-hydroxy-2,2-dimethylchroman with aroylchloride by the Baker-Venkataraman method to establish their identity. Proof of structure of **4** was further confirmed by ^{13}C nmr of the methoxy derivative **4b**. In its decoupled spectrum, the pyran ring C-3 and C-4 signals, δ 127.346 and 114.193 ppm, were comparable to those reported (21) for 2,2-dimethylchromene.

Similarly, chromenochalcones **5a–5d**, **6b–6d**, dihydropyranoaurones **8a–8d**, **9b–9d**, and dihydropyranoflavones **11a–11d**, **12b–12d** were obtained from the corresponding pyranochalcones **2a–2d**, and **3b–3d** (Scheme 1). Products **4**, **5**, and **6** are the dehydrogenated compounds of the corresponding chalcones **1**, **2**, and **3**, and the other two structural types, viz. aurones **7**, **8**, **9** and flavones **10**, **11**, **12**, are cyclo-oxidation products. The position of electron-donating substituents in the B ring has very little effect on yields. On the other hand, in the case of chalcones with substituents in the A ring we noted considerable influence: the yields of angular pyranoflavones **11**, **12** obtained from the corresponding chalcones **2**, **3** were comparable to the yield of linear pyranoflavone **10** obtained from chalcones **1**, while yields of angular aurones **8**, **9** were low when compared with those of linear aurone **7**.



SCHEME 1

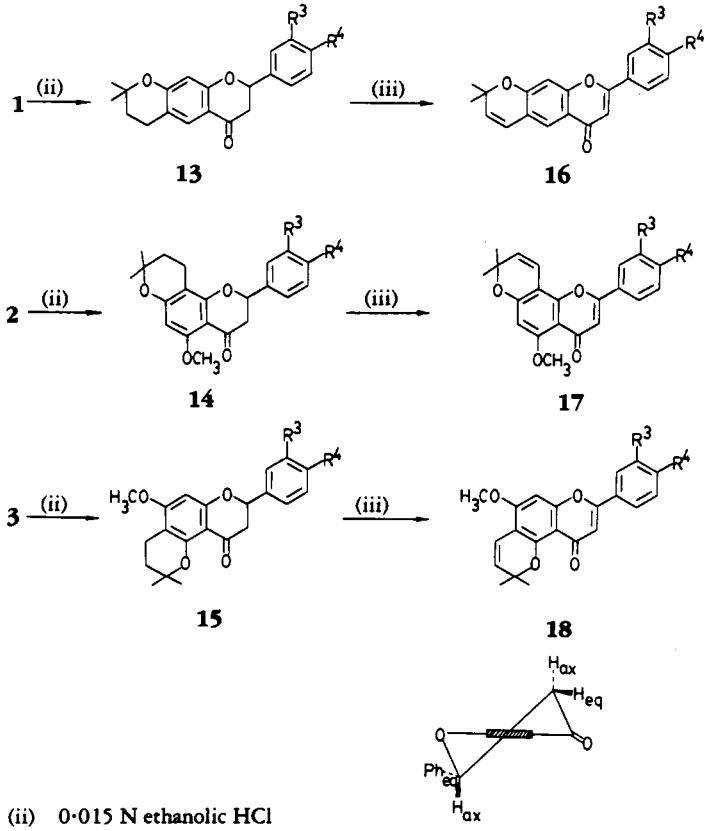
Flavanones are isomeric with chalcones which are observed to by synthetic as well as biosynthetic precursors of the former group. Isomerization-cyclization of the chalcones **1** with acids forming dihydropyranoflavanones followed by dehydrogenation constitutes an important method among those hitherto known for the synthesis of pyranoflavones **16**. Though dehydrogenation of dihydropyranoflavanone has proved useful for the synthesis of flavone, the overall yield of the flavone was poor; the reason being that the method (22) for deriving the precursor, viz., prenylated flavanone (from prenylbromide and corresponding flavanone), was not as productive and gave a mixture.

It was felt that methodology that would provide an alternative and convenient access to the hitherto unknown dihydropyranoflavanone should make the acid-catalyzed isomerization-cyclization technique more expedient and widely applicable. Chalcone **1a**, when refluxed with a solution of 0.015 N ethanolic HCl for 20 h gave a single compound (mp 150–151°) in 60% yield (95% based on unrecovered **1a**). It was identified as the corresponding flavanone, 2-phenyl-8,8-dimethyl-2,3,6,7-tetrahydro-4*H*,8*H*-benzo[1,2-*b*:5,4-*b'*]dipyran-4-one [**13a**]. The absorption at 1660 cm^{-1} in its ir spectrum was ascribable to a carbonyl group. The structure was confirmed by ^{1}H-nmr, and the chromanone ring (H-2) proton appeared as a doublet of doublets at δ 5.35 ppm. The double doublets centered at δ 3.0 ppm, $J = 16.5$ and 12.9 Hz, were assignable to H_{ax}-3, and a doublet of doublets (overlapping with methylene protons at C-6) at δ 2.79 ppm was assigned to H_{eq}-3 forming an ABX system. The coupling constant of proton H-2 [viz. 13.5 Hz (ax-ax), and 2.7 Hz (ax-eq)] indicated it to be axial in the quasi-chair conformation of the chromanone ring, with phenyl equatorial.

Extension of this isomerization-cyclization technique to chalcones **1b–1d**, **2a–2d**, and **3b–3d** gave rise to the corresponding flavanones **13b–13d**, **14a–14d**, and **15b–15d**, respectively (Scheme 2). A critical factor noted in this reaction is that a slight increase in acid concentration above 0.015 N had an immense counter-productive effect as observed (23) in the case of simple chalcone-flavanone systems. Structures assigned for flavanones were also confirmed by ^{13}C-nmr spectra of the methoxy compound **13b**. The signals at δ 44.127 and 79.331 ppm were characteristic of C-3 methylene and C-2 oxymethine carbons of flavanone [C-3 and C-2 carbon signals of flavone, chalcone occur downfield (110–165 ppm) when compared to flavanone (40–80 ppm)] (24).

Dehydrogenation of both flavanone and dihydropyrans using DDQ and NBS followed by pyridine has been reported (26–28). Treatment of dihydropyranoflavanone **13a** with DDQ in dioxane and with NBS/pyridine in CCl_4 separately gave **16a**. These two methodologies were extended to the dihydropyranoflavones **13b–13d**, **14a–14d**, and **15b–15d** to obtain the corresponding pyranoflavones **16b–16d**, **17a–17d**, and **18b–18d**, respectively (Scheme 2).

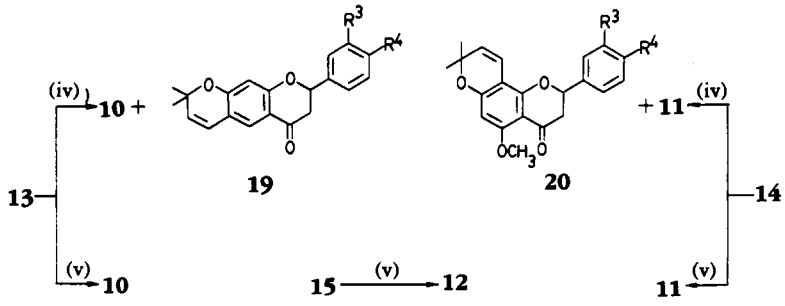
Expecting to derive the titled pyranoflavanone, mixtecacin, and their analogues, we treated dihydropyranoflavanone **13a** with DDQ (1 mmol) in boiling dioxane for 6 h. Workup of the product showed two spots on tlc which were identified as the pyranoflavanone **19a** and dihydropyranoflavone **10a**. On similar treatment, dihydropyranoflavanones **13c**, **14a**, and **14c** gave the pyranoflavanones **19c**, **20a**, and **20c** and the dihydropyranoflavones **10c**, **11a**, and **11c**, respectively (Scheme 3). Thus, the simple high yield conversion **1**→→**16**, in two steps, represents a productive approach to the titled flavonoid systems, viz., candidin [**17a**] (7) [isopongaflavone [**17a**] (8)], atalantoflavone dimethylether [**17b**] (25), recemoflavone dimethylether [**17d**] (25) and mixtecacin [**20a**] (10) [obovatin methylether [**20a**] (23)]. Structures of pyranoflavanones **19** and **20** were further confirmed by acid isomerization-cyclization of the corresponding chromenochalcones **4** and **5**.



