Total Synthesis of Dictamnol, a Trinor-Guaiane Type Sesquiterpene from the Roots of *Dictamnus dasycarpus* TURCZ.

Takeshi KOIKE,* Katsuya YAMAZAKI, Naoko FUKUMOTO, Kayoko YASHIRO, Naoki TAKEUCHI, and Seisho TOBINAGA

Showa College of Pharmaceutical Sciences, Higashitamagawagakuen, Machida-shi, Tokyo 194, Japan.
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Dictamnol (1), a trinor-guaiane type sesquiterpene from the roots of *Dictamnus dasycarpus* TURCZ., was synthesized from 4α-acetoxy-3,4,4a,5,6,8aβ-hexahydro-4aα-methyl-2*H*,8*H*-naphthalene-1,7-dione (3) by the utilization of an intramolecular base-induced rearrangement with sodium *tert*-amylate as a key step (27→28). Compound 3 was prepared from a chiral dione, (*S*)-3,4,8,8a-tetrahydro-8aα-methyl-2*H*,7*H*-naphthalene-1,6-dione (2) according to the procedure of de Groot *et al.* [*J. Org. Chem.*, 48, 4380 (1983)] and was transformed into dictamnol (1) *via* 22, 23, 24, 26, 27, 28, and 30. Thus, the absolute configuration of dictamnol is as represented by formula 1.

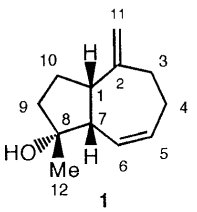
Key words *Dictamnus dasycarpus*; dictamnol; trinor-guaiane type sesquiterpene; synthesis; absolute configuration

In the previous paper,[1] we reported the isolation and structural elucidation of dictamnol, a trinor-guaiane type sesquiterpene, from the roots of *Dictamnus dasycarpus* TURCZ. (Japanese name: Hakusen-pi; Rutaceae). The structure of dictamnol was concluded to be 8α-methyl-2-methylene-1α,7α-bicyclo[3.5.0]dec-5-en-8β-ol (**1**) mainly on the basis of spectroscopic analyses. We next sought to synthesize **1**, starting from a chiral dione, (*S*)-3,4,8,8a-tetrahydro-8aβ-methyl-2*H*,7*H*-naphthalene-1,6-dione (**2**), $[\alpha]_D$ +70.2° (c=0.9, chloroform),[2] which was transformed successively into **3**,[3] **4**,[4] and **5**[5] according to the procedures of de Groot *et al.* (Chart 1).

We first, attempted to synthesize dictamnol (**1**) from the easily obtainable perhydroazulene **7**, followed by suitable dehydration reaction (Chart 2). That is, the tosylate **4** was reduced with $NaBH_4$ in methanol to give the diol **6**, mp 144—146 °C (dec.) (94.7% yield), which was treated with sodium *tert*-amylate in benzene to afford the perhydroazulene **7**, mp 133—135 °C, *via* intramolecular base-induced rearrangement[4,5] in 90.9% yield.

The target compound, dictamnol (**1**), is simply a dehydration product of **7**. Therefore, **7** was transformed into the mesylate **8** (92.1% yield) with methanesulfonyl chloride (MsCl) in pyridine for dehydration reaction. Treatment of **8** with sodium *tert*-amylate did not afford the desired compound, but gave only the bond cleavage compound **9** (63.9% yield). Next, the Bamford–Stevens reaction[6] was tried. That is, **7** was oxidized with Jones' reagent to yield the hemiketal **10**, mp 65—67 °C (98.3% yield), and then **10** was treated with *p*-toluenesulfonyl hydrazide and sodium hydride in tetrahydrofuran (THF) to afford a hydrazine **11**, mp 133—135 °C in 69.4% yield. Treatment of the hydrazine **11** with methyllithium in the presence of *N*,*N*,*N*′,*N*′-tetramethylenediamine (TMEDA) in THF afforded a dehydration product **12**, a double bond isomer of dictamnol **1**, in 38.5% yield. The structure of **12** was determined from the presence of the cross-peaks due to the vicinal couplings between a proton on C(6) and the protons of C(5), C(6), and C(7) in the ^1H–^1H correlation spectroscopy (COSY) spectrum.

An alternative dehydration reaction through dehydrochlorination of the chloride **16** was explored. Compound **7** was treated with *tert*-butyldimethylsilyl chloride (TBDMSCl) and imidazole in *N*,*N*-dimethylformamide (DMF) to yield the silyl ether **13** (84.4% yield), which was acetylated with acetic anhydride and 4-(*N*,*N*-dimethyl-



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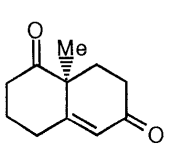

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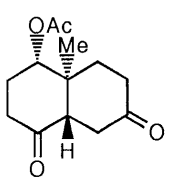

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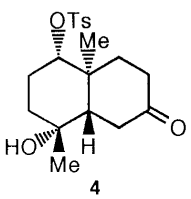

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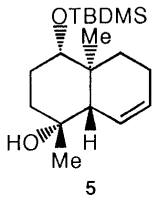

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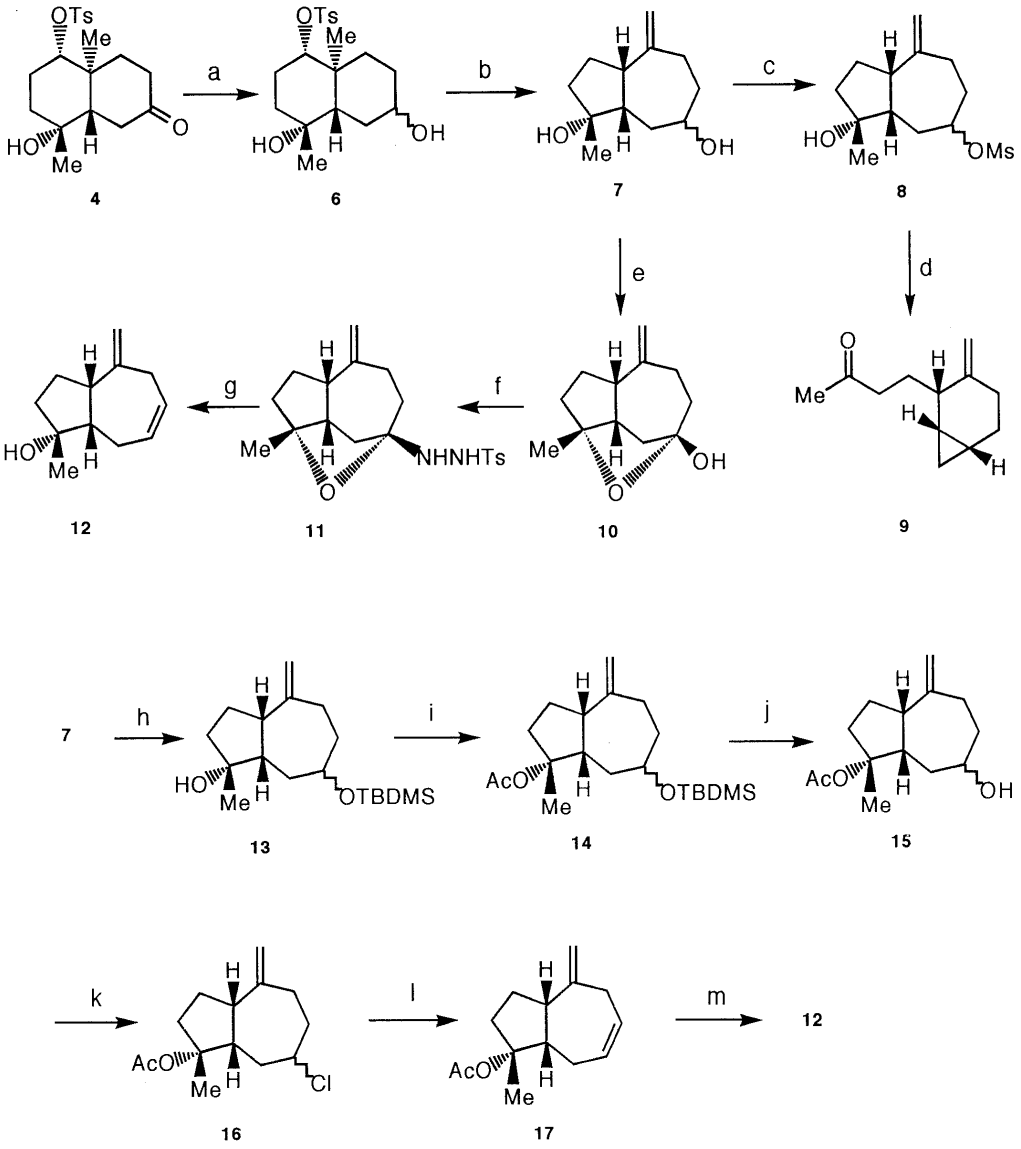
Chart 1

