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# CHALCONES FROM *ANGELICA KEISKEI**

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**Key Word Index**—*Angelica keiskei*; Umbelliferae; roots; prenylated chalcone; xanthoangelols B–E.

**Abstract**—Four new chalcones, xanthangelols B–E were isolated from roots of *Angelica keiskei* and their structures determined to be 2′,4,4′-trihydroxy-3′-[(*E*)-6-hydroxy-3,7-dimethyl-2,7-octadienyl]chalcone, 2′,4,4′-trihydroxy-3′-[(*E*)-3-methyl-6-oxo-2-hexenyl]chalcone, 2′,4-dihydroxy-4′-methoxy-3′-(2-hydroxy-3-methyl-3-butenyl)chalcone and 2′,4-dihydroxy-4′-methoxy-3′-(2-hydroperoxy-3-methyl-3-butenyl)chalcone, respectively, by means of chemical and spectral analyses.

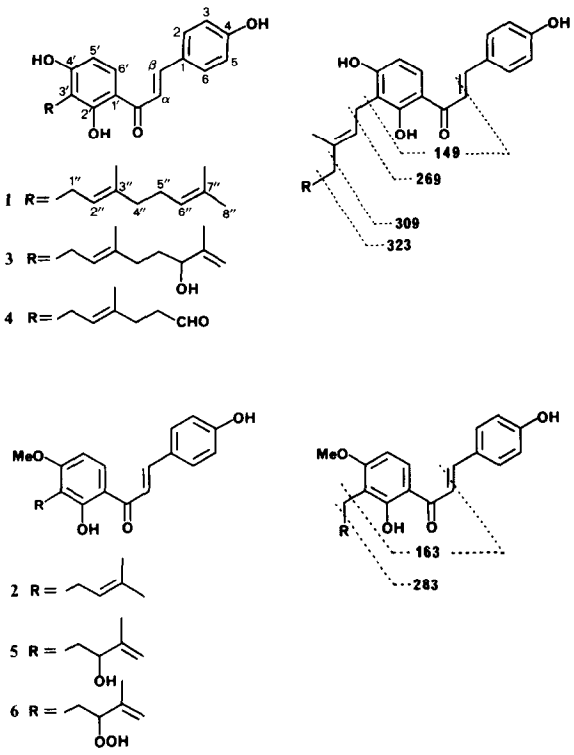
## INTRODUCTION

In previous papers [1, 2], we reported the isolation of two chalcones, xanthoangelol (**1**) and 4-hydroxyderricin (**2**) together with several coumarins from *Angelica keiskei* Koidzumi (Japanese name 'ashitaba'), a plant which has traditionally been used as a diuretic, analeptic and lactogogue in Japan. We have now reinvestigated and isolated four new chalcones, xanthoangelol B–E (**3**–**6**).

## RESULTS AND DISCUSSION

The ethyl acetate extract of fresh roots of *A. keiskei* collected in Hachijyo Island in March 1989, was subjected to a combination of normal and reversed phase silica gel chromatography in various solvent systems to give compounds **3**, $C_{25}H_{28}O_5$([M]$^+$ 408.1933), **4**, $C_{22}H_{22}O_5$([M]$^+$ 366.1469), **5**, $C_{21}H_{22}O_5$([M]$^+$ 354.1468) and **6**, $C_{21}H_{22}O_6$([M]$^+$ 370.1415) together with two chalcones (**1** and **2**) and 11 coumarins, viz., bergapten, isolaserpitin, isopimpinellin, laserpitin, marmesin, psolaren, pteryxin, scopoletin, selinidin, umbelliferone and xanthotoxin. Compounds **3**–**6** gave a red colouration with $H_2SO_4$–methanol on TLC and showed a chelated hydroxyl group by $^1$H NMR, and had UV spectral characteristic of oxychalcones.