(ii) 0·015 N ethanolic HCl
(iii) DDQ or NBS/pyridine

SCHEME 2

In continuation of our efforts aimed at developing a new and simple route for converting the dihydropyranoflavanones **13–15** into pyranoflavones **16–18** it was felt that I_2 and KOAc could be employed for the transformation. Accordingly, dihydropyranoflavanone **13a** was heated with I_2 in the presence of freshly fused KOAc in HOAc at 120° for 5 h. A single product (mp 145–146°) was obtained in 80% yield and identified as the dihydropyranoflavone **16a**. Extension of the technique to **13b–13d**, **14a–14d**,



(iv) DDQ in dioxane
(v) I_2, KOAc/HOAc

SCHEME 3

and **15b–15d** gave a similar series of compounds. By choosing the proper reagent and conditions, the selected ring could be dehydrogenated.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Melting points were determined on Boetius microheating table and Mettler FP 5 apparatus and are uncorrected. Cc was performed on columns of Si gel (Merck, 60–120 mesh). Analytical tlc was performed on Si gel-G (Merck). Ir were recorded on a Perkin Elmer 597 spectrophotometer in KBr. ^{1}H-nmr were recorded on a Varian EM-360 (90 MHz), XL 100 (80 MHz), and General Electric QE-300 (300 MHz) spectrometers in solution of $CDCl_3$. ^{13}C nmr were obtained on General Electric QE-300 (75 MHz) and VXR-300 standard (75 MHz) spectrometers. Chemical shifts for both the ^{1}H nmr and ^{13}C nmr are reported in δ units downfield of TMS and coupling constants are in Hz. Microanalyses were performed on Carlo Erba 1106 and Perkin Elmer-Model 240 CHN analysers. Resorcinol, phloroglucinol, anhydrous $AlCl_3$, $POCl_3$, DDQ, NBS, MeCN, C_5H_5N, HOAc, benzaldehyde, anisaldehyde, piperanal, vanillin, zinc dust, and KOAc were purchased from SISCO Industrial Ltd., Bombay, India. All hydroxychromans **1–3** were prepared in our laboratory according to usual methods (29,30).

PREPARATION OF CHALCONES **1–3**.—To a mixture of hydroxysubstituted 2,2-dimethylchroman (29,30) (10 mmol), cinnamic acid (10 mmol), and anhydrous $AlCl_3$ (10 g) was added $POCl_3$ (25 ml), and the mixture was allowed to stand at room temperature for 24 h. The reaction mixture was then poured into crushed ice with stirring. The separated solid was filtered and purified by Si gel cc using petroleum ether-EtOAc (10:1). The following pyranochalcones were obtained. **1a**: mp 192–193° [lit. (19) 192–193°]. **1b**: mp 145–146° [lit. (19) 147–148°]. **1c**: mp 202–203° [lit. (19) 201–203°]. **1d**: mp 118–119° [lit. (19) 120–121°]. **2a**: mp 120–121° [lit. (19) 120–121°]. **2b**: mp 113–114° [lit. (19) 112–113°]. **2c**: mp 127–129° [lit. (30) 125–126°]. **2d**: mp 119–120° [lit. (30) 117—118°]. **3b**: mp 130–131°. **3c**: mp 175–176°. **3d**: mp 140–142°.

PREPARATION OF CHROMENOCHALCONES **4–6**, DIHYDROPYRANOAURONES **7–9**, AND DIHYDROPYRANOFLAVONES **10–12**.—A mixture of dihydropyranochalcones **1–3** (1 mmol) and DDQ (2 mmol) in dry dioxane (20 ml) was refluxed for 15 h. The reaction mixture was then poured into saturated Na_2CO_3 solution (20 ml) and extracted with $CHCl_3$ (2 × 25 ml). The $CHCl_3$ extract was washed with H_2O and dried over anhydrous Na_2SO_4. The residue obtained on evaporation of the solvent was chromatographed on Si gel. Elution with petroleum ether/EtOAc gave the respective chromenochalcones, aurones, and flavones. The physical and spectral data of chromenochalcones **4a–4d**, **5a–5d**, **6b–6d**, aurones **7a–7d**, **8a–8d**, **9b–9d**, and flavones **10a–10d**, **11a–11d**, and **12b–12d** are given in Tables 1, 2, and 3, respectively.

ISOMERIZATION-CYCLIZATION OF CHALCONES **1–3** INTO FLAVANONES **13–15**.—To a solution of dihydropyranochalcones **1–3** (2 mmol) in EtOH (150 ml) was added 0.1 N HCl (25 ml). The solution was refluxed on a steam bath for 20 h and concentrated to a small volume under reduced pressure. After cooling, the residual solution was diluted with H_2O and extracted with $CHCl_3$ (3 × 20 ml). The $CHCl_3$ extract was washed successively with dilute $NaHCO_3$ (100 ml) and H_2O (200 ml) and dried over anhydrous Na_2SO_4. Removal of the solvent furnished a residue which when subjected to cc on Si gel eluted with petroleum ether/EtOAc afforded the corresponding dihydropyranoflavanones **13**, **14**, and **15** (yield above 90% based on unrecovered chalcones). The physical and spectral data of the dihydropyranoflavanones are listed in Table 4.

CONVERSION OF FLAVANONES **13–15** INTO FLAVONES **16–18**.—*DDQ method*.—A mixture of dihydropyranoflavanones **13–15** (1 mmol) and DDQ (454 mg, 2 mmol) in dioxane (15 ml) was refluxed for 6 h. Reaction mixture was then filtered and the residue obtained by evaporation of the solvent was dissolved in $CHCl_3$ and washed successively with aqueous $NaHCO_3$ and H_2O. Evaporation of the dried extract furnished the pyranoflavones **16–18**.

NBS method.—A solution of the dihydropyranoflavanones **13–15** (1 mmol), NBS (356 mg, 2 mmol), and dibenzoyl peroxide (25 mg) in anhydrous CCl_4 (25 ml) was refluxed for 6 h. The reaction mixture was cooled, and the precipitated succinimide was filtered. The residue obtained after removal of the solvent was refluxed with pyridine (3 ml) for 1 h, cooled, diluted with H_2O, and extracted with $CHCl_3$. The $CHCl_3$ extract was washed with dilute HCl and H_2O and dried. Evaporation of the solvent afforded the pyranoflavones **16–18**. The physical and spectral data of pyranoflavones **16–18** are listed in Tables 5 and 6.

