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3-Benzylchroman Derivatives Related to Brazilin from Sappan Lignum

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Six aromatic compounds **1**—**6** were isolated from Sappan Lignum, the dried heartwood of *Caesalpinia sappan* L., and were characterized as 3-benzylchroman derivatives by spectroscopic means. They seem to be closely related biosynthetically to brazilin; **2** and **3** may be precursors and **4**—**6** may be key intermediates in the biogenesis of brazilin.

Keywords——*Caesalpinia sappan*; Leguminosae; heartwood; Sappan Lignum; brazilin; 3-benzylchroman derivative; biogenesis

Sappan Lignum, the dried heartwood of *Caesalpinia sappan* L. (Leguminosae) has long been used as an oriental medicine,[1] for example, as an anti-inflammatory agent. In the course of a systematic screening for antihypercholesteremic activity, the methanolic extractive of this plant was shown to have a significant effect. From this extractive, we obtained seventeen aromatic compounds (compounds **1**—**17**) together with brazilin[2] and sappanchalcone,[3] and reported the chemical characterization of four [compounds **7**, **8**,[4] caesalpin J (**9**) and caesalpin P (**10**)[5]] among them. This paper deals with the structural characterization of six aromatic compounds **1**—**6**, closely related biosynthetically to brazilin.

Compound **1**, colorless needles, mp 192—194 °C, $[\alpha]_D$ −10.3 °, showed M^+ at *m/z* 286 in the electron-impact mass spectrum (EI-MS), giving the molecular formula $C_{16}H_{14}O_5$, which is consistent with the results of elementary analysis. The infrared (IR) spectrum exhibited bands at 3250 (hydroxyl), 1640 (flavanone carbonyl) and 1600 (arom. ring) cm^{-1}. The ultraviolet (UV) spectrum showed absorptions at 312 (3.98), 276 (4.25), 231 (4.26) and 204 (4.65) nm (log ε). The carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectrum (Table I) revealed a total of sixteen carbon signals due to four aromatic carbons (δ 164.3, 163.0, 145.0, 143.6) each bearing an oxygen function, two alkyl-substituted aromatic carbons (δ 128.7, 113.1), six aromatic carbons (δ 129.1, 110.5, 102.2, 115.5, 116.2, 119.5) each carrying a proton, one flavanone carbonyl carbon (δ 191.4), one methylene carbon (δ 69.4) having an oxygen function, one methine carbon (δ 46.5) and one methylene carbon (δ 31.2). Furthermore, the proton nuclear magnetic resonance (^{1}H-NMR) spectrum showed the presence of two aromatic ABX system [δ 7.65 (1H, d, J=9 Hz), 6.51 (1H, dd, J=2, 9 Hz), 6.32 (1H, d, J=2 Hz); 6.66 (1H, d, J=8 Hz), 6.47 (1H, dd, J=2, 8 Hz), 6.62 (1H, d, J=2 Hz), one methylene [δ 4.09 (1H, dd, J=8, 11 Hz) and 4.29 (1H, dd, J=4, 11 Hz)] linked to an oxygen atom, the benzylic protons [δ 2.47 (1H, dd, J=9, 13 Hz) and 2.93 (1H, dd, J=5, 13 Hz)] and one methine proton [δ 2.79 (1H, m)]. From the above spectral data, compound **1** was assumed to be a 3-benzylchroman-4-one analogue.[6] A signal at δ 102.2 in the ^{13}C-NMR spectrum was assigned

to the *ortho*-, *ortho*-oxygen substituted aromatic carbon by estimating the substitution effect[7]; therefore, this should be assigned to C-8, and there should be a hydroxyl group at C-7 in the A-ring. Moreover, the appearance of the dihydroxytropylium fragment at *m/z* 123 in the EI-MS, and of the aromatic ABX system in the ^{1}H-NMR spectrum indicated the presence of a 3,4-dihydroxybenzyl moiety. Therefore, the structure of **1** could be represented as 3-(3′,4′-dihydroxybenzyl)-7-hydroxychroman-4-one.

