Two Novel Diarylheptanoid Glucosides from *Myrica gale* var. *tomentosa* and Absolute Structure of Plane-Chiral Galeon

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From *Myrica gale* var. *tomentosa*, two new diarylheptanoids, myricatomentosides I and II, were isolated together with a plane-chiral diarylheptanoid, galeon. The absolute stereochemistry of (+)-galeon was determined as *R*. Myricatomentoside I, was identified as the glucoside of myricatomentogenin, a new diarylheptanoid of diphenyl ether type, and myricatomentoside II, as the glucoside of 12-hydroxymyricanone.

Key words myricatomentoside (I and II); galeon; plane-chirality; *Myrica gale* var. *tomentosa*; diarylheptanoid; 12-hydroxymiricanone

Myrica gale L. var. *tomentosa* C. DC. (yachi-yanagi in Japanese, Myricaceae) is distributed in marshlands of Northern Japan, Sakhalin and Eastern Siberia. In a previous paper,[1] we have reported the isolation and structure determination of myricalactone along with some known triterpenoids, serratenedione, serratenediol, myricadiol and so on. In our continuing research on diarylheptanoid components of the plant,[2] we isolated three compounds **1**, **2** and **3**, of which the former two are new glucosides named myricatomentosides I and II.

Compound **3**, $C_{20}H_{22}O_4$, mp 180 °C was isolated from a phenolic fraction of benzene solubles out of the methanolic extract of the branches of the plant. Spectral, physicochemical and chromatographic data, except for rotatory polarization, indicated that **3** is identical with galeon, a diphenyl ether type of diarylheptanoid isolated by Malterud *et al.* from *M. gale*.[3] Compound **3** showed $[\alpha]_D$ +24.9°, while galeon reportedly has $[\alpha]_D$ −16°. Since galeon has no chiral center or chiral axis, but has a chiral plane in the molecule, the opposite sign of their optical rotations indicated that **3** is the enantiomer of (−)-galeon.

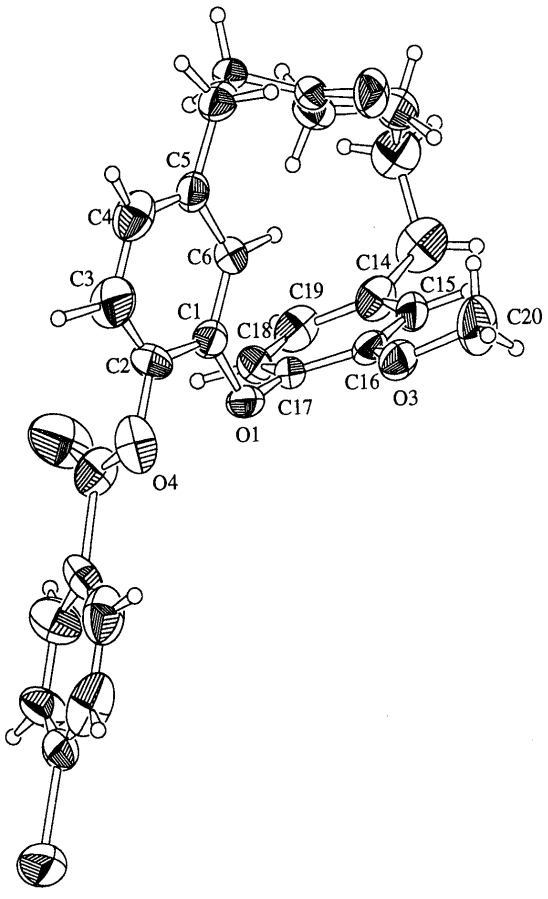
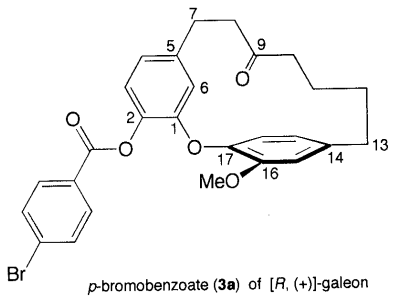


Fig. 1. The Absolute Structure of the *p*-Bromobenzoate (**3a**) of [*R*, (+)]-Galeon

In order to determine the unsolved absolute structure, the *p*-bromobenzoate (**3a**) of (+)-galeon, $C_{27}H_{25}O_5Br$, mp 147 °C, was prepared and subjected to an X-ray crystallographic analysis. The molecular structure, including absolute stereochemistry, is shown in Fig. 1; the chiral plane of (+)-galeon is expressed as *R* (Chart 1).