PREPARATION OF PYRANOFLAVANONES **19** AND **20**.—*2-Phenyl-8,8-dimethyl-2,3-dihydro-4H,8H-benzo[1,2-b:5,4-b′]dipyran-4-one* [**19a**].—A mixture of flavanone **13a** (308 mg, 1 mmol) and DDQ (227 mg, 1 mmol) in dioxane (15 ml) was refluxed at 120° for 6 h. The precipitated hydroquinone was filtered, and the solution was concentrated to a small volume under reduced pressure. The residue ob-

TABLE 1. Data for Chromenochalcones **4**, **5**, and **6**.

Compound	Mp (solvent)[a]	Yield (%)	Ir (KBr) ν max cm^{-1}	Molecular formula	Analysis % observed C,H (calcd C,H)	^{1}H nmr ($CDCl_3$), δ ppm J in Hz
4a	148–149 (100:0)	25	1630,1600	$C_{20}H_{18}O_3$ (306.36)	78.41,5.95 (78.43,5.92)	1.45 (s, 6H, CMe_2, 5.70 (d, 1H, H-3, J = 10), 6.38 (d, 2H, H-4, H-8, J = 10), 7.35–7.60 (m, 5H, H_{arom}), 7.73 (d, 2H, H-5, H-α, J = 16), 8.0 (d, 1H, H-β, J = 16), 13.60 (s, 1H, 7-OH)
4b[b]	151–152 (99:1)	20	1630,1600	$C_{21}H_{20}O_4$ (336.39)	74.90,6.00 (74.79,5.99)	1.44 (s, 6H, CMe_2), 3.84 (s, 3H, 4′-OMe), 5.70 (d, 1H, H-3, J = 10), 6.41 (d, 2H, H-4, H-8, J = 10), 7.01 (d, 2H, H-3′, H-5′, J = 9), 7.20–7.80 (m, 4H, H-2′, H-5, H-6′, H-α), 7.90 (d, 1H, H-β, J = 16), 13.60 (s, 1H, 7-OH)
4c	163–164 (98:2)	25	1620,1550	$C_{21}H_{18}O_5$ (350.37)	72.04,5.22 (71.88,5.18)	1.42 (s, 6H, CMe_2, 5.59 (d, 1H, H-3, J = 10), 6.05 (s, 2H, -OCH_2O-), 6.30 (d, 2H, H-4, H-8, J = 10), 6.83 (d, 1H, H-5′, J = 9), 7.08 (d, 2H, H-2′, H-6′, J = 9), 7.32 (d, 1H, H-α, J = 16), 7.45 (s, 1H, H-5), 7.77 (d, 1H, H-β, J = 16), 13.65 (s, 1H, 7-OH)
4d	165–166 (98:2)	18	1620,1545	$C_{22}H_{22}O_5$ (366.42)	72.08,6.07 (72.12,6.05)	1.42 (s, 6H, CMe_2, 3.90, 3.96 (2s, 3H, each, 3′-OMe, 4′-OMe, 5.60 (d, 1H, H-3, J = 10), 6.31 (d, 2H, H-4, H-8, J = 10), 6.90 (d, 1H, H-5′, J = 9), 7.13–7.28 (m, 2H, H-2′, H-6′), 7.39 (d, 1H, H-α, J = 16), 7.47 (s, 1H, H-5), 7.80 (d, 1H, H-β, J = 16), 13.63 (s, 1H, 7-OH)
5a	106–107 (99:1)	20	1625,1585	$C_{21}H_{20}O_4$ (336.39)	75.03,6.03 (74.99,5.99)	1.45 (s, 6H, Me_2), 3.92 (s, 3H, 7-OMe), 5.46 (d, 1H, H-3, J = 10), 5.90 (s, 1H, H-8), 6.64 (d, 1H, H-4, J = 10), 7.30–7.51 (m, 5H, H_{arom}), 7.64–7.81 (m, 2H, H-α, H-β), 14.49 (s, 1H, 5-OH)
5b	90–92 (100:0)	22	1630,1605	$C_{22}H_{22}O_5$ (366.42)	72.15,6.08 (72.12,6.05)	1.45 (s, 6H, CMe_2), 3.81, 3.92 (2s, 3H each, 7-OMe, 4′-OMe, 5.45 (d, 1H, H-3, J = 10), 5.92 (s, 1H, H-8), 6.68 (d, 1H, H-4, J = 10), 6.91 (d, 2H, H-3′, H-5′, J = 9), 7.55 (d, 2H, H-2′, H-6′, J = 9), 7.70–7.81 (m, 2H, H-α, H-β), 14.45 (s, 1H, 5-OH)

TABLE 1. (Continued)

Compound	Mp (solvent)[a]	Yield (%)	Ir (KBr) ν max cm^{-1}	Molecular formula	Analysis % observed C,H (calcd C,H)	^1H nmr ($CDCl_3$), δ ppm J in Hz
5c	124–125 (98:2) [lit. (31) 126°]	20	1649,1580	$C_{22}H_{20}O_6$ (380.40)	69.50,5.35 (69.46,5.30)	—
5d	115–116 (100:0)	20	1620,1600	$C_{23}H_{24}O_6$ (396.44)	69.60,6.15 (69.68,6.10)	1.45 (s, 6H, CMe_2), 3.91, 3.92, 3.93 (3s, 3H each, 7-OMe, 3′-OMe, 4′-OMe), 5.46 (d, 1H, H-3, J = 10), 5.92 (s, 1H, H-8), 6.68 (d, 1H, H-4, J = 10), 6.89 (d, 1H, H-5′, J = 9), 7.12 (s, 1H, H-2′), 7.23 (d, 1H, H-6′, J = 9), 7.76–7.81 (m, 2H, H-α, H-β), 14.45 (s, 1H, 5-OH)
6b	159–160 (99:1)	21	1625,1600	$C_{22}H_{22}O_5$ (366.42)	72.08,6.10 (72.15,6.09)	1.50 (s, 6H, CMe_2), 3.85 (s, 6H, 5-OMe, 4′-OMe), 5.45 (d, 1H, H-3, J = 10), 6.07 (s, 1H, H-6), 6.60 (d, 1H, H-4, J = 10), 6.91 (d, 2H, H-3′, H-5′, J = 9), 7.58 (d, 2H, H-2′, H-6′, J = 9), 7.82–8.13 (m, 2H, H-α, H-β), 14.43 (s, 1H, 7-OH)
6c	164–165 (98:2)	20	1635,1605	$C_{22}H_{20}O_6$ (380.40)	69.50,5.28 (69.46,5.30)	1.53 (s, 6H, CMe_2), 3.84 (s, 3H, 5-OMe), 5.46 (d, 1H, H-3, J = 10), 6.01 (s, 2H, $-OCH_2O-$), 6.06 (s, 1H, H-6), 6.60 (d, 1H, H-4, J = 10), 6.83 (s, 1H, H-5′), 7.00–7.20 (m, 2H, H-2′, H-6′), 7.70 (d, 1H, H-α, J = 16), 8.00 (d, 1H, H-β, J = 16), 14.42 (s, 1H, 7-OH)
6d	120–122 (100:0)	15	1630,1600	$C_{23}H_{24}O_6$ (396.44)	69.70,6.12 (69.68,6.10)	1.53 (s, 6H, CMe_2), 3.84, 3.86 (2s, 9H, 5-OMe, 3′-OMe, 4′-OMe), 5.45 (d, 1H, H-3, J = 10), 6.06 (s, 1H, H-6), 6.61 (d, 1H, H-4, J = 10), 6.82 (s, 1H, H-5′), 7.03–7.10 (m, 2H, H-2′, H-6′), 7.65–8.10 (m, 2H, H-α, H-β), 14.45 (s, 1H, 7-OH)

[a]Solvent in each case is petroleum ether-EtOAc in ratio shown in parentheses.