Compound **2**, $C_{16}H_{12}O_5$, yellow needles, mp 220—221 °C (dec.), $[\alpha]_D$ ±0°, UV λ_{max}^{EtOH} nm (log ε): 370 (4.35), 310 (4.14), 258 (4.11), 2.08 (4.76), IR ν_{max}^{KBr} cm^{-1}: 3300, 1645, 1610, 1575, could be deduced to be a dehydro derivative of **1** by comparing its EI-MS [M^+ at *m/z* 284] and the ^{13}C-NMR spectrum with those of **1**. That is, the sp^3 carbon signals due to C-3 and C-9 in **1** were replaced by sp^2 carbons [δ 125.4 (s) and 136.0 (d)] in the ^{13}C-NMR spectrum of **2**. The ^{1}H-NMR spectrum of **2** showed signals assignable to a methylene group (2H, br s, at δ 5.37) carrying an oxygen atom, located at the allylic position, and one olefinic proton (1H, br s, at δ 7.53), which could be assigned to 2-H_2 and 9-H, respectively. Thus, compound **2** was considered to be an eucomin-type substance.[8] The geometry of the double bond between C-3 and C-9 was concluded to be *E* from the chemical shifts of 2-H_2 and 9-H in the ^{1}H-NMR spectrum.[8]

Compound **3**, $C_{16}H_{14}O_6$ (by the EI-MS), a white powder, $[\alpha]_D$ +51.6°, showed absorptions at 311 (3.89), 277 (4.18), 231 (4.18), 205 (4.61) nm (log ε) in the UV and at 3300, 1660 and 1600 cm^{-1} in the IR spectrum. It was concluded to be an oxy-derivative of **1** by comparing the ^{13}C-NMR spectrum of **3** with that of **1**. The signal at δ 72.1 (s) in the ^{13}C-NMR spectrum of **3** was attributed to C-3 by reference to that of **1**. Therefore, the quaternary carbon at C-3 was substituted by a hydroxyl group. This was supported by the appearance of two sets of broad singlet signals due to 2-H_2 and 9-H_2, suggesting that compound **3** is an eucomol-type compound.[8]

Compound **4**, $C_{16}H_{16}O_6$, colorless needles, mp 157—160 °C, $[\alpha]_D$ +3.7°, showed a fragment pattern superimposable on that of brazilin in the EI-MS, but the peaks $[M+Na]^+$ and $[M]^+$ at *m/z* 327 and 304 in the fast atom bombardment (FAB)-MS corresponded to a hydrogenated derivative of **3**. Compound **4** was deduced to be a 3-(3′,4′-dihydroxybenzyl)-3,4,7-trihydroxychroman from the occurrence of the signal at δ 69.0, assignable to the methine carbon carrying an oxygen atom in **4**, instead of the signals at δ 192.9 due to C-4 in **3** by comparing the ^{13}C-NMR spectra. Usual acetylation of **4** afforded a tetraacetate whose EI-MS ($C_{24}H_{24}O_{10}^+$, M^+ at *m/z* 472) showed four acetyl groups at δ 2.07 (3H, s), 2.28 (6H, s) and 2.29 (3H, s), the benzylic protons at δ 2.78 (2H, s, 9-H_2), one methylene bearing an oxygen atom at δ 3.82 (1H, dd, *J*=1, 10 Hz, 2-H) and 3.95 (1H, d, *J*=10 Hz, 2-H′) and an acetoxymethine proton at δ 5.74 (1H, d, *J*=1 Hz) assignable to 4-H. Compound **4** readily changed, even upon heating at 70 °C, into brazilin, as well as compound **5** (see below) and its isomer **6**. The identity of the EI-MS of **4** with that of brazilin might arise from the ready conversion of compound **4** to brazilin under electron impact. Consequently, the structure of **4** was characterized as shown in the formula.