Compound **1** (myricatomentoside I), $C_{26}H_{32}O_{10}$, $[\alpha]_D$ +8.6°, $FeCl_3$ (+), showed an absorption maximum at 281 nm ($\log\varepsilon = 3.58$) in the UV spectrum. The ^{1}H-NMR spectrum of **1** (methanol-d_4) showed aromatic proton signals consisting of an AB pattern at δ 6.79 and 7.02 (J = 8 Hz) and an ABX pattern at 6.73, 6.57 and 5.56. The unusual high field resonance of the X spin of the latter pattern reminded us of the resonance of 6-H of galeon (**3**)[3] and acerogenin B,[4] both diarylheptanoids of diphenyl ether type.[5] Taking into consideration the chemical shifts of the ABX pattern, we concluded that **1** contains a trisubstituted benzene ring (ring A in Chart 2).

In the ^{13}C-NMR spectrum (pyridine-d_5) of **1**, twenty-six signals were observed, ascribable to a β-D-glucopy-



p-bromobenzoate (**3a**) of [*R*, (+)]-galeon

Chart 1

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ranosyloxy group, two benzene rings (rings A and B in Chart 2), six methylenes, a ketonic carbonyl, and a methoxyl. The ^1H–^1H shift correlated spectroscopy (COSY) and heteronuclear multiple quantum coherence (HMQC) spectra clearly indicated that the heptane chain of **1** consists of an ethylene, a tetramethylene and a carbonyl, in addition to allowing the assignment of chemical shifts of the respective protons and carbons. In the heteronuclear multiple bond connectivity (HMBC) spectrum of **1**, long-range couplings were observed among the four protons at positions 7 and 8 and the two carbons at positions 5 and 9, between one (δ 2.74) of the two protons at position 7 and the carbon at position 6, and between the aromatic proton (δ 7.03 in pyridine-d_5, 7.02 in methanol-d_4) on ring B and the carbon at position 13. These NMR data showed that the carbonyl on the heptane chain of **1** is located at C-9.

Myricatomentoside I (**1**) has two benzene rings (rings A and B), and ring B is a 1,2,3,4-tetrasubstituted benzene, because it has two *ortho*-located protons (*vide supra*). The methoxy group, one of the four substituents on ring B, resonated at δ 61.6, a usual chemical shift for *ortho*-disubstituted anisoles, in the ^{13}C-NMR spectrum (Table 1), and not at around δ 55 (*ortho*-non or monosubstituted anisoles).[6] In the nuclear Overhauser effect (NOE) difference spectra (pyridine-d_5) of **1**, irradiation on the methoxy protons caused NOE at 6-H, but not at any other aromatic or aliphatic protons. Further, irradiation of 6-H caused NOE at the methoxy protons and an aromatic proton resonating at δ 6.86 (6.79 in methanol-d_4). This experiment indicated that 6-H on ring A is located spatially close to both the methoxy protons and the aromatic proton on ring B. This fact, together with positive coloration of the genin (**1a**) of **1** to Gibbs reagent (*vide infra*), excluded the possibility of alternative diphenyl ether systems (C and D in Chart 2) other than a *metapara*-cyclophane system (such as **1** and **3** in Chart 2). At the same time, the methoxy group must be located at C-16: it follows the glucopyranosyloxy group at C-15.

