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TOTAL SYNTHESIS OF (±)-SIGMOIDIN-A [3',4',5,7-TETRAHYDROXY-2-(γ,γ-DIMETHYLALLYL)FLAVANONE] AND OF ANTIARONE-F†

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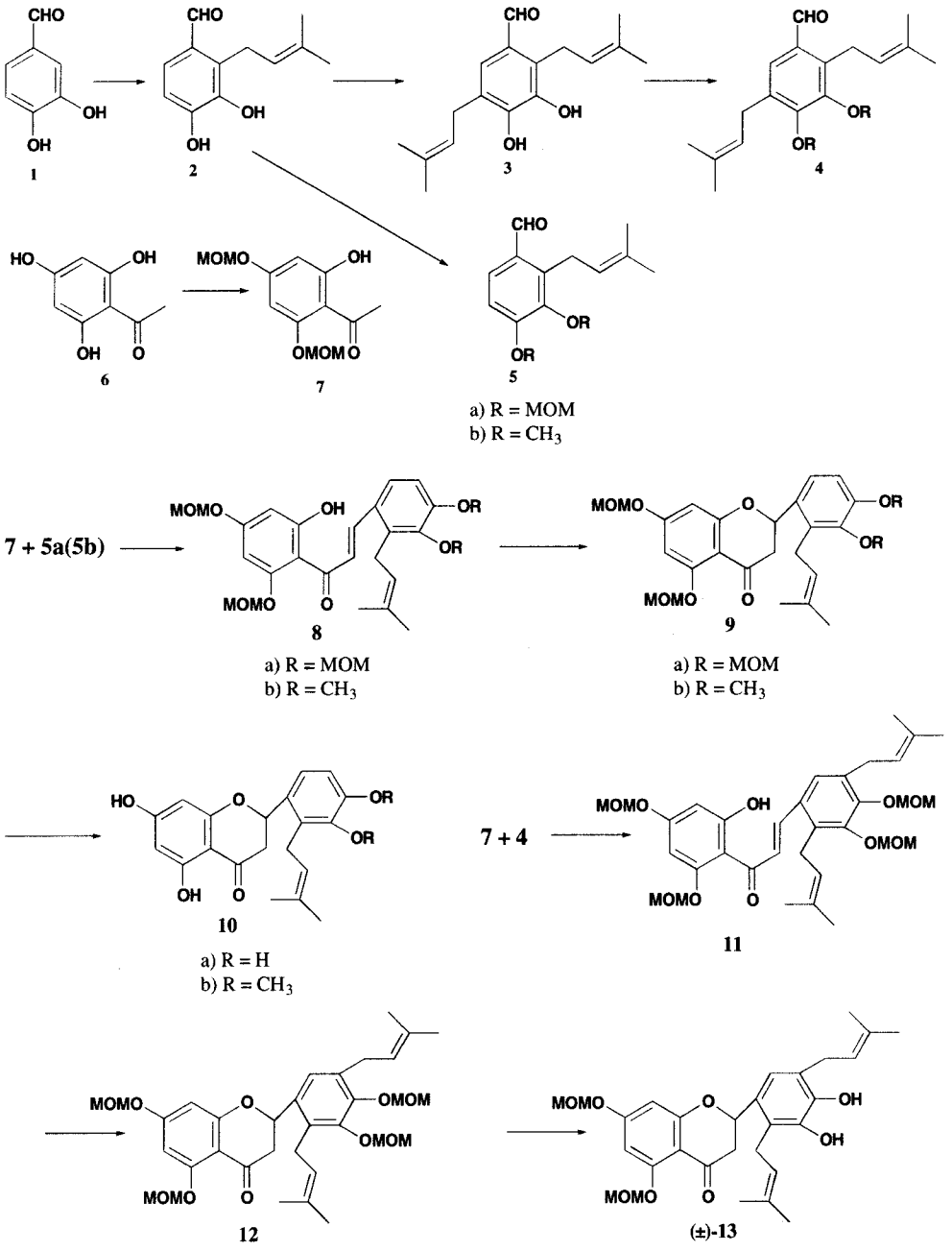
Prenylflavonoids are an interesting and large class of flavonoids. Their synthesis and biological activity have attracted much attention.[1-4] A systematic investigation of the prenylflavonoids has led to the total syntheses of lespedezaflavanone-A,[5] (±)-amoritin,[6] (±)-lespedezaflavanone-E.[7] We undertook the synthesis of a series of new prenylflavonoids with a view to evaluate their biological properties. Prenylflavonoids with two prenyl group on the C ring have not been synthesized before. This paper describes the synthesis of the racemate of 3',4',5,7-tetrahydroxy-2',5',-di-(γ,γ-dimethylallyl)-(2S)-flavanone (**13**), named Sigmoidin-A,[8] isolated from *Erythrina sigmoidea* Hua and characterized by antibiotic activity against Gram-positive bacteria. Also described are the syntheses of 3',4',5,7-tetrahydroxy-2'-(γ,γ-dimethylallyl)flavanone (**10a**) which isolated from *Erythrina* suberosa roots,[9] and of 5,7-dihydroxy-3',4'-dimethoxy-2'-(γ,γ-dimethylallyl)flavanone (**10b**) obtained from the root of *Antiaris Toxicaria* and named antiarone-F.[10] The synthetic routes are shown in the Scheme.