Compound **5**, $C_{17}H_{18}O_6$, a white powder, $[\alpha]_D$ +53.6°, showed the same fragment peaks as **4** in the EI-MS, but a peak of $[M+Na]^+$ at *m/z* 341 appeared in the FAB-MS. In the ^{1}H-NMR spectrum of **5**, a methoxyl signal appeared at δ 3.30. The ^{13}C-NMR spectrum indicated that **5** is a derivative of **4** methylated at C_4-OH, because the C-4 signal was shifted toward lower field by 9.3 ppm compared with that of **4**. Usual acetylation of **5** yielded the triacetate, whose ^{1}H-NMR spectrum showed three phenolic acetoxyl signals at δ 2.27, 2.28, 2.29, also suggesting that **5** was methylated at C_4-OH. Compound **5** was also unstable, and even upon heating at 70 °C it changed into a mixture of **4**, **6** and brazilin. Consequently, the plain structure of **5** was represented as shown in the formula.

Compound **6**, $C_{17}H_{18}O_6$, a white powder, $[\alpha]_D$ −34.8°, was recognized to be a

stereoisomer of **5** from the following facts: 1) the EI-MS of **6** was coincident with that of **5**, though a peak at *m/z* 341 due to $[M+Na]^+$ appeared in the FAB-MS; 2) the ^1H- and ^{13}C-NMR spectra of **6** and its acetate showed signals comparable with those of **5** and its acetate. Compound **6** was supposed to be a configurational isomer at C_4-OMe; it behaved in the same way as **4** and **5** upon heating.

TABLE I. ^{13}C-NMR Data for Compounds **1**—**6** (in DMSO-d_6)

	1	2	3	4	5	6
2	69.4 t	67.5 t	72.0 t	66.9 t	66.7 t	68.9 t
3	46.5 d	125.4 s	72.1 s	67.7 s	69.5 s	69.4 s
4	191.4 s	179.5 s	192.9 s	69.0 d	78.3 d	76.2 d
4a	113.1 s	114.3 s	111.8 s	114.8 s	112.1 s	111.6 s
5	129.1 d	129.3 d	129.1 d	131.3 d	132.2 d	132.1 d
6	110.5 d	111.0 d	110.9 d	108.3 d	107.9 d	106.9 d
7	164.3 s	164.4 s	164.5 s	157.9 s	158.9 s	158.4 s
8	102.2 d	102.3 d	102.3 d	101.0 d	102.5 d	102.4 d
8a	163.0 s	162.3 s	162.7 s	154.0 s	154.1 s	154.7 s
9	31.2 t	136.0 d	30.6 t	*a)*	*a)*	*a)*
1′	128.7 s	127.7 s	126.0 s	127.4 s	127.2 s	127.2 s
2′	115.5 d	115.8 d	115.0 d	115.4 d	114.9 d	115.0 d
3′	145.0 s	145.3 s	144.5 s	144.3 s	144.7 s	144.5 s
4′	143.6 s	147.4 s	143.3 s	143.5 s	143.7 s	143.6 s
5′	116.2 d	117.5 d	118.0 d	118.8 d	118.2 d	118.4 d
6′	119.5 d	123.0 d	121.4 d	121.2 d	121.4 d	121.7 d
OMe	—	—	—	—	56.6 q	55.3 q

a) Hidden by DMSO-d_6.

