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DIBENZOCYCLOOCTADIENE LIGNANS FROM *KADSURA JAPONICA*

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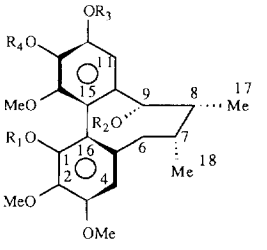
Key Word Index—*Kadsura japonica*; Schisandraceae; fruits; lignan; dibenzocyclooctadiene; acetylbinankadsurin B; angeloylbinankadsurin B; deangeloylschisantherin F.

Abstract—Two new dibenzocyclooctadiene lignans, angeloylbinankadsurin B, acetylbinankadsurin B, and a known lignan, deangeloylschisantherin F, were isolated from the fruits of *Kadsura japonica*. Their structures were determined on the basis of chemical and spectral studies.

INTRODUCTION

Kadsura japonica Dunal is a climbing species growing in the southern part of Japan. Its dried fruits were used as an antitussive and a tonic under the name of 'Nangomishi' as a substitute for the fruits of *Schisandra chinensis* Baill. Two dibenzocyclooctadiene lignans (kadsurin and kadsurarin) have been isolated from the stems of this species [1] and three lignans (acetyl-, angeloyl- and caproyl-binankadsurin A) from the fruits [2]. The present paper describes the structural elucidation of two new dibenzocyclooctadiene lignans, angeloylbinankadsurin B (**1**) and acetylbinankadsurin B (**2**) and the first isolation of a known lignan, deangeloylschisantherin F (**3**) [3], from a natural source.



1 : R_1=H, R_2=Angeloyl, R_3=R_4=Me

1a: R_1=R_2=H, R_3=R_4=Me

2 : R_1=H, R_2=$COCH_3$, R_3=R_4=Me

3 : R_1=R_2=R_3=H, R_4=Me

3a: R_1=R_3=$COCH_3$, R_2=H, R_4=Me

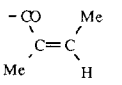
4 : R_1=R_2=H, R_3+R_4=CH_2

4a: R_1=H, R_2=$COCH_3$, R_3+R_4=CH_2

4b: R_1=R_2=$COCH_3$, R_3+R_4=CH_2

4c: R_1=R_2=$COCH_3$, R_3=R_4=Me

4d: R_1=R_2=$COCH_3$, R_3=R_4=Me

Angeloyl= 

RESULTS AND DISCUSSION

Angeloylbinankadsurin B (**1**), acetylbinankadsurin B (**2**) and deangeloylschisantherin F (**3**) were obtained as needles, a white powder and prisms, respectively. The molecular formulae of **1**–**3** were estimated from HR-mass spectrometry to be $C_{28}H_{36}O_8$, $C_{25}H_{32}O_8$ and $C_{22}H_{28}O_7$, respectively. The UV and CD spectra (**1**, $[\theta]_{205}$ + 104000, $[\theta]_{232}$ + 6100sh, $[\theta]_{249}$ − 5700 and $[\theta]_{272}$ − 6900sh; **2**, $[\theta]_{249}$ − 57400, $[\theta]_{269}$ − 9200sh, $[\theta]_{287}$ + 1800; **3**, $[\theta]_{205}$ + 139000, $[\theta]_{248}$ − 104000 and $[\theta]_{288}$ + 7000) of these compounds show that they are dibenzocyclooctadiene lignans with an *S* configuration of the biphenyl moiety [4].

The ^1H and ^{13}C NMR 2 (Tables 1 and 2, respectively) spectra of **1** reveal that it has a phenolic hydroxyl and five methoxyl groups on the aromatic rings, and also two secondary methyls, a benzylic methine and an angeloyl group [5] on the cyclooctadiene ring. The mass spectrum, with peaks at *m/z* 400 [M − MeCH=C(Me)COOH]$^+$ and 83 [MeCH=C(Me)CO]$^+$ supports the presence of an angeloyl group in **1**. The ^1H and ^{13}C NMR spectra of **2** resemble those of **1**, except for the signals of the ester moiety. By comparison of the ^1H and ^{13}C NMR spectra of **2** with those of **1**, it was assumed that the angeloyl group in **1** was replaced by an acetyl group in **2**. The mass spectrum, with peaks at *m/z* 460 [M]$^+$ and 400 [M − Me COOH]$^+$ supported the presence of an acetyl group in **2**.