3,4-Dihydroxybenzaldehyde (**1**) was prenylated with 1-bromo-3-methyl-2-butene according to the reported method[11] to afford **2** as a yellowish solid in 24% yield. If **2** was treated again with 1-bromo-3-methyl-2-butene, **3** was obtained in 20% yield. Compound **3** was methoxymethylated with methoxymethyl chloride to give **4** in 82% yield. If **2** was methoxymethylated with methoxymethyl chloride or methylated with dimethyl sulfate, **5a** and **5b** were produced in 85% and 92% yield. 2,4,6-Trihydroxyacetophenone (**6**) was selectively methoxymethylated with methoxymethyl chloride to give **7** in 63% yield. The condensation of **7** with **5a** or **5b** in a mixture of ethanol and 50% aq. potassium hydroxide (v:v/ 4:1) for 36 hrs at room temperature gave chalcone **8a** and **8b** in 88% and 89% yield. When **8a** and **8b** were treated with sodium acetate in ethanol, flavanones **9a** and **9b** were obtained in 72% and 80% yields, but the yields were poor unless several drops of water were added in the reaction mixture to dissolve the solid sodium acetate. Demethoxymethylation of **9a** and **9b** gave target molecule **10a** and **10b** in 85% and 92% yields, respectively.

The condensation of **7** with **4** under the same conditions as described before gave the chalcone **11** in 71% yield. Cyclization followed by demethoxymethylation of **11** gave (±)-sigmoidin-A (**13**). In this paper, fourteen new products of **2-5**, **8-12**, and (±)-**13** were synthesized and their struc-

tures were confirmed by their IR,^{1}H NMR and MS data.



EXPERIMENTAL SECTION

Mps were measured on a Kofler melting points apparatus and are uncorrected. IRs spectra were recorded on a NICOLET 170 XFT-IR spectrophotometer as KBr disks and are reported in cm^{-1}. ^{1}H

NMR were recorded on FT-80A and AC-80 spectrometers, and all spectra were determined in $CDCl_3$ unless noted otherwise. MS were performed on ZAB-HS, MAT 445 and HP-5988 spectrometers and EA on a MOD-1106 elemental analyzer.