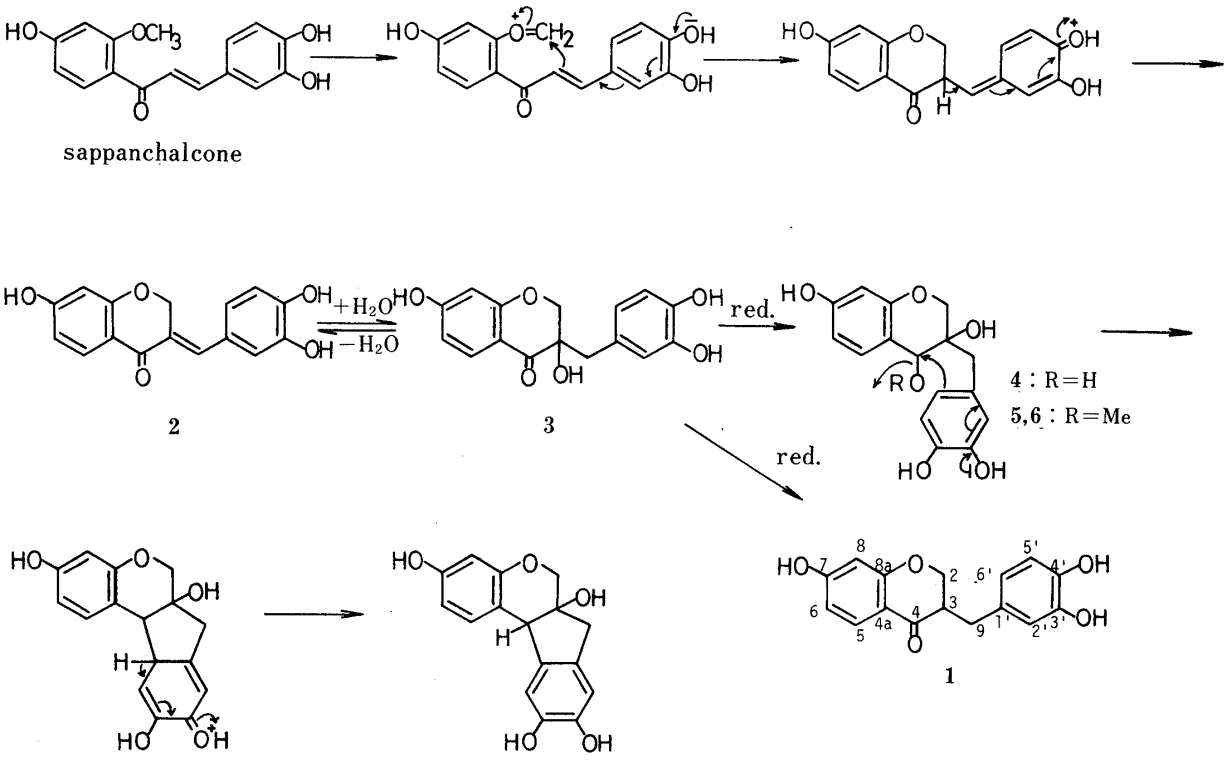


Chart 1

Brazilin is interesting from the viewpoint of pharmacological activity[9] and its skeleton is rare among natural compounds. As regards the biogenesis of brazilin, Tamm and Heller proposed a biogenetic pathway from chalcone *via* 3-benzylchroman analogs as shown in Chart 1.[10] We have here isolated the key intermediates, compounds **4**—**6**, which upon heating are converted partly into brazilin, together with sappanchalcone and compounds **1**—**3**, which are considered to be precursors of brazilin, in accordance with Tamm's scheme. This is believed to be the first report of the isolation of isoflavonoids such as compounds **1**—**6** from the Leguminosae plant. The configurations at C-3 in **1**, **3**—**6** and at C-4 in **4**—**6** have not been determined.

Experimental[11]

Isolation——The methanolic extractive (300 g) of Sappan Lignum, the dried heartwood of *Caesalpinia sappan* L. (Leguminosae), purchased in the market in Hong Kong, was separated as shown in Chart 2 to give a total of nineteen substances (compounds **1**—**17** along with brazilin and sappanchalcone). Compounds **7** and **8** in this text correspond to **2** and **3** in the foregoing paper.[4]

