Plant Bioregulators, 4[+]

Synthesis and Structure of Orobanchol, the Germination Stimulant for *Orobanche minor*

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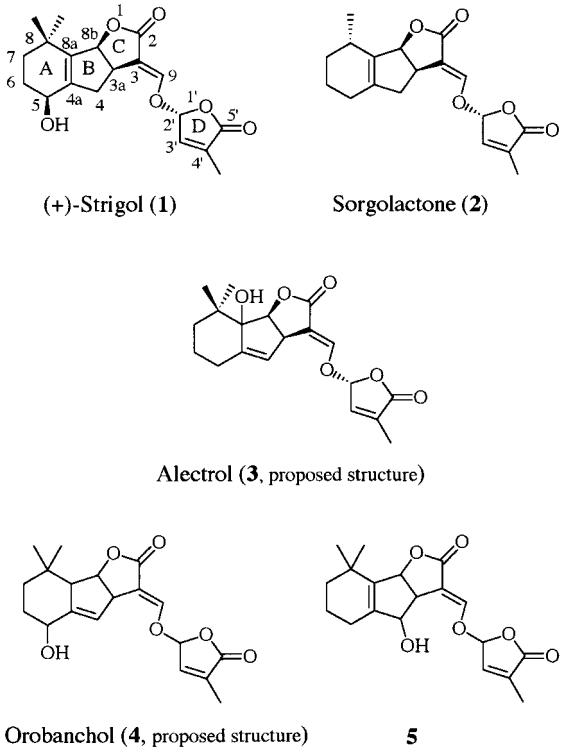
The structure of orobanchol, a new seed germination stimulant for clover broomrape (*Orobanche minor*), was proposed as **5a** (tentative absolute configuration) on the basis of GC-MS comparison of the natural product with several synthetic compounds [(±)-**4a**–(±)-**4h**, (±)-**5a** and (±)-**5b**]. All of the synthetic compounds showed significant seed germination activities for *Orobanche minor* and witchweed (*Striga asiatica*).

The phenomenon that the seeds of root parasitic weeds of the genera *Orobanche*, *Striga* and *Alectra* remain dormant in soil until exudates from their host plants induce germination has been a topic of intense interest, since the above weeds attack the important crops including corn, sugarcane and sorghum to cause severe yield losses in many countries.[1][2] Chemists′ endeavor to solve this agricultural problem culminated in the isolation and identification of the active principles of the exudates. (+)-Strigol (**1**, Scheme 1) was first isolated in 1972 from cotton (a non-host plant) root exudates and shown to be a potent germination stimulant for the seeds of such weeds, in particular for *Striga* seeds.[3] It was later isolated from the host plants of *Striga*, such as maize, proso millet and sorghum[4] and its structure was rigorously determined by X-ray analysis.[3][5] Two decades later in 1992, a German group isolated two germination stimulants, sorgolactone from *Sorghum bicolor*, a genuine host for *Striga asiatica* and *Striga hermonchica*[6] and alectrol from *Vigna unguiculata*, a genuine host for *Alectra vogelii* and *Striga gesnerioides*.[7] Even with insufficient spectral information due to the scarcity of the isolated samples and the presence of some impurities, they proposed strigol-related structures **2** for the former stimulant and **3** for the latter. Synthesis and ^{1}H-NMR analysis of (±)-**2** and (+)-**2**, however, did not perfectly support the structure **2**.[8] The correctness of the structure **3** was also disproved by the comparison of ^{1}H-NMR data of the several synthetic compounds related to **3** with those reported for the natural alectrol.[9] The scarcity of the material and instability during the purification process of the germination stimulants make their structure elucidation rather difficult and indefinite.



Scheme 1. Structures of the germination stimulants

Recently, Yokota and his co-workers isolated three seed germination stimulants for clover broomrape (*Orobanche minor*) from root exudates of its host, red clover (*Trifolium pratense*).[10][11] One of them was a novel isomer of strigol and named orobanchol.[11] The structure of orobanchol was proposed as **4**, mainly on the basis of the mass-spectral data of it and its trimethylsilyl (TMS) ether, although the positions of the OH group at C-5 and the 4(4a)-double

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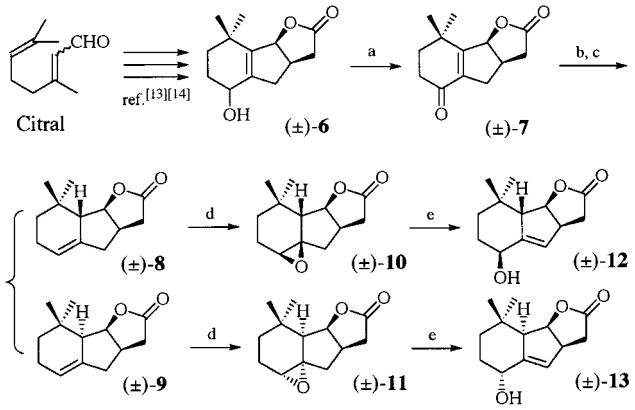
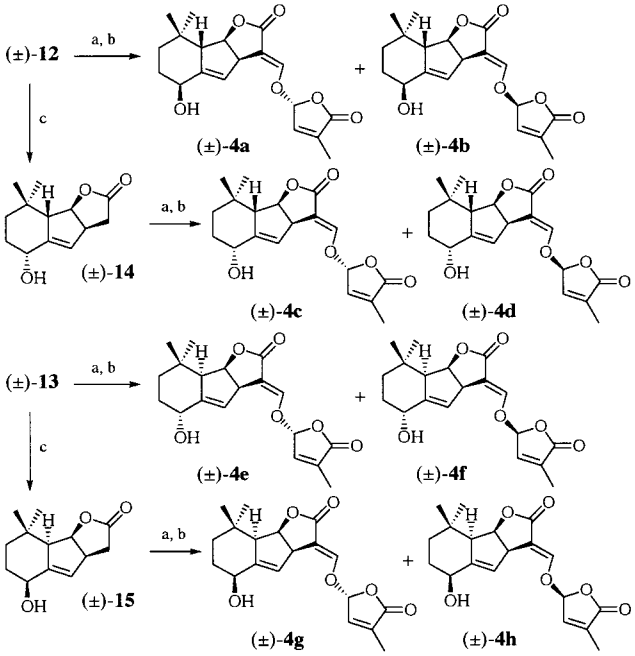
bond were uncertain. In the previous work which was reported as a preliminary communication,[12] we synthesized various stereoisomers of **4** and **5** as the racemates and executed GC-MS comparison of their TMS ethers with natural orobanchol TMS ether. That work enabled us to propose **5a** as the structure of orobanchol. This paper describes the full account of the synthesis, GC-MS analysis and bioassay of the racemates with the structures **4** and **5**.

Schemes 2 and 3 summarize the synthesis of the eight stereoisomers (±)-**4a**−(±)-**4h** of the proposed structure **4**. By the procedures of Sih,[13] Brooks,[14] and their co-workers, citral was converted to the known hydroxylactone (±)-**6** as a diastereomeric mixture. This was oxidized to the oxolactone (±)-**7**.[14] Reduction of (±)-**7** via its tosylhydrazone[15] gave (±)-**8** and (±)-**9** in moderate yields, which could readily be separated by silica-gel column chromatography. These were separately epoxidized with *m*-chloroperbenzoic acid (*m*CPBA) to give (±)-**10** and (±)-**11**. Their treatment with aluminum 2-propoxide in toluene under reflux generated the allylic alcohols (±)-**12** and (±)-**13**, respectively. The stereochemistry assigned to (±)-**8**, (±)-**10** and (±)-**12** was supported by the later X-ray analysis of (±)-**4a** derived from (±)-**12**. The stereochemistry of (±)-**9**, (±)-**11** and (±)-**13** was based on the ^{1}H-NMR comparison with their stereoisomers (±)-**8**, (±)-**10** and (±)-**12**. The hydroxylactone (±)-**12** yielded a mixture of (±)-**4a** and (±)-**4b** in two steps, formylation and alkylation, according to the conventional procedure reported previously.[8,9,13,14] The two isomers were separated by silica-gel column chromatography to give crystalline (±)-**4a** and (±)-**4b**, whose ^{1}H-NMR spectra were almost identical. The structure of (±)-**4a**, m.p. 229−231°C, was solved by its X-ray analysis, and its perspective view is shown in Figure 1. Mitsunobu inversion[16] of the configuration of the OH group of (±)-**12** gave (±)-**14**, which furnished (±)-**4c** and (±)-**4d**. Mass spectra of the TMS ethers of the four stereoisomers (±)-**4a**−(±)-**4d** were almost identical to one another. The mass spectrum of TMS-(±)-**4a** together with those of TMS-strigol and TMS-orobanchol are shown in Figure 2a and 2b. The fragmentation pattern of TMS-(±)-**4a** (A) was similar to that of TMS-strigol (D) and clearly distinct from that of TMS-orobanchol (E), indicating that none of **4a**, **4b**, **4c** and **4d** was orobanchol. Similarly, (±)-**13** was converted into (±)-**4e**, (±)-**4f**, (±)-**4g** and (±)-**4h**. Mass spectra of their TMS ethers were almost identical to each other and slightly different from that of TMS-(±)-**4a** due to the difference in the configuration of the tricyclic part. The mass spectrum of the TMS-(±)-**4e** is shown in Figure 2a. Importantly, the fragmentation pattern of TMS-(±)-**4e** (B) was also different from that of TMS-orobanchol (E). Therefore orobanchol was not **4e**, (±)-**4f**, (±)-**4g** nor (±)-**4h**. The GC-MS analysis of the TMS ethers revealed that the proposed structure **4** was incorrect.