3,4-Dihydroxy-2-prenylbenzaldehyde (2).- 3,4-Dihydroxybenzaldehyde (**1**) (414 mg, 3 mmol) and potassium hydroxide (336 mg, 6 mmol) were dissolved in water (4 mL) and cooled to 0°. Then, prenyl bromide (444 mg, 3 mmol) was added dropwise over 10 min with stirring. The mixture was stirred at 0° for 1hr and at room temperature for 24 hrs, and then poured into ice-water and acidified to pH2 with aq. HCl, and extracted with ethyl acetate. The extract was dried over anhydrous Na_2SO_4 and the solvent was evaporated. The residue was chromatographed on silica gel with benzene as the eluent to give **2** (150 mg, 24%) as a yellowish solid, mp. 102-104°.

IR: 1739, 1645, 1595, 1501. ^{1}H NMR: δ 1.71, 1.81 (each 3H, s, each CH_3), 3.87 (2H, d, J = 6.6Hz, CH_2), 5.21 (1H, t, J = 6.6Hz, CH=), 6.87 (1H, d, J = 8.3Hz, C_5-H), 7.35 (1H, d, J = 8.3Hz, C_6-H), 10.00 (1H, s, CHO). MS (EI): m/e 206 (M^+), 177, 151, 138.

Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 69.79; H, 6.78

3,4-Dihydroxy-2,5-diprenylbenzaldehyde (3).- Compound **2** (206 mg, 1 mmol) and potassium hydroxide (112 mg, 2 mmol) were dissolved in water (1.3 mL) and cooled to 0°. Then prenyl bromide (148 mg, 1 mmol) was added and the mixture was treated in the same manner as **1**. Compound **3** (55 mg, 20%) was obtained as a yellow solid, mp. 78-80°.

IR: 1734, 1647, 1570, 1557, 1510. ^{1}H NMR: δ 1.80 (12H, br s, CH_3 4), 3.41 (2H, d, J = 7.0Hz, CH_2), 3.89 (2H, d, J = 7.0Hz, CH_2), 5.00-5.40 (2H, m, CH= 2), 7.30 (1H, s, C_6-H), 10.04 (1H, s, CHO). MS (EI): m/e 274 (M^+), 258, 245, 229, 216, 177, 150, 91

Anal. Calcd for $C_{17}H_{22}O_3$: C, 74.42; H, 8.08. Found: C, 74.28; H, 8.14

3,4-Dimethoxymethoxy-2,5-diprenylbenzaldehyde (4).-The mixture of compound **3** (274 mg, 1 mmol), anhydrous potassium carbonate (1.35 g), acetone (5.5 mL) and excess methoxymethyl chloride (241 mg, 3.0 mmol) was refluxed for 30 min, and then worked up in the usual manner to give compound **4** as a yellowish oil (297 mg, 82%).

IR: 1736, 1645, 1571, 1559, 1502, 1159. ^{1}H NMR: δ 1.78 (12H, br s, CH_3 4), 3.35-3.65 (8H, m, OCH_3 2 and CH_2), 3.86 (2H, d, J = 7.0Hz, CH_2), 5.00-5.45 (6H, m, OCH_2O 2 and CH= 2), 7.36 (1H, s, C_6-H), 10.07 (1H, s, CHO). MS (EI): m/e 362 (M^+), 347, 345, 330, 316, 284, 270, 216, 188, 162, 135.

Anal. Calcd for $C_{21}H_{30}O_5$: C, 69.58; H, 8.34. Found: C, 69.63; H, 8.47

3,4-Dimethoxymethoxy-2-prenylbenzaldehyde (5a).- Compound **2** (206 mg, 1 mmol) was mixed with anhydrous potassium carbonate (1.35 g), acetone (5.5 mL) and methoxymethyl chloride (241 mg, 3.0 mmol) and refluxed for 30 min. After treatment as described for compound **4**, **5a** was obtained as a colorless oil (250 mg, 85%).