Compound 1——Colorless needles, mp 192—194 °C, $[\alpha]_D^{24}$ −10.3° (c=1.00, MeOH). UV λ_{max}^{MeOH} nm (log ε): 204 (4.65), 231 (4.26), 276 (4.25), 312 (3.98). IR ν_{max}^{KBr} cm^{-1}: 3250 (OH), 1640, 1600, 1570. EI-MS m/z: 286 ($C_{16}H_{14}O_5^+$, M^+, 47%), 164 ($C_6H_8O_3^+$, base peak), 137 ($C_7H_5O_3^+$, 72%), 123 ($C_7H_7O_2^+$, 67%). ^{1}H-NMR δ: 2.47 (1H, dd, J=9, 13 Hz, 9-H), 2.79 (1H, m, 3-H), 2.93 (1H, dd, J=5, 13 Hz, 9-H′), 4.09 (1H, dd, J=8, 11 Hz, 2-H), 4.29 (1H, dd, J=4, 11 Hz, 2-H′), 6.32 (1H, d, J=2 Hz, 8-H), 6.47 (1H, dd, J=2, 8 Hz, 6′-H), 6.51 (1H, dd, J=2, 9 Hz, 6-H), 6.62 (1H, d, J=2 Hz, 2′-H), 6.66 (1H, d, J=8 Hz, 5′-H), 7.65 (1H, d, J=9 Hz, 5-H), 8.71, 8.78 (each 1H, s, 2 × arom. OH). *Anal.* Calcd for $C_{16}H_{14}O_5$: C, 67.12; H, 4.93. Found: C, 67.21; H, 4.90.

Compound 2——Yellow needles, mp 220—221 °C (dec.), $[\alpha]_D^{25}$ ±0° (c=1.00, MeOH). UV λ_{max}^{MeOH} nm (log ε): 208 (4.76), 258 (4.11), 310 (4.14), 370 (4.35). IR ν_{max}^{KBr} cm^{-1}: 3300 (OH), 1645, 1610, 1575. EI-MS m/z: 284 ($C_{16}H_{12}O_5^+$, M^+, 47%), 137 ($C_7H_5O_3^+$, 80%). ^{1}H-NMR δ: 5.37 (2H, br s, 2-H), 6.35 (1H, d, J=2 Hz, 8-H), 6.55 (1H, dd, J=2, 8 Hz, 6-H), 6.83 (3H, br s, 2′,5′,6′-H), 7.53 (1H, br s, 9-H), 7.74 (1H, d, J=8 Hz, 5-H).