* To whom correspondence should be addressed.

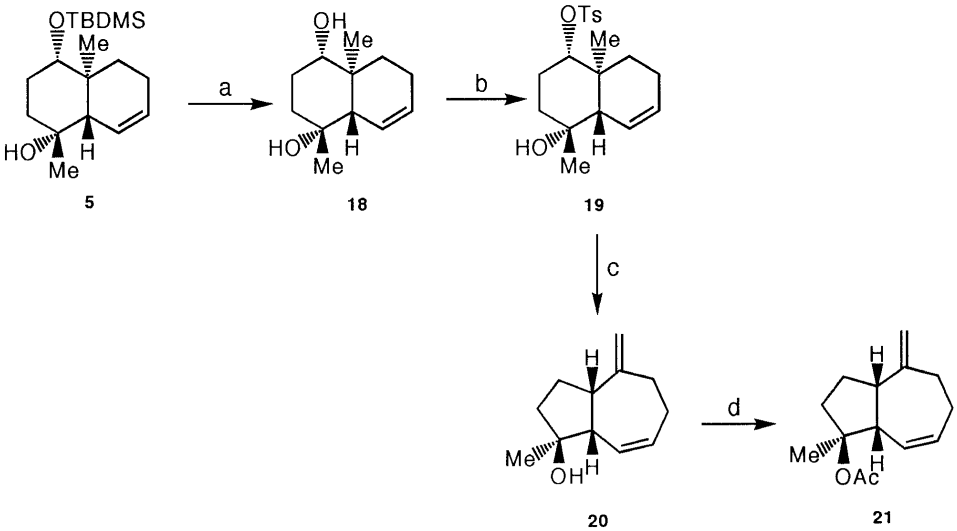


a) $NaBH_4$, MeOH; b) Na *tert*-amylate, benzene; c) MsCl, pyridine; d) Na *tert*-amylate, toluene; e) Jones' reagent, acetone; f) *p*-$TsNHNH_2$, NaH, THF; g) MeLi, TMEDA, THF; h) TBDMSCl, imidazole, DMF; i) Ac_2O, Et_3N, DMAP; j) $Bu_4N^+F^-$, THF; k) $POCl_3$, pyridine; l) DBU; m) MeONa, MeOH

Chart 2

amino)pyridine (DMAP) in triethylamine to give the acetate **14** in 74.3% yield. Desilylation of **14** with tetrabutylammonium fluoride ($(Bu)_4N^+F^-$) in THF afforded the alcohol **15** (95.2% yield), which was transformed into the chloride **16**, mp 105—107 °C (62.3% yield) by chlorination with phosphorus oxychloride in pyridine. Thus, the chloride **16** was treated with 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) to yield **17** (62.8% yield), which was hydrolyzed with sodium methoxide in methanol to give **12** (73.3% yield), the same double bond isomer of dictamnol (**1**) that had been obtained by the above methods.

Further, we attempted to synthesize **1** through formation of the tosylate **19**, followed by intramolecular base-induced rearrangement with sodium *tert*-amylate as shown in Chart 3. The monoene **5** gave the alcohol **18**, mp 109—111 °C (94.3% yield) on treatment with $(Bu)_4N^+F^-$ in THF, and this product was transformed into the tosylate **19**, mp 93—95 °C (96.0% yield) by treatment with TsCl in pyridine. The tosylate **19** was rearranged to the perhydroazulene **20** (75.6% yield) by treatment with sodium *tert*-amylate in benzene, and the acetylation of **20** with acetic anhydride and DMAP in triethylamine gave the acetate **21** in 64.4% yield. The ^1H- and ^{13}C-NMR spectra of dictamnol were unfortunately not identical with those of compound **20**, a stereoisomer of **1** at C(8), prepared by the present method. In particular, the nuclear Overhauser and exchange spectroscopy (NOESY) spectrum of **20** showed the presence of cross-peaks between the proton of C(1) and the proton of C(7) and between



a) $Bu_4N^+F^-$, THF; b) *p*-TsCl, pyridine; c) Na *tert*-amylate, benzene; d) Ac_2O, Et_3N, DMAP

Chart 3

the protons of C(12) and the protons of C(7) and C(11), and did not show the presence of a cross-peak between the proton of C(1) and the protons of C(12), indicating that the protons of C(1) and C(7) are in *cis*-configuration and the methyl group and the proton of C(1) are in *trans*-configuration. Therefore, the structure of **20** is represented by the formula **20**, a stereoisomer of dictamnol (**1**) at C(8). Presumably because of the steric interaction arising from the presence of the double bond in a six-membered ring, the rearrangement of **19** proceeded with inversion between C(1) and C(7) of **20**.

Subsequently, we examined a new synthetic plan for compound **1**, consisting of preparation of the tosylate **27** starting from the diketone **3**, followed by base-catalyzed rearrangement to give the perhydroazulene **28** and C-methylation of the ketone **30** to afford the final product **1**, as shown in Chart 4. The diketone **3** was transformed into the alcohol **22**, mp 143—146 °C (80.3% yield) by treatment with sodium methoxide in methanol and **22** was tosylated with *p*-TsCl in pyridine to give **23**, mp 132—135 °C (dec.) in 92.8% yield. Reduction of **23** with $NaBH_4$ in methanol afforded two alcohols **24**, an oil, and **25**, mp 136—138 °C (dec.), in 74.0% and 20.6% yields, respectively. Oxidation of **25** with Jones' reagent gave the diketone **23** in 82.5% yield. The structure of the alcohol **24** was confirmed by its transformation into the diol **6**, mp 144—146 °C (dec., 82.4% yield) on treatment with methyllithium in THF. This product was identical with the compound **6** described previously. Compound **24** was mesylated with MsCl in pyridine to give **26** (96.5% yield), which was reduced with $NaBH_4$ in methanol to afford the alcohols **27** [α-OH : β-OH (8 : 1)] in 98.6% yield. The alcohols **27** were transformed into the new perhydroazulenes **28** (40.2% yield) and **29** (28.0% yield) by treatment with sodium *tert*-amylate in benzene. Compound **28** was oxidized to the ketone **30** with Jones' reagent in 71.5% yield. Finally, reaction of **30** with methylmagnesium iodide in ether afforded the desired trinor-guaiane sesquiterpene alcohol, dictamnol (**1**), mp 72—73 °C, $[\alpha]_D$ +36.3° (*c* = 0.4, MeOH) (53.1% yield) and acetylation of **1** with acetic anhydride and DMAP in triethylamine gave the acetate **31** in 74.3% yield. The spectroscopic data for this synthetic **1** were identical with those for the natural product.[1)]