On enzymatic hydrolysis, **1** afforded its genin (named myricatomentogenin) **1a**, $C_{20}H_{22}O_5$, $[\alpha]_D$ $-50°$ and glucose. Compound **1a** showed a positive coloration with Gibbs reagent, while the glucoside **1** itself showed a negative one: thus **1a** is a *para*-nonsubstituted phenol. Myricatomentogenin (**1a**) has a plane-chirality, for it is optically active. We failed to prepare the di-*p*-bromobenzoate of **1a**, but obtained a monoester at the C-2 hydroxyl group.

In conclusion, the structure of myricatomentoside I was determined as **1** (Chart 2), although the absolute stereochemistry of its genin part remained undetermined.

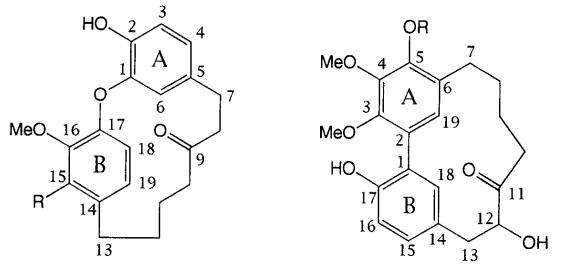
Myricatomentoside II (**2**), $C_{27}H_{34}O_{11}$, mp 150 °C, $[\alpha]_D$ $+31.3°$, gave the genin **2a**, $C_{21}H_{24}O_6$, $[\alpha]_D$ $+15.5°$, on enzymatic hydrolysis. The genin **2a** was identified as 12-hydroxymyricanone, a biphenyl-type diarylheptanoid isolated previously from *M. gale* var. *tomentosa*,[2] by comparison of its TLC behavior, IR spectrum (CCl_4) and ^1H-NMR spectrum with those of an authentic sample, except for rotatory polarization. The binding site of the β-D-glucopyranosyl in **2** was determined to be the C-5 hydroxyl group of **2a**, because the anomeric proton 1′-H of the sugar and C-5 of the genin part were correlated in the HMBC spectrum of **2**, and because the 1′-H and methoxy protons at C-4 showed NOE in the NOE difference spectrum of **2**. Myricatomentoside II is thus 12-hydroxymyricanone 5-*O*-β-D-glucopyranoside (**2** in Chart 2).

In summary, we isolated from the branches of *Myrica gale* var. *tomentosa*, two new diarylheptanoid glucosides,

Table 1. ^{13}C-NMR Chemical Shifts for Compounds **1**, **2** and **3**

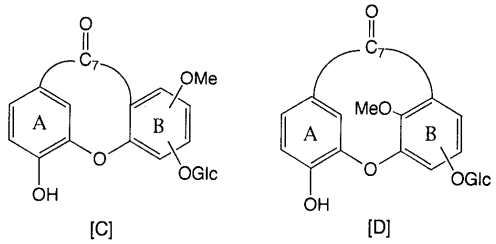
Carbon	**1**[a]	**2**[a]	**3**[b]
1	148.9	127.7	147.4
2	145.7	128.7	143.2
3	117.4	146.3	115.1
4	122.6	149.6[d]	122.0
5	132.8[c]	150.0[d]	133.3
6	114.2	130.5	112.4
7	27.5	29.2	27.5
8	41.1	25.0	41.4
9	209.9	21.1	210.1
10	46.4	43.5	46.3
11	19.8	218.8	19.2
12	25.7	77.6	27.7
13	31.1	40.8	36.0
14	133.1[c]	129.0	140.2
15	150.7	131.7	115.1
16	147.8	116.7	152.3
17	148.9	154.1	143.0
18	120.5	134.3	124.1
19	126.7	129.9	122.1
OCH_3	61.6	61.0	56.1
OCH_3		61.5	
1′	106.1	105.6	
2′	75.8	75.7	
3′	78.7	78.2	
4′	71.6	71.5	
5′	78.7	78.4	
6′	62.6	62.4	

a, *b*) Chemical Shifts (δ: ppm) were measured in pyridine-d_5[a] and in $CDCl_3$[b]. *c*) Assignments of these signals may be interchangeable. *d*) Signals overlapped with pyridine signals.