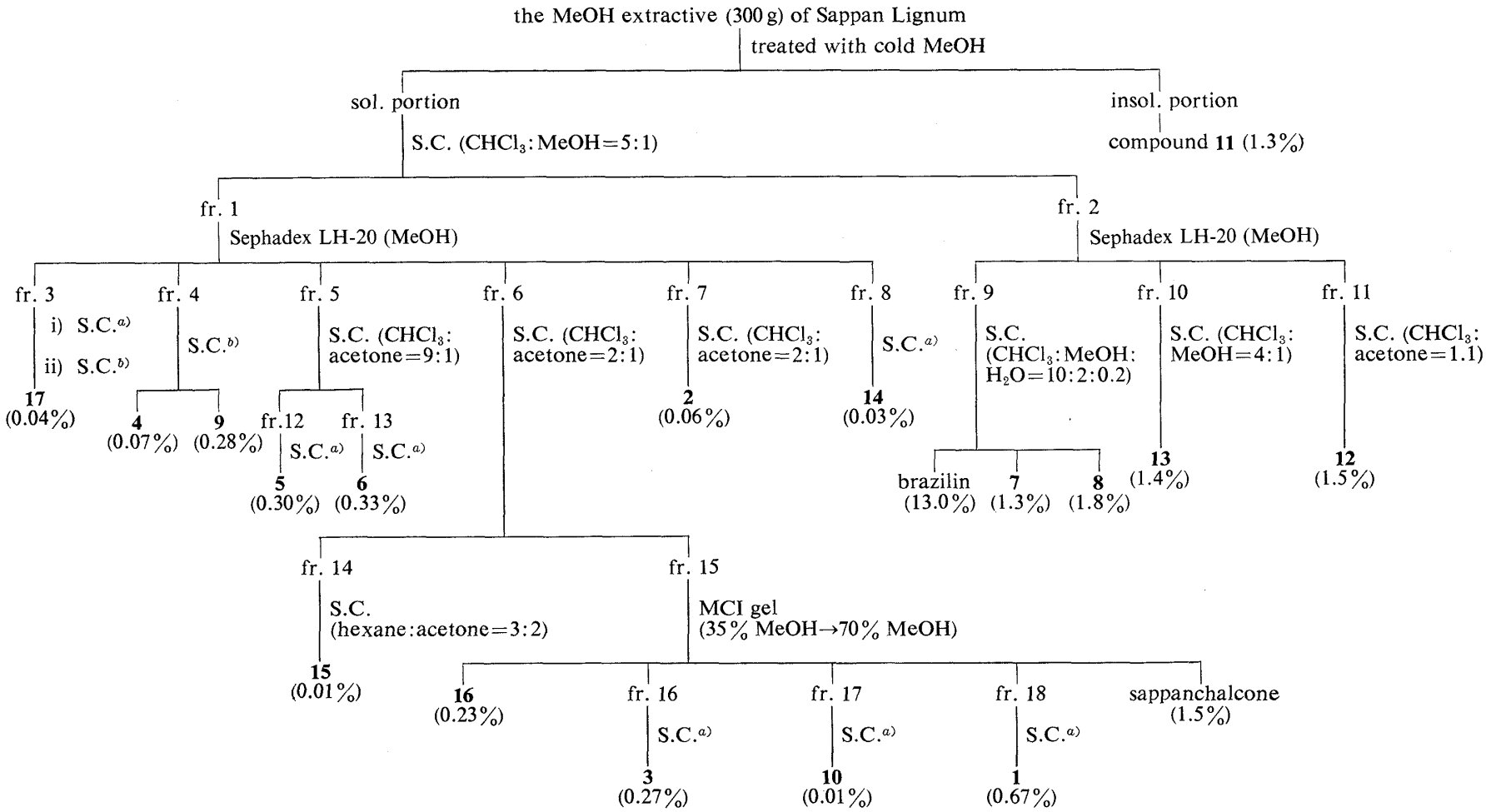
Compound 3——A white powder, $[\alpha]_D^{24}$ +51.6° (c=1.00, MeOH). UV λ_{max}^{MeOH} nm (log ε): 205 (4.61), 231 (4.18), 277 (4.18), 311 (3.89). IR ν_{max}^{KBr} cm^{-1}: 3300, 1660, 1600. EI-MS m/z: 302 ($C_{16}H_{14}O_6^+$, M^+, 12%), 284 (6%), 180 ($C_9H_8O_4^+$, base peak), 137 ($C_7H_5O_3^+$, 72%), 123 ($C_7H_7O_2^+$, 91%). ^{1}H-NMR δ: 2.69 (2H, br s, 9-H_2), 3.98 (2H, br s, 2-H_2), 6.33—6.83 (5H, m, 6,8,2′,5′,6′-H), 7.65 (1H, d, J=9 Hz, 5-H).

Compound 4——Colorless needles, mp 157—160 °C, $[\alpha]_D^{29}$ +3.7° (c=0.50, MeOH). UV λ_{max}^{MeOH} nm (log ε): 205 (4.80), 219 (4.26), 280 (3.81), 285 (3.79). EI-MS m/z: 286 ($M^+ - H_2O$, 78%), 268 (37%), 267 (37%), 229 (22%). FAB-MS m/z: 327 $[M+Na]^+$, 304 [M^+, $C_{16}H_{16}O_6^+$], 287, 277, 269, 207, 185, 147, 123, 115. A small amount of **4** in MeOH was heated at 70 °C for about 1 h; thin-layer chromatography (TLC) monitoring indicated the formation of compounds **5** and **6**, and brazilin.