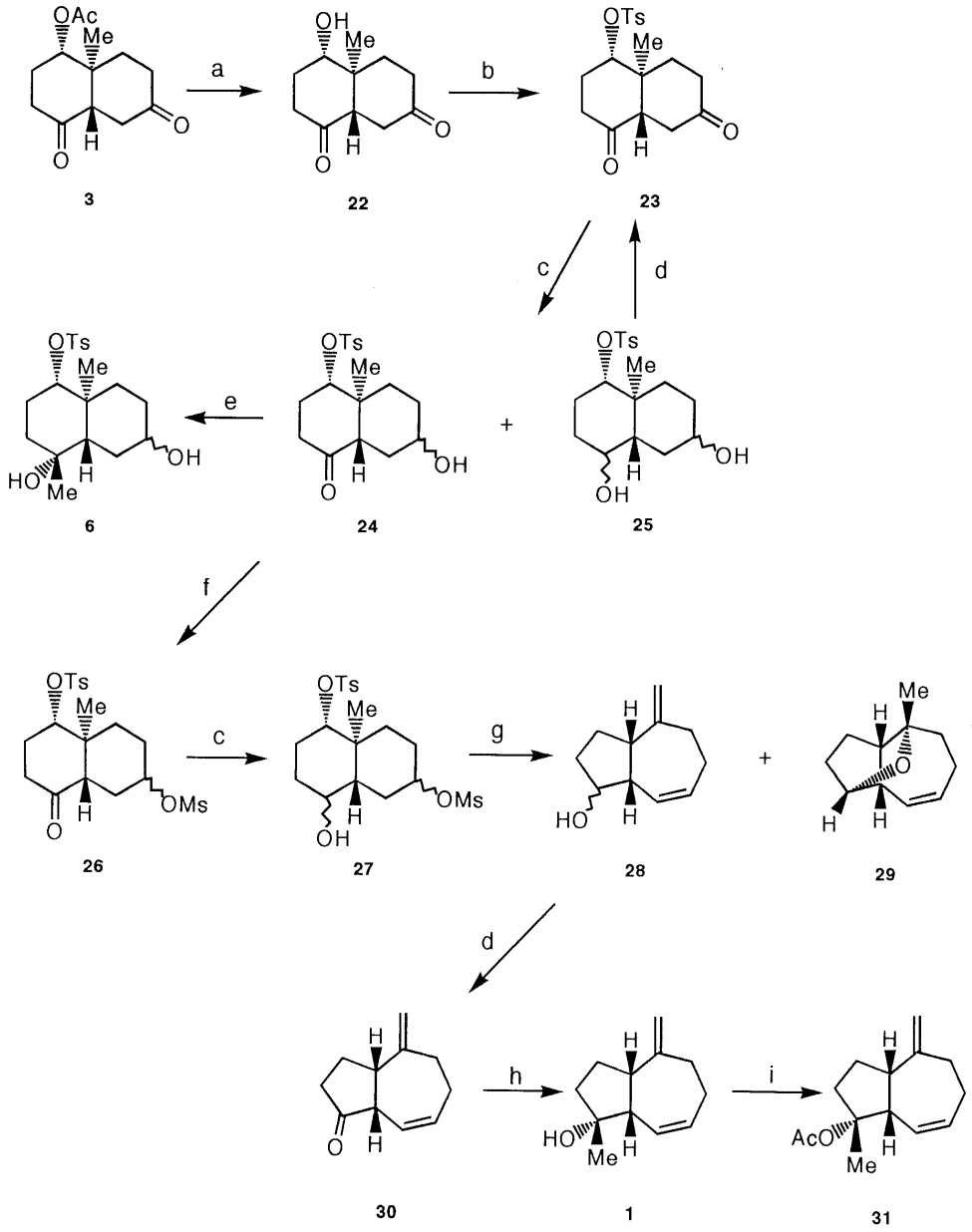
In conclusion, dictamnol (**1**) was synthesized from the chiral dione **2** *via* **3**, **22**, **23**, **24**, **26**, **27**, **28**, and **30**, as shown in Chart 4. Thus, the absolute configuration of **1** was demonstrated to be 1*S*, 7*S*, and 8*R*.

Experimental

All melting points were determined on a Yanagimoto melting point apparatus and are uncorrected. IR spectra were recorded with a JASCO FT/IR-200 or JASCO FT/IR-8000 spectrometer, and ^{1}H- and ^{13}C-NMR spectra with a JEOL EX-90 or JEOL JNM-α500 spectrometer with tetramethylsilane as an internal standard. ^{1}H–^{1}H, ^{1}H–^{13}C, and ^{1}H–^{1}H long-range COSY and NOESY spectra were obtained with the usual pulse sequence and data processing was performed with the standard JEOL software. MS were recorded with a JEOL JMS-D 300 spectrometer. Elemental analyses were done by Kissei Pharmaceutical Company, Ltd., Matsumoto, Japan. Wakogel C-200 (silica gel) and Merck Kieselgel G nach Stahl (silica gel) were used for column chromatography and thin layer chromatography (TLC), respectively.

1,2,3,4,4a,5,6,7,8,8aβ-Decahydro-1β,4aα-dimethylnaphthalene-1α,4α,7-triol 4-(4′-Methylbenzenesulfonate) (6) $NaBH_4$ (76 mg) was added to a solution of **4**[4)] (200 mg) in methanol (5 ml) and the mixture was stirred at room temperature for 1 h, then poured into ice-water and extracted with ethyl acetate. The organic layer was washed with saturated NaCl, then dried and evaporated. The residue was subjected to silica gel column chromatography. The eluate with 10% methanol in chloroform gave 190.4 mg (94.7%) of **6** as colorless needles (chloroform), mp 144—146 °C (dec.). IR ν_{max}^{KBr} cm^{-1}: 3393, 1599. ^{1}H-NMR (90 MHz, CD_3OD) δ: 1.07 (3H, s, 4a-Me), 1.09 (3H, s, 1-Me), 1.15—1.82 (11H, m, 8a-H, 2,3,5,6,8-H_2), 2.44 (3H, s, 4′-Me), 3.54 (1H, m, 7-H), 4.16 (1H, m, 4-H), 7.41 (2H, d, *J* = 8.2 Hz, 3′,5′-H), 7.78 (2H, d, *J* = 8.2 Hz, 2′,6′-H). CI-MS *m/z*: 197 ($M^+ + 1 - TsOH$).