	R
myricatomentoside I (1)	O-β-D-glc (p)
myricatomentogenin (1a)	OH
galeon (3)	H

	R
myricatomentoside II (2)	β-D-glc (p)
12-hydroxymyricanone (2a)	H



[C] [D]

Chart 2

myricatomentosides I and II, together with a plane-chiral diarylheptanoid, (+)- galeon. The absolute structure of (+)-galeon was determined as *R*. The structures of the glucosides were identified as **1** and **2** in Chart 2.

Experimental

Instruments and TLC procedures used in this work were essentially the same as described in our previous paper.[2] Circular dichroism (CD) spectra were recorded with a JEOL J-600 spectrometer. NMR spectra were measured with Bruker AM-500 and JEOL LA 400 spectrometers. The Gibbs test was carried out on TLC plates by spraying a 3% solution of 2,6-dibromoquinone chloroimide in MeOH followed by heating at 80 °C. For column chromatography, Chromatorex ODS DM 1020T (Fuji Silysia) and Polyamide C-200 (Wako Pure Chemical) were used. For preparative HPLC, an LC-10AD pump (Shimadzu), RID-6A (Shimadzu) or UV S-310A model II (Soma) detector and YMC-Pack ODS-AQ (20 × 250 mm) or NEOPAK 120-5C18 (10 × 250 mm) column were used.

Extraction and Isolation The phenolic fraction (11 g) obtained in the previous paper[2] was chromatographed with hexane–EtOAc (3 : 2) and benzene–EtOAc (7 : 3) as eluents to afford **3** (30 mg). The H_2O extract (2.5 l) described in the previous paper,[2] was passed through a Polyamide C-200 column. The column was washed with water, and absorbed materials were eluted with 50% aqueous MeOH and MeOH, successively. The 50% aqueous MeOH eluate was concentrated, and the residue was chromatographed with benzene–EtOAc–MeOH (5 : 2 : 1) to give three fractions (A—C). Fraction B was chromatographed on an ODS column with CH_3CN–H_2O–MeOH (1 : 4 : 1) to give four fractions (D—G). From fractions G and E, **1** (10 mg) and a mixture of **2** and minor contaminants were isolated. Compound **2** (10 mg) was purified by preparative HPLC.

Myricatomentoside I (1) White amorphous powder. $[\alpha]_D$ +8.6° (c=0.5, MeOH). $FeCl_3$: positive (dark blue). Gibbs reagent: negative (no coloration). Positive FAB-MS m/z : 505 $[M+H]^+$. HR-FAB-MS m/z: Calcd for $C_{26}H_{32}O_{10}Na$: 527.1893. Found: 527.1900. EIMS m/z (%): 342 (100). HR-MS m/z: Calcd for $C_{20}H_{22}O_5$: 342.1465. Found: 342.1457. UV λ_{max} (MeOH) nm (log ε): 281 (3.58). IR ν_{max} (KBr) cm^{-1}: 3500—3290, 1701, 1589, 1520, 1286, 1072, 891, 829. ^{13}C-NMR (pyridine-d_5): Table 1. ^{1}H-NMR (CD_3OD) δ: 3.82 (3H, s, OMe), 5.56 (1H, d, J=2 Hz, 6-H), 6.57 (1H, dd, J=2, 8 Hz, 4-H), 6.73 (1H, d, J=8 Hz, 3-H), 6.79 (1H, d, J=8 Hz, 18-H), 7.02 (1H, d, J=8 Hz, 19-H). ^{1}H-NMR (pyridine-d_5) δ: 1.68 (1H, m, 12-H), 1.70 (2H, m, 11-H_2), 1.86 (1H, m, 10-H), 2.05 (1H, m, 12-H), 2.21 (1H, m, 10-H), 2.26 (1H, m, 8-H), 2.40 (1H, m, 13-H), 2.45 (1H, m, 8-H), 2.74 (1H, dd, J=7, 16 Hz, 7-H), 3.15 (1H, dd, J=10, 16 Hz, 7-H), 3.84 (1H, m, 13-H), 4.08 (3H, s, OMe), 6.04 (1H, d, J=2 Hz, 6-H), 6.73 (1H, dd, J=2, 8 Hz, 4-H), 6.86 (1H, d, J=8 Hz, 18-H), 7.03 (1H, d, J=8 Hz, 19-H), 7.19 (1H, d, J=8 Hz, 3-H).