Tetraacetate of 4——Compound **4** (20 mg) was acetylated with Ac_2O–pyridine to give an acetate as a white powder (15 mg). $[\alpha]_D^{28}$ +68.9° (c=0.50, $CHCl_3$). EI-MS m/z: 472 ($C_{24}H_{24}O_{10}$, M^+, 5%), 412 (55%), 206 (base peak), 164 (77%), 123 (56%). ^{1}H-NMR ($CDCl_3$) δ: 2.07, 2.28, 2.29 (each 3H, 6H, 3H, s, 4 × OAc), 2.78 (2H, s, 9-H_2), 3.82 (1H, dd, J=1, 10 Hz, 2-H), 3.95 (1H, d, J=10 Hz, 2-H′), 5.74 (1H, d, J=1 Hz, 4-H), 7.08—7.16 (3H, m, 2′,5′,6′-H), 7.33 (1H, d, J=9 Hz, 5-H). ^{13}C- NMR ($CDCl_3$) δ: 67.0 (t), 69.2 (s), 71.0 (d), 117.1 (s), 132.3 (d), 114.9 (d), 152.4 (s), 110.2 (d), 154.7 (s), 40.1 (t), 133.7 (s), 123.1 (d), 141.8 (s),* 141.2 (s),* 125.7 (d), 128.8 (d) [C-2-4, 4a, 5—8, 8a, 9, 1′—6′, respectively], 170.9, 169.0, 168.2, 20.6, 21.1 (Ac signals) (signals marked * may be interchanged).

Compound 5——A white powder, $[\alpha]_D^{29}$ +53.6° (c=1.50, MeOH). UV λ_{max}^{MeOH} nm (log ε): 205 (4.74), 219 (4.20), 280 (3.72), 285 (3.70). EI-MS m/z: 286 (M^+ − MeOH, base peak), 268 (42%), 267 (46%), 229 (31%). FAB-MS m/z: 359 $[M+K]^+$, 341 $[M+Na]^+$, 327, 287, 269, 207, 185, 163, 153. ^{1}H-NMR δ: 2.41 (2H, br s, 9-H), 3.30 (3H, s, OMe), 6.2—7.1 (6H, m, arom. H), 8.57 (2H, br s, 2 × arom. OH), 9.46 (1H, br s, arom. OH). (Signals due to 2-H and 4-H were obscured by the solvent peaks). Compound **5**, upon heating as described for **4**, yielded a mixture of compounds **4** and **6**, and brazilin.

Triacetate of 5——Compound **5** (15 mg) was acetylated in the usual manner to afford an acetate as a white powder (12 mg). $[\alpha]_D^{28}$ +34.1° (c=0.33, $CHCl_3$). EI-MS m/z: 444 ($C_{23}H_{24}O_9^+$, M^+, 33%), 401 (57%), 260 (44%), 231 (40%), 218 (60%), 195 ($C_{10}H_{11}O_4^+$, base peak), 152 ($C_8H_8O_3^+$, 67%), 123 ($C_7H_7O_2^+$, 56%). ^{1}H-NMR ($CDCl_3$) δ: 2.27, 2.28, 2.29 (each 3H, s, 3 × OAc), 2.63, 2.87 (2H, ABq, J=14 Hz, 9-H), 3.40 (3H, s, OMe), 3.88 (1H, dd, J=1, 10 Hz, 2-H), 4.06 (1H, d, J=1 Hz, 4-H), 4.24 (1H, d, J=10 Hz, 2-H′), 6.70 (1H, dd, J=2, 9 Hz, 6-H), 6.70 (1H, d, J=2 Hz, 8-H), 7.07 (1H, d, J=2 Hz, 2′-H), 7.10 (2H, br s, 5′,6′-H), 7.16 (1H, d, J=9 Hz, 5-H). ^{13}C-NMR ($CDCl_3$) δ: 65.1 (t), 76.0 (s), 77.8 (d), 117.9 (s), 131.4 (d), 113.5 (d), 152.2 (s), 110.3 (d), 154.4 (s), 37.1 (t), 134.3 (s), 122.8 (d), 141.7 (s), 141.0 (s), 125.5 (d), 128.7 (d) [C-2-4, 4a, 5—8, 8a, 9, 1′—6′, respectively], 168.9, 168.1, 20.7, 20.6, 21.1 [all s, acetyl signals], 56.5 [q, OMe].