The $^1$H and $^{13}$C NMR spectra of **3** and **4** (Tables 1 and 2) were closely related to those of xanthoangelol (2′, 4, 4′-trihydroxy-3′-geranylchalcone) (**1**) except for the presence of signals assignable to a 6-hydroxy-3,7-dimethyl-2,7-octadienyl moiety [$\delta$3.38 (2H, *d*, $J$ = 6.9 Hz, H-1″), 5.31 (1H, *t*, $J$ = 6.9 Hz, H-2″), 2.02 (2H, *m*, H-4″), 1.63 (2H, *m*, H-5″), 3.98 (1H, *t*, $J$ = 6.2 Hz, H-6″), 4.88 (1H, *br s*, H-8″), 4.77 (1H, *br s*, H-8″), 1.82 (3H, *s*, Me-3″), 1.69 (3H, *s*, Me-7″), 2.74 (1H, *br*, OH); $\delta_C$ 21.83 (C-1″), 123.13 (C-2″), 148.17 (C-3″), 36.08 (C-4″), 33.35 (C-5″), 75.75 (C-6″), 135.78 (C-7″), 111.11 (C-8″), 16.37 (3″-Me), 17.88 (7″-Me)] and a 3-methyl-6-oxo-2-hexenyl moiety [$\delta$3.41 (2H, *d*, $J$ = 7.0 Hz, H-1″), 5.34 (1H, *t*, $J$ = 7.0 Hz, H-2″), 2.32 (2H, *t*, $J$ = 7.9 Hz, H-4″), 2.52 (2H, *td*, $J$ = 7.9, 1.8 Hz, H-5″), 9.74 (1H, *t*, $J$ = 1.8 Hz, H-6″), 1.83 (3H, *s*, 3″-Me); $\delta_C$ 21.65 (C-1″), 123.22 (C-2″), 133.62 (C-3″), 31.88 (C-4″), 42.09 (C-5″), 189.56 (C-6″), 16.30 (3″-Me)] instead of signals due to a geranyl moiety. In the $^{13}$C NMR spectra of **3** and **4**, the carbonyl carbons were observed as double-double-doublet signals (each $J$ = 5 Hz) ascribable to the long range coupling with α-, β- and 6′-protons. The mass spectra of **3**




*Part 7 in the series 'Chemical Components of *Angelica keiskei*'. For part 6 see Inamori, Y., Baba, K., Tsujibo, M., Taniguchi, M., Nakata, K. and Kozawa, M. (1990) *Chem. Pharm. Bull.* submitted.

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Table 1. $^1$H NMR data for compounds **1**, **3** and **4** (in $CDCl_3$, values in parentheses are coupling constants in Hz)

| H | 1 | 3 | 4 |
|---|---|---|---|
| α | 7.43 *d* (15.4) | 7.43 *d* (15.3) | 7.42 *d* (15.3) |
| β | 7.81 *d* (15.4) | 7.79 *d* (15.3) | 7.82 *d* (15.3) |
| 2,6 | 7.52 *d* (8.6) | 7.52 *d* (8.6) | 7.52 *d* (8.6) |
| 3,5 | 6.89 *d* (8.6) | 6.89 *d* (8.6) | 6.89 *d* (8.6) |
| 5′ | 6.47 *d* (8.8) | 6.48 *d* (8.8) | 6.46 *d* (8.8) |
| 6′ | 7.66 *d* (8.8) | 7.65 *d* (8.8) | 7.66 *d* (8.8) |
| 1″ | 3.41 *d* (7.0) | 3.38 *d* (6.9) | 3.41 *d* (7.0) |
| 2″ | 5.30 *t* (7.0) | 5.31 *t* (6.9) | 5.34 *t* (7.0) |
| 4″ | 2.01 *m* | 2.02 *m* | 2.32 *t* (7.9) |
| 5″ | 2.05 *m* | 1.63 *m* | 2.52 *td* (7.9, 1.8) |
| 6″ | 5.07 *m* | 3.98 *t* (6.2) | 9.74 *t* (1.8) |
| 8″ | 1.65 *s* | 4.88 *br s* | — |
| | | 4.77 *br s* | |
| 3″-Me | 1.81 *s* | 1.82 *s* | 1.83 *s* |
| 7″-Me | 1.57 *s* | 1.69 *s* | |
| 4,4′-OH | 9.16 *s*, 8.85 *s* | 9.50 *s*, 9.46 *br s* | 8.91 *s*, 8.81 *s* |
| 2′-OH | 13.81 *s* | 13.79 *s* | 13.80 *s* |
| 6″-OH | — | 2.74 *br* | — |

Assignments were confirmed by spin decoupling experiments.