Enzymatic Hydrolysis of 1 A mixture of a solution of **1** (5 mg) in MeOH (2 ml), AcOH–AcONa buffer (pH 5.0) (10 ml) and molsin (*Aspergillus saitoi*) (20 mg) in water (5 ml) was incubated at 37 °C for 2 d. The MeOH was removed *in vacuo* and the residue was extracted with EtOAc. The EtOAc extract was washed with H_2O, dried with Na_2SO_4 and concentrated to dryness. The residue was purified by column chromatography with $CHCl_3$–MeOH (20 : 1) to give **1a** (2 mg). The water-soluble part was passed through an Amberlite MB-3 column, and concentrated under reduced pressure. The residue was subjected to TLC with *n*-BuOH–acetone–H_2O (4 : 5 : 1), and identified as glucose. *Rf*: 0.36.

Myricatomentogenin (1a) White amorphous powder. $[\alpha]_D$ −50° (c=0.1, $CHCl_3$). Gibbs reagent: positive (blue). EIMS m/z (%): 342 (100). HR-MS m/z: Calcd for $C_{20}H_{22}O_5$: 342.1467. Found: 342,1468. ^{1}H-NMR (pyridine-d_5) δ: 1.69 (1H, m, 12-H), 1.73 (2H, m, 11-H_2), 1.88 (1H, m, 10-H), 2.01 (1H, m, 12-H), 2.19 (1H, m, 10-H), 2.30 (2H, m, 8-H_2), 2.42 (1H, m, 13-H), 2.74 (1H, dd, J=7, 16 Hz, 7-H), 3.18 (1H, dd, J=10, 16 Hz, 7-H), 3.52 (1H, m, 13-H), 3.77 (3H, s, OMe), 6.05 (1H, d, J=2 Hz, 6-H), 6.64 (1H, d, J=8 Hz, 18-H), 6.74 (1H, dd, J=2, 8 Hz, 4-H), 7.01 (1H, d, J=8 Hz, 19-H), 7.19 (1H, d, J=8 Hz, 3-H). ^{1}H-NMR ($CDCl_3$) δ: 3.93 (3H, s, OMe), 5.47 (1H, s, Ph-OH, disappeared with D_2O), 5.49 (1H, d, J=2 Hz, 6-H), 5.94 (1H, s, Ph-OH, disappeared with D_2O), 6.53 (1H, d, J=8 Hz, 18-H), 6.64 (1H, dd, J=2, 8 Hz, 4-H), 6.84 (1H, d, J=8 Hz, 3-H), 6.91 (1H, d, J=8 Hz, 19-H).