8β-Methyl-2-methylene-1β,7β-bicyclo[3.5.0]decane-5,8α-diol (7) Sodium hydride (240 mg) was added to a solution of dry *tert*-amyl alcohol (1.1 ml) in dry benzene (15 ml). The solution was refluxed for 45 min, then allowed to come to room temperature, and a solution of **6** (720 mg) in dry benzene (15 ml) was added. The mixture was refluxed for 2 h under



a) MeONa, MeOH; b) *p*-TsCl, pyridine; c) $NaBH_4$, MeOH; d) Jones' reagent, acetone; e) MeLi, THF; f) MsCl, pyridine; g) Na *tert*-amylate, benzene; h) MeMgI, ether; i)Ac_2O, Et_3N, DMAP

Chart 4

a nitrogen atmosphere, then poured into 10% HCl at 0 °C and extracted with ether. The organic layer was washed with saturated NaCl, then dried and evaporated. The residue was subjected to silica gel column chromatography. The eluate with 25% hexane in ethyl acetate gave 349 mg (90.9%) of **7** as colorless needles (ether), mp 133—135 °C. IR ν_{max}^{KBr} cm^{-1}: 3375, 1637. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.30 (3H, s, 8-Me), 1.42 (1H, m, 4-H), 1.49 (1H, m, 6-H), 1.58 (1H, m, 10-H), 1.69 (3H, m, 6,9,10-H), 1.87 (1H, m, 3-H), 1.91 (1H, m, 9-H), 1.96 (1H, m, 1-H), 2.08 (1H, m, 4-H), 2.48 (1H, ddd, J=13.4, 6.1, 3.3 Hz, 3-H), 2.73 (1H, dd, J=18.1, 10.5 Hz, 7-H), 3.72 (1H, tdd, J=9.7, 3.9, 2.6 Hz, 5-H), 4.84 (1H, s, 11-H), 4.88 (1H, s, 11-H). ^{13}C-NMR (500 MHz, $CDCl_3$) δ: 27.1 (C9), 27.4 (C12), 33.7 (C3), 34.9 (C6), 39.5 (C4), 40.9 (C10), 48.2 (C1), 48.5 (C7), 73.8 (C5), 80.6 (C8), 110.1 (C11), 150.0 (C2). HREI-MS m/z Calcd for $C_{12}H_{20}O_2$ (M^+): 196.1460. Found: 196.1455. *Anal.* Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.18; H, 10.22.

8β-Methyl-2-methylene-1β,7β-bicyclo[3.5.0]decane-5,8α-diol 5-Methanesulfonate (8) MsCl (45.6 mg) was added to a solution of **7** (20 mg) in dry pyridine (1 ml) and the mixture was stirred at 40 °C for 2.5 h, then poured into 10% HCl and extracted with dichloromethane. The organic layer was washed with saturated $NaHCO_3$ and NaCl, then dried and evaporated. The residue was subjected to silica gel column chromatography. The eluate with 25% hexane in ethyl acetate gave 25.7 mg (92.1%) of **8** as a colorless oil. IR ν_{max}^{neat} cm^{-1}: 3449, 1736, 1650. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.32 (3H, s, 8-Me), 1.60—2.03 (9H, m, 1,3,4-H, 6,9,10-H_2), 2.25 (1H, m, 4-H), 2.54 (1H, ddd, J=14.0, 6.7, 3.7 Hz, 3-H), 2.74 (1H, m, 7-H), 3.00 (3H, s, 5-OSO_2Me), 4.74 (1H, m, 5-H), 4.89 (1H, s, 11-H), 4.95 (1H, s, 11-H). CI-MS m/z: 275 (M^++1).

4-(3′-Methylene-1′β,6′β-bicyclo[1.4.0]hept-2′α-yl)butan-2-one (9) Sodium hydride (12 mg) was added to a solution of dry *tert*-amyl alcohol (54 μl) in dry toluene (2 ml). The solution was refluxed for 30 min, then allowed to come to room temperature, and a solution of **8** (15 mg) in dry toluene (1 ml) was added. The mixture was refluxed for 2 h under a nitrogen atmosphere, then poured into 10% HCl at 0 °C and extracted with ethyl acetate. The organic layer was washed with saturated NaCl, then dried and evaporated. The residue was subjected to silica gel column

chromatography. The eluate with 25% hexane in ethyl acetate gave 6.2 mg (63.9%) of **9** as a colorless oil. IR ν_{max}^{neat} cm^{-1}: 1716, 1649. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 0.11 (1H, m, 7′-H), 0.41 (1H, m, 7′-H), 0.97—1.08 (2H, m, 1′,6′-H), 1.71—1.78 (3H, m, 4-H, 3-H_2), 1.89—1.98 (3H, m, 4-H, 4′-H_2), 2.16 (3H, s, 1-H_3), 2.48—2.61 (3H, m, 2′-H, 5′-H_2), 4.59 (1H, s, 1″-H), 4.71 (1H, s, 1″-H). ^{13}C-NMR (500 MHz, $CDCl_3$) δ: 5.7 (C7′), 10.7 (C1′), 16.8 (C6′), 26.5 (C4), 27.7 (C3), 29.9 (C1), 30.1 (C4′), 38.3 (C2′), 41.7 (C5′), 108.5 (C1″), 149.7 (C3′), 209.4 (C2). HREI-MS *m/z* Calcd for $C_{12}H_{18}O$ (M^+): 178.1358. Found: 178.1375.

5α,8α-Epoxy-8β-methyl-2-methylene-1β,7β-bicyclo[3.5.0]decan-5β-ol (10) Jones' reagent (150 μl) [obtained by adding water (6 ml) to a mixture of CrO_3 (2.67 g) and concentrated H_2SO_4 (2.3 ml)] was added to a solution of **7** (80 mg) in acetone (15 ml) and the mixture was stirred at 10—15 °C for 1 h, then poured into ice-water and extracted with chloroform. The organic layer was washed with saturated $NaHCO_3$ and NaCl, then dried and evaporated. The residue was subjected to silica gel column chromatography. The eluate with 17% hexane in ethyl acetate gave 77.8 mg (98.3%) of **10** as colorless needles (hexane–ether), mp 65—67 °C. IR ν_{max}^{KBr} cm^{-1}: 3414, 1635. ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 1.41 (3H, s, 8-Me), 1.64—3.15 (12H, m, 1,7-H, 3,4,6,9,10-H_2), 4.74 (1H, s, 11-H), 4.76 (1H, s, 11-H). HREI-MS *m/z* Calcd for $C_{12}H_{18}O_2$ (M^+): 194.1304. Found: 194.1292.

***N*-(5α,8α-Epoxy-8β-methyl-2-methylene-1β,7β-bicyclo[3.5.0]dec-5β-yl)-*N*′-(4′-methylbenzenesulfonyl)hydrazine (11)** Sodium hydride (4 mg) was added to a solution of *p*-$TsNHNH_2$ (30 mg) in dry THF (3 ml). The solution was stirred at room temperature for 45 min and then **10** (20 mg) was added. The mixture was stirred at room temperature for 2 h, then poured into water and extracted with chloroform. The organic layer was washed with saturated NaCl, then dried and evaporated. The residue was subjected to silica gel column chromatography. The eluate with 5% methanol in chloroform gave 25.6 mg (69.4%) of **11** as colorless needles (chloroform), mp 133—135 °C. IR ν_{max}^{KBr} cm^{-1}: 3310, 3244, 1630, 1600. ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 1.39 (3H, s, 8-Me), 1.52—3.15 (12H, m, 1,7-H, 3,4,6,9,10-H_2), 2.42 (3H, s, 4′-Me), 3.70 (1H, br, 5-NH), 4.69 (2H, s, 11-H), 6.03 (1H, br, 1′-NH), 7.30 (2H, d, J=7.4 Hz, 2′,6′-H), 7.77 (2H, d, J=7.4 Hz, 3′,5′-H). CI-MS *m/z*: 363 ($M^+ + 1$).