We then synthesized (±)-**5a** and (±)-**5b** (Scheme 4) as the possible candidates for (±)-alectrol[9] and (±)-orobanchol. The known tricyclic lactone (±)-**16**[17] was oxidized to give (±)-**17** as the minor product. The major product (±)-**7** could be recycled by its reduction to (±)-**6**. Reduction of (±)-**17**

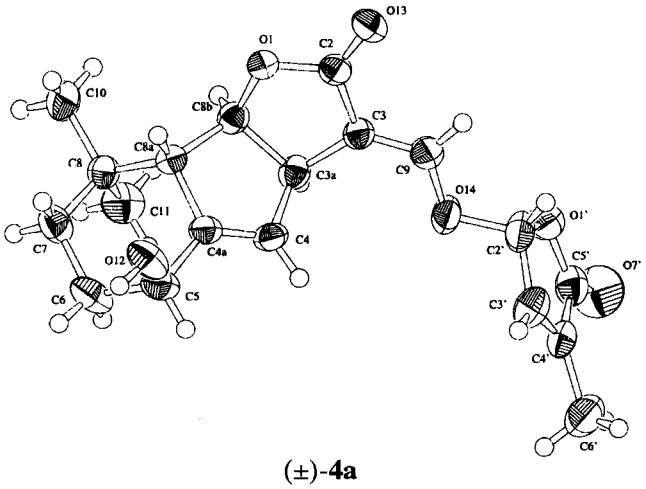


Scheme 2. Synthesis of (±)-**12** and (±)-**13**; reagents: (a) PCC, CH_2Cl_2 (87%); (b) *p*TsNHNH$_2$, EtOH; (c) $NaBH_3CN$, *p*TsOH, DMF, sulfolane [13% for (±)-**8** and 11% for (±)-**9**]; (d) *m*CPBA, CH_2Cl_2 [69% for (±)-**10**; 72% for (±)-**11**]; (e) Al(O*i*Pr)$_3$, toluene, heat [75% for (±)-**11**; 38% for (±)-**12**]



Scheme 3. Synthesis of (±)-**4a**−(±)-**4h**; reagents: (a) NaH, HCO_2Et, Et_2O, THF; (b) i) K_2CO_3, (±)-4-bromo-2-methyl-2-buten-4-olide, *N*-methylpyrrolidone; ii) SiO_2 chromatography (54%−86%; α isomer/β isomer ≈ 1:1); (c) i) $EtO_2CN{=}NCO_2Et$, Ph_3P, $PhCO_2H$, THF; ii) K_2CO_3, MeOH [61% for (±)-**14**; 49% for (±)-**15**]

furnished the alcohols (±)-**18** and (±)-**19**. The structure of (±)-**18** with *cis* relationship between the hydroxy group at C-4 and the lactone ring was confirmed by its X-ray analysis. The minor product (±)-**19** with a 1 H singlet at δ = 4.45 (C*H*OH) could be further secured by Mitsunobu inversion of the isomer (±)-**18**. Its perspective view is shown in Figure 3. Finally, (±)-**19** was converted to (±)-**5a** (m.p. 200−201°C) and (±)-**5b** (m.p. 170−172°C), whose structures were confirmed by the X-ray analysis of (±)-**5b**. Its perspective view is also shown in Figure 3. We also attempted to synthesize stereoisomers of **5a** and **5b** with β-OH group at C-4. Formylation of (±)-**18** was unsuccessful due to translactonization and other side-reactions, and at-



(±)-**4a**

Figure 1. Perspective view of (±)-**4a**

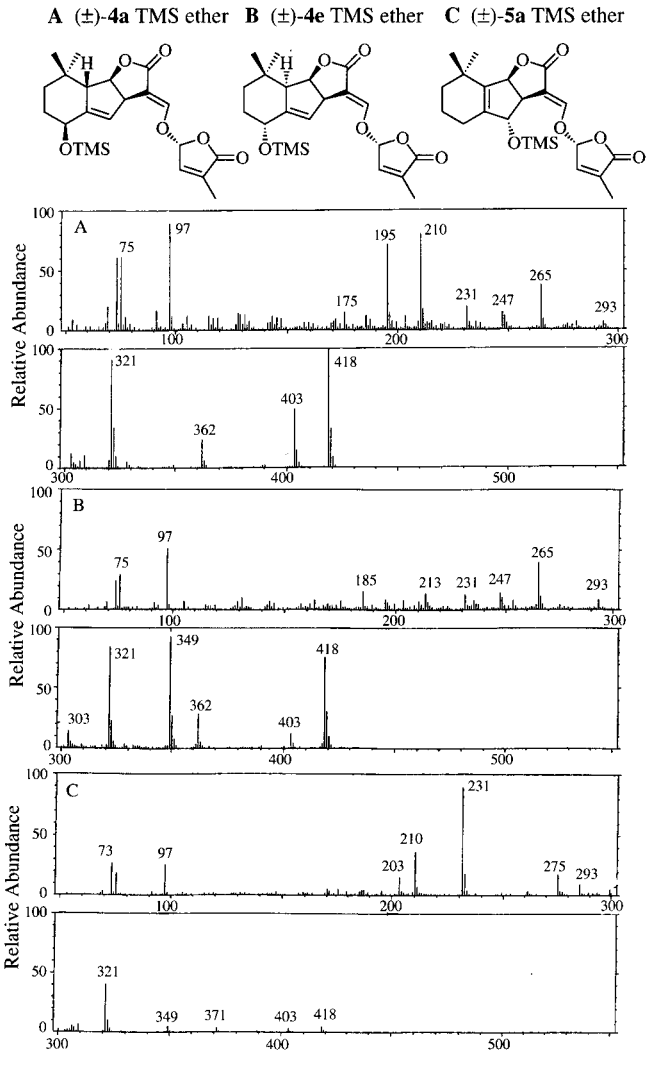


Figure 2a. Mass spectra of TMS ethers of (±)-**4a** (A), (±)-**4e** (B) and (±)-**5a** (C)

tempted Mitsunobu inversion of (±)-**5a** failed. Synthesis of a compound with the structure of **5** with the β-OH group will be reported later.