On hydrolysis with 3% KOH in EtOH, **1** afforded compound **1a**, named binankadsurin B, as a white powder, $C_{23}H_{30}O_7$, and a mixture of angelic and tiglic acids. On the other hand, reduction of **2** with $LiAlH_4$ similarly afforded **1a**. These facts indicate that **1** and **2** are the compounds with angeloyl and acetyl groups attached to the hydroxyl group of **1a**, respectively. The singlet at δ4.67 in the ^1H NMR spectrum of **1a**, which appeared at δ5.69 in **1** and 5.62 in **2**, was assigned to a benzylic methine. This shows that the angeloyl group in **1** and the acetyl group in **2** are linked to a benzylic hydroxyl group of **1a**. The ^{13}C NMR spectrum of **1a** is very similar to

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Table 1. ^{1}H NMR spectral data of compounds **1**, **1a**, **2**, **3**, **3a**, and **4** in $CDCl_3$(500 MHz)

C	H-4, *s* H-11, *s*	H-9β	H-6α, *dd* (*J* = Hz)	H-6β, *dd* (*J* = Hz)	H-7, *m*	H-8, *m*	C-7-Me, *d* (*J* = Hz)	C-8-Me, *d* (*J* = Hz)	OMe *s*	ArOH *br s*	OCH_2O
1*	6.38	5.69 *br s*	2.62	2.59	2.11	2.11	0.95	1.14	3.59, 3.86, 3.88	5.40	
	6.60		(13.6, 6.2)	(13.6, 2.3)			(7.2)	(6.9)	3.91		
1a	6.41	4.67 *s*	2.64	2.61	2.10	1.94	0.95	1.20	3.65, 3.88, 3.89	5.84	
	6.43		(13.5, 6.4)	(13.5, 2.9)			(7.5)	(7.3)	3.89,3.92		
2*	6.40	5.62 *br s*	2.64	2.59	2.06	2.06	0.91	1.11	3, 62, 3.88, 3.90		
	6.55		(13.7, 6.4)	(13.7, 2.3)			(7.1)	(7.0)	3.90, 3.91		
3†	6.34	4.52 *s*	2.58	2.53	2.02	1.84	0.88	1.12	3.58, 3.80, 3.85	7.86	
	6.39		(13.6, 7.1)	(13.6, 2.2)			(7.4)	(7.3)	3.90	8.71	
3a*	6.73	4.75 *s*	2.69	2.64	2.04	1.83	1.01	1.17	3.60, 3.82, 3.85		
	6.60		(13.8, 7.0)	(13.8, 2.3)			(7.4)	(7.3)	3.90		
4	6.41	4.60 *s*	2.62	2.65	2.07	1.91	0.94	1.16	3.87, 3.88, 3.91	5.82	5.95, *d* (1.5)
	6.36		(13.6, 6.6)	(13.6, 3.1)			(7.5)	(7.3)			5.97, *d* (1.5)

*Other singals: **1**, angeloyl: 1.30 (3H, *quintet*, J = 1.6 Hz, α-Me), 1.89 (3H, *dq*, J = 7.2, 1.6 Hz, β-Me), 5.88(1H, *qq*, J = 7.2, 1.6 Hz); **2**, acetyl: 1.57 (3H, *s*); **3a**, acetyl: 1.99 and 2.33 (each 3H, *s*).

†This compound was measured in $CDCl_3$-DMSO-d_6 (3:1).

that of binankadsurin A (**4**) [2], having the C-7 α methyl, C-8 α methyl and C-9α hydroxyl groups, except for the signals given by the functional groups on the aromatic rings. By comparison of the ^{1}H and ^{13}C NMR spectra of **1a** with those of **4** (Tables 1 and 2), it was assumed that the methylenedioxy moiety at the C-12 and C-13 positions in **4** was replaced by two methoxyl groups in **1a**. This was confirmed by chemical correlation of **1a** with acetylbinankadsurin A (**4a**), as described below.