Table 2. $^{13}$C NMR data for compounds **1**, **3** and **4** (in $CDCl_3$)

| C | 1 | 3 | 4 |
|---|---|---|---|
| α | 118.32 | 117.76 | 117.35 |
| β | 145.10 | 144.59 | 144.11 |
| CO | 193.24 | 192.64 | 192.03 |
| 1 | 127.97 | 126.92 | 126.59 |
| 2,6 | 131.19 | 130.92 | 130.41 |
| 3,5 | 116.58 | 116.64 | 116.16 |
| 4 | 158.98 | 160.54 | 159.80 |
| 1′ | 114.44 | 113.94 | 113.63 |
| 2′ | 162.57 | 162.69 | 161.87 |
| 3′ | 114.80 | 115.84 | 115.01 |
| 4′ | 164.47 | 164.73 | 164.16 |
| 5′ | 108.55 | 107.96 | 107.48 |
| 6′ | 129.94 | 129.23 | 128.80 |
| 1″ | 21.94 | 21.83 | 21.65 |
| 2″ | 121.50 | 123.13 | 123.22 |
| 3″ | 140.04 | 148.17 | 133.62 |
| 4″ | 39.97 | 36.08 | 31.88 |
| 5″ | 26.59 | 33.35 | 42.09 |
| 6″ | 124.28 | 75.75 | 189.56 |
| 7″ | 132.60 | 135.78 | — |
| 8″ | 25.89 | 111.11 | — |
| 3″-Me | 16.46 | 16.37 | 16.30 |
| 7″-Me | 17.90 | 17.88 | — |

Assignments were confirmed by $^1$H–$^{13}$C COSY and $^1$H–$^{13}$C long range COSY experiments.

and **4** revealed the same peaks at *m/z* 323 ($C_{20}H_{19}O_4$), *m/z* 309 ($C_{19}H_{17}O_4$), *m/z* 269 ($C_{16}H_{13}O_4$), *m/z* 203 ($C_{12}H_{11}O_3$) and *m/z* 149 ($C_8H_5O_3$) as that of **1**. From these spectral data, compounds **3** and **4** were identified as 2′,4,4′-trihydroxy-3′-[(*E*)-6-hydroxy-3,7-dimethyl-2,7-octadieyl]chalcone and 2′,4,4′-trihydroxy-3′-[(*E*)-3-methyl-6-oxo-2-hexenyl]chalcone, respectively.

The $^1$H and $^{13}$C NMR spectra of **5** (Tables 3 and 4) were closely related to those of 4-hydroxyderricin [2′,4-dihydroxy-3′-(3,3-dimethyl allyl)-4′-methoxychalcone] (**2**) except for the presence of signals assignable to a 2-hydroxy-3-methyl-3-butenyl moiety [$\delta$3.01 (1H, *dd*, $J$ = 13.4, 5.0 Hz, H-1″), 2.92 (1H, *dd*, $J$ = 13.4, 8.1 Hz, H-1″), 4.29 (1H, *dd*, $J$ = 8.1, 5.0 Hz, H-2″), 4.87 (1H, *br s*, H-4″), 4.75 (1H, *br s*, H-4″), 1.84 (3H, *s*, 3″-Me), 3.35 (1H, *br*, OH); $\delta_C$ 29.56 (C-1″), 75.98 (C-2″), 148.38 (C-3″), 110.39 (C-4″), 18.22 (3″-Me)] instead of signals due to a 3,3-dimethylallyl moiety. In the $^{13}$C NMR spectra of **5**, the carbonyl carbon was observed as double-double-doublet signals (each $J$ = 5 Hz) arising from long range coupling with the α-, β- and 6′-protons. In the difference NOE experiment in the $^1$H NMR spectrum of **5**, NOE was observed between OMe and H-5′ ($\delta$6.55, *d*, $J$ = 9.1 Hz). The mass spectrum of **5** showed the same peaks at *m/z* 283 ($C_{17}H_{15}O_4$) and *m/z* 163 ($C_9H_7O_3$) as that of **2**. From the above spectral data, compound **5** was confirmed to be 2′,4-dihydroxy-4′-methoxy-3′-(2-hydroxy-3-methyl-3-butenyl)chalcone.