8β-Methyl-2-methylene-1β,7β-bicyclo[3.5.0]dec-4-en-8α-ol (12) A solution of 1.2 M MeLi in ether (0.6 ml) was added to a solution of **11** (20 mg) and TMEDA (174 mg) in dry THF (2 ml) with stirring at −78 °C under a nitrogen atmosphere and the mixture was stirred for 1.5 h under the same conditions, then poured into saturated NH_4Cl and extracted with ethyl acetate. The organic layer was washed with saturated NaCl, then dried and evaporated. The residue was subjected to silica gel column chromatography. The eluate with 40% ethyl acetate in hexane gave 3.7 mg (38.5%) of **12** as a colorless oil. IR ν_{max}^{neat} cm^{-1}: 3420, 1643. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.28 (3H, s, 8-Me), 1.61 (1H, m, 10-H), 1.73—1.85 (2H, m, 9,10-H), 1.94—2.04 (2H, m, 6,9-H), 2.17 (1H, m, 6-H), 2.23 (1H, m, 1-H), 2.88 (1H, d, J=18.0 Hz, 3-H), 2.90 (1H, dd, J=18.0, 9.5 Hz, 7-H), 3.06 (1H, dd, J=18.0, 2.1 Hz, 3-H), 4.88 (1H, s, 11-H), 4.94 (1H, s, 11-H), 5.49 (1H, m, 4-H), 5.71 (1H, m, 5-H). ^{13}C-NMR (500 MHz, $CDCl_3$) δ: 22.9 (C6), 26.7 (C9), 27.3 (C12), 40.7 (C3), 41.0 (C10), 47.6 (C7), 53.4 (C1), 80.7 (C8), 110.6 (C11), 128.2 (C4), 128.5 (C5), 149.0 (C2). CI-MS *m/z*: 179 ($M^+ + 1$).

5-(*tert*-Butyldimethylsilyloxy)-8β-methyl-2-methylene-1β,7β-bicyclo-[3.5.0]decan-8α-ol (13) TBDMSCl (280 mg) and imidazole (250 mg) was added to a solution of **7** (260 mg) in dry DMF (5 ml) and the mixture was stirred at room temperature for 1 h, then poured into 10% HCl and extracted with chloroform. The organic layer was washed with saturated NaCl, then dried and evaporated. The residue was subjected to silica gel column chromatography. The eluate with 5% MeOH in chloroform gave 350.6 mg (84.4%) of **13** as a colorless oil. IR ν_{max}^{neat} cm^{-1}: 3396, 1660. ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 0.06 (6H, s, 5-OSi$\underline{Me}_2$$CMe_3$), 0.89 (9H, s, 5-OSi$Me_2$$\underline{CMe}_3$), 1.29 (3H, s, 8-Me), 1.56—2.91 (12H, m, 1,7-H, 3,4,6,9,10-H_2), 3.73 (1H, m, 5-H), 4.80 (1H, s, 11-H), 4.82 (1H, s, 11-H). CI-MS *m/z*: 311 ($M^+ + 1$).

8α-Acetoxy-5-(*tert*-butyldimethylsilyloxy)-8β-methyl-2-methylene-1β,7β-bicyclo[3.5.0]decane (14) Compound **13** (280 mg) was added to a solution of acetic anhydride (0.5 ml) and DMAP (20 mg) in triethylamine (0.9 ml) and the mixture was stirred at room temperature for 1 d, then poured into 10% HCl and extracted with ether. The organic layer was washed with saturated $NaHCO_3$ and NaCl, then dried and evaporated. The residue was subjected to silica gel column chromatography. The eluate with 13% ethyl acetate in hexane gave 262 mg (74.3%) of **14** as a colorless oil. IR ν_{max}^{neat} cm^{-1}: 1736, 1610. ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 0.05 (6H, s, 5-OSi$\underline{Me}_2$$Me_3$), 0.88 (9H, s, 5-OSi$Me_2$$\underline{CMe}_3$), 1.24—2.97 (12H, m, 1,7-H, 3,4,6,9,10-H_2), 1.53 (3H, s, 8-Me), 1.96 (3H, s, 8-OCOMe), 3.64 (1H, m, 5-H), 4.73 (1H, s, 11-H), 4.88 (1H, s, 11-H). CI-MS *m/z*: 353 ($M^+ + 1$).

8α-Acetoxy-8β-methyl-2-methylene-1β,7β-bicyclo[3.5.0]decan-5-ol (15) A solution of 1.0 M $Bu_4N^+F^-$ in THF (0.9 ml) was added to a solution of **14** (250 mg) in dry THF (2 ml) and the mixture was stirred at 50° for 3 h, then poured into water and extracted with chloroform. The organic layer was washed with saturated $NaHCO_3$ and NaCl, then dried and evaporated. The residue was subjected to silica gel column chromatography. The eluate with 25% ethyl acetate in hexane gave 161 mg (95.2%) of **15** as colorless needles (hexane–ether), mp 104—107 °C. IR ν_{max}^{KBr} cm^{-1}: 3300, 1720, 1641. ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 1.22—2.82 (12H, m, 1,7-H, 3,4,6,9,10-H_2), 1.55 (3H, s, 8-Me), 1.96 (3H, s, 8-OCOMe), 3.70 (1H, m, 5-H), 4.78 (1H, s, 11-H), 4.91 (1H, s, 11-H). HREI-MS *m/z* Calcd for $C_{14}H_{22}O_3$ (M^+): 238.1566. Found: 238.1526. *Anal.* Calcd for $C_{14}H_{22}O_3$: C, 70.39; H, 9.47. Found: C, 70.56; H, 9.30.

8α-Acetoxy-5-chloro-8β-methyl-2-methylene-1β,7β-bicyclo-[3.5.0]-decane (16) Phosphorus oxychloride (5.6 μl) was added to a solution of **15** (10 mg) in dry pyridine (1 ml) and the mixture was stirred at 50 °C for 1 h, then poured into 10% HCl and extracted with chloroform. The organic layer was washed with saturated $NaHCO_3$ and NaCl, then dried and evaporated. The residue was subjected to silica gel column chromatography. The eluate with 13% ethyl acetate in hexane gave 6.7 mg (62.3%) of **16** as colorless plates (hexane–ethyl acetate), mp 105—107 °C. IR ν_{max}^{KBr} cm^{-1}: 1734, 1643. ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 1.25—2.98 (12H, m, 1,7-H, 3,4,6,9,10-H_2), 1.56 (3H, s, 8-Me), 1.93 (3H, s, 8-OCOMe), 4.52 (1H, m, 5-H), 4.80 (1H, s, 11-H), 4.91 (1H, s, 11-H). HREI-MS *m/z* Calcd for $C_{14}H_{21}ClO_2$ (M^+): 256.1228, 258.1199. Found: 256.1198, 258.1154.

8α-Acetoxy-8β-methyl-2-methylene-1β,7β-bicyclo[3.5.0]dec-4-ene (17) A solution of **16** (10 mg) in DBU (1 ml) was stirred at 150 °C for 1 d, then poured into 10% HCl and extracted with chloroform. The organic layer was washed with saturated NaCl, then dried and evaporated. The residue was subjected to silica gel column chromatography. The eluate with 13% ethyl acetate in hexane gave 5.4 mg (62.8%) of **17** as a colorless oil. IR ν_{max}^{neat} cm^{-1}: 1734, 1620. ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 1.25—2.15 (8H, m, 1,7-H, 6,9,10-H_2), 1.25 (3H, s, 8-Me), 1.55 (3H, s, 8-OCOMe), 2.98 (2H, m, 3-H_2), 4.78 (1H, s, 11-H), 4.92 (1H, s, 11-H), 5.50—5.85 (2H, m, 4,5-H). CI-MS *m/z*: 221 ($M^+ + 1$).

Preparation of 12 from 17 A solution of **17** (5 mg) in methanol (0.5 ml) was added to a solution of sodium (0.3 mg) in methanol (1 ml) and the mixture was stirred at room temperature for 1 d, then evaporated and extracted with chloroform. The organic layer was washed with saturated NaCl, then dried and evaporated. The residue was subjected to silica gel column chromatography. The eluate with 14% ethyl acetate in hexane gave 2.5 mg (73.3%) of **12** as a colorless oil. This compound **12** was identical with **12** previously described.