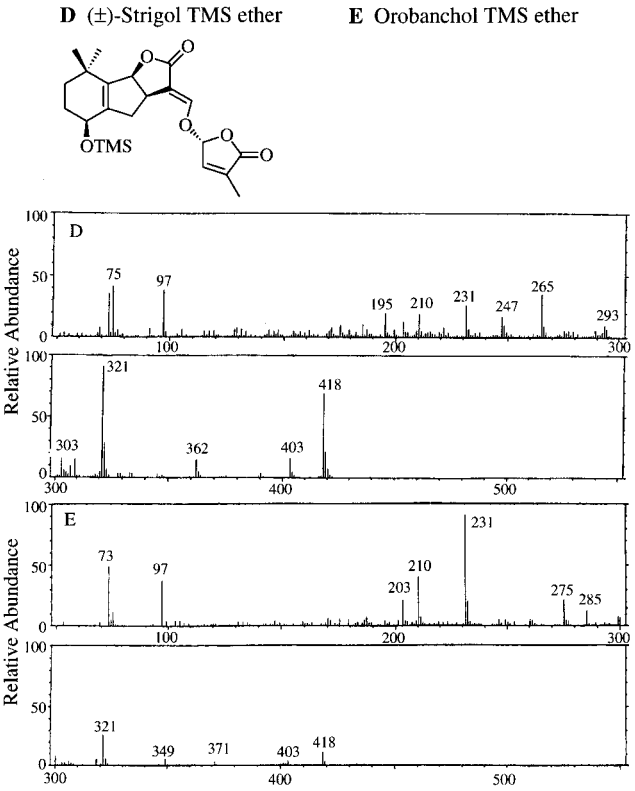
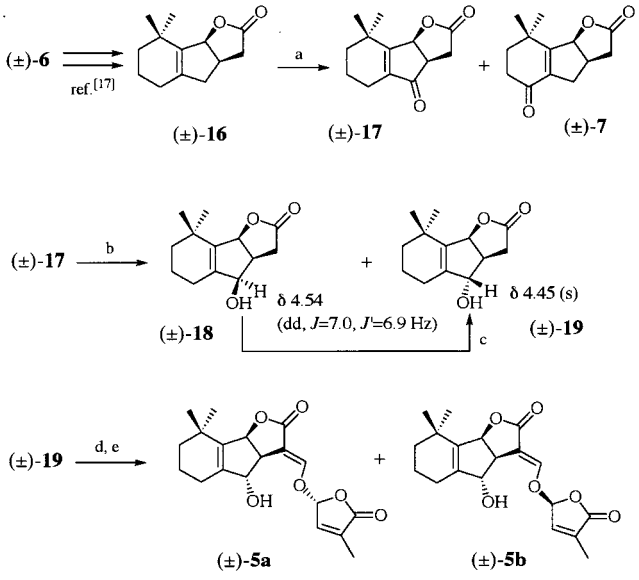
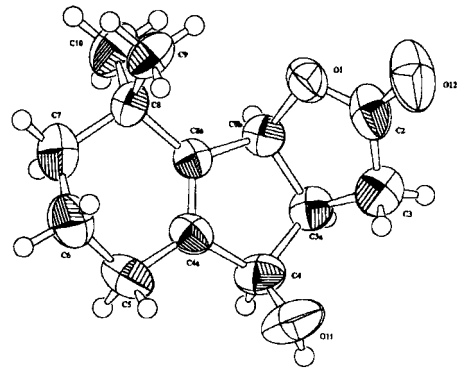


Figure 2b. Mass spectra of TMS ethers of strigol (D) and orobanchol (E)

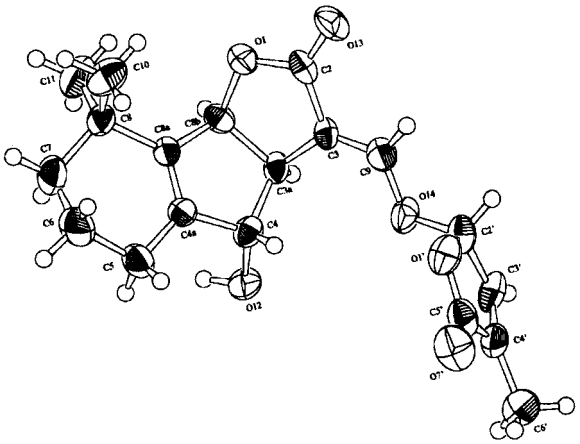


Scheme 4. Synthesis of (±)-**5a** and (±)-**5b**; reagents: (a) CrO_3, 3,5-dimethylpyrazole, CH_2Cl_2 [23% for (±)-**17** and 75% for (±)-**7**]; (b) $NaBH_4$, $CeCl_3 \cdot 7\ H_2O$, EtOH [79% for (±)-**18** and 5% for (±)-**19**]; (c) i) $EtO_2CN{=}NCO_2Et$, Ph_3P, $PhCO_2H$, THF; ii) K_2CO_3, MeOH (98%); (d) NaH, HCO_2Et, Et_2O; (e) i) K_2CO_3, (±)-4-bromo-2-methyl-2-buten-4-olide, *N*-methylpyrrolidone; ii) SiO_2 chromatography [38% for (±)-**5a** and 31% for (±)-**5b**]

The final products, (±)-**5a** and (±)-**5b**, were then analyzed by GC-MS in the similar manner. The mass spectra of the TMS ethers of (±)-**5a** and (±)-**5b** were superimposable. The mass spectrum of TMS-(±)-**5a** is also shown in Figure 2a.



(±)-**18**



(±)-**5b**

Figure 3. Perspective views of (±)-**18** and (±)-**5b**

It is worth noting that the fragmentation pattern of TMS-(±)-**5a** is totally different from that of TMS-strigol, but identical with that of TMS-orobanchol. The GC relative retention times of TMS-(±)-**5a** (t_R = 4′45″) and TMS-(±)-**5b** (t_R = 4′42″) were virtually the same as TMS-orobanchol (t_R = 4′45″). We thus tentatively conclude that orobanchol is **5a**, considering the known absolute configuration of strigol.

Finally, bioactivity of the synthetic compounds [(±)-**4a**−(±)-**4h**, (±)-**5a** and (±)-**5b**] as seed germination stimulants was evaluated. The seeds of clover broomrape (*Orobanche minor*)[18] and witchweed (*Striga asiatica*)[19] were used as test parasitic weed seeds. The results were summarized in Tables 1 and 2. All of the compounds were good stimulants for the germination of *Orobanche minor* at a concentration of 10^{-8} M and of *Striga asiatica* at a concentration of 10^{-7} M, supporting the view that bioactivity as the germination stimulant resides on the C/D-ring part of the molecule.

Table 1. Germination stimulating activity for *Orobanche minor* seeds

Compound	Relative germination of *Orobanche minor* seeds (%)[a] 10^{-8} M	10^{-9} M	10^{-10} M	10^{-11} M
(±)-**4a**	45.0 ± 3.9	23.2 ± 1.5	3.0 ± 0.5	0
(±)-**4b**	39.4 ± 4.7	12.3 ± 5.6	6.8 ± 3.2	5.7 ± 3.2
(±)-**4c**	75.0 ± 1.4	62.3 ± 5.8	45.9 ± 6.6	1.4 ± 0.1
(±)-**4d**	62.0 ± 2.5	52.3 ± 7.4	3.3 ± 1.0	0
(±)-**4e**	57.1 ± 7.4	1.1 ± 1.0	0	0
(±)-**4f**	67.7 ± 8.0	50 6 ± 4.1	21.9 ± 1.3	20.0 ± 6.2
(±)-**4g**	62.4 ± 7.7	35.9 ± 6.0	3.4 ± 0.6	0
(±)-**4h**	66.4 ± 5.2	42.1 ± 10.2	2.5 ± 0.8	0
(±)-**5a**	62.2 ± 5.6	38.0 ± 4.1	12.7 ± 3.3	0
(±)-**5b**	66.9 ± 2.3	50.5 ± 4.1	20.5 ± 5.2	1.6 ± 1.5
(±)-strigol	70.4 ± 4.3	60.6 ± 4.4	17.5 ± 4.0	1.8 ± 0.5

[a] Control, 0%.

Table 2. Germination stimulating activity for *Striga asiatica* seeds

Compound	Relative germination of *Striga asiatica* seeds (%)[a] 10^{-7} M	10^{-8} M	10^{-9} M	10^{-10} M
(±)-**4a**	87.4 ± 6.3	73.2 ± 6.5	12.5 ± 9.4	2.9 ± 2.9
(±)-**4b**	88.8 ± 4.2	42.2 ± 5.8	9.6 ± 2.5	0
(±)-**4c**	92.4 ± 2.4	80.0 ± 2.5	8.7 ± 6.4	3.0 ± 1.5
(±)-**4d**	87.4 ± 4.7	23.8 ± 5.1	1.0 ± 0.9	1.6 ± 1.5
(±)-**4e**	86.7 ± 1.8	3.4 ± 2.4	4.0 ± 4.0	1.9 ± 1.0
(±)-**4f**	92.0 ± 1.8	90.5 ± 4.2	56.0 ± 8.2	15.7 ± 1.3
(±)-**4g**	88.5 ± 2.1	87.1 ± 4.0	28.2 ± 7.0	8.3 ± 2.6
(±)-**4h**	88.5 ± 2.5	33.0 ± 2.5	3.5 ± 2.4	0
(±)-**5a**	82.5 ± 1.3	69.9 ± 3.4	39.7 ± 1.1	12.8 ± 6.1
(±)-**5b**	87.5 ± 3.0	57.2 ± 9.4	32.3 ± 4.2	16.1 ± 4.2
(±)-strigol	93.3 ± 2.7	93.9 ± 0.7	80.3 ± 1.9	19.9 ± 2.9

[a] Control, 3.7 ± 3.7%.