The $^1$H NMR and $^{13}$C NMR spectra of **6** (Tables 3 and 4) were similar to those of **5** except for signals arising from the side chain. The long range coupling of the carbonyl carbon with the α-, β- and 6′ protons and the NOE between OMe and 5′-H were also observed as found in **5**. The mass spectrum of **6** showed the same peaks at *m/z* 283 ($C_{17}H_{15}O_4$) and *m/z* 163 ($C_9H_7O_3$) as that of **5**. All of the above findings indicated that **6** is also a 3′-substituted 2′,4-dihydroxy-4′-methoxychalcone.

The side chain at C-3′ of **6** was concluded to be 2-oxy-3-methyl-3-butenyl by NMR spectra [$\delta$3.19 (1H, *dd*, $J$ = 13.5, 8.1 Hz, H-1″), 3.03 (1H, *dd*, $J$ = 13.5, 5.4 Hz, H-1″), 4.52 (1H, *dd*, $J$ = 8.1, 5.4 Hz, H-2″), 4.93 (1H, *br s*, H-4″), 4.89 (1H, *br s*, H-4″), 1.89 (3H, *s*, 3″-Me), 10.45 (1H, *s*, OH); $\delta_C$ 24.28 (C-1″), 87.14 (C-2″), 145.63 (C-3″), 113.00 (C-4″), 18.41 (3″-Me)]. However, their chemical shifts were dis-

Table 3. $^1$H NMR data for compounds **2**, **5** and **6** (in $CDCl_3$, values in parentheses are coupling constants in Hz)

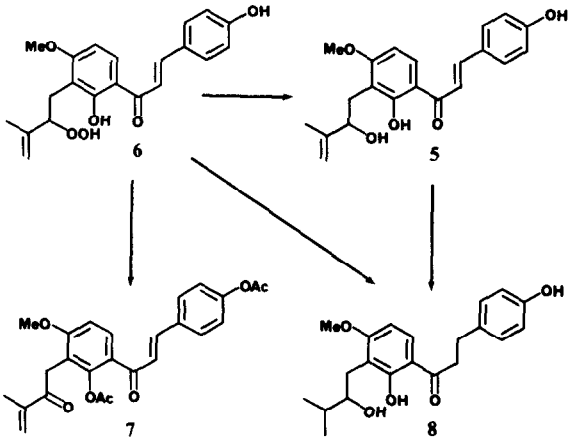
| H | 2 | 5 | 6 |
|---|---|---|---|
| α | 7.48 *d* (15.4) | 7.48 *d* (15.3) | 7.45 *d* (15.4) |
| β | 7.84 *d* (15.4) | 7.83 *d* (15.3) | 7.87 *d* (15.4) |
| 2,6 | 7.57 *d* (8.5) | 7.55 *d* (8.6) | 7.55 *d* (8.7) |
| 3,5 | 6.89 *d* (8.5) | 6.90 *d* (8.6) | 6.91 *d* (8.7) |
| 5′ | 6.50 *d* (9.0) | 6.55 *d* (9.1) | 6.53 *d* (9.1) |
| 6′ | 7.80 *d* (9.0) | 7.89 *d* (9.1) | 7.87 *d* (9.1) |
| 1″ | 3.40 *d* (7.6) | 3.01 *dd* (13.4, 5.0) | 3.19 *dd* (13.5, 8.1) |
| | | 2.92 *dd* (13.4, 8.1) | 3.03 *dd* (13.5, 5.4) |
| 2″ | 5.23 *t* (7.6) | 4.29 *dd* (8.1, 5.0) | 4.52 *dd* (8.1, 5.4) |
| 4″ | 1.80 *s* | 4.87 *br s* | 4.93 *br s* |
| | | 4.75 *br s* | 4.89 *br s* |
| 3″-Me | 1.69 *s* | 1.84 *s* | 1.89 *s* |
| 4′-OMe | 3.92 *s* | 3.92 *s* | 3.91 *s* |
| 2′-OH | 13.50 *s* | 13.81 *s* | 14.05 *s* |
| 4-OH | 5.78 *s* | 9.58 *s* | 9.51 *s* |
| 2″-OH | — | 3.35 *br s* | — |
| 2″-OOH | — | — | 10.45 *s* |

Assignments were confirmed by spin decoupling experiments.