On acetylation, **4a** afforded a compound **4b**, $C_{26}H_{30}O_9$. The ^{1}H NMR spectrum of **4b** showed a new acetyl signal at δ1.98 and no phenolic hydroxyl signal, indicating that the C-1 hydroxyl group in **4** was acetylated. In a previous paper [6], we reported on the selective cleavage of the methylenedioxy moiety with $Pb(OAc)_4$ in dry benzene. Treatment of **4b** with this reagent followed by hydrolysis with 80% HOAc afforded a diphenol (**4c**), $C_{25}H_{30}O_9$, whose ^{1}H NMR spectrum showed no methylenedioxyl signal. Methylation of **4c** with Me_2SO_4 and K_2CO_3 gave compound **4d**, $C_{27}H_{34}O_9$ [^{1}H NMR ($CDCl_3$): δ3.57 (3H, *s*), 3.87 (6H, *s*), 3.90 (3H, *s*), 3.93 (3H, *s*) (5 × OMe)]. On hydrolysis, **4d** afforded **1a**. This indicates that the methylenedioxy moiety at the C-12 and C-13 positions in **4** is replaced by two methoxyl groups in **1a**.

On the basis of the above results, the structures of angeloylbinankadsurin B and acetylbinankadsurin B were thus determined as (7*R*, 8*R*, 9*R*, *S*-biar)-9-angeloyloxy-6,7,8,9-tetrahydro-2,3,12,13,14-pentamethoxy-7,8-dimethyl-1-dibenzo [a, c] cyclooctenol (**1**), and (7*R*,8*R*,9*R*,*S*-biar)-9-acetoxy-6,7,8,9-tetrahydro-2,3,12,13,14-pentamethoxy-7, 8-dimethyl-1-dibenzo [a, c] cyclooctenol (**2**), respectively. In addition, the J value between the C-8 proton and the C-9 proton ($J_{8,9}$ = 0 Hz, $\phi_{8,9} \fallingdotseq 90°$) in **1** and **2** supports that the conformations of the cyclooctadiene ring of **1** and **2** are in a twist-boat-chair form.

The ^{1}H and ^{13}C NMR spectra of deangeloylschisantherin F (**3**) showed two phenolic hydroxyl signals and a benzylic methine signal attached to the carbon carrying a hydroxyl group. On methylation with MeI and K_2CO_3, **3** afforded a monomethyl ether, which was identified as **1a** possessing the C-1 phenolic hydroxyl group. This indicates that **3** corresponds to norbinankadsurin B. The position of the other phenolic hydroxyl group was determined by ^{13}C NMR spectral analysis of **1a**, **3** and the acetate (**3a**) of **3**. In the ^{13}C NMR spectral analysis of dibenzocyclooctadiene lignans, it was reported that replacement of the methoxyl group at the C-3 or C-12 positions by a hydroxyl group and an acetoxyl group produces downfield shifts of *ca* 3 and *ca* 10 ppm, respectively, for the C-4 or C-11 carbon signal [7]. The C-11 signals of **3** and **3a** show downfield shifts of 2.9–3.4 and 9.8–10.3 ppm, respectively, compared with that of **1a**. This indicates the presence of a C-12 hydroxyl group in **3**.