Myricatomentoside II (2) Colorless needles (from MeOH–H_2O), mp 148—150 °C. $[\alpha]_D$ +31.3° (c=0.5, MeOH). Positive FAB-MS m/z: 535 $[M+H]^+$. Negative FAB-MS m/z: 533 $[M-H]^-$. HR-FAB-MS m/z: Calcd for $C_{27}H_{34}O_{11}Na$: 557.1999. Found: 557.2004. EIMS m/z (%): 372 (100), 273 (25). HR-MS m/z: Calcd for $C_{21}H_{24}O_6$: 372.1573. Found: 372.1563. UV λ_{max} (MeOH) nm (log ε): 295 (3.67), 249 (3.99), 213 (4.48). IR ν_{max} (KBr) cm^{-1}: 3500—3255, 1701, 1641, 1589, 1508, 1083, 1043, 895, 820, 810. ^{13}C-NMR (pyridine-d_5): Table 1. ^{1}H-NMR (pyridine-d_5) δ: 1.50 (1H, m, 8-H), 1.97 (3H, m, 9-H_2, 8-H), 3.01 (2H, m, 7, 10-H), 3.14 (1H, dd, J=7, 14 Hz, 13-H), 3.38 (1H, dd, J=12, 17 Hz, 7-H), 3.55 (1H, dd, J=10, 18 Hz, 10-H), 3.72 (1H, d, J=14 Hz, 13-H), 3.85 (3H, s, OMe), 4.05 (3H, s, OMe), 4.30 (4H, m, 2′, 5′-H, 6′-H_2), 4.40 (1H, t, J=8 Hz, 4′-H), 4.78 (1H, dd, J=2, 7 Hz, 12-H), 5.74 (1H, d, J=7 Hz, 1′-H), 6.83 (1H, s, 19-H), 7.08 (1H, d, J=2 Hz, 18-H), 7.15 (1H, d, J=8 Hz, 16-H), 7.22 (1H, dd, J=2, 8 Hz, 15-H), 8.51 (1H, s, Ph-OH).

Enzymatic Hydrolysis of 2 Compound **2** (5 mg) was hydrolyzed as described for hydrolysis of **1**. The aglycone part was purified by column chromatography with hexane–EtOAc (3 : 2) to give **2a** (1 mg). **2a**: white powder, $[\alpha]_D$ +15.5° (c=0.2, $CHCl_3$). ORD (c=0.2, $CHCl_3$) (nm): +21.5° (577), +29.2° (546), +123.3° (435), +492.2° (365). EIMS m/z (%): 372 (M^+, 100), 273 (30). HR-MS m/z: Calcd for $C_{21}H_{24}O_6$: 372.1573. Found: 372.1575. IR ν_{max} (CCl_4) cm^{-1}: 3551, 3531, 3400—3200, 1704, 1230, 1075. ^{1}H-NMR ($CDCl_3$) δ: 3.81 (3H, s, OMe), 3.99 (3H, s, OMe), 4.38 (1H, ddd J=2, 6, 8 Hz, 12-H), 6.47 (1H, s, 19-H), 6.68 (1H, d, J=2 Hz, 18-H), 6.93 (1H, d, J=8 Hz, 16-H), 7.08 (1H, dd, J=2, 8 Hz, 15-H). Compound **2a** was identified as 12-hydroxymyricanone[2] on the basis of co-TLC, IR and ^{1}H-NMR spectral comparison with an authentic sample. TLC: *Rf* 0.38 {$CHCl_3$–MeOH (30 : 1)}, *Rf* 0.34 {hexane–EtOAc (1 : 1)}. Glucose was identified by TLC as the sugar in the water soluble part of the hydrolysis products. TLC: *Rf* 0.38 {*n*-BuOH–acetone–H_2O (4 : 5 : 1)}.

(+)-Galeon (3) Colorless plates (from hexane–EtOAc), mp 178—180 °C (lit. mp 179—181 °C).[3] $[\alpha]_D$ +24.9° (c=1.4, $CHCl_3$). EIMS m/z (%): 326 (M^+, 100), 162 (10), 147 (10), 137(10), 121 (20). HR-MS m/z: Calcd for $C_{20}H_{22}O_4$: 326.1516. Found: 326.1513. UV λ_{max} (MeOH) nm (log ε): 280 (3.81), 204 (4.73). CD (c=3.46 × 10^{-5}, MeOH) $\Delta\varepsilon$ (nm): +6.6 (280), 0 (256), −2.3 (250), 0 (244), +38.5 (228), 0 (218), −67.4 (203). IR ν_{max} (KBr) cm^{-1}: 3355, 1701, 1599, 1519, 1514, 1271, 887, 821. ^{1}H-NMR ($CDCl_3$) δ: 1.57 (3H, m, 10, 11, 12-H), 1.68 (1H, m, 12-H), 1.86 (1H, m, 10-H), 2.25 (1H, m, 8-H), 2.36 (1H, m, 8-H), 2.64 (1H, m, 13-H), 2.71 (1H, m, 7-H), 2.84 (1H, m, 13-H), 2.99 (1H, m, 7-H), 3.72 (3H, s, OMe), 5.56 (1H, d, J=2 Hz, 6-H), 5.66 (1H, s, Ph-OH), 6.61 (1H, dd, J=2, 8 Hz, 4-H), 6.83 (1H, d, J=8 Hz, 3-H), 6.87 (1H, d, J=2 Hz, 15-H), 6.88 (1H, dd, J=2, 8 Hz, 19-H), 7.02 (1H, d, J=8 Hz, 18-H). ^{13}C-NMR: Table 1. Compound **3** was identified as galeon on the basis of co-TLC, MS, IR and ^{1}H-NMR spectral comparison with an authentic sample.