In conclusion, we achieved the synthesis of the racemates of possible eight stereoisomers of the structure **4** proposed for orobanchol and two stereoisomers with the related structure **5**. From GC-MS comparison of the TMS ethers of synthetic products with that of natural orobanchol, **5a** was proposed for the structure of orobanchol. The importance of GC-MS analysis in structure elucidation is well established in pheromone chemistry, and it has also been proved in the present phytochemical work dealing with a scarce bioregulator. Since mass-spectrometric fragmentation patterns of densely functionalized molecules are less predictable and cannot be calculated, structures deduced from mass spectra are less conclusive than those from NMR data. Synthesis and bioassay of the optically active orobanchol (**5a**) will be reported in due course.

Experimental Section

General: Boiling points and melting points: Uncorrected values. − IR: Shimadzu FT IR-8100 or Jasco IRA-102. − ^{1}H NMR: Jeol JNM-EX 90A (90 MHz), Jeol JNM-EX 270 L (270 MHz), Bruker DPX 300 (300 MHz), or Jeol JNM-LA 400 (400 MHz, TMS at δ_H = 0.00, $CHCl_3$ at δ_H = 7.26 as internal standards). − ^{13}C NMR: Jeol JNM-EX 270 L (67.8 MHz), Bruker DPX 300 (75.5 MHz) or Jeol JNM-LA 400 (100.4 MHz, $CDCl_3$ at δ_C = 77.0

as an internal standard). − MS: Jeol JMX-DX 303 (70 eV). − M.p.s: Yanaco MP-S3. − CC: Merck Kieselgel 60 Art 1.07734. − TLC: 0.25 mm Merck silica gel plate (60F-254).

(±)-(3a*R,8b*S**)-8,8-Dimethyl-5-oxo-3,3a,4,5,6,7,8,8b-octahydroindeno[1,2-*b*]-furan-2-one [(±)-7]:** To a stirred suspension of pyridinium chlorochromate (PCC) (5.82 g, 27 mmol) in CH_2Cl_2 (40 mL) was added a solution of the hydroxylactone **6**[13][14] (4.00 g, 18 mmol) in CH_2Cl_2 (15 mL). After stirring for 2 h, diethyl ether (120 mL) was added and stirring was continued for further 2 h. Filtration through Hyflo Super-Cell® and evaporation of the solvent under reduced pressure gave a crude product, which was purified by silica-gel chromatography (hexane/ethyl acetate = 6:1−3:1) to afford 3.45 g (87%) of the α,β-unsaturated ketone (±)-**7**[14] as colorless needles, m.p. 84−86°C (hexane/diethyl ether). − IR (KBr): $\tilde{\nu}$ = 1775 cm^{-1} (s, C=O), 1675 (s, C=C), 1165 (s, C−O), 1025 (m, C−O). − ^1H NMR (300 MHz, $CDCl_3$): δ = 1.27 (s, 3 H, 8-Me), 1.29 (s, 3 H, 8-Me), 1.89 (m, 2 H, 7-CH_2), 2.32 (dd, 1 H, *J* = 18.4, *J*′ = 5.9 Hz, 3-H), 2.47 (dt, 1 H, *J* = 17.4, *J*′ = 2.7 Hz, 6-H), 2.47 (m, 1 H, 4-H), 2.58 (ddd, 1 H, *J* = 17.5, *J*′ = 9.3, *J*′′ = 6.3 Hz, 6-H′), 2.84 (dd, 1 H, *J* = 17.0, *J*′ = 8.4 Hz, 4-H′), 2.85 (dd, 1 H, *J* = 18.4, *J*′ = 10.3 Hz, 3-H′), 3.15 (m, 1 H, 3a-H), 5.63 (dd, 1 H, *J* = 7.6, 1.8 Hz, 8b-H).

(±)-(3a*R,8a*R**,8b*S**)- and (±)-(3a*R**,8a*S**,8b*S**)-8,8-Dimethyl-3,3a,4,6,7,8,8a,8b-octahydroindeno[1,2-*b*]furan-2-one [(±)-8 and (±)-9]:** A mixture of the α,β-unsaturated ketone (±)-**7** (330 mg, 1.5 mmol) and *p*-toluenesulfonyl hydrazide (335 mg, 1.8 mmol) in ethanol (0.8 mL) was stirred and heated under reflux for 2 h. The mixture was cooled to room temperature and then concentrated under reduced pressure to afford the crude *p*-toluenesulfonyl hydrazone, which was directly used in the next step. Under argon, the above crude hydrazone was dissolved in dry DMF (4.2 mL) and dry sulfolane (4.2 mL). To the solution were added *p*-toluenesulfonic acid (67 mg) and sodium cyanotrihydroborate (425 mg, 6.8 mmol). The mixture was stirred and heated at 110°C for 3 h, cooled to room temperature and diluted with water. The mixture was extracted with diethyl ether. The organic layer was washed with brine, dried with $MgSO_4$, and concentrated under reduced pressure. The yellowish residue was chromatographed on silica gel (hexane/ethyl acetate = 15:1) to give first 39 mg (13%) of (±)-**8** (R_f = 0.74, hexane/ethyl acetate = 1:1) as white solids and then 34 mg (11%) of (±)-**9** (R_f = 0.63, hexane/ethyl acetate = 1:1) as a pale yellowish paste. Although (±)-**8** was purified by recrystallization from hexane to afford colorless needles, (±)-**9** was employed in the next transformation without further purification. The stereostructures of (±)-**8** and (±)-**9** were determined after conversion of (±)-**8** to (±)-**4a**, which was analyzed by X-ray crystallography. − (±)-**8**: M.p. 59−60°C (hexane). − IR (KBr): $\tilde{\nu}$ = 2945 cm^{-1} (m, C−H), 1765 (s, C=O), 1700 (w, C=C), 1170 (s, C=O), 1005 (m, C=O). − ^1H NMR (300 MHz, $CDCl_3$): δ = 0.76 (s, 3 H, 8-Me), 1.09 (s, 3 H, 8-Me), 1.37−1.43 (m, 2 H, 7-CH_2), 2.02 (m, 2 H, 6-CH_2), 2.16 (m, 1 H), 2.32−2.37 (m, 1 H), 2.38 (dd, 1 H, *J* = 17.6, *J*′ = 2.2 Hz, 3-H), 2.53−2.79 (m, 2 H, 3a-H and 4-H), 2.74 (dd, 1 H, *J* = 17.6, *J*′ = 8.8 Hz, 3-H′), 4.73 (dd, 1 H, *J* = 7.1, *J*′ = 4.0 Hz, 8b-H), 5.45 (t, 1 H, *J* = 3.0 Hz, 5-H). − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 19.4, 22.9, 29.8, 30.3, 35.3, 36.8, 37.8, 37.9, 55.1, 85.8, 118.6, 138.4, 177.3. − $C_{13}H_{18}O_2$ (206.3): calcd. C 75.69, H 8.80; found C 75.72, H 8.86. − (±)-**9**; n_D^{23} = 1.5162. − IR (film): $\tilde{\nu}$ = 2950 cm^{-1} (m, C−H), 1775 (s, C=O), 1665 (w, C=C), 1155 (m, C−O). − ^1H NMR (300 MHz, $CDCl_3$): δ = 1.04 (s, 3 H, 8-Me), 1.08 (s, 3 H, 8-Me), 1.18−1.43 (m, 3 H), 1.91−2.12 (m, 2 H), 2.13 (m, 1 H), 2.26 (dd, 1 H, *J* = 17.6, *J*′ = 1.5 Hz, 3-H), 2.71 (dd, 1 H, *J* = 17.4, *J*′ = 8.7 Hz, 3-H′), 2.72 (m, 1 H), 2.84 (m, 1 H, 3a-H), 4.93 (t, 1 H, *J* = 4.8 Hz, 8b-H), 5.27 (br. s, 1 H, 5-H).