On the basis of the above data **3** was identified as (7*R*, 8*R*, 9*R*, *S*-biar)-6,7,8,9-tetrahydro-2,3,13,14-tetramethoxy-7,8-dimethyl-1,9,12-dibenzo [a, c] cyclooctenetriol. Compound **3** has already been reported as the hydrolysis

Table 2. ^{13}C NMR spectral data of compounds **1**, **1a**, **2**, **3**, **3a** and **4** in $CDCl_3$ (125 MHz)

C	1*	1a	2	3†	3a‡	4
1	146.9	147.2	146.5	147.7	141.3	147.1
2	134.0	134.2	133.8	134.3	139.2	133.9
3	150.6	151.4	150.5	151.0[a]	151.8	151.3
4	107.3[a]	107.6[a]	107.3[a]	106.6	113.3	107.5
5	133.1	133.7	133.5	133.4	134.4	133.9
6	38.6	38.8	38.7	38..6	38.9	38.8
7	34.9	35.1	35.2	35.0	35.1	34.9
8	41.9	43.2	41.8	42.9	43.1	43.1
9	82.7	83.9	82.7	82.8	82.5	83.7
10	137.3	140.1	137.0	140.5	141.1	138.9
11	107.1[a]	107.1[a]	107.0[a]	110.5	117.4	102.8
12	153.0	153.0	153.1	149.0	143.7[a]	148.9
13	141.1	140.9	141.2	139.1	143.3[a]	135.7
14	151.6	151.8	151.7	151.4[a]	151.4	141.3
15	120.2	119.1	119.9	120.2[b]	125.0[b]	118.3
16	117.4	115.5	117.5	119.4[b]	122.5[b]	115.3
17	19.9	19.9	19.8	20.0	20.1	19.7
18	14.8	15.3	14.8	15.0	15.2	15.4
C-1, 14	—, 60.5	, 60.9	—, 60.9	, 60.5[c]	—, 60.5[c]	—, 59.8
OMe C-2, 13	60.8, 60.8	61.1, 60.9	60.9, 60.9	60.2, 60.2[c]	60.6[c], 60.6[c]	61.1, —
C-3, 12	55.9[b], 56.0[b]	55.8[b], 56.0[b]	55.9[b], 56.0[b]	56.0, —	—	55.8, —
OCH_2O	—	—	—	—	—	101.2
CO-CH_3			170.3, 20.4	—	170.5, 20.5 168.9, 20.7	—

* Other signals: **1**, 15.7 (β-Me), 20.4 (α-Me), 127.3 (α-olefin), 139.4 (β-olefin), 166.8 (C=O) (angeloyl).

† This compound was measured in DMSO-d_6–$CDCl_3$ (1:3).

‡ This compound was measured at 80 MHz.

[a–b] Assignments within any vertical column may be interchanged.

product of schisantherin F by Liu and Ma [3], but this is the first report of this compound from a natural source.

EXPERIMENTAL

General. See ref. [2].

Extraction and isolation. Dried fruits (1.28 kg) of *K. japonica* (provided by the Herbal Garden of Tokyo Metropolitan Government) were pulverized and extracted with petrol (31 × 4, 7 hr each) under reflux. The petrol extracts were concd to give a brown mass (471 g). This afforded 15 frs on silica gel CC (2.5 kg) with *n*-hexane–benzene–Me_2CO. The frs eluted with benzene–Me_2CO (9:1) and (22:13) were combined and concd. This residue (12.28 g) was purified by prep. TLC: (i) benezene–Et_2O (1:1), R_f 0.48; (ii) *n*-hexane–Me_2CO (3:2), R_f 0.45, to give **1** (576 mg, yield 0.045%). The frs eluted with benzene–Me_2CO (21:14) and (41:19) were combined and concd. The residue (2.33 g) was purified by prep. TLC: (i) *n*-hexane–Me_2CO(3:2), R_f 0.42; (ii) benzene–EtOH (19:1), R_f 0.34, to give **2** (289 mg, yield 0.023%). The frs eluted with benzene–Me_2CO (1:1) were concd (2.6 g) and purified by prep. TLC: *n*-hexane–Me_2CO (3:2), R_f 0.30 to give **3** (535 mg, yield 0.042%).