(+)-Galeon *p*-Bromobenzoate (3a) *p*-Bromobenzoyl chloride (30 mg) was added to a solution of **3** (3 mg) in pyridine (2 ml), and the mixture was stirred at room temperature overnight. The solvent was removed *in vacuo* and the residue was extracted with EtOAc. The EtOAc extract was washed with H_2O, dried with Na_2SO_4 and concentrated to dryness. The residue was purified by column chromatography with hexane–EtOAc (8 : 2) to give **3a** (3 mg), colorless plates (from MeOH), mp 146—147 °C. EIMS m/z (%): 510 (20), 508 (20), 326 (30), 185 (100), 183 (100). UV λ_{max} (MeOH) nm (log ε): 273 (3.77), 245 (4.29), 202 (4.70). CD (c=2.22 × 10^{-5}, MeOH) $\Delta\varepsilon$ (nm): +6.3 (271), 0 (253), −0.8 (249), 0 (246), +18.3 (230), 0 (217), −47.3 (202). ^{1}H-NMR ($CDCl_3$) δ: 3.77 (3H, s, OMe), 5.69 (1H, d, J=2 Hz, 6-H), 6.74 (1H, dd, J=2, 8 Hz, 4-H), 6.83 (1H, dd, J=2, 8 Hz, 19-H), 6.86 (1H, d, J=2 Hz, 15-H), 7.01 (1H, d, J=8 Hz, 2-H), 7.03 (1H, d, J=8 Hz, 18-H), 7.64 , 8.13 (each 2H, d, J=9 Hz, benzoyl-H_4).

X-Ray Crystallographic Analysis[7] of 3a Crystals were grown from MeOH as colorless plates (mp 146—147 °C). Crystal data: $C_{27}H_{25}O_5Br$, orthorhombic, space group $P2_12_12_1$, a=13.525(1), b=22.998(2), c=7.8057(8) Å, V=2427.9(3) Å^3, Z=4, Dc=1.393 g cm^{-3}, F(000)=1048, μ (CuK_α)=26.00 cm^{-1}. The diffraction intensities were collected at 20 °C on a Rigaku AFC-7R diffractometer using graphite-monochromated CuK_α radiation. The structure was solved by the direct method using MULTAN88[8] and DIRDIF92[9] and refined finally with anisotropic thermal parameters for non-hydrogen atoms. The R (Rw) value was 8.4 (11.3) % after a final least-squares calculation done for 2884 reflections including the Bijvoet pairs when the initial structure was chosen, but this value was reduced to 7.4 (9.8) % when the antipodal (correct) structure was chosen. Moreover, the absolute structure was confirmed by comparison of the observed intensity ratios of the Bijvoet pairs with the calculated values.

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5) The main planes of the two aryl rings in the *p*-bromobenzoate of galeon are set at 83° to each other, and the torsion angle C_6–C_1–O_1–C_{17} is −14.4°. The aromatic hydrogen H-6 on ring A is located above the plane of the neighboring aromatic ring B and thus experiences a strong upfield shift due to anisotropy of the aromatic ring B.
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