[b]**4b**: ^{13}C nmr ($CDCl_3$, 75 MHz) δ 28.541 Me_2, 55.370 (OMe), 76.578 (C-2), 104.670 (C-5a), 113.428 (C-8), 114.193 (C-4), 114.396 (C-2′, C-6′), 117.729 (C-α), 121.095 (C-1), 127.095 (C-1′), 127.346 (C-3), 128.747 (C-5), 130.320 (C-3′ and C-5′), 144.151 (C-β), 160.395 (C-8a), 161.735 (C-4′), 166.453 (C-7), 191.608 (C=O).

TABLE 2. Data for Dihyropyranoaurones **7**, **8**, and **9**.

Compound	Mp (solvent)[a]	Yield (%)	Ir (KBr) ν max cm^{-1}	Molecular formula	Analysis % observed C,H (calcd C,H)	^1H nmr ($CDCl_3$), δ ppm J in Hz
7a	196–197 (96:4)	15	1690,1630	$C_{20}H_{18}O_3$ (306.36)	78.43,5.90 (78.43,5.92)	1.34 (s, 6H, CMe_2), 1.90 (t, 2H, H-6, $J=7$), 2.85 (t, 2H, H-5, $J=7$), 6.45 (s, 1H, =CH-), 7.30 (s, 1H, H-9), 7.42–7.80 (m, H_{arom}), 7.90 (s, 1H, H-4)
7b	144–145 (97:3)	13	1685,1635	$C_{21}H_{20}O_4$ (336.39)	74.85,6.06 (74.79,5.99)	1.45 (s, 6H, CMe_2), 1.95 (t, 2H, H-6, $J=7$), 2.85 (t, 2H, H-5, $J=7$), 3.82 (s, 3H, OMe), 6.42 (s, 1H, =CH-), 7.00 (d, 2H, H-3′, H-5′, $J=8.7$), 7.30 (d, 2H, H-2′, H-6′, $J=8.7$), 7.40, 7.50 (2s, 2H, H-9, H-4)
7c	213–214 (94:6)	15	1700,1630	$C_{21}H_{18}O_5$ (350.37)	72.03,5.15 (71.99,5.18)	1.53 (s, 6H, CMe_2), 1.82 (t, 2H, H-6, $J=7$), 2.80 (t, 2H, H-5, $J=7$), 6.50 (s, 1H, =CH-), 6.10 (s, 2H, $-OCH_2O-$), 6.90–7.30 (m, 3H, H_{arom}), 7.60 (s, 1H, H-9), 7.70 (s, 1H, H-4)
7d	169–170 (95:5)	12	1700,1625	$C_{22}H_{22}O_5$ (366.42)	72.15,6.08 (72.12,6.05)	1.40 (s, 6H, CMe_2), 1.85 (t, 2H, H-6, $J=7$), 2.80 (t, 2H, H-5, $J=7$), 3.95, 4.00 (2s, 6H, 2 × OMe), 6.35 (s, 1H, =CH-), 6.85–7.20 (m, 2H, H-5′, H-6′), 7.45 (s, 1H, H-2′), 7.60 (s, 1H, H-9), 7.90 (s, 1H, H-4)
8a	160–162 (97:3)	10	1680,1630	$C_{21}H_{20}O_4$ (336.39)	74.95,6.00 (74.99,5.99)	1.38 (s, 6H, CMe_2), 2.00 (t, 2H, H-8, $J=7$), 2.60 (t, 2H, H-9, $J=7$), 3.84 (s, 3H, OMe), 6.05 (s, 1H, H-5), 6.60–7.20 (m, 6H, =CH-, H_{arom})
8b	190–193 (98:2)	10	1685,1625	$C_{22}H_{22}O_5$ (366.42)	72.10,6.10 (72.12,6.05)	1.43 (s, 6H, CMe_2), 1.87 (t, 2H, H-8, α7), 2.65 (t, 2H, H-9, $J=7$), 3.85, 3.89 (2s, 3H each, 2 × OMe), 6.10 (s, 1H, H-5), 6.90–7.00 (m, 3H, =CH-, H-3′, H-5′), 7.30 (d, 2H, H-2′, H-6′, $J=8.7$)
8c	230–232 (95:5)	11	1700,1640	$C_{22}H_{20}O_6$ (380.40)	69.50,5.25 (69.46,5.30)	1.44 (s, 6H, CMe_2), 1.80 (t, 2H, H-8, $J=7$), 2.70 (t, 2H, H-9, $J=7$), 3.89 (s, 3H, OMe), 6.00 (s, 3H, $-OCH_2O-$, H-5), 6.70–6.90 (m, 2H, H-5′, H-6′), 6.95 (s, 1H, =CH-), 7.70 (s, 1H, H-2′)

TABLE 2. (Continued)

Compound	Mp (solvent)[a]	Yield (%)	Ir (KBr) ν max cm^{-1}	Molecular formula	Analysis % observed C,H (calcd C,H)	^{1}H nmr ($CDCl_3$), δ ppm J in Hz
8d	205–207 (93:7)	10	1685,1645	$C_{23}H_{24}O_6$ (396.44)	69.65,6.13 (69.68,6.10)	1.45 (s, 6H, CMe_2), 1.90 (t, 2H, H-8, J = 7), 2.85 (t, 2H, H-9, J = 7), 3.85 (s, 9H, 3 × OMe), 6.02 (s, 1H, H-5), 6.55 (s, 1H, =CH-), 7.00–7.70 (m, 3H, H_{arom})
9b	171–174 (94:6)	8	1680,1625	$C_{22}H_{22}O_5$ (366.42)	72.10,6.10 (72.15,6.09)	1.45 (s, 6H, CMe_2), 1.85 (t, 2H, H-6, J = 7), 2.90 (t, 2H, H-7, J = 7), 3.85 (s, 6H, 2 × OMe), 6.10 (s, 1H, H-9), 6.90–7.80 (m, 5H, =CH-, H_{arom})
9c	193–195 (95:5)	9	1690,1625	$C_{22}H_{20}O_6$ (380.40)	69.51,5.32 (69.46,5.30)	1.50 (s, 6H, CMe_2), 1.85 (t, 2H, H-6, J = 7), 2.85 (t, 2H, H-7, J = 7), 3.80 (s, 3H, OMe), 6.0 (s, 2H, -OCH_2O-), 6.10 (s, 1H, H-9), 6.85 (s, 1H, =CH-), 7.10–7.30 (m, 3H, H_{arom})
9d	140–142 (97:3)	8	1690,1625	$C_{23}H_{24}O_6$ (396.44)	69.72,6.08 (69.68,6.10)	1.50 (s, 6H, CMe_2), 1.85 (t, 2H, H-6, J = 7), 2.85 (t, 2H-7, J = 7), 3.84 (s, 9H, 3 × OMe), 6.05 (s, 1H, H-9), 6.90–7.40 (m, 4H, =CH-, H_{arom})

[a]Solvent in each case is petroleum ether-EtOAc in the ratio shown in parentheses.

TABLE 3. Data for Dihydropyranoflavones **10**, **11**, and **12**.