(±)-(3a*R,4a*R**,5*S**,8a*R**,8b*S**)-8,8-Dimethyl-3,3a,4,4a,5,6,7,8,8a,8b-decahydro-4a,5-epoxyindeno[1,2-*b*]furan-2-one [(±)-10]:** To a stirred and ice-cooled solution of the unsaturated lactone (±)-**8** (688 mg, 3.34 mol) in CH_2Cl_2 (125 mL) was carefully added *m*-chloroperbenzoic acid (*m*CPBA) (ca. 70%, 1.06 g, ca. 4.34 mmol) in several portions. The mixture was stirred for 15 h at room temperature, quenched by the addition of satd. $Na_2S_2O_3$ solution and satd. $NaHCO_3$ solution, and then extracted with CH_2Cl_2. The organic layer was washed with satd. $NaHCO_3$ solution and brine, and dried with $MgSO_4$. Evaporation of the solvent gave a crude product, which was purified by silica-gel column chromatography (hexane/ethyl acetate = 3:1−1:1) to give 558 mg (75%) of (±)-**10** as colorless needles. The stereostructures of (±)-**10** was assigned after conversion to (±)-**4a**, which was analyzed by X-ray crystallography, m.p. 98−99°C (hexane/diethyl ether). − IR (KBr): $\tilde{\nu}$ = 2925 cm^{-1} (m, C−H), 1775 (s, C=O), 1205 (m, C−O), 1170 (s, C−O). − ^1H NMR (300 MHz, $CDCl_3$): δ = 0.80 (s, 3 H, 8-Me), 1.02 (s, 3 H, 8-Me), 1.10 (ddd, 1 H, *J* = 13.6, *J*′ = 6.1, *J*′′ = 1.6 Hz, 7-H), 1.27 (td, 1 H, *J* = 13.3, *J*′ = 5.6 Hz, 7-H′), 1.81 (dddd, 1 H, *J* = 15.5, *J*′ = 12.4, *J*′′ = 6.1, *J*′′′ = 2.4 Hz, 6-H), 1.93−2.07 (m, 3 H, 4-CH_2 and 6-H′), 2.09 (d, 1 H, *J* = 1.5 Hz, 8a-H), 2.47 (dd, 1 H, *J* = 20.2, *J*′ = 5.8 Hz, 3-H), 2.74 (dd, 1 H, *J* = 20.2, *J*′ = 7.7 Hz, 3-H′), 2.77 (m, 1 H, 3a-H), 3.16 (s, 1 H, 5-H), 4.71 (dd, 1 H, *J* = 5.6, 2.1 Hz, 8b-H). − ^{13}C NMR (22.4 MHz, $CDCl_3$): δ = 20.5, 21.6, 29.4, 31.8, 35.6, 36.8, 37.9, 54.0, 58.5, 65.2, 86.1, 176.1. − $C_{13}H_{18}O_3$ (222.3): calcd. C 70.24, H 8.16; found C 70.05, H 8.29.

(±)-(3a*R,4a*S**,5*R**,8a*S**,8b*S**)-8,8-Dimethyl-3,3a,4,4a,5,6,7,8,8a,8b-decahydro-4a,5-epoxyindeno[1,2-*b*]furan-2-one [(±)-11]:** In the same manner as described for (±)-**10**, the unsaturated lactone (±)-**9** (597 mg, 2.9 mmol) was converted to the epoxide (±)-**11** (colorless needles, 465 mg, 72%) with *m*-chloroperbenzoic acid (*m*CPBA), m.p. 84−85°C (hexane/diethyl ether). − IR (KBr): $\tilde{\nu}$ = 2950 cm^{-1} (m, C−H), 1765 (s, C=O), 1200 (m, C−O), 1160 (m, C−O). − ^1H NMR (300 MHz, $CDCl_3$): δ = 1.03 (s, 3 H, 8-Me), 1.06 (s, 3 H, 8-Me), 1.13−1.30 (m, 2 H, 7-CH_2), 1.82 (dd, 1 H, *J* = 15.1, *J*′ = 9.7 Hz, 4-H), 1.90 (m, 2 H, 6-CH_2), 1.99 (d, 1 H, *J* = 5.3 Hz, 8a-H), 2.13 (dd, 1 H, *J* = 15.0, 9.0 Hz, 4-H′), 2.36 (d, 1 H, *J* = 17.5 Hz, 3-H), 2.71 (dd, 1 H, *J* = 17.5, 7.4 Hz, 3-H′), 3.01 (m, 1 H, 3a-H), 3.24 (s, 1 H, 5-H), 5.03 (t, 1 H, *J* = 5.1 Hz, 8b-H). − $C_{13}H_{18}O_3$ (222.3): calcd. C 70.24, H 8.16; found C 70.19, H 8.30.

(±)-(3a*R,5*S**,8a*R**,8b*S**)-5-Hydroxy-8,8-dimethyl-3,3a,5,6,7,8,8a,8b-octahydroindeno[1,2-*b*]furan-2-one [(±)-12]:** A mixture of the epoxide (±)-**10** (16 mg, 0.072 mmol) and aluminum 2-propoxide (73 mg, 0.36 mmol) in toluene (2.0 mL) was stirred and refluxed for 13 h under argon. The cooled reaction mixture was treated with 2 N HCl and extracted with ethyl acetate. The organic layer was washed with brine, dried with $MgSO_4$, and concentrated under reduced pressure. The yellowish residue was purified by silica-gel column chromatography (hexane/ethyl acetate = 2.5:1) to afford 12 mg (75%) of the alcohol (±)-**12** as colorless crystals, m.p. 148−149°C (hexane/diethyl ether). − IR (KBr): $\tilde{\nu}$ = 3530 cm^{-1} (s, O−H), 2935 (m, C−H), 1770 (s, C=O), 1200 (m, C−O), 1045 (m, C−O), 1005 (m, C−O). − ^1H NMR (400 MHz, $CDCl_3$): δ = 0.67 (s, 3 H, 8-Me), 1.11 (s, 3 H, 8-Me), 1.18 (ddd, 1 H, *J* = 13.9. *J*′ = 3.7, 3.1 Hz, 7-H), 1.43 (br s, 1 H, OH), 1.55−1.66 (m, 1 H, 7-H′), 1.73−1.86 (m, 2 H, 6-CH_2), 2.39 (dd, 1 H, *J* = 18.2, *J*′ = 1.8 Hz, 3-H), 2.72 (dd, 1 H, *J* = 18.0, *J*′ = 10.2 Hz, 3-H′), 2.88 (s, 1 H, 8a-H), 3.36 (m, 1 H, 3a-H), 4.49 (s, 1 H, 5-H), 4.89 (d, 1 H, *J* = 6.6 Hz, 8b-H), 5.40 (t, 1 H, *J* = 1.7 Hz, 4-H). − ^{13}C NMR (100.4 MHz, $CDCl_3$): δ = 19.0, 29.4, 30.0, 32.9, 34.3, 34.8, 44.6,

58.1, 65.7, 84.4, 123.9, 145.9, 176.7. − $C_{13}H_{18}O_3$ (222.3): calcd. C 70.24, H 8.16; found C 70.16, H 8.28.

(±)-(3a*R,5*R**,8a*S**,8b*S**)-5-Hydroxy-8,8-dimethyl-3,3a,5,6,7,8,8a,8b-octahydroindeno[1,2-*b*]furan-2-one [(±)-13]:** In the same manner as described for (±)-**12**, the epoxide (±)-**11** (597 mg, 2.9 mmol) was treated with aluminum isopropoxide (1.71 g, 8.36 mmol) to afford the allylic alcohol (±)-**13** (177 mg, 38%) as colorless needles, m.p. 85−86°C (hexane/diethyl ether). − IR (KBr): $\tilde{\nu}$ = 3465 cm^{-1} (s, O−H), 2960 (m, C−H), 1735 (s, C=O), 1205 (s, C−O), 1035 (m, C−O). − ^{1}H NMR (300 MHz, $CDCl_3$): 0.90 (s, 3 H, 8-Me), 1.20 (s, 3 H, 8-Me), 1.15−1.27 (m, 1 H, 7-H), 1.54 (m, 1 H, 7-H′), 1.67−1.80 (m, 2 H, 6-CH_2), 1.75 (s, 1 H, OH), 2.33 (dd, 1 H, J = 18.3, J' = 4.0 Hz, 3-H), 2.72 (dd, 1 H, J = 18.3, J' = 10.6 Hz, 3-H′), 2.88 (d, 1 H, J = 7.3 Hz, 8a-H), 3.51 (m, 1 H, 3a-H), 4.52 (br s, 1 H, 5-H), 5.28 (t, 1 H, J = 7.5 Hz, 8b-H), 5.59 (t, 1 H, J = 2.3 Hz, 4-H). − $C_{13}H_{18}O_3$ (222.3): calcd. C 70.24, H 8.16; found C 70.17, H 8.23.