IR: 1690, 1591, 1269, 1156. ^{1}H NMR: δ 1.62, 1.71 (each 3H, s, each CH_3), 3.43 (3H, s, OCH_3), 3.51 (3H, s, OCH_3), 3.74 (2H, d, J = 6.6Hz, CH_2), 5.00-5.30 (5H, m, OCH_2O 2 and CH=), 7.00 (1H, d, J = 8.5Hz, C_5-H), 7.51 (1H, d, J = 8.5Hz, C_6-H), 10.07 (1H, s, CHO). MS (EI): m/e 294 (M^+), 262, 249,

233, 218, 203, 189, 175, 162, 145, 115.

Anal. Calcd for $C_{16}H_{22}O_5$: C, 65.29; H, 7.54. Found: C, 65.17; H, 7.42

3,4-Dimethoxy-2-prenylbenzaldehyde (5b).- Compound **2** (120 mg, 0.58 mmol), excess dimethyl sulfate (240 mg, 1.88 mmol) and anhydrous potassium carbonate (600 mg) was added to acetone (4.0 mL) and the mixture was refluxed for 3 hrs. Work up was the same as described for compound **4**, gave **5b** as a colorless oil (125 mg, 92%).

IR: 1687, 1589, 1569. ^{1}H NMR: δ 1.65, 1.78 (each 3H, s, each CH_3), 3.65-3.83 (5H, m, CH_2 and OCH_3), 3.92 (3H, s, OCH_3), 5.14 (1H, t, J = 7.8Hz, CH=), 6.87 (1H, d, J = 8.7Hz, C_5-H), 7.62 (1H, d, J = 8.7Hz, C_6-H), 10.09 (1H, s,CHO). MS (EI): m/e 234 (M^+), 219, 191, 178, 177, 163, 150.

Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.49; H, 7.68

2-Hydroxy-4,6-dimethoxymethoxyacetophenone (7).- 2,4,6-Trihydroxyacetophenone (**6**) (168 mg, 1 mmol), anhydrous potassium carbonate (1.0 g) and methoxymethyl chloride (177 mg, 2.2 mmol) were dissolved in acetone (5.0 mL) and treated as before, the selectively methoxymethylated compound **7** (160 mg, 63%) was obtained as a yellowish solid, mp. 50-52°, lit.[12] 52°. (CAUTION should be used with methoxymethyl chloride).

^{1}H NMR: δ 2.61 (3H, s, CH_3), 3.43 (3H, s, OCH_3), 3.49 (3H, s, OCH_3), 5.13 (2H, s, OCH_2O), 5.22 (2H, s, OCH_2O), 6.20 (2H, s, C_3-H and C_5-H), 13.63 (1H, s, OH, disappeared after D_2O addition).

3,4,4',6'-Tetramethoxymethoxy-2'-hydroxy-2-prenylchalcone (8a).- To a cold solution of the acetophenone (**7**) (50 mg, 0.20 mmol) and benzaldehyde (**5a**) (50 mg, 0.17 mmol) in ethanol (2.0 mL), a cooled solution of potassium hydroxide (2.0 g) in water (0.8 mL)-ethanol (1.2 mL) was added with stirring. The resulting mixture was stirred under argon at room temperature for 36 hrs. The whole was poured into ice-water, acidified to pH2, and extracted with CH_2Cl_2. The extract was dried, evaporated and chromatographed to give chalcone **8a** (80 mg, 88%) as a yellow solid, mp. 105-108°.

IR: 3330, 1624, 1578, 1554, 1484, 1153. ^{1}H NMR: δ 1.68, 1.84 (each 3H, s, each CH_3), 3.25-3.70 (14H, m, OCH_3 4 and CH_2), 5.08-5.35 (9H, m, OCH_2O 4 and CH=), 6.20 (1H, d, J = 2.0Hz, C_5'-H), 6.28 (1H, d, J = 2.0Hz, C_3'-H), 6.99 (1H, d, J = 8.2Hz, C_5-H), 7.37 (1H, d, J = 8.2Hz, C_6-H), 7.65 (1H, d, J = 16.0Hz, CH=), 8.00 (1H, d, J = 16.0Hz, CH=), 13.88 (1H, s, OH). MS (EI): m/e 532 (M^+), 514, 487, 461, 443, 429, 411, 379, 355, 276, 241, 201, 197, 167.