1,2,3,4,4a,5,6,8aβ-Octahydro-1β,4aα-dimethylnaphthalene-1α,4α-diol (18) A solution of 1.0 M $Bu_4N^+F^-$ in THF (0.3 ml) was added to a solution of **5**[5] (62 mg) in THF (2 ml) and the mixture was refluxed for 1 d, then poured into water and extracted with chloroform. The organic layer was washed with saturated $NaHCO_3$ and NaCl, then dried and evaporated. The residue was subjected to silica gel column chromatography. The eluate with 25% hexane in ethyl acetate gave 36.7 mg (94.3%) of **18** as colorless needles (hexane–ether), mp 109—111 °C. IR ν_{max}^{KBr} cm^{-1}: 3385, 1640. ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 1.04 (3H, s, 4a-Me), 1.23 (3H, s, 1-Me), 1.35—2.23 (9H, m, 8a-H, 2,3,5,6-H_2), 3.33 (1H, dd, J=10.5, 4.2 Hz, 4-H), 5.75 (2H, s, 7,8-H). CI-MS *m/z*: 197 ($M^+ + 1$).

1,2,3,4,4a,5,6,8aβ-Octahydro-1β,4aα-dimethylnaphthalene-1α,4α-diol 4-(4′-Methylbenzenesulfonate) (19) *p*-TsCl (420 mg) was added to a solution of **18** (173 mg) in dry pyridine (8 ml) and the mixture was stirred at room temperature for 4 d, then poured into 10% HCl and extracted with chloroform. The organic layer was washed with saturated $NaHCO_3$ and NaCl, then dried and evaporated. The residue was subjected to silica gel column chromatography. The eluate with 25% hexane in ethyl acetate gave 298 mg (96.0%) of **19** as colorless needles (hexane–ethyl acetate), mp 93—95 °C. IR ν_{max}^{KBr} cm^{-1}: 3553, 1599. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.06 (3H, s, 4a-Me), 1.13 (1H, m, 5-H), 1.20 (3H, s, 1-Me), 1.49 (1H, td, J=14.5, 4.9 Hz, 2-H), 1.62 (1H, m, 5-H), 1.68—1.75 (2H, m, 2,3-H), 1.92 (1H, m, 8a-H), 2.00—2.05 (2H, m, 6-H_2), 2.17 (1H, m, 3-H), 2.44 (3H, s, 4′-Me), 4.31 (1H, dd, J=12.0, 4.0 Hz, 4-H), 5.66 (1H, dq, J=10.3,

1.5 Hz, 7-H), 5.77 (1H, m, 8-H), 7.33 (2H, d, J=8.0 Hz, 2′,6′-H), 7.79 (2H, d, J=8.0 Hz, 3′,5′-H). CI-MS m/z: 351 ($M^+ + 1$).

8α-Methyl-2-methylene-1β,7β-bicyclo[3.5.0]dec-5-en-8β-ol (20) Sodium hydride (9.6 mg) was added to a solution of dry *tert*-amyl alcohol (44 μl) in dry benzene (1 ml). The solution was refluxed for 30 min, then allowed to come to room temperature, and a solution of **19** (28 mg) in dry benzene (1 ml) was added. The mixture was refluxed for 1 h under a nitrogen atmosphere, then poured into 10% HCl at 0 °C and extracted with ethyl acetate. The organic layer was washed with saturated NaCl, then dried and evaporated. The residue was subjected to silica gel column chromatography. The eluate with 25% ethyl acetate in hexane gave 11.5 mg (75.6%) of **20** as a colorless oil. IR ν_{max}^{neat} cm^{-1}: 3445, 1725, 1645. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.29 (3H, s, 8-Me), 1.65 (1H, m, 9-H), 1.80 (1H, m, 10-H), 1.89—2.04 (2H, m, 9,10-H), 2.16—2.28 (3H, m, 3-H, 4-H_2), 2.55 (1H, m, 3-H), 2.68 (1H, ddd, J=10.7, 5.6, 1.7 Hz, 7-H), 3.07 (1H, dd, J=10.7, 8.2 Hz, 1-H), 4.76 (1H, s, 11-H), 4.82 (1H, s, 11-H), 5.58 (1H, ddt, J=11.9, 5.6, 1.7 Hz, 6-H), 5.84 (1H, m, 5-H). ^{13}C-NMR (500 MHz, $CDCl_3$) δ: 27.0 (C12), 29.2 (C10), 30.3 (C4), 32.6 (C3), 40.3 (C9), 48.9 (C1), 53.2 (C7), 80.4 (C8), 109.9 (C11), 125.6 (C6), 132.3 (C5), 152.5 (C2). CI-MS m/z: 179 ($M^+ + 1$).

8β-Acetoxy-8α-methyl-2-methylene-1β,7β-bicyclo[3.5.0]dec-5-ene (21) Compound **20** (39.1 mg) was added to a solution of acetic anhydride (1 ml) and DMAP (4 mg) in triethylamine (1.6 ml), and the mixture was stirred at room temperature for 1 d, then poured into 10% HCl and extracted with ethyl acetate. The organic layer was washed with saturated $NaHCO_3$ and NaCl, then dried and evaporated. The residue was subjected to silica gel column chromatography. The eluate with 9% ethyl acetate in hexane gave 31 mg (64.4%) of **21** as a colorless oil. IR ν_{max}^{neat} cm^{-1}: 1735, 1640. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.58 (3H, s, 8-Me), 1.78 (3H, m, 9-H, 10-H_2), 1.98 (3H, s, 8-OCOMe), 2.18 (1H, m, 4-H), 2.31 (1H, m, 4-H), 2.38 (3H, m, 9-H, 3-H_2), 2.98 (2H, s, 1,7-H), 4.74 (1H, s, 11-H), 4.81 (1H, s, 11-H), 5.58 (1H, d, J=11.6 Hz, 6-H), 5.65 (1H, m, 5-H). ^{13}C-NMR (500 MHz) δ: 22.2 (C2′), 23.6 (C12), 26.1 (C10), 29.5 (C4), 33.8 (C3), 36.1 (C9), 47.2 (C1), 51.3 (C7), 89.2 (C8), 109.9 (C11), 126.6 (C6), 129.5 (C5), 151.2 (C2), 170.3 (C1′). HREI-MS m/z Calcd for $C_{14}H_{20}O_2$ (M^+): 220.1525. Found: 220.1532.

3,4,4a,5,6,8aβ-Hexahydro-4aα-methyl-2*H*,8*H*-naphthalene-1,7-dion-4α-ol (22) A solution of **3** (3.1 g), mp 150—152 °C, $[\alpha]_D$ +12.89° (c=0.953, MeOH), prepared from **2** according to the procedure of de Groot *et al.*,[3] in dry methanol (10 ml) was added to a solution of sodium (200 mg) in dry methanol (60 ml). The mixture was stirred at room temperature for 3 h, then poured into water and extracted with methylene chloride. The organic layer was washed with saturated NaCl, then dried and evaporated. The residue was subjected to silica gel column chromatography. The eluate with 25% hexane in ethyl acetate gave 2.05 g (80.3%) of **22** as colorless needles (ethyl acetate), mp 143—146 °C. $[\alpha]_D$ + 0.88° (c=0.826, MeOH). IR ν_{max}^{KBr} cm^{-1}: 3281, 1718, 1710. ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 1.00 (3H, s, 4a-Me), 1.37—2.72 (11H, m, 8a-H, 2,3,5,6,8-H_2), 3.93 (1H, m, 4-H). HREI-MS m/z Calcd for $C_{11}H_{16}O_3$ (M^+): 196.1097. Found: 196.1071.