S.C.: silica gel column chromatography
solvent *a*) $CHCl_3$: MeOH = 9 : 1
b) hexane : acetone = 1 : 1

Chart 2

Compound 6——A white powder, $[\alpha]_D^{29}$ −34.8° (c=1.0, MeOH). UV λ_{max}^{MeOH} nm (log ε): 207 (4.86), 220 (4.39), 280 (4.01), 285 (3.99). EI-MS m/z: 286 (M^+ − MeOH, base peak), 268 (63%), 267 (56%), 229 (38%). FAB-MS m/z: 341 $[M+Na]^+$, 318 $[M]^+$, 287, 261, 153, 123. ^{1}H-NMR δ: 2.61 (2H, m, 9-H), 3.23 (3H, s, OMe), 3.69, 3.97 (2H, ABq, J= 11 Hz, 2-H), 4.56 (1H, s, 3-OH), 6.2—7.0 (6H, m, 6 × arom. H), 8.53, 8.60, 9.27 (each 1H, 3 × arom. OH). (The signal due to 4-H was obscured by the solvent peak). Compound **6**, upon heating as described for **5** gave compounds **4** and **5**, and brazilin.

Triacetate of 6——Compound **6** (25 mg) was acetylated to afford the corresponding acetate as a white powder (22 mg). $[\alpha]_D^{28}$ −14.1° (c=3.0, $CHCl_3$). EI-MS m/z: 443 (6%), 426 (50%), 401 (13%), 260 (15%), 218 (33%), 195 (34%), 177 (20%), 167 (21%), 165 (25%), 152 (59%), 123 (base peak). ^{1}H-NMR ($CDCl_3$) δ: 2.26 (3H, s, OAc), 2.87 (6H, s, 2 × OAc), 2.89, 3.03 (2H, ABq, J=14 Hz, 9-H), 3.22 (3H, s, OMe), 3.67 (1H, d, J=1 Hz, 4-H), 4.25 (1H, d, J= 12 Hz, 2-H), 4.30 (1H, dd, J=1, 12 Hz, 2-H′), 7.0—7.2 (6H, m, arom. H). ^{13}C-NMR ($CDCl_3$) δ: 65.1 (t), 76.0 (s), 74.7 (d), 117.4 (s), 132.1 (d), 113.0 (d), 151.6 (s), 109.6 (d), 154.8 (s), 34.4 (t), 134.4 (s), 122.9 (d), 141.8 (s), 140.9 (s), 125.6 (d), 128.7 (d) [C-2-4, 4a, 5—8, 8a, 9, 1′—6′, respectively], 169.0, 168.2, 21.1, 20.7, 20.6 [all s, acetyl signals], 55.6 [q, OMe].

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11) The following instruments were used to obtain physical data: melting points, Yanagimoto micro-melting point apparatus; specific rotations, JASCO DIP-360 and DIP-4 digital polarimeters; IR spectra, JASCO A-100 infrared spectrometer; ^{1}H-NMR spectra, JEOL 60, PS-100, JNM-FX 200 NMR spectrometers (solvent: dimethyl sulfoxide-d_6 (DMSO-d_6) unless otherwise specified, with TMS as an internal standard); ^{13}C-NMR spectra, JEOL JNM-FX 200 FT-NMR spectrometer (solvent: DMSO-d_6 unless otherwise specified); EI-MS JEOL JMS-01SG mass spectrometer; high-resolution MS and FAB-MS, JEOL JMS-new D-300 mass spectrometer. The following experimental conditions were used for column chromatography: Silica gel (Kanto gel 300 mesh up) as the adsorbent; TLC, precoated TLC plates Silica gel $60F_{254}$ (0.25 mm), detection by spraying with 10% aq. H_2SO_4 following by heating.