(±)-(3a*R,5*R**,8a*R**,8b*S**)-5-Hydroxy-8,8-dimethyl-3,3a,5,6,7,8,8a,8b-octahydroindeno[1,2-*b*]furan-2-one [(±)-14]:** To a stirred mixture of the alcohol (±)-**12** (211 mg, 0.95 mmol), triphenylphosphane (747 mg, 2.85 mmol) and benzoic acid (348 mg, 2.85 mmol) in THF (15 mL) was added a solution of diethyl azodicarboxylate (DEAD, ca. 40% toluene solution, 827 mg, ca. 1.90 mmol) in THF (6 mL). The mixture was stirred for 12 h and then concentrated under reduced pressure. Silica-gel chromatography (hexane/ethyl acetate = 6:1) of the residue gave the crude benzoate, which was used directly in the subsequent transformation. The mixture of the above benzoate (ca. 0.95 mmol) and K_2CO_3 (131 mg, 0.95 mmol) in methanol (15 mL) was stirred for 2 h, acidified with 1 N HCl and then extracted with ethyl acetate. The organic layer was washed with brine and dried with $MgSO_4$. Evaporation of the solvent gave a crude product, which was purified by silica-gel column chromatography (hexane/ethyl acetate = 2:1−1:1) to afford 128 mg [61% from (±)-**12**] of the epimerized alcohol (±)-**14** as colorless needles, m.p. 155−156°C (hexane/diethyl ether). − IR (KBr): $\tilde{\nu}$ = 3455 cm^{-1} (s, O−H), 2940 (s, C−H), 1765 (s, C=O), 1305 (m, O−H), 1215 (s, C−O), 1065 (m, C−O), 1030 (m, C−O). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.72 (s, 3 H, 8-Me), 1.10 (s, 3 H, 8-Me), 1.31−1.49 (m, 3 H, 6-H and 7-CH_2), 1.79 (d, 1 H, J = 5.0 Hz, OH), 1.96 (m, 1 H, 6-H′), 2.41 (dd, 1 H, J = 18.1, J' = 2.1 Hz, 3-H), 2.51 (s, 1 H, 8a-H), 2.73 (dd, 1 H, J = 18.1, J' = 9.9 Hz, 3-H′), 3.42 (m, 1 H, 3a-H), 4.21 (m, 1 H, 5-H), 4.90 (d, 1 H, J = 6.4 Hz, 8b-H), 5.42 (d, 1 H, J = 1.7 Hz, 4-H). − $C_{13}H_{18}O_3$ (222.3): calcd. C 70.24, H 8.16; found C 70.23, H 8.33.

(±)-(3a*R,5*S**,8a*S**,8b*S**)-5-Hydroxy-8,8-dimethyl-3,3a,5,6,7,8,8a,8b-octahydroindeno[1,2-*b*]furan-2-one [(±)-15]:** In the same manner as described for (±)-**14**, esterification of the alcohol (±)-**13** (140 mg, 0.63 mmol) and subsequent hydrolysis gave the epimerized alcohol (±)-**15** (69 mg, 49%) as a pale yellowish paste; n_D^{23} = 1.5180. − IR (film): $\tilde{\nu}$ = 3420 cm^{-1} (s, O−H), 2940 (s, C−H), 1760 (s, C=O), 1360 (m, O−H), 1170 (s, C−O), 1050 (s, C−O). − ^{1}H NMR (90 MHz, $CDCl_3$): δ = 0.90 (s, 3 H, 8-Me), 1.14 (s, 3 H, 8-Me), 1.00−2.06 (m, 4 H, 6-CH_2 and 7-CH_2), 2.10−2.96 (m, 4 H, 3-CH_2, 8a-H and OH), 3.48 (m, 1 H, 3a-H), 4.08 (br d, 1 H, J = 7.0 Hz, 5-H), 5.26 (t, 1 H, J = 7.7 Hz, 8b-H), 5.56 (d, 1 H, J = 2.0 Hz, 4-H). − HRMS calcd. for $C_{13}H_{18}O_3$ 222.1256; found 222.1243. − MS (EI, 70 eV); *m/z*: 222 [M^+], 204, 189, 163, 154, 144, 129, 107, 95, 70, 55, 41.

(±)-(3a*R,5*S**,8a*R**,8b*S**,2′*R**)- and (±)-(3a*R**,5*S**,8a*R**,8b*S**,2′*S**)-3-[(*E*)-2′,5′-Dihydro-4′-methyl-5′-oxo-2′-furanyloxymethylene]-5-hydroxy-8,8-dimethyl-3,3a,5,6,7,8,8a,8b-octahydroindeno[1,2-*b*]furan-2-one [(±)-4a and (±)-4b]:** To a stirred suspension of NaH (ca. 60% suspension in oil, 46 mg, ca. 1.04 mmol), washed with dry diethyl ether several times, in dry diethyl ether (2.0 mL) at room temperature under argon, was added a solution of the hydroxylactone (±)-**12** (84 mg, 0.38 mmol) in dry diethyl ether (3.0 mL) and dry THF (3.0 mL), followed by ethyl formate (0.45 mL, ca. 2.25 mmol). After stirring for 13 h, the mixture was acidified with 1 N HCl and then extracted with ethyl acetate. The organic layer was washed with water and brine, and dried with $MgSO_4$. Evaporation of the solvent under reduced pressure gave the crude hydroxymethylene lactone as pale orange foam, which was used directly in the subsequent transformation without further purification. To a stirred mixture of the above hydroxymethylene lactone (ca. 0.38 mmol) and K_2CO_3 (105 mg, 0.76 mmol) in anhydrous *N*-methylpyrrolidone (3.3 mL), at room temperature under argon, was added a solution of (±)-4-bromo-2-methyl-2-buten-4-olide[20] (135 mg, 0.76 mmol) in anhydrous *N*-methylpyrrolidone (2.0 mL). After stirring for 13 h at room temperature, the reaction mixture was poured into 1 N HCl (10 mL) and extracted with ethyl acetate. The organic layer was washed with water twice and brine, and dried with $MgSO_4$. Evaporation of the solvent under reduced pressure gave a yellowish residue, which was purified by silica-gel chromatography (hexane/ethyl acetate = 1:1) to afford 42 mg (32%) of (±)-**4a** (R_f = 0.18, $CHCl_3$/acetone = 4:1) as colorless prisms and 42 mg (32%) of its 2′-epimer (±)-**4b** (R_f = 0.33, $CHCl_3$/acetone = 4:1) as colorless crystals. The structures of (±)-**4a** and (±)-**4b** were determined by the X-ray analysis of (±)-**4a**. − **(±)-4a:** M.p. 229−231°C (hexane/ethyl acetate). − IR (KBr): $\tilde{\nu}$ = 3465 cm^{-1} (m, O−H), 2950 (m, C−H), 1790 (s, C=O), 1725 (s, C=O), 1680 (s, C=C), 1345 (m, O−H), 1200 (s, C−O), 1100 (s), 1050 (m, C−O), 1020 (s, C−O), 1005 (s, C−O), 965 (s), 885 (m). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.68 (s, 3 H, 8-Me), 1.12 (s, 3 H, 8-Me), 1.21 (m, 1 H, 7-H), 1.52 (s, 1 H, OH), 1.64 (dt, 1 H, J = 14.4, J' = 3.5 Hz, 7-H′), 1.72−1.89 (m, 2 H, 6-CH_2), 2.02 (t, 3 H, J = 1.5 Hz, 4′-Me), 2.89 (d, 1 H, J = 0.9 Hz, 8a-H), 3.96 (dq, 1 H, J = 7.0, J' = 2.0 Hz, 3a-H), 4.48 (s, 1 H, 5-H), 4.86 (d, 1 H, J = 7.2 Hz, 8b-H), 5.52 (t, 1 H, J = 1.8 Hz, 4-H), 6.16 (t, 1 H, J = 1.4 Hz, 2′-H), 6.94 (t, 1 H, J = 1.6 Hz, 3′-H), 7.40 (d, 1 H, J = 2.1 Hz, 9-H). − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 10.8, 19.0, 29.3, 29.8, 34.4, 34.7, 47.2, 57.9, 65.7, 82.4, 100.5, 110.8, 121.5, 136.0, 140.9, 145.6, 149.9, 171.1, 171.6. − $C_{19}H_{22}O_6$ (346.2): calcd. C 65.88, H 6.40; found C 65.84, H 6.44. − **(±)-4b:** M.p. 166−167°C (ethyl acetate). − IR (KBr): $\tilde{\nu}$ = 3505 cm^{-1} (w, O−H), 2960 (w, C−H), 1770 (s, C=O), 1755 (s, C=O), 1685 (s, C=C), 1340 (m, O−H), 1185 (s, C−O), 1090 (s), 1050 (s, C−O), 1020 (s, C−O), 960 (s). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.69 (s, 3 H, 8-Me), 1.12 (s, 3 H, 8-Me), 1.21 (m, 1 H, 7-H), 1.47 (br. s, 1 H, OH), 1.62 (dt, 1 H, J = 14.3, J' = 3.6 Hz, 7-H′), 1.74−1.90 (m, 2 H, 6-CH_2), 2.03 (t, 3 H, J = 1.5 Hz, 4′-Me), 2.89 (d, 1 H, J = 1.2 Hz, 8a-H), 3.95 (dq, 1 H, J = 7.1, 2.0 Hz, 3a-H), 4.48 (s, 1 H, 5-H), 4.86 (d, 1 H, J = 7.1 Hz, 8b-H), 5.51 (t, 1 H, J = 1.9 Hz, 4-H), 6.15 (s, 1 H, 2′-H), 6.92 (t, 1 H, J = 1.6 Hz, 3′-H), 7.39 (d, 1 H, J = 2.1 Hz, 9-H). − $C_{19}H_{22}O_6$ (346.2): calcd. C 65.88, H 6.40; found C 66.02, H 6.51.