Angeloylbinankadsurin B (**1**). Plates from *n*-hexane–Et_2O, mp 146.5–148°. $[\alpha]_D^{25}$ + 33.6° ($CHCl_3$; *c* 1.07). IR ν_{max}^{KBr} cm^{-1}: 3432 (OH), 1710 (C=O), 1644 (C=C), 1586 (aromatic ring). UV λ_{max}^{EtOH} nm(log ε): 215 (4.61), 252 sh (4.00), 278 (3.47). EIMS *m/z* (rel. int.): 500 $[M]^+$ (26), 400 [M − Me CH = C Me COOH]$^+$ (97), 369 (100), 357 (9.8), 83 [Me CH = C Me CO]$^+$ (6.4), 55 (12.6). HRMS *m/z*: 500. 2409 (calc. for $C_{28}H_{36}O_8$: 500. 2410). CD (MeOH; *c* 0.00983) $[\phi]^{28}$ (nm): 104 000(205), + 6100sh(232), − 57 700(249), − 6900sh(272), + 4600 (287).

Acetylbinankadsurin B (**2**). White powder. $[\alpha]_D^{28}$ + 7.70° ($CHCl_3$; *c* 1.30). IR ν_{max}^{KBr} cm^{-1}: 3420 (OH), 1735 (C=O), 1604, 1595, 1580 (aromatic ring). UV λ_{max}^{EtOH} nm (log ε): 211 (4.59), 254sh (3.95), 277 (3.48). EIMS *m/z* (*rel. int.*): 460 $[M]^+$ (35), 401 (23), 400 [M-Me COOH]$^+$ (89), 370 (27), 369 (100), 357 (14). HRMS *m/z*: 460.2099 (calc. for $C_{25}H_{32}O_8$: 460.2097). CD (MeOH; *c* 0.00947) $[\phi]^{30}$ (nm): − 57 400(249), − 9200sh (269), + 1800 (287).

Deangeloylschisantherin F (**3**). Prisms from Me_2CO, mp 195–196°. $[\alpha]_D^{24}$ − 12.5° (dioxane; *c* 0.88). IR ν_{max}^{KBr} cm^{-1}: 3500, 3472 (OH), 1605, 1585, 1575 (aromatic ring). UV λ_{max}^{EtOH} nm(log ε): 217 (4.58), 251sh (4.03), 278 (3.45). EIMS *m/z* (rel. int): 404 $[M]^+$ (83), 387 (24), 386 (100), 355 (45), 348 (28), 273 (16). HRMS *m/z*: 404. 1831 (calc. for $C_{22}H_{28}O_7$: 404. 1835). CD (MeOH; *c* 0.0121) $[\phi]^{29}$ (nm): + 139 000 (205), − 30 000sh (230), − 104 000(248), − 11 900sh (272), + 7000 (288).

Hydrolysis of **1**. A soln of **1** (34.8 mg) in 3% KOH–EtOH (2 ml) was kept at 75–80° for 6 hr, then diluted with H_2O (15 m) and extracted with Et_2O. The Et_2O extract was washed with H_2O, dried over Na_2SO_4 and concd. The residue was purified by prep. TLC [benzene–Et_2O, 1:1] to give **1a** (20.4 mg) as a white powder. $[\alpha]_D^{27}$ − 32.8° ($CHCl_3$; *c* 2.04). IR ν_{max}^{KBr} cm^{-1}: 3540, 3500 (OH), 1608, 1595, 1580 (aromatic ring). UV λ_{max}^{EtOH} nm(log ε): 213 (4.58), 250sh (4.06), 281sh (3.44). EIMS *m/z* (rel. int.):418 $[M]^+$ (91), 400 (100), 369 (84), 362 (32), 347 (14), 224 (15). HRMS *m/z*:418.1995 (calc. for $C_{23}H_{30}O_7$:418.1992). The aq. soln was acidified with N HCl and extracted with Et_2O. The Et_2O extract was washed with H_2O, dried over Na_2SO_4 and evapd. Sublimation (70°, 15 mmHg) of the residue gave needles. The presence of angelic and tiglic acids in this sublimate in a ratio 1:99 was verified by GC [column, SP1200 (10%) + H_3PO_4 (1%) on Chromosorb WAW (80–100 mesh) (3 mm i.d. × 2 m); column temp., 130°; inj. temp., 150°; N_2 29.4 ml min^{-1}]; angelic acid, R_t, 6.4 min; tiglic acid, R_t, 8.3 min.