Table 4. $^{13}$C NMR data for compounds **2**, **5** and **6** (in $CDCl_3$)

| C | 2 | 5 | 6 |
|---|---|---|---|
| α | 118.26 | 117.19 | 117.09 |
| β | 145.04 | 145.64 | 145.28 |
| CO | 193.39 | 193.12 | 193.10 |
| 1 | 127.81 | 126.67 | 126.54 |
| 2,6 | 131.16 | 131.14 | 131.14 |
| 3,5 | 116.58 | 116.71 | 116.69 |
| 4 | 159.20 | 160.90 | 160.95 |
| 1′ | 115.07 | 115.22 | 114.85 |
| 2′ | 163.51 | 163.95 | 163.84 |
| 3′ | 118.02 | 115.09 | 114.38 |
| 4′ | 164.04 | 164.08 | 164.20 |
| 5′ | 102.77 | 102.61 | 102.59 |
| 6′ | 129.90 | 130.28 | 130.32 |
| 1″ | 21.94 | 29.56 | 24.28 |
| 2″ | 122.53 | 75.98 | 87.14 |
| 3″ | 132.57 | 148.38 | 145.63 |
| 4″ | 26.03 | 110.39 | 113.00 |
| 3″-Me | 18.03 | 18.22 | 18.41 |

Assignments were confirmed by $^1$H–$^{13}$C COSY and $^1$H–$^{13}$C long range COSY experiments.




tinct from those of 2-hydroxy-3-methyl-3-butenyl observed in **5** and auraptenol [3], especially the C-2″ signal which was shifted downfield (11.16 ppm), suggesting that the C-2″ position was attached to a hydroperoxy group [4]. Further support for a hydroperoxide was obtained from a prominent peak at *m/z* 337 $[M-HO_2]^+$ in the mass spectrum, an intense ferrous thiocyanate test [4] and by the following results. Upon acetylation with pyridine–acetic anhydride, **6** gave a ketone [4], 2′,4,-diacetoxy-4′-methoxy-3′-(3-methyl-2-oxo-3-butenyl)chalcone (**7**). Catalytic hydrogenation of **6** formed 2′,4-dihydroxy-4′-methoxy-3′-(2-hydroxy-3-methylbutyl)dihydrochalcone (**8**), which was also derived from **5** by the same reaction. Reduction of **6** with triphenylphosphine gave a hydroxy compound [4], identified as **5**. Thus, the structure of **6** was elucidated to be 2′,4-dihydroxy-4′-methoxy-3′-(2-hydroperoxy-3-methyl-3-butenyl)chalcone.

## EXPERIMENTAL

*General.* Mps: uncorr; EIMS: 70 eV; $^1$H NMR: 300 or 500 MHz, $^{13}$C NMR: 75.4 or 125.8 MHz, with TMS as an int. standard. CC: Merck silica gel 60 $F_{254}$ (70–230 mesh) and Merck RP-18; TLC and prep. TLC: Merck silica gel 60 $F_{254}$ plates (0.25 mm) and Whatman silica gel 150A PLK 5F (1 mm). Spots and bands were detected by UV irradiation (254 and 365 nm).

*Plant material.* Roots of *A. keiskei* Koidzumi were collected at the full leaf stage on March, 1989 at Hachjo Island, Tokyo, Japan, and identified by Dr Jin Murata, Botanical Garden,

Faculty of Sciences, University of Tokyo. A voucher specimen is deposited in the University of Tokyo and Osaka University of Pharmaceutical Sciences.

*Extraction and isolation.* Air-dried roots (9.5 kg) were chopped into small pieces and extracted with EtOAc (10 l × 5) under reflux. The combined EtOAc exts were concd to give a brown viscous mass (298 g), which was chromatographed on silica gel. The column was eluted with increasing concns of EtOAc in hexane. The 20% EtOAc eluates (106.5 g) were rechromatographed on silica gel with $CHCl_3$–MeOH (100:1 to 30:1) and RP-18 with 80% MeOH to give selinidin (2.1 g), psoralen (6.3 g), bergapten (0.035 g), xanthotoxin (4.4 g), laserpitin (11.6 g), isolaserpitin (17.5 g), isopimpinellin (0.07 g), xanthoangelol (**1**) (14.3 g), 4-hydroxyderricin (**2**) (13.5 g), xanthoangelol B (**3**) (0.54 g), xanthoangelol C (**4**) (0.025 g), xanthoangelol D (**5**) (0.03 g) and xanthoangelol E (**6**) (0.68 g). The 30–40% EtOAc eluates (26.3 g) gave umbelliferone (0.3 g), scopoletin (0.18 g) and marmesin (0.07 g).