Exact Mass Calcd for $C_{28}H_{36}O_{10}$: 532.2308. Found: 532.2320

Anal. Calcd for $C_{28}H_{36}O_{10}$: C, 63.14; H, 6.06. Found: C, 63.27; H, 6.10

3,4-Dimethoxy-4,6-dimethoxymethoxy-2'-hydroxy-2-prenylchalcone (8b).- In a similar manner, condensation of acetophenone (**7**) with benzaldehyde (**5b**) in strong basic solution gave **8b** (89%) as a yellowish solid, mp. 121-123°.

IR: 1709, 1622, 1578, 1558. ^{1}H NMR: δ 1.72, 1.89 (each 3H, s, each CH_3), 3.37-3.66 (8H, m, OCH_3 2 and CH_2), 3.86 (3H, s, OCH_3), 3.94 (3H, s, OCH_3), 4.99-5.25 (3H, m, OCH_2O and CH=), 5.32 (2H, s, OCH_2O), 6.30 (1H, d, J = 2.2Hz, C_5'-H), 6.37 (1H, d, J = 2.2 Hz, C_3'-H), 6.87 (1H, d, J = 8.6Hz, C_5-H), 7.50 (1H, d, J = 8.6Hz, C_6-H), 7.77 (1H, d, J = 15.4Hz, CH=), 8.14 (1H, d, J = 15.4Hz, CH=), 13.58 (1H, s, OH). MS (EI): m/e 472 (M^+), 427, 371, 241, 217, 197, 167, 115.

Anal. Calcd for $C_{26}H_{32}O_8$: C, 66.08; H, 6.83. Found: C, 65.97; H, 6.87

3',4',5,7-Tetramethoxymethoxy-2'-prenylflavanone (9a).- The solution of **8a** (50 mg, 0.094 mmol) and sodium acetate (150 mg) in ethanol (4.0 mL) with two drops of water was refluxed for 24 hrs. The reaction mixture was poured into cold water and extracted with CH_2Cl_2. After removal of the solvent, the residue was chromatographed on silica gel to give flavanone **9a** (36 mg, 72%) as a yellowish solid, mp. 60-63°.

IR: 1681, 1641, 1608, 1573, 1267, 1152. ^{1}H NMR: δ 1.70 (6H, br s, CH_3 2), 2.74 (1H, dd, J = 4.0Hz and 17.0Hz, C_3-H), 3.05 (1H, dd, J = 4.0Hz and 17.0Hz, C_3-H), 3.48-3.72 (14H, m, OCH_3 4 and CH_2), 5.12-5.40 (9H, m, OCH_2O 4 and CH=), 5.54 (1H, dd, J = 4.0Hz and 12.0Hz, C_2-H), 6.35 (1H, d, J = 2.0Hz, C_6-H), 6.44 (1H, d, J = 2.0Hz, C_8-H), 7.07 (1H, d, J = 8.2Hz, C_5'-H), 7.28 (1H, d, J = 8.2Hz, C_6'-H). MS (EI): m./e 532 (M^+), 517, 501, 488, 478, 461, 443, 432, 411, 358, 241, 201, 197, 167, 143, 69.

Exact Mass Calcd for $C_{28}H_{36}O_{10}$: 532.2308. Found: 532.2300

Anal. Calcd for $C_{28}H_{36}O_{10}$: C, 63.14; H, 6.06. Found: C, 63.30; H, 6.10

3',4',-Dimethoxy-5,7-dimethoxymethoxy-2'-prenylflavanone (9b).- Treated the compound **8b** as described for compound **8a** to give flavanone **9b** (80%) as a yellowish solid, mp. 82-84°.