3,4,4a,5,6,8aβ-Hexahydro-4aα-methyl-2*H*,8*H*-naphthalene-1,7-dion-4α-ol 4-(4′-Methylbenzenesulfonate) (23) *p*-TsCl (2 g) was added to a solution of **22** (1.8 g) in pyridine (20 ml) and the mixture was stirred at room temperature for 4 d, then poured into 10% HCl and extracted with chloroform. The organic layer was washed with saturated $NaHCO_3$ and NaCl, then dried and evaporated. The residue was subjected to silica gel column chromatography. The eluate with 30% hexane in ethyl acetate gave 2.8 g (92.8%) of **23** as colorless needles (hexane–ethyl acetate), mp 132—135 °C. IR ν_{max}^{KBr} cm^{-1}: 1714, 1599. ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 1.02 (3H, s, 4a-Me), 1.45—2.75 (11H, m, 8a-H, 2,3,5,6,8-H_2), 2.46 (3H, s, 4′-Me), 4.71 (1H, m, 4-H), 7.36 (2H, d, J=8.4 Hz, 2′,6′-H), 7.82 (2H, d, J=8.4 Hz, 3′,5′-H). CI-MS m/z: 351 ($M^+ + 1$).

Reaction of 23 with $NaBH_4$ $NaBH_4$ (27 mg) was added to a solution of **23** (1.4 g) in dry methanol (50 ml) and the mixture was stirred at 0 °C for 1 h, then poured into ice-water and extracted with ethyl acetate. The organic layer was washed with saturated NaCl, then dried and evaporated. The residue was subjected to silica gel column chromatography. The eluate with 25% hexane in ethyl acetate gave 1.04 g (74.0%) of 3,4,4a,5,6,7,8,8aβ-octahydro-4aα-methyl-2*H*-naphthalen-1-one-4α,7-diol 4-(4′-methylbenzenesulfonate) (**24**) as a colorless oil. IR ν_{max}^{neat} cm^{-1}: 3410, 1710, 1600. ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 0.83 (3H, s, 4a-Me), 1.12 (11H, m, 8a-H, 2,3,5,6,8-H_2), 2.46 (3H, s, 4′-Me), 3.54 (1H, m, 7-H), 4.70 (1H, dd, J=12.0, 4.0 Hz, 4-H), 7.35 (2H, d, J=8.2 Hz, 2′,6′-H), 7.81 (2H, d, J=8.2 Hz, 3′,5′-H). CI-MS m/z: 353 ($M^+ + 1$). The second eluate with 25% hexane in ethyl acetate gave 292 mg (20.6%) of 1,2,3,4,4a,5,6,7,8,8aβ-decahydro-4aα-methylnaphthalene-1,4α,7-triol 4-(4′-methylbenzenesulfonate) (**25**) as colorless needles (hexane–ethyl acetate), mp 136—138 °C (dec.). IR ν_{max}^{KBr} cm^{-1}: 3385, 1599. ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 1.11 (3H, s, 4a-Me), 1.16—2.25 (11H, m, 8a-H, 2,3,5,6,8-H_2), 2.44 (3H, s, 4′-Me), 3.40—3.81 (2H, m, 1,7-H), 4.22 (1H, dd, J=12.0, 4.0 Hz, 4-H), 7.32 (2H, d, J=8.2 Hz, 2′,6′-H), 7.78 (2H, d, J=8.2 Hz, 3′,5′-H). CI-MS m/z: 183 ($M^+ + 1 - TsOH$).

Preparation of 23 from 25 Jones' reagent (10 ml) was added to a solution of **25** (660 mg) in acetone (60 ml) and the mixture was stirred at room temperature for 20 min, then poured into ice water and extracted with ethyl acetate. The organic layer was washed with saturated $NaHCO_3$ and NaCl, then dried and evaporated. The residue was subjected to silica gel column chromatography. The eluate with 30% hexane in ethyl acetate gave 538 mg (82.5%) of **23** as colorless needles (hexane–ethyl acetate), mp 132—135 °C. This product was identical with **23** previously described.

Preparation of 6 from 24 A solution of 1.2 M MeLi in ether (0.6 ml) was added to a solution of **24** (60 mg) in dry THF (3 ml) and the mixture was stirred at −78 °C for 1 h, then poured into saturated NH_4Cl and extracted with chloroform. The organic layer was washed with saturated NaCl, then dried and evaporated. The residue was subjected to silica gel column chromatography. The eluate with 10% methanol in chloroform gave 57 mg (82.4%) of **6** as colorless needles (chloroform), mp 144—146 °C (dec.). This product was identical with **6** previously described.

3,4,4a,5,6,7,8,8aβ-Octahydro-4aα-methyl-2*H*-naphthalen-1-one-4α,7-diol 7-Methanesulfonate 4-(4′-Methylbenzenesulfonate) (26) MsCl (22 μl) was added to a solution of **24** (50 mg) in dry pyridine (2 ml) and the mixture was stirred at 40 °C for 2 h, then poured into 10% HCl and extracted with chloroform. The organic layer was washed with saturated $NaHCO_3$ and NaCl, then dried and evaporated. The residue was subjected to silica gel column chromatography. The eluate with 30% hexane in ethyl acetate gave 61.3 mg (96.5%) of **26** as a colorless oil. IR ν_{max}^{neat} cm^{-1}: 1725, 1600. ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 0.85 (3H, s, 4a-Me), 1.39—2.42 (11H, m, 8a-H, 2,3,5,6,8-H_2), 2.47 (3H, s, 4′-Me), 3.00 (3H, s, 7-OSO_2Me), 4.36—4.72 (2H, m, 4,7-H), 7.36 (2H, d, J=8.1 Hz, 2′,6′-H), 7.81 (2H, d, J=8.1 Hz, 3′,5′-H). CI-MS m/z: 431 ($M^+ + 1$).

1,2,3,4,4a,5,6,7,8,8aβ-Decahydro-4aα-methylnaphthalene-1,4α,7-triol 7-Methanesulfonate 4-(4′-Methylbenzenesulfonate) (27) $NaBH_4$ (36 mg) was added to a solution of **26** (1.2 g) in dry methanol (40 ml) and the mixture was stirred at room temperature for 1 h, then poured into ice-water and extracted with ethyl acetate. The organic layer was washed with saturated NaCl, then dried and evaporated. The residue was subjected to silica gel column chromatography. The eluate with 30% hexane in ethyl acetate gave 1.2 g (98.6%) of **27** as a colorless oil. IR ν_{max}^{neat} cm^{-1}: 3550, 1600. ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 1.12 (3H, s, 4a-Me), 1.25—2.21 (11H, m, 8a-H, 2,3,5,6,8-H_2), 2.45 (3H, s, 4′-Me), 3.00 (3H, s, 7-OSO_2Me), 3.71 (1H, br, 1-H), 4.17 (1H, m, 4-H), 4.39 (1H, m, 7-H), 7.33 (2H, d, J=8.2 Hz, 2′,6′-H), 7.78 (2H, d, J=8.2 Hz, 3′,5′-H). CI-MS m/z: 337 ($M^+ + 1 - MsOH$).