Compound	Mp (solvent)[a]	Yield (%)	Ir (KBr) ν max cm^{-1}	Molecular formula	Analysis % observed C,H (calcd C,H)	^1H nmr ($CDCl_3$), δ ppm J in Hz
10a	145–146 (90:10) [lit. (12) 146°]	20	1635,1605	$C_{20}H_{18}O_3$ (306.36)	78.40,6.00 (78.43,5.92)	1.37 (s, 6H, CMe_2), 1.85 (t, 2H, H-7, J = 7), 2.90 (t, 2H, H-6, J = 7), 6.72 (s, 1H, H-3), 6.90 (s, 1H, H-10), 7.45–8.00 (m, 6H, H_{arom})
10b	161–162 (95:5) [lit. (20) 161–162]	25	1630,1605	$C_{21}H_{20}O_4$ (336.39)	74.70,5.90 (74.79,5.99)	1.40 (s, 6H, CMe_2), 1.86 (t, 2H, H-7, J = 7), 2.90 (t, 2H, H-6, J = 7), 3.88 (s, 3H, OMe), 6.56 (s, 1H, H-3), 6.84 (s, 1H, H-10), 6.96 (d, 2H, H-3′, H-5′, J = 9), 7.82 (d, 2H, H-2′, H-6′, J = 9), 7.90 (s, 1H, H-5)
10c	223–224 (90:10) [lit. (20) 223–224]	25	1630,1595	$C_{21}H_{18}O_5$ (350.37)	71.90,5.10 (71.99,5.18)	1.42 (s, 6H, CMe_2), 1.92 (t, 2H, H-7, J = 7), 2.94 (t, 2H, H-6, J = 7), 6.12 (s, 2H, $-OCH_2$), 6.66 (s, 1H, H-3), 6.92 (s, 1H, H-10), 7.42 (s, 1H, H-2′), 7.52 (d, 1H, H-5′, J = 9), 7.86 (d, 1H, H-6′, J = 9), 7.98 (s, 1H, H-5)
10d[b]	165–166 (92:8)	26	1630,1610	$C_{22}H_{22}O_5$ (366.42)	72.00,6.15 (72.12,6.05)	1.42 (s, 6H, CMe_2), 1.88 (t, 2H, H-7, J = 7), 2.90 (t, 2H, H-6, J = 7), 3.96 (s, 6H, 3′-OMe, 4′-OMe), 6.64 (s, 1H, H-3), 6.90 (s, 1H, H-10), 7.02–7.60 (m, 3H, H_{arom}), 7.90 (s, 1H, H-5)
11a[c]	205–206 (95:5)	25	1640,1600	$C_{21}H_{20}O_4$ (336.39)	74.95,6.00 (74.98,5.99)	1.43 (s, 6H, CMe_2), 1.94 (t, 2H, H-9, J = 7), 2.97 (t, 2H, H-10, J = 7), 3.95 (s, 2H, 4-OMe), 6.33 (s, 1H, H-6), 6.73 (s, 1H, H-3), 7.53–7.90 (m, 5H, H_{arom})
11b	220–221 (94:6)	25	1635,1620	$C_{22}H_{22}O_5$ (366.42)	72.16,6.00 (72.12,6.05)	1.35 (s, 6H, CMe_2), 1.85 (t, 2H, H-9, J = 7), 2.90 (t, 2H, H-10, J = 7), 3.82, 3.88 (2s, 3H each 5-OMe, 4′-OMe), 6.23 (s, 1H, H-6), 6.54 (s, 1H, H-3), 6.93 (d, 2H, H-3′, H-5′, J = 9), 7.75 (d, 2H, H-2′, H-6′, J = 9)
11c	277–278 (90:10)	30	1635,1610	$C_{22}H_{20}O_6$ (380.40)	69.50,5.25 (69.46,5.30)	1.50 (s, 6H, CMe_2), 1.93 (t, 2H, H-9, J = 7), 2.95 (t, 2H, H-10, J = 7), 3.95 (s, 3H, 5-OMe), 6.10 (s, 2H, $-OCH_2O-$), 6.35 (s, 1H, H-6), 6.60 (s, 1H, H-3), 6.90 (d, 1H, H-5′, J = 9), 7.35 (s, 1H, H-2′), 7.50 (d, 1H, H-6′ J = 9)

TABLE 3. (Continued)

Compound	Mp (solvent)[a]	Yield (%)	Ir (KBr) ν max cm^{-1}	Molecular formula	Analysis % observed C,H (calcd C,H)	^{1}H nmr ($CDCl_3$), δ ppm *J* in Hz
11d	255–256 (91:9)	25	1630,1590	$C_{23}H_{24}O_6$ (396.44)	69.65,6.13 (69.68,6.10)	1.30 (s, 6H, CMe_2), 1.80 (t, 2H, H-9, *J* = 7), 2.82 (t, 2H, H-10, *J* = 7), 3.85 (s, 9H, 5-OMe, 3′-OMe, 4′-OMe), 6.20 (s, 1H, H-6), 6.50 (s, 1H, H-3), 6.85 (d, 1H, H-5′, *J* = 9), 7.25 (s, 1H, H-2′), 7.40 (d, 1H, H-6′, *J* = 9)
12b[a]	203–204 (90:10) [lit. (20) 203–204]	35	1640,1605	$C_{22}H_{22}O_5$ (366.42)	72.00,6.02 (72.12,6.05)	1.40 (s, 6H, CMe_2), 1.80 (t, 2H, H-7, *J* = 7), 2.66 (t, 2H, H-8, *J* = 7), 3.83, 3.90 (2s, 3H each, 9-OMe, 4′-OMe), 6.40 (s, 1H, H-3), 6.45 (s, 1H, H-10), 6.92 (d, 2H, H-3′, H-5′, *J* = 9), 7.90 (d, 2H, H-2′, H-6′, *J* = 9)
12c[b]	222–224 (88:12)	30	1630–1590	$C_{20}H_{20}O_6$ (380.40)	69.40,5.39 (69.46,5.30)	1.40 (s, 6H, CMe_2), 1.78 (t, 2H, H-7, *J* = 7), 2.58 (t, 2H, H-8, *J* = 7), 3.82 (s, 3H, 9-OMe), 5.98 (s, 2H, $-OCH_2O-$), 6.40 (s, 1H, H-3), 6.65–7.40 (m, 4H, H_{arom})
12d[d]	210–212 (90:10)	35	1630,1590	$C_{23}H_{24}O_6$ (396.44)	69.60,6.13 (69.68,6.10)	1.40 (s, 6H, CMe_2), 1.78 (t, 2H, H-7, *J* = 7), 2.60 (t, 2H, H-8, *J* = 7), 3.88 (s, 9H, 9-OMe, 3′-OMe, 4′OMe), 6.38 (s, 1H, H-3), 6.40 (s, 1H, H-10), 6.82 (d, 1H, H-5′, *J* = 9), 7.24 (s, 1H, H-2′), 7.40 (d, 1H, H-6′, *J* = 9)

[a]Solvent in each case is petroleum ether-EtOAc in the ratio shown in parentheses.

[b]**10d**: ^{13}C nmr ($CDCl_3$, 75 MHz) δ 22.434 (C-6), 27.353 (Me_2), 32.849 (C-7), 56.400, 56.462 (2 × OMe), 76.387 (C-8), 104.751 (C-5a), 106.306 (C-3), 109.085 (C-5′), 111.501 (C-2′), 117.472 (C-4a), 120.115 (C-6′), 120.568 (C-10), 124.967 (C-5′), 126.615 (C-5), 149.571 (C-3′), 152.169 (C-4′), 156.500 (C-2), 159.608 (C-10a), 163.263 (C-9a), 178.465 (C=O).

[c]**11a**: ^{13}C nmr ($CDCl_3$, 75 MHz) δ 16.686 (C-10), 26.639 (Me_2), 31.873 (C-9), 56.259 (OMe), 75.993 (C-8), 96.982 (C-6), 101.380 (C-4a), 108.833 (C-3, C-10a), 125.781 (C-2′, C-6′), 128.951 (C-3′, C-5′), 131.071 (C-4′), 131.824 (C-1′), 159.300 (C-2), 159.125 (C-6a), 159.996 (C-5, C-10b), 177.947 (C=O).