IR: 1681, 1609, 1573. ^{1}H NMR: δ 1.68 (6H, br s, CH_3 2), 2.80 (2H, dd, J = 3.0Hz and 13.0Hz, C_3-H), 3.30-3.65 (8H, m, OCH_3 2 and CH_2), 3.82, 3.88 (each 3H, s, each OCH_3), 4.94-5.10 (1H, m, CH=), 5.16, 5.28 (each 2H, s, each OCH_2O), 5.51 (1H, d, J = 3.0Hz and 13.0Hz, C_2-H), 6.37 (1H, d, J = 2.0Hz, C_6-H), 6.44 (1H, d, J = 2.0Hz, C_8-H), 6.86 (1H, d, J = 8.5Hz, C_5'-H), 7.27 (1H, d, J = 8.5Hz, C_6'-H). MS (EI): m/e 472 (M^+), 427, 416, 371, 241, 197, 189, 158.

Anal. Calcd for $C_{26}H_{32}O_8$: C, 66.08; H, 6.83. Found: C, 66.02; H, 6.89

3',4',5,7-Tetrahydroxy-2'-prenylflavanone (10a).- To the solution of **9a** (50 mg, 0.094 mmol) in methanol (5.0 mL), 3N HCl (1.0 mL) was added. The resulting mixture was refluxed for 15min, then poured into cold water and extracted with ethyl acetate. After the treatment as usual, compound **10a** (28 mg, 85%) was obtained as colorless needles, mp. 220-221°, lit.[9] 219-220°.

IR: 3598, 3329, 1635, 1286. ^{1}H NMR (400 MHz, acetone-d_6): δ 1.75, 1.78 (each 3H, s, each CH_3), 2.73 (1H, dd, J = 4.0Hz and 17.0Hz, C_3-H), 3.18 (1H, dd, J = 4.0Hz and 17.0Hz, C_3-H), 3.30 (2H, d, J = 8.0Hz, CH_2), 5.20 (1H, t, J = 7.9Hz, CH=), 5.60 (1H, dd, J = 4.0Hz and 12.0Hz, C_2-H), 5.94 (1H, d, J = 2.0Hz, C_6-H), 6.01 (1H, d, J = 2.0Hz, C_8-H), 6.85 (1H, d, J = 8.4Hz, C_5'-H), 7.07 (1H, d, J = 8.4Hz, C_6'-H), 12.08 (1H, s, OH). MS (EI): m/e 356 (M^+), 338, 300, 295, 283, 204, 189, 153, 152, 149.

Exact Mass Calcd for $C_{20}H_{20}O_6$: 356.1260. Found: 356.1248

Anal. Calcd for $C_{20}H_{20}O_6$: C, 67.40; H, 5.66. Found: C, 67.43; H, 5.70

Antiarone-F (10b).- Compound **9b** was treated as **9a** to give compound **10b** (antiarone-F, 92%) as colorless needles, mp. 195-197°, lit.[10] 197-200°.

IR: 3282, 1707, 1640, 1602. ^{1}H NMR (400 MHz, acetone-d_6): δ 1.67 (6H, br s, CH_3 2), 2.70 (1H, dd, J = 3.4Hz and 16.9Hz, C_3-H), 3.15 (1H, dd, J = 12.7Hz and 17.2Hz, C_3-H), 3.46 (2H, br d, J = 7.8Hz, CH_2), 3.82, 3.88 (each 3H, s, C_3'-OCH_3 and C_4'-OCH_3), 4.87-5.18 (1H, m, CH=), 5.50 (1H, d, J =

3.3Hz and 12.6Hz, C_2-H), 5.96 (1H, d, J = 2.2Hz, C_6-H), 6.01 (1H, d, J = 2.2Hz, C_8-H), 6.87 (1H, d, J = 8.6Hz, C_5'-H), 7.27 (1H, d, J = 8.6Hz, C_6'-H), 12.03 (1H, s, OH). MS (EI): m/e 384 (M^+), 328, 315, 231, 217, 189, 153.