Acetylation of **4a**. A soln of **4a** (100.1 mg) in a mixt. of dry pyridine (2.5 ml), Ac_2O (2 ml) and dimethylaminopyridine (50 mg) was kept at 55–60° for 10 min, then diluted with Et_2O. The Et_2O soln was washed with N HCl, then H_2O, dried over Na_2SO_4 and concd. The residue was purified by prep. TLC (benzene–Et_2O 1:1) to **4b** (124 mg) as prisms (from *n*-hexane–Et_2O), mp 130–132°. $[\alpha]_D^{24}$ + 22.1° ($CHCl_3$; *c* 1.22). IR ν_{max}^{KBr} cm^{-1}:1782, 1775, 1735 (C=O), 1615, 1601, 1575 (aromatic ring). UV λ_{max}^{EtOH} nm(log ε): 219 (4.63), 254sh (4.03), 278sh (3.50). ^1H NMR ($CDCl_3$, 60 MHz):δ0.93 (3H, *d*, *J* = 7 Hz, Me-7), 1.03 (3H, *d*, *J*-7 Hz, Me-8), 1.62 (3H, *s*, AcO-9), 2.00 (2H, *m*, H-7 and H-8), 2.02 (3H, *s*, OAc-1), 2.33 (2H, *d*, *J* = 4 Hz, H-6), 3.85 (6H, *s*, OMe), 3.90 (3H, *s*), 5.67 (1H, *br s*, H-9β), 5.95 (2H, *s*, OCH_2O), 6.45 (1H, *s*, H-11), 6.72 (1H, *s*, H-4). (found:C, 63.91; H, 6.27. $C_{26}H_{30}O_9$ requires:C, 64.18; H, 6.22%).

Treatment of **4b** *with Pb(OAc)$_4$ in dry benzene, to give* **4c**. A soln of **4b** (124.0 mg) and $Pb(OAc)_4$ (442.9 mg) in dry benzene (8 ml) was stirred at 50–55° for 7 hr, then diluted with Et_2O. The mixt. was washed with H_2O, dried over Na_2SO_4 and concd. The residue was purified by prep. TLC (*n*-hexane–Me_2CO, 3:2) to give a pale brown oil and unchanged **4b** (39.0 mg). A soln of the pale brown oil in 80% HOAC (3 ml) was stirred at room temp. for 15 hr. The mixt. was concd and purified by prep. TLC (*n*-hexane–EtOAc, 3:4) to give **4c** (37 mg) as an amorphous powder. $[\alpha]_D^{30}$ − 8.8° ($CHCl_3$; *c* 1.59). IR $\nu_{max}^{CHCl_3}$ cm^{-1}:3510, 3350 (OH), 1765, 1735 (C=O), 1601,1585 (aromatic ring). EIMS *m/z* (rel. int.):474 $[M]^+$ (12), 414 (9.7), 373 (23), 372 (100), 341 (16), 43 (16). HRMS *m/z*:474.1891 (calc. for $C_{25}H_{30}O_9$:474.1890). ^1H NMR ($CDCl_3$, 500 MHz):δ0.96 (3H, *d*, *J* = 7.3 Hz, Me-7), 1.06 (3H, *d*, *J* = 7.3 Hz, Me-8), 1.59(3H, *s*, AcO-9), 1.98 (3H, *s*, OAc-1), 2.00 (1H, *m*, H-8), 2.08 (1H, *m*, H-7), 2.72(2H, *d*, *J* = 4.7 Hz, H-6), 3.29, 3.85, 3.92 (each 3H, *s*, 3 × OMe), 5.66 (1H, *s*, H-9β), 6.60 (1H, *s*, H-11), 6.72 (1H, *s*, H-4).