[d]**12d**: ^{13}C nmr ($CDCl_3$, 75 MHz) δ 16.644 (C-8), 26.018 (Me_2), 30.833 (C-7), 55.329, 55.555, 55.644 (3 × OMe), 74.928 (C-6), 89.838 (C-10), 106.239 (C-3), 107.600 (C-2′), 108.085 (C-5′), 108.663 (C-4a), 110.526 (C-8a), 118.893 (C-6′), 123.955 (C-1′), 148 (C-3′), 150.940 (C-4′), 154.271 (C-2), 157.603 (C-4b), 159.608 (C-10a), 160.805 (C-9), 170.042 (C=O).

TABLE 4. Data for Dihydropyranoflavanones **13**, **14**, and **15**.

Compound	Mp (solvent)[a]	Yield (%)	Ir (KBr) ν max cm^{-1}	Molecular formula	Analysis % observed C,H (calcd C,H)	^1H nmr ($CDCl_3$), δ ppm J in Hz
13a	150–151 (97:3)	60	1685,1610	$C_{20}H_{20}O_3$ (308.38)	77.85,6.65 (77.90,6.54)	1.35 (s, 6H, CMe_2), 1.82 (t, 2H, H-7, J = 7), 2.77 (t, 2H, H-6, J = 7), 2.79 (d of d, 1H, H_{eq}-3, J = 13.5, 2.7), 3.00 (dd, 1H, H_{ax}-3, J = 16.5, 12.9), 5.35 (d of d, 1H, H-2, J = 13.5, 2.7), 6.38 (s, 1H, H-10), 6.97–7.47 (m, 5H, H_{arom}), 7.60 (s, 1H H-5)
13b[b]	126–127 (98:2)	55	1660,1600	$C_{21}H_{22}O_4$ (338.41)	74.58,6.58 (74.54,6.55)	1.34 (s, 6H, CMe_2), 1.81 (t, 2H, H-7, J = 7), 2.76 (t, 2H, H-6, J = 7), 2.80 (d of d, 1H, H_{eq}-3, J = 13.5, 2.7), 3.02 (dd, 1H, H_{ax}-3, J = 16.5, 12.5), 3.82 (s, 3H, 4′-OMe), 5.34 (d of d, 1H, H-2, J = 13.5, 2.5), 6.38 (s, 1H, H-10), 6.94 (d, 2H, H-3′, H-5′, J = 8.4), 7.38 (d, 2H, H-2′, H-6′, J = 8.4), 7.68 (s, 1H, H-5)
13c	130–131 (95:5)	70	1675,1620	$C_{21}H_{20}O_5$ (352.39)	71.50,5.68 (71.58,5.72)	1.34 (s, 6H, CMe_2), 1.82 (t, 2H, H-7, J = 7), 2.75 (t, 2H, H-6, J = 7), 2.81 (d of d, 1H, H_{eq}-3, J = 13.5, 2.7), 3.01 (dd, 1H, H_{ax}-3, J = 16.5, 12.9), 5.37 (d of d, 1H, H-2, J = 13.5, 2.7), 6.03 (s, 2H, -OCH_2O-), 6.35 (s, 1H, H-10), 6.85 (d, 1H, H-5′, J = 8.7), 6.98 (d, 1H, H-6′, J = 8.7), 7.15 (s, 1H, H-2′), 7.65 (s, 1H, H-5)
13d[c]	124–125 (98:2)	60	1660,1605	$C_{22}H_{24}O_5$ (368.43)	71.70,6.52 (71.72,6.57)	1.34 (s, 6H, CMe_2), 1.81 (t, 2H, H-7, J = 7), 2.76 (t, 2H, H-6, J = 7), 2.81 (d of d, 1H, H_{eq}-3, J = 13.5, 2.7), 3.03 (dd, 1H, H_{ax}-3, J = 16.5, 13.0), 3.89, 3.91 (2s, 3H each, 3′-OMe, 4′OMe), 5.36 (d of d, 1H, H-2, J = 13.7, 2.5), 6.39 (s, 1H, H-10), 6.88 (d, 1H, H-5′, J = 8.7), 6.97 (d, 1H, H-6′, J = 8.7), 7.0 (s, 1H, H-2′), 7.68 (s, 1H, H-5)
14a	169–170 (97:3)	55	1660,1600	$C_{21}H_{22}O_4$ (338.41)	74.50,6.53 (74.54,6.55)	1.36 (s, 6H, CMe_2), 1.78 (t, 2H, H-9, J = 7), 2.64 (t, 2H, H-10, J = 7), 2.83 (d of d, 1H, H_{eq}-3, J = 13.5, 2.7), 3.00 (dd, 1H, H_{ax}-3, J = 16.5, 12.8), 3.86 (s, 3H, 5-OMe), 5.43 (d of d, 1H, H-2, J = 13.5, 2.5), 6.02 (s, 1H, H-6), 7.36–7.46 (m, 5H, H_{arom})

TABLE 4. (Continued)

Compound	Mp (solvent)[a]	Yield (%)	Ir (KBr) ν max cm^{-1}	Molecular formula	Analysis % observed C,H (calcd C,H)	^1H nmr ($CDCl_3$), δ ppm J in Hz
14b[d]	160–161 (98:2)	60	1665,1600	$C_{22}H_{24}O_5$ (368.43)	71.78,6.61 (71.72,6.57)	1.34, 1.35 (2s, 6H, CMe_2), 1.77 (t, 2H, H-9, J = 7), 2.60 (t, 2H, H-10, J = 7), 2.80 (d of d, 1H, H_{eq}-3, J = 13.5, 2.7), 2.98 (dd, 1H, H_{ax}-3, J = 16.5, 12.9), 3.83, 3.86 (2s, 3H each, 5-OMe, 4′-OMe), 5.36 (d of d, 1H, H-2, J = 13.5, 2.5), 6.01 (s, 1H, H-6), 6.94 (d, 2H, H-3′, H-5′, J = 8.7), 7.40 (d, 2H, H-2′, H-6′, J = 8.7)
14c	175–176 (94:6)	65	1660,1600	$C_{22}H_{22}O_6$ (382.42)	69.06,5.80 (69.10,5.80)	1.33, 1.35 (2s, 6H, CMe_2), 1.77 (t, 2H, H-9, J = 7), 2.60 (t, 2H, H-10, J = 7), 2.75 (d of d, 1H, H_{eq}-3, J = 13.5, 2.7), 2.94 (dd, 1H, H_{ax}-3, J = 16.5, 13.0), 3.85 (s, 3H, 5-OMe), 5.31 (d of d, 1H, H-2, J = 13.5, 2.5), 5.98 (s, 2H, OCH_2O-), 6.00 (s, 1H, H-6), 6.82 (d, 1H, H-5′, J = 8.4), 6.88 (d, 1H, H-6′, J = 8.4), 6.97 (s, 1H, H-2′)
14d	148–149 (97:3)	55	1650,1580	$C_{23}H_{26}O_6$ (398.0)	69.30,6.30 (69.34,6.53)	1.33, 1.36 (2s, 6H, CMe_2), 1.78 (t, 2H, H-9, J = 7), 2.61 (t, 2H, H-10, J = 7), 2.80 (d of d, 1H, H_{eq}-3, J = 13.5, 2.7), 3.00 (dd, 1H, H_{ax}-3, J = 16.5, 13.0), 3.87, 3.89, 3.92, (3s, 3H each, 5-OMe, 3′-OMe, 4′-OMe), 5.36 (d of d, 1H, H-2, J = 13.5, 2.5), 6.02 (s, 1H, H-6), 6.88 (d, 1H, H-5′, J = 8.4), 7.00 (d, 2H, H-2′, H-6′, J = 8.4)
15b	125–126 (98:2)	60	1675,1575	$C_{22}H_{24}O_5$ (368.43)	71.70,6.53 (71.72,6.57)	1.38, 1.41 (2s, 6H, CMe_2), 1.78 (t, 2H, H-7, J = 7), 2.56 (t, 2H, H-8, J = 7), 2.70 (d of d, 1H, H_{eq}-3, J = 13.5, 2.7), 3.06 (dd, 1H, H_{ax}-3, J = 16.5, 13.0), 3.81, 3.82 (2s, 3H each, 9-OMe, 4′-OMe), 5.31 (d of d, 1H, H-2, J = 13.5, 2.5), 6.08 (s, 1H, H-10), 6.93 (d, 2H, H-3′, H-5′, J = 8.7), 7.38 (d, 2H, H-2′, H-6′, J = 8.7)