Anal. Calcd for $C_{22}H_{24}O_6$: C, 68.73; H, 6.29. Found: C, 68.81; H, 6.33

3,4,4',6'-Tetramethoxymethoxy-2'-hydroxy-2,5-diprenylchalcone (11).- In a similar manner, condensation of acetophenone (**7**) with benzaldehyde (**4**) in basic solution gave chalcone **11** (71%) as a yellow solid, mp. 86-88°.

IR: 1630, 1574, 1550, 1478, 1151. ^{1}H NMR: δ 1.72 (12H, br s, CH_3 4), 3.30-3.80 (16H, m, OCH_3 4 and CH_2 2), 5.00-5.51 (10H, m, OCH_2O 4 and CH= 2), 6.34 (1H, d, J = 2.0Hz, C_3'-H), 6.38 (1H, d, J = 2.0Hz, C_5'-H), 7.06 (1H, s, C_6-H), 7.86 (1H, d, J = 16.5Hz, CH =), 8.27 (1H, d, J = 16.5Hz, CH =), 13.81 (1H, s, OH). MS (EI): m/e 600 (M^+), 582, 555, 529, 511, 479, 447, 344, 309, 269, 245, 197, 135.

Anal. Calcd for $C_{33}H_{44}O_{10}$: C, 65.98; H, 7.38. Found: C, 66.03; H, 7.44

3',4',5,7-Tetramethoxymethoxy-2',5'-diprenylflavanone (12).- Compound **11** was treated as compound **8a** with sodium acetate to give flavanone **12** (70%) as a colorless needle, mp. 39-41°.

IR: 1651, 1610, 1507, 1460, 1172, 1160. ^{1}H NMR: δ 1.71 (12H, br s, CH_3 4), 2.76 (1H, dd, J = 4.0Hz and 17.0Hz, C_3-H), 3.07 (1H, dd, J = 4.0Hz and 17.0Hz, C_3-H),3.28-3.76 (16H, m, OCH_3 4 and CH_2 2), 4.98-5.46 (11H, m, OCH_2O 4 and C_2-H, CH= 2), 5.96 (2H, s, C_6-H and C_8-H), 6.81 (1H, s, C_6'-H). MS (EI): m/e 600 (M^+), 585, 555, 529, 479, 468, 447, 344, 294, 269, 245, 197, 157, 135, 115.

Anal. Calcd for $C_{33}H_{44}O_{10}$: C, 65.98; H, 7.38. Found: C, 66.07; H, 7.31

(±)-Sigmoidin-A (13).- Compound **12** was treated as **9a** with 3N HCl to give compound **(±13)** (87%) as a white solid, mp. 180-182°, lit.[8] 181-182°.

IR: 3485, 3288, 1642, 1602, 1507, 1443, 1291, 1183, 1158, 1081. ^{1}H NMR (acetone-d_6): δ 1.69 (12H, br s, CH_3 4), 2.82 (1H, dd, J = 4.0Hz and 17.0Hz, C_3-H), 3.12 (1H, dd, J = 4.0Hz and 17.0Hz, C_3-H), 3.24 (4H, d, J = 7.2Hz, CH_2 2), 5.19-5.36 (3H, m, CH= 2 and C_2-H), 5.80 (1H, d, J = 2.0Hz, C_6-H), 5.86 (1H, d, J = 2.0Hz, C_8-H), 6.74 (1H, s, C_6'-H), 12.03 (1H, s, OH, disappeared after D_2O addition). MS (EI): m/e 424 (M^+), 407, 406, 368, 363, 351, 300, 283, 204, 189, 188, 153, 143, 115.

Anal. Calcd for $C_{25}H_{28}O_6$: C, 70.74; H, 6.41. Found: C, 70.66; H, 6.35

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