*Xanthoangelol B* (**3**). Fine yellow needles, mp 167.4–169.3°. $[\alpha]_D^{18}$ +12° (MeOH; *c* 0.50). UV $\lambda_{max}^{MeOH}$ nm (log ε): 369.0 (4.52), 307.0 (sh 4.02), 243.5 (sh 4.04), 221.5 (sh 4.18); IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3600–2400, 1629, 1606, 1564. HRMS *m/z*: 408.1933 $[M]^+$ (Calcd. for $C_{25}H_{28}O_5$, 408.1935), 323.1277 ($C_{20}H_{19}O_4$, 323.1281), 309.1117 ($C_{19}H_{17}O_4$, 309.1125), 269.0852 ($C_{16}H_{13}O_4$, 269.0813), 203.0711 ($C_{12}H_{11}O_3$, 203.0707), 149.0231 ($C_8H_5O_3$, 149.0238). $^1H$ and $^{13}C$ NMR see Tables 1 and 2.

*Xanthoangelol C* (**4**). Fine yellow needles, mp 134.7–136.1°. UV $\lambda_{max}^{MeOH}$ nm (log ε): 368.0 (4.64), 312.0 (sh 4.18), 237.5 (sh 4.23), 223.0 (sh 4.32). IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3800–2400, 1715, 1627, 1605, 1558. HRMS *m/z*: 366.1469 $[M]^+$ (Calcd for $C_{22}H_{22}O_5$, 366.1466), 323.1250 ($C_{20}H_{19}O_4$, 323.1281), 309.1117 ($C_{19}H_{17}O_4$, 309.1125), 269.0821 ($C_{16}H_{13}O_4$, 269.0813), 203.0720 ($C_{12}H_{11}O_3$, 203.0707), 149.0228 ($C_8H_5O_3$, 149.0238). $^1H$ and $^{13}C$ NMR see Tables 1 and 2.

*Xanthoangelol D* (**5**). Yellow crystalline powder, mp 148.9–150.1°. $[\alpha]_D^{18}$ 0° (MeOH; *c* 0.5). UV $\lambda_{max}^{MeOH}$ nm (log ε): 366.5 (4.50), 307.0 (sh 4.07), 240.0 (sh 4.11), 222.5 (sh 4.20). IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3400–2400, 1632, 1608, 1567. HRMS *m/z*: 354.1468 $[M]^+$ (Calcd for $C_{21}H_{22}O_5$, 354.1466), 337.1438 ($C_{21}H_{21}O_4$, 337.1439), 283.0957 ($C_{17}H_{15}O_4$, 283.0969), 163.0377 ($C_9H_7O_3$, 163.0395). $^1H$ and $^{13}C$ NMR see Tables 3 and 4.

*Xanthoangelol E* (**6**). Yellow needles, mp 185.5–187.2°. $[\alpha]_D^{18}$ 0° (MeOH, *c* 0.5). UV $\lambda_{max}^{MeOH}$ nm (log ε): 369.0 (4.39), 307.0 (sh 3.95), 243.0 (sh 3.99), 221.5 (sh 4.06). IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3800–2350, 1632, 1608, 1514, 1496. HRMS *m/z*: 370.1415 $[M]^+$ (Calcd. for $C_{21}H_{22}O_6$, 370.1415), 337.1445 ($C_{21}H_{21}O_4$, 337.1439), 283.0970 ($C_{17}H_{15}O_4$, 283.0969), 163.0399 ($C_9H_7O_3$, 163.0395). $^1H$ and $^{13}C$ NMR see Tables 3 and 4.