Methylation of **4c**. A soln of **4c** (33.9 mg) in dry Me_2CO(3 ml) containing MeI (0.3 ml) and K_2CO_3 (300 mg) was stirred at room temp. for 4 hr, then diluted with Et_2O. The mixt. was washed with H_2O, concd and purified by prep. TLC (benzene–Et_2O, 1:1) to give **4d** (23 mg) as an amorphous powder. IR $\nu_{max}^{CHCl_3}$ cm^{-1}:1765, 1735, 1725 (C=O), 1595, 1577 (aromatic ring). EIMS *m/z* (rel. int.):502 $[M]^+$ (34), 460 (12), 400 (100), 369 (83). ^1H NMR ($CDCl_3$, 500 MHz):δ0.97 (3H, *d*, *J* = 7.3 Hz, Me-7), 1.08 (3H, *d*, *J* = 7.2 Hz, Me-8), 2.00 (1H, *m*, H-8), 2.07(1H, *m*, H-7), 2.65 (1H, *dd*, *J* = 13.8, 2.3 Hz, H-6β), 2.71 (1H, *dd*, *J* = 13.8, 7.0 Hz, H-6α), 3.56, 3.85, 3.86, 3.87 (each 3H, *s*, 4 × OMe), 5.73 (1H, *d*, *J* = 0.8 Hz, H-9β), 6.50 (1H, *s*, H-11), 6.72 (1H, *s*, H-4).

Hydrolysis of **4c**. A soln of **4c** (15 mg) in 3% KOH–EtOH (2 ml) was kept at 65° for 1 hr, then diluted with Et_2O. The Et_2O extract was washed with H_2O, dried over Na_2SO_4 and evapd. The residue was purified by prep. TLC (benzene–Et_2O, 1:1) to give an amorphous powder (10.7 mg). $[\alpha]_D^{24}$ − 35.9° ($CHCl_3$; *c* 1.07). HRMS *m/z*:418.1999 (*calc. for* $C_{23}H_{30}O_7$:418.1991). This compound was identified as **1a** ($[\alpha]_D$, IR, EIMS and ^1H NMR).

Reduction of **2** with $LiAlH_4$. $LiAlH_4$ (20 mg) was added to a soln of **2** (24.1 mg) in dry THF (2 ml). The mixt. was stirred at room temp. for 1 hr, then wet Et_2O was added. The reaction mixt. was then filtered and evapd. The residue was purified by prep. TLC (benzene–Et_2O, 1:1) to give an amorphous powder (17.3 mg). $[\alpha]_D^{26}$ − 30.1° ($CHCl_3$; *c* 0.87,). HRMS *m/z*:418.1989 (calc. for $C_{23}H_{30}O_7$:418.1991). This compound was identified as **1a** ($[\alpha]_D$, IR, EIMS and ^1H NMR).

Acetylation of **3**. A soln of **3** (46.5 mg) in a mixt. of dry pyridine (2 ml) and Ac_2O (1 ml) was kept at room temp. overnight. The reaction mixt. was treated as described above for the acetylation of **4a** to give **3a** (36.4 mg) as prisms (from *n*-hexane–Et_2O), mp 155–156°. $[\alpha]_D^{24}$ + 5.0° ($CHCl_3$; *c* 1.0). IR ν_{max}^{KBr} cm^{-1}:3498 (OH), 1775, 1735 (C=O), 1608, 1575 (aromatic ring). UV λ_{max}^{EtOH} nm(log ε): 211 (4.59), 251 (3.96), 283sh (3.42). EIMS *m/z* (rel. int.):488 $[M]^+$ (36), 470 (29), 446 (35), 428 (77), 397 (43), 386 (100). HRMS *m/z*:488.2047 (calc. for $C_{22}H_{32}O_9$:488.2046).

Methylation of **3**. A soln of **3** (80.4 mg) in dry Me_2CO (3 ml) containing MeI (0.3 ml) and K_2CO_3 (300 mg) was stirred at room temp. for hr, then diluted with Et_2O. The mixt. was treated as described above for the methylation of **4c**, to give unchanged **3** (40.1 mg) and an amorphous powder (15.8 mg). $[\alpha]_D^{27}$ − 35.2° ($CHCl_3$; *c* 0.79). This compound was identified as **1a** $[\alpha]_D$, IR, EIMS and ^1H NMR).

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