TABLE 4. (Continued)

Compound	Mp (solvent)[a]	Yield (%)	Ir (KBr) ν max cm^{-1}	Molecular formula	Analysis % observed C,H (calcd C,H)	^{1}H nmr ($CDCl_3$), δ ppm J in Hz
15c	150–153 (95:5)	60	1665,1590	$C_{22}H_{22}O_6$ (382.42)	69.17,5.75 (69.10,5.80)	1.38, 1.41 (2s, 6H, CMe_2), 1.77 (t, 2H, H-7, J = 7), 2.55 (t, 2H, H-8, J = 7), 2.69 (d of d, 1H, H_{eq}-3, J = 13.5, 2.7), 2.96 (dd, 1H, H_{ax}-3, J = 16.5, 12.8), 3.81 (s, 3H, 9-OMe), 5.98 (s, 2H, -OCH_2O-), 5.27 (d of d, 1H, H-2, J = 13.5, 2.5), 6.07 (s, 1H, H-10), 6.82 (d, 1H, H-5′, J = 8.1), 6.89 (d, 1H, H-6′, J = 8.1), 6.97 (s, 1H, H-2′)
15d	118–119 (97:3)	50	1665,1600	$C_{23}H_{26}O_6$ (398.0)	69.38,6.50 (69.34,6.53)	1.38, 1.40 (2s, 6H, CMe_2), 1.78 (t, 2H, H-7, J = 7), 2.56 (t, 2H, H-8, J = 7), 2.70 (d of d, 1H, H_{eq}-3, J = 13.5, 2.7), 2.98 (dd, 1H, H_{ax}-3, J = 16.5, 12.9), 3.81, 3.84, 3.86 (3s each, 9-OMe, 3′-OMe, 4′-OMe), 5.30 (d of d, 1H, H-2, J = 13.5, 2.5), 6.08 (s, 1H, H-10), 6.83 (d, 1H, H-5′, J = 8.1), 6.92 (d, 1H, H-6′, J = 8.1), 6.99 (s, 1H, H-2′)

[a]Solvent in each case is petroleum ether-EtOAc in the ratio shown in parentheses.

[b]**13b**: ^{13}C-nmr ($CDCl_3$, 75 MHz) δ 21.60 (C-6), 26.819, 27.069 (Me_2), 32.623 (c-7), 44.317 (C-3), 55.338 (OMe), 75.947 (C-8), 79.331 (C-2), 104.640 (C-4a, C-5a), 114.116 (C-3′, C-5′), 115.779 (C-10), 127.689 (C-2′, C-6′), 128.244 (C-5), 131.156 (C-1′), 159.821 (C-9a, C-10a), 161.363 (C-4′), 191.223 (C=O).

[c]**13d**: ^{13}C-nmr ($CDCl_3$, 75 MHz) δ 16.942 (C-6), 22.176, 22.356 (Me_2), 28.002 (C-7), 39.961 (C-3), 51.301 (OMe_2), 71.243 (C-8), 74.819 (C-2), 99.94 (C-10), 104.974 (C-5a), 106.632 (C-4a), 109.841 (C-2′), 111.157 (C-5′), 114.075 (C-6′), 123.557 (C-5), 127.020 (C-1′), 156.710 (C-3′, C-4′), 167.200 (C-9a, C-10a), 186.284 (C=O).

[d]**14b**: ^{13}C-nmr ($CDCl_3$, 75 MHz) δ 16.567 (C-10), 26.395, 27.035 (Me_2), 32.027 (C-9), 45.338 (C-3), 55.321, 55.976 $(OMe)_2$, 75.947 (C-8), 78.479 (C-2), 93.888 (C-6), 101.790 (C-4a), 106.313 (C-10a), 114.025 (C-2′, C-6′), 127.381 (C-3′, C-5′), 131.283 (C-1′), 159.660 (C-10b), 160.569 (C-5, C-4′), 161.777 (C-6a), 189.743 (C=O).

TABLE 5. Physical and Analytical Data for **16–18**.

Compound	Yield (%)		Mp (solvent)	IR (KBr) ν max cm^{-1}	Molecular Formula	Analysis % observed C,H (calcd C,H)
	DDQ	NBS				
16a	80	70	154–156 A lit. (13) 156	1635,1610	$C_{20}H_{16}O_3$ (304.32)	79.00,5.20 (78.93,5.29)
16b	75	70	169–170 A	1630,1610	$C_{21}H_{18}O_4$ (334.35)	75.38,5.47 (75.43,5.42)
16c	78	72	210–211 A	1640,1620	$C_{21}H_{16}O_5$ (348.36)	72.50,4.57 (42.41,4.63)
16d	80	70	157–158 A	1640,1615	$C_{22}H_{20}O_5$ (364.50)	72.55,5.50 (72.51,5.53)
17a	85	80	199–201 A lit. (8) 201–205	1640,1600	$C_{21}H_{18}O_4$ (334.35)	75.48,5.45 (75.43,5.42)
17b	80	70	207–208 A lit. (25) 207–209	1660,1610	$C_{22}H_{20}O_5$ (364.50)	72.40,5.50 (72.51,5.53)
17c	75	70	242–243 A lit. (32) 242–244	1635,1610	$C_{22}H_{18}O_6$ (378.39)	70.00,4.70 (69.84,4.79)
17d	90	80	195–196 B lit. (25) 194–196	1635,1610	$C_{23}H_{22}O_6$ (394.43)	70.00,5.65 (70.04,5.62)
18b	75	67	205–206 B	1655,1620	$C_{22}H_{20}O_5$ (364.40)	72.57,5.55 (72.51,5.53)
18c	70	65	220–221 C	1645,1625	$C_{22}H_{18}O_6$ (378.39)	69.86,4.75 (69.84,4.79)

[a]Solvent A, petroleum ether/C_6H_6; Solvent B, C_6H_6; Solvent C, C_6H_6/EtOAc.

tained was separated by chromatography on Si gel in petroleum ether-EtOAc (98:2) into pyranoflavanone **19a** (138 mg, 45% and dihydropyranoflavone **10a** (92 mg, 30%). **19a**: mp 119–120°; ir (KBr) 1665, 1615, 1380 cm^{-1}; ^{1}H-nmr (300 MHz) δ 1.40 (s, 6H, CMe_2), 2.72 (d of d, 1H, H_{eq}-3, J = 13.5, 2.7), 3.0 (dd, 1H, H_{ax}-3, J = 16, 12.9), 5.45 (d of d, 1H, H-2, J = 13.5, 2.7), 5.65 (d, 1H, H-7, J = 10), 6.35 (s, 1H, H-10), 6.45 (d, 1H, H-6, J = 10), 7.40–7.50 (m, 5H, H_{arom}), 7.60 (s, 1H, H-5). *Anal.* calcd for $C_{20}H_{18}O_3$ (306.36) C 78.41, H 5.92; observed C 78.45, H 5.95.