(±)-(3a*R,5*R**,8a*R**,8b*S**,2′*R**)- and (±)-(3a*R**,5*R**,8a*R**,8b*S**,2′*S**)-3-[(*E*)-2′,5′-Dihydro-4′-methyl-5′-oxo-2′-furanyloxymethylene]-5-hydroxy-8,8-dimethyl-3,3a,5,6,7,8,8a,8b-octahydroindeno[1,2-*b*]furan-2-one [(±)-4c and (±)-4d]:** In the same manner as described for (±)-**4a** and (±)-**4b**, the lactone (±)-**14** (127 mg, 0.57 mmol) was converted to (±)-**4c** [colorless crystals, 81 mg, 41%, R_f = 0.30 ($CHCl_3$/acetone = 4:1)] and (±)-**4d** [colorless crystals, 90 mg, 45%, R_f = 0.41 ($CHCl_3$/acetone = 4:1)] . The relative configurations at C-2′ in (±)-**4c** and (±)-**4d** were assigned on the basis of their m.p. and R_f values. − **(±)-4c:** M.p. 220−222°C (ethyl acetate). − IR (KBr): $\tilde{\nu}$ = 3550 cm^{-1} (m, O−H), 2965 (m, C−H), 1785

(s, C=O), 1750 (s, C=O), 1680 (s, C=C), 1385 (m, O−H), 1340 (m, O−H), 1190 (s, C−O), 1095 (s), 1020 (s, C−O), 955 (s), 865 (m). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.71 (s, 3 H, 8-Me), 1.09 (s, 3 H, 8-Me), 1.34−1.50 (m, 3 H, 7-CH_2 and OH), 1.89−1.98 (m, 2 H, 6-CH_2), 2.01 (t, 3 H, *J* = 1.5 Hz, 4′-Me), 2.50 (s, 1 H, 8a-H), 4.00 (dt, 1 H, *J* = 6.9, *J*′ = 2.0 Hz, 3a-H), 4.18 (m, 1 H, 5-H), 4.85 (dd, 1 H, *J* = 6.9, *J*′ = 0.7 Hz, 8b-H), 5.52 (q, 1 H, *J* = 1.9 Hz, 4-H), 6.15 (t, 1 H, *J* = 1.4 Hz, 2′-H), 6.94 (t, 1 H, *J* = 1.6 Hz, 3′-H), 7.40 (d, 1 H, *J* = 2.1 Hz, 9-H). − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 10.7, 19.3, 28.9, 32.3, 34.1, 38.8, 47.3, 61.8, 69.8, 82.7, 100.5, 111.0, 117.1, 135.8, 141.0, 147.1, 150.0, 170.3, 171.1. − $C_{19}H_{22}O_6$ (346.2): calcd. C 65.88, H 6.40; found C 65.95, H 6.46. − **(±)-4d:** M.p. 133−135°C (ethyl acetate). − IR (KBr): ṽ = 3400 cm^{-1} (m, O−H), 2950 (m, C−H), 1780 (s, C=O), 1750 (s, C=O), 1685 (s, C=C), 1345 (m, O−H), 1210 (m, C−O), 1185 (s, C−O), 1095 (s), 1025 (s, C−O), 960 (m). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.72 (s, 3 H, 8-Me), 1.09 (s, 3 H, 8-Me), 1.33−1.50 (m, 3 H, 7-CH_2 and OH), 1.90−1.98 (m, 2 H, 6-CH_2), 2.02 (t, 3 H, *J* = 1.5 Hz, 4′-Me), 2.50 (s, 1 H, 8a-H), 4.00 (ddd, 1 H, *J* = 6.9, *J*′ = 2.1, *J*′′ = 2.0 Hz, 3a-H), 4.18 (m, 1 H, 5-H), 4.85 (dd, 1 H, *J* = 6.9, *J*′ = 0.9 Hz, 8b-H), 5.50 (q, 1 H, *J* = 1.9 Hz, 4-H), 6.15 (t, 1 H, *J* = 1.4 Hz, 2′-H), 6.93 (t, 1 H, *J* = 1.6 Hz, 3′-H), 7.38 (d, 1 H, *J* = 2.1 Hz, 9-H). − $C_{19}H_{22}O_6$ (346.2): calcd. C 65.88, H 6.40; found C 66.06, H 6.45.

(±)-(3a*R,5*R**,8a*S**,8b*S**,2′*R**)- and (±)-(3a*R**,5*R**,8a*S**,8b*S**,2′*S**)-3-[(*E*)-2′,5′-Dihydro-4′-methyl-5′-oxo-2′-furanyloxymethylene]-5-hydroxy-8,8-dimethyl-3,3a,5,6,7,8,8a,8b-octahydroindeno[1,2-*b*]furan-2-one [(±)-4e and (±)-4f]:** In the same manner as described for (±)-**4a** and (±)-**4b**, the hydroxylactone (±)-**13** (38 mg, 0.17 mmol) was converted to (±)-**4e** [colorless crystals, 16 mg, 27%, R_f = 0.36 (hexane/ethyl acetate = 1:4)] and (±)-**4f** [white foams, 16 mg, 27%, R_f = 0.43 (hexane/ethyl acetate = 1:4)]. The relative configurations at C-2′ in (±)-**4e** and (±)-**4f** were assigned on the basis of their R_f values. − **(±)-4e:** M.p. 119−123°C (ethyl acetate). − IR (KBr): ṽ = 3450 cm^{-1} (w, O−H), 2945 (m, C−H), 1775 (s, C=O), 1755 (s, C=O), 1685 (s, C=C), 1350 (m, O−H), 1180 (m, C−O), 1165 (m, C−O), 1100 (s), 1035 (s, C−O), 1015 (s, C−O), 950 (s). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.85 (s, 3 H, 8-Me), 1.21 (s, 3 H, 8-Me), 1.10−1.30 (m, 2 H), 1.57 (m, 1 H), 1.65−1.81 (m, 2 H, 6-CH_2), 2.04 (t, 3 H, *J* = 1.5 Hz, 4′-Me), 2.95 (dd, 1 H, *J* = 7.9, *J*′ = 2.1 Hz, 8a-H), 4.05 (d, 1 H, *J* = 7.9 Hz, 3a-H), 4.49 (s, 1 H, 5-H), 5.28 (t, 1 H, *J* = 8.0 Hz, 8b-H), 5.67 (t, 1 H, *J* = 2.4 Hz, 4-H), 6.14 (t, 1 H, *J* = 1.4 Hz, 2′-H), 6.94 (t, 1 H, *J* = 1.6 Hz, 3′-H), 7.41 (d, 1 H, *J* = 2.5 Hz, 9-H). − $C_{19}H_{22}O_6$ (346.2): calcd. C 65.88, H 6.40; found C 65.62, H 6.46. − **(±)-4f:** IR (KBr): ṽ = 3450 cm^{-1} (m, O−H), 2945 (m, C−H), 1785 (s, C=O), 1745 (s, C=O), 1680 (s, C=C), 1340 (m, O−H), 1180 (s, C−O), 1095 (s), 1035 (s, C−O), 1020 (s, C−O), 955 (s). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.85 (s, 3 H, 8-Me), 1.21 (s, 3 H, 8-Me), 1.10−1.50 (m, 2 H, 7-H and OH), 1.58 (m, 1 H, 7-H′), 1.67−1.82 (m, 2 H, 6-CH_2), 2.03 (t, 3 H, *J* = 1.4 Hz, 4′-Me), 2.95 (dd, 1 H, *J* = 8.0, *J*′ = 1.8 Hz, 8a-H), 4.07 (d, 1 H, *J* = 7.8 Hz, 3a-H), 4.48 (s, 1 H, 5-H), 5.28 (t, 1 H, *J* = 8.0 Hz, 8b-H), 5.69 (t, 1 H, *J* = 2.3 Hz, 4-H), 6.16 (t, 1 H, *J* = 1.3 Hz, 2′-H), 6.94 (t, 1 H, *J* = 1.5 Hz, 3′-H), 7.40 (d, 1 H, *J* = 2.5 Hz, 9-H). − HRMS calcd. for $C_{19}H_{22}O_6$ 346.1415; found 346.1439.