Reaction of 27 with Sodium *tert*-Amyl Alcohol Sodium hydride (29 mg) was added to a solution of *tert*-amyl alcohol (130 μl) in dry benzene (1 ml). The solution was refluxed for 30 min, and then a solution of **27** (50 mg) in dry benzene (2 ml) was added. The mixture was refluxed for 2 h under a nitrogen atmosphere, then poured into 10% HCl and extracted with chloroform. The organic layer was washed with saturated NaCl, then dried and evaporated. The residue was subjected to silica gel column chromatography. The eluate with 15% ethyl acetate in hexane gave 5.3 mg (28.0%) of 2α,8α-epoxy-2β-methyl-1β,7β-bicyclo[3.5.0]dec-5-ene (**29**) as a colorless oil. IR ν_{max}^{neat} cm^{-1}: 1630. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.28 (3H, s, 2-Me), 1.50 (1H, m, 4-H), 1.57 (2H, m, 3-H_2), 1.69 (1H, m, 9-H), 1.82 (1H, m, 4-H), 1.89 (1H, m, 9-H), 2.09 (1H, m, 10-H), 2.27 (1H, m, 10-H), 2.36 (1H, d, J=6.1 Hz, 7-H), 2.51 (1H, d, J=3.4 Hz, 1-H), 3.97 (1H, s, 8-H), 5.63 (1H, ddd, J=11.3, 6.4, 2.1 Hz, 6-H), 5.79 (1H, m, 5-H). ^{13}C-NMR (500 MHz, $CDCl_3$) δ: 24.0 (C10), 24.7 (C4), 27.9 (C11), 29.3 (C3), 42.3 (C9), 46.9 (C1), 52.6 (C7), 81.6 (C2), 82.0 (C8), 128.2 (C5), 130.2 (C6). HREI-MS m/z Calcd for $C_{11}H_{16}O$ (M^+): 164.1198. Found: 164.1193. The second eluate with 15% ethyl acetate in hexane gave 7.6 mg (40.2%) of 2-methylene-1β,7β-bicyclo[3.5.0]dec-5-en-8-ol (**28**) as a colorless oil. IR ν_{max}^{neat} cm^{-1}: 3400, 1695, 1630. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.77—1.87 (3H, m, 9-H, 10-H_2), 1.99 (1H, m, 9-H), 2.24—2.28 (3H, m, 3-H, 4-H_2), 2.49 (1H, m, 3-H), 2.88 (1H, m, 7-H), 2.96 (1H, dd, J=16.7, 8.2 Hz, 1-H), 4.13 (1H,

m, 8-H), 4.76 (1H, s, 11-H), 4.80 (1H, s, 11-H), 5.60 (1H, ddt, $J=12.4$, 4.9, 1.5 Hz, 6-H), 5.84 (1H, m, 5-H). ^{13}C-NMR (500 MHz, $CDCl_3$) δ: 29.4 (C9), 30.8 (C4), 32.6 (C3), 33.3 (C10), 47.9 (C1), 49.1 (C7), 75.3 (C8), 110.1 (C11), 126.0 (C6), 132.2 (C5), 152.7 (C2). HREI-MS m/z Calcd for $C_{11}H_{16}O$ (M^+): 164.1178. Found: 164.1148.

2-Methylene-1β,7β-bicyclo[3.5.0]dec-5-en-8-one (30) Jones' reagent (350 μl) was added to a solution of **28** (35 mg) in acetone (15 ml) and the mixture was stirred at room temperature for 3 min, then poured into ice-water and extracted with ether. The organic layer was washed with saturated $NaHCO_3$ and NaCl, then dried and evaporated. The residue was subjected to silica gel column chromatography. The eluate with 15% ethyl acetate in hexane gave 24.2 mg (71.5%) of **30** as a colorless oil. $[\alpha]_D$ $-62.32°$ ($c=0.0267$, MeOH). IR ν_{max}^{neat} cm^{-1}: 1740, 1640. ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 1.13—2.62 (10H, m, 1,7-H, 3,4,9,10-H_2), 4.81 (1H, s, 11-H), 4.87 (1H, s, 11-H), 5.94 (2H, s, 5,6-H). HREI-MS m/z Calcd for $C_{11}H_{14}O$ (M^+): 162.1044. Found: 162.1079.

Dictamnol (1) A solution of 1.0 M methylmagnesium iodide in ether (0.9 ml) was added to a solution of **30** (18.5 mg) in dry ether (10 ml) and the mixture was stirred at 0 °C for 2 h, then poured into saturated NH_4Cl and extracted with ethyl acetate. The organic layer was washed with saturated NaCl, then dried and evaporated. The residue was subjected to silica gel column chromatography. The eluate with 15% ethyl acetate in hexane gave 10.9 mg (53.1%) of **1** as colorless needles (ether), mp 72—73 °C, $[\alpha]_D$ $+36.3°$ ($c=0.4$, MeOH), (lit.,[1] mp 72—73 °C, $[\alpha]_D$ $+55°$ ($c=0.1$, MeOH)). IR ν_{max}^{neat} cm^{-1}: 3270, 1633. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.22 (3H, s, 8-Me), 1.25 (1H, s, 8-OH), 1.73—1.78 (2H, m, 9-H_2), 1.80 (1H, m, 10-H), 1.89 (1H, m, 10-H), 2.11 (1H, m, 4-H), 2.20 (1H, dd, $J=13.6$, 8.9 Hz, 3-H), 2.28 (1H, m, 4-H), 2.38 (1H, d, $J=11.6$ Hz, 7-H), 2.43 (1H, m, 1-H), 2.56 (1H, t, $J=13.6$ Hz, 3-H), 4.74 (1H, s, 11-H), 4.82 (1H, s, 11-H), 5.78 (1H, d, $J=11.6$ Hz, 6-H), 5.86 (1H, m, 5-H). ^{13}C-NMR (500 MHz, $CDCl_3$) δ: 24.0 (C12), 25.1 (C10), 28.6 (C4), 36.6 (C3), 39.9 (C9), 46.9 (C1), 55.4 (C7), 80.3 (C8), 107.2 (C11), 129.9 (C6), 131.8 (C5), 153.6 (C2). HREI-MS m/z Calcd for $C_{12}H_{18}O$ (M^+): 178.1355. Found: 178.1354. This product was identical with an authentic sample[1] on the basis of IR and NMR spectral comparisons.

8α-Acetoxy-8β-methyl-2-methylene-1β,7β-bicyclo[3.5.0]dec-5-ene (31) Compound **1** (12 mg) was added to a solution of acetic anhydride (0.3 ml) and DMAP (1 mg) in triethylamine (0.4 ml) and the mixture was stirred at room temperature for 1 d, then poured into 10% HCl and extracted with ethyl acetate. The organic layer was washed with saturated $NaHCO_3$ and NaCl, then dried and evaporated. The residue was subjected to silica gel column chromatography. The eluate with 5% ethyl acetate in hexane gave 11 mg (74.3%) of **31** as a colorless oil. IR ν_{max}^{neat} cm^{-1}: 1740, 1635. ^{1}H-NMR (500 MHz $CDCl_3$) δ: 1.44 (3H, s, 8-Me), 1.78—1.92 (2H, m, 10-Hz), 1.98 (3H, s, 8-COMe), 2.08 (2H, m, 9-H_2), 2.12 (1H, m, 4-H), 2.20 (1H, dd, $J=13.7$, 8.6 Hz, 3-H), 2.29 (1H, m, 4-H), 2.39 (1H, $J=19.5$, 12.2 Hz, 1-H), 2.55 (1H, t, $J=12.2$ Hz, 3-H), 2.63 (1H, d, $J=12.2$ Hz, 7-H), 4.75 (1H, s, 11-H), 4.82 (1H, s, 11-H), 5.85 (2H, s, 5,6-H). ^{13}C-NMR (500 MHz, $CDCl_3$) δ: 21.2 (C12), 22.2 (C2'), 26.3 (C10), 28.7 (C4), 36.7 (C3), 37.3 (C9), 46.2 (C1), 54.0 (C7), 89.4 (C8), 107.6 (C11), 129.9 (C5 or C6), 131.3 (C5 or C6), 152.8 (C2), 170,6 (C1'). HREI-MS m/z Calcd for $C_{14}H_{20}O_2$ (M^+): 220.1464. Found: 220.1497.

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