*2-(3′,4′-Methylenedioxy)phenyl-8,8-dimethyl-2,3-dihydro-4*H,*8*H-*benzo*[*1,2*-b:*5,4*-b′]*dipyran-4-one* [**19c**].—Flavanone **13c** (352 mg, 1 mmol) was reacted with DDQ (227 mg, 1 mmol) in the same manner as described for the preparation of **19a**. Chromatographic separation on Si gel in petroleum ether-EtOAc (97:3) afforded the pyranoflavanone **19c** (175 mg, 50%) together with dihydropyranoflavone **10c** (87 mg, 25%). **19c**: mp 120–122°; ir (KBr) 1660, 1620, 1380, 1340 cm^{-1}; ^{1}H nmr (300 MHz) δ 1.45 (s, 6H, CMe_2), 2.82 (d of d, 1H, H_{eq}-3, J = 13.5, 2.7), 3.05 (dd, 1H, H_{ax}-3, J = 16.5, 12.9), 5.56 (d of d, 1H, H-2, J = 13.5, 2.7), 5.69 (d, 1H, H-7, J = 10), 6.01 (s, 2H, -OCH_2O-), 6.34 (s, 1H, H-10), 6.42 (d, 1H, H-8, J = 10), 6.89 (d, 1H, H-5′, J = 8.7), 7.25–7.34 (m, 2H, H-2′, H-6′), 7.65 (s, 1H, H-5). *Anal.* calcd for $C_{21}H_{18}O_5$ (350.37), C 71.99, H 5.18; observed C 72.03, H 5.15.

Mixtecacin [**20a**].—A mixture of flavanone **14a** (338 mg, 1 mmol) and DDQ (227 mg, 1 mmol) in dioxane (15 ml) was refluxed for 6 h and filtered. After concentrating in vacuo, the residue was separated by chromatography on Si gel in petroleum ether-EtOAc (97:3) yielding mixtecacin [**20a**] (168 mg, 50%), mp 135–136° [lit. (10) mp 136–137°] and dihydropyranoflavone **11a** (84 mg, 25%).

*5-Methoxy-2-(3′,4′-methylenedioxy)phenyl-2,3-dihydro-8,8-dimethyl-4*H,*8*H-*benzo*[*1,2*-b:*3′4*-b′]*dipyran-4-one* [**20c**].—Flavanone **14c** (382 mg, 1 mmol) was dehydrogenated with DDQ (1 mmol) as described for the preparation of mixtecacin [**20a**]. Chromatographic purification on Si gel in petroleum ether-EtOAc (97:3) afforded pyranoflavanone **20c** (209 mg, 55%), mp 168–170° [lit. (31) mp 168–169°], together with dihydropyranoflavone **11c** (76 mg, 20%).

CONVERSION OF FLAVANONES **13–15** INTO FLAVONES **10–12**: I_2, KOAc/HOAc METHOD.—A solution of I_2 (254 mg, 1 mmol) in glacial HOAc (15 ml) was added dropwise during 20 min to a stirred

TABLE 6. ^{1}H-nmr Data of Pyranoflavones **16**, **17**, and **18**.

Flavone	CMe_2 s	>C-CH= d, J = 10	=CH-Ar d, J = 10	H-3 s	Aromatic Protons (J is in Hz)	Other Protons
16a	1.48	5.74	6.46	6.76	6.89 (s, 1H, H-10), 7.45–7.55 (m, 3H), 7.82–7.92 (m, 3H)	
16b	1.46	5.86	6.48	6.58	6.70 (s, 1H, H-10), 7.06 (d, 2H, H-3′, H-5′, J = 9), 7.88 (d, 2H, H-2′, H-6′, J = 9), 8.28 (s, 1H, H-5)	3.98 (s, 3H, 4′-OMe)
16c	1.44	5.84	6.54	6.62	6.88 (s, 1H, H-10), 7.44 (d, 1H, H-5′, J = 9), 7.52 (s, 1H, H-2′), 7.88 (d, 1H, H-6′, J = 9), 8.08 (s, 1H, H-5)	6.08 (s, 2H, -OCH_2O-)
16d	1.45	5.85	6.50	6.56	6.80 (s, 1H, H-10), 7.40–7.80 (m, 3H), 8.05 (s, 1H, H-5)	3.97 (s, 6H, 3′-OMe, 4′-OMe)
17a	1.56	5.70	6.96	6.86	6.45 (s, 1H, H-6), 7.60 (m, 3H), 8.30 (m, 2H)	4.00 (s, 3H, 5-OMe)
17b	1.50	5.62	6.84	6.58	6.32 (s, 1H, H-6), 7.01 (d, 2H, H-3′, H-5′, J = 8.5), 7.81 (d, 2H, H-2′, H-6′, J = 8.5)	3.88, 3.95 (2s, 6H, 5-OMe, 4′-OMe)
17c	1.55	5.60	6.80	6.50	6.25 (s, 1H, H-6), 7.25–7.70 (m, 3H)	3.95 (s, 3H, 5-OMe), 6.05 (s, 2H, -OCH_2O-)
17d	1.52	5.63	6.83	6.60	6.34 (s, 1H, H-6), 6.98 (d, 1H, H-5, J = 8.5), 7.32 (d, 1H, H-2′), 7.51 (d, 1H, H-6′, J = 8.5)	3.97 (s, 6H, 3′-OMe, 4′-OMe), 3.98 (s, 3H, 5-OMe)
18b	1.42	5.56	6.64	6.48	6.38 (s, 1H, H-10), 6.96 (d, 2H, H-3′, H-5′, J = 9), 7.72 (d, 2H, H-2′, H-6′, J = 9)	3.88, 3.96 (2s, 6H, 9-OMe, 4′-OMe)
18c	1.44	5.56	6.64	6.48	6.35 (s, 1H, H-10), 6.99 (d, 1H, H-5′, J = 8.7), 7.25–7.50 (m, 2H, H-2′, H-6′)	3.96 (s, 3H, 9-OMe), 6.01 (s, 2H, -OCH_2O-)

solution of the dihydropyranoflavanone **13** (1 mmol) and freshly fused KOAc (1 g) in glacial HOAc (10 ml) at 120° and refluxed for 5 h. The reaction mixture was then cooled, diluted with H_2O (15 ml), and extracted with $CHCl_3$ (2 × 25 ml). The $CHCl_3$ extract was successively washed with a dilute solution of $NaHCO_3$, $Na_2S_2O_3$, and H_2O and dried (Na_2SO_4). Evaporation of the solvent furnished the dihydropyranoflavone **10** which was recrystallized using petroleum ether/EtOAc.

The dihydropyranoflavanones **14** and **15** also furnished the flavones **11** and **12**, respectively, on treatment with I_2/KOAc in HOAc as described above. The yields were **10a** (90%), **10b** (85%), **10c** (83%), **10d** (79%), **11a** (80%), **11b** (90%), **11c** (80%), **11d** (75%), **12b** (85%), **12c** (78%), and **12d** (83%). The physical and spectral data of flavones **10–12** are listed in Table 3.

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