*Acetylation of* **6**. A soln of **6** (50 mg) in a mixt. of $Ac_2O$ (2 ml) and pyridine (2 ml) was allowed to stand at room temp. overnight. The reaction mixt. was treated in the usual way and the product recrystallized from *n*-hexane–EtOAc to give **7** (15 mg). Compound **7**: yellow crystalline powder, mp 124.9–126.0°. UV $\lambda_{max}^{MeOH}$ nm (log ε): 302.0 (4.19), 223.0 (sh 4.31). IR $\nu_{max}^{KBr}$ $cm^{-1}$: 1763, 1687, 1660, 1601, 1506. HRMS *m/z*: 436.1531 $[M]^+$ (Calcd. for $C_{25}H_{24}O_7$, 436.1521). $^1H$ NMR ($CDCl_3$): δ7.76 (1H, *d*, *J* = 8.6 Hz, H-6′), 7.61 (1H, *d*, *J* = 15.7 Hz, H-β), 7.60 (2H, *d*, *J* = 8.6 Hz, H-2, 6) 7.20 (1H, *d*, *J* = 15.7 Hz, H-α), 7.14 (2H, *d*, *J* = 8.6 Hz, H-3, 5), 6.86 (1H, *d*, *J* = 8.6 Hz, H-5′), 6.07 (1H, *br s*, H-3″), 5.82 (1H, *br s*, H-3″), 3.99 (2H, *s*, H-1″), 3.88 (3H, *s*, OMe), 2.32 (3H, *s*, OAc), 2.24 (3H, *s*, OAc), 1.91 (3H, *s*, 3″-Me). $^{13}C$ NMR ($CDCl_3$): δ198.67 (*s*), 190.15 (*s*), 169.77 (*s*) × 2, 161.71 (*s*), 152.78 (*s*), 149.83 (*s*), 144.79 (*s*), 143.69 (*d*), 133.06 (*s*), 130.94 (*d*), 129.97 (*d*) × 2, 125.42 (*d*), 125.17 (*t*), 125.17 (*s*), 122.68 (*d*) × 2, 119.60 (*s*), 107.98 (*d*), 56.39 (*q*), 33.69 (*t*), 21.34 (*q*), 21.04 (*q*), 17.96 (*q*).

*Catalytic hydrogenation of* **6**. A soln of **6** (50 mg) in EtOH (10 ml) was added to pre-reduced Adams catalyst ($PtO_2$; 50 mg) in EtOH (10 ml) and the mixt. stirred in the presence of $H_2$ until consumption ceased. The catalyst was filtered off and the filtrate evapd to dryness. The product was purified by prep. TLC (*n*-hexane–EtOAc, 3:1) to give **8** (20 mg). Compound **8**: glassy substance. UV $\lambda_{max}^{MeOH}$ nm (log ε): 385.5 (sh 3.15), 329.5 (sh 3.84), 283.5 (4.33), 220.0 (4.50). IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3700–2400, 1721, 1515, 1500. HRMS *m/z*: 358.1783 $[M]^+$ (Calcd for $C_{21}H_{26}O_5$, 358.1787). $^1H$ NMR ($CDCl_3$): δ7.63 (1H, *d*, *J* = 9.1 Hz, H-6′), 7.02 (2H, *d*, *J* = 8.4 Hz, H-2, 6), 6.67 (2H, *d*, *J* = 8.4 Hz, H-3, 5), 6.46 (1H, *d*, *J* = 9.1 Hz, H-5′), 3.88 (3H, *s*, OMe), 3.61 (1H, *m*, H-2″), 3.18 (2H, *t*, *J* = 7.7 Hz, H-α), 2.94 (2H, *t*, *J* = 7.7 Hz, H-β), 2.93 (1H, *dd*, *J* = 13.5, 2.9 Hz, H-1″), 2.79 (1H, *dd*, *J* = 13.5, 9.4 Hz, H-1″), 1.77 (1H, *m*, H-3″), 1.02 (6H, *d*, *J* = 6.75 Hz, Me). $^{13}C$ NMR ($CDCl_3$): δ205. 18 (*s*), 164.04 (*s*), 162.69 (*s*), 155.25 (*s*), 132.65 (*s*), 130.64 (*d*), 129.83 (*d*) × 2, 115.90 (*d*) × 2, 115.82 (*s*), 114.38 (*s*), 102.88 (*d*), 77.82 (*d*), 56.22 (*q*), 40.36 (*t*), 34.41 (*d*), 29.93 (*t*), 27.37 (*t*), 18.80 (*q*), 17.66 (*q*).

*Reduction of* **6** *with triphenylphosphine.* Compound **6** (50 mg) was dissolved in MeOH (10 ml) and triphenylphosphine (50 mg) added. The mixt. was allowed to stand at room temp. for 1 hr, dild with $H_2O$ (50 ml) and extracted with EtOAc. The EtOAc soln was dried and evapd to dryness. The residue was purified by prep. TLC (*n*-hexane–EtOAc, 2:1) to give **5** (35 mg).

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