(±)-(3a*R,5*S**,8a*S**,8b*S**,2′*R**)- and (±)-(3a*R**,5*S**,8a*S**,8b*S**,2′*S**)-3-[(*E*)-2′,5′-Dihydro-4′-methyl-5′-oxo-2′-furanyloxymethylene]-5-hydroxy-8,8-dimethyl-3,3a,5,6,7,8,8a,8b-octahydroindeno[1,2-*b*]furan-2-one [(±)-4g and (±)-4h]:** In the same manner as described for (±)-**4a** and (±)-**4b**, the hydroxylactone (±)-**15** (62 mg, 0.28 mmol) was converted to (±)-**4g** (28 mg, 29%, R_f = 0.36, hexane/ethyl acetate = 1:4), white foams] and (±)-**4h** (30 mg, 31%, R_f = 0.40, hexane/ethyl acetate = 1:4), white foams] . The relative configurations at C-2′ in (±)-**4g** and (±)-**4h** were assigned on the basis of their R_f values. − **(±)-4g:** IR (KBr): ṽ = 3450 cm^{-1} (m, O−H), 2945 (m, C−H), 1785 (s, C=O), 1745 (s, C=O), 1680 (s, C=C), 1350 (m, O−H), 1185 (s, C−O), 1100 (s), 1020 (s, C−O), 955 (s). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (s, 3 H, 8-Me), 1.19 (s, 3 H, 8-Me), 1.04−1.30 (m, 1 H), 1.36−1.50 (m, 2 H), 1.58−1.82 (m, 1 H), 1.90 (m, 1 H, 6-H), 2.02 (t, 3 H, *J* = 1.4 Hz, 4′-Me), 2.60 (d, 1 H, *J* = 8.2 Hz, 8a-H), 4.07 (m, 1 H, 3a-H), 4.15 (m, 1 H, 5-H), 5.29 (t, 1 H, *J* = 8.1 Hz, 8b-H), 5.70 (q, 1 H, *J* = 2.3 Hz, 4-H), 6.14 (t, 1 H, *J* = 1.4 Hz, 2′-H), 6.95 (t, 1 H, *J* = 1.6 Hz, 3′-H), 7.42 (d, 1 H, *J* = 2.5 Hz, 9-H). − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 10.7, 22.1, 29.3, 31.3, 34.8, 41.9, 47.3, 57.9, 69.9, 82.2, 100.5, 111.1, 117.9, 135.8, 141.0, 147.4, 150.2, 170.2, 171.4. − HRMS calcd. for $C_{19}H_{22}O_6$ 346.1415; found 346.1391. − **(±)-4h:** IR (KBr): ṽ = 3450 cm^{-1} (m, O−H), 2950 (m, C−H), 1780 (s, C=O), 1745 (s, C=O), 1685 (s, C=C), 1350 (m, O−H), 1185 (s, C−O), 1100 (s), 1020 (s, C−O), 955 (s). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87 (s, 3 H, 8-Me), 1.18 (s, 3 H, 8-Me), 1.04−1.22 (m, 1 H), 1.35−1.50 (m, 2 H), 1.73 (br s, 1 H), 1.90 (m, 1 H, 6-H), 2.03 (t, 3 H, *J* = 1.5 Hz, 4′-Me), 2.59 (dd, 1 H, *J* = 8.3, *J*′ = 1.9 Hz, 8a-H), 4.03−4.19 (m, 2 H, 3a-H and 5-H), 5.29 (t, 1 H, *J* = 8.1 Hz, 8b-H), 5.68 (q, 1 H, *J* = 2.2 Hz, 4-H), 6.15 (t, 1 H, *J* = 1.3 Hz, 2′-H), 6.94 (t, 1 H, *J* = 1.6 Hz, 3′-H), 7.40 (d, 1 H, *J* = 2.4 Hz, 9-H). − $C_{19}H_{22}O_6$ (346.2): calcd. C 65.88, H 6.40; found C 65.35, H 6.39.

(±)-(3a*R,8b*S**)-8,8-Dimethyl-4-oxo-3,3a,4,5,6,7,8,8b-octahydroindeno[1,2-*b*]-furan-2-one [(±)-17]:** To a stirred suspension of chromium trioxide (26.0 g, 0.26 mol) in dry CH_2Cl_2 (200 mL) was added 3,5-dimethylpyrazole (25.0 g, 0.26 mol) in one portion at −20°C under argon. The mixture was stirred for 30 min at −20°C and then a solution of the lactone (±)-**16**[17] (536 mg, 2.6 mmol) in dry CH_2Cl_2 (40 mL) was added at −20°C. After stirring for 5 h at −20°C, 5 N NaOH (122 mL) was added in one portion. The mixture was stirred for 20 min at 0°C and extracted with CH_2Cl_2. The organic layer was washed successively with water, 1 N HCl, water, satd. $NaHCO_3$ solution and brine, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was chromatographed on silica gel (hexane/ethyl acetate = 6:1) to afford first 130 mg (23%) of (±)-**17** (R_f = 0.48, hexane/ethyl acetate = 1:1) as colorless rods and then 427 mg (75%) of (±)-**7** (R_f = 0.36, hexane/ethyl acetate = 1:1) as colorless needles. − **(±)-17:** M.p. 69−71°C (hexane/diethyl ether). − IR (KBr): ṽ = 2955 cm^{-1} (m, C−H), 1770 (s, C=O), 1710 (s, C=O), 1645 (m, C=C), 1235 (m, C−O), 1175 (s, C−O), 1030 (m, C−O), 1005 (s, C−O). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.25 (s, 3 H, 8-Me), 1.26 (s, 3 H, 8-Me), 1.46−1.78 (m, 4 H, 6-CH_2 and 7-CH_2), 2.11 (dtd, 1 H, *J* = 18.3, *J*′ = 6.9, *J*′′ = 2.0 Hz, 5-H), 2.23 (dt, 1 H, *J* = 18.6, *J*′ = 5.3 Hz, 5-H′), 2.64 (dd, 1 H, *J* = 19.0, *J*′ = 4.6 Hz, 3-H), 2.90 (dd, 1 H, *J* = 19.0, *J*′ = 12.4 Hz, 3-H′), 3.19 (ddd, 1 H, *J* = 12.4, *J*′ = 6.2, *J*′′ = 4.6 Hz, 3a-H), 5.54 (dd, 1 H, *J* = 6.2, *J*′ = 2.1 Hz, 8b-H). − $C_{13}H_{16}O_3$ (220.3): calcd. C 70.89, H 7.32; found C 70.94, H 7.34.

(±)-(3a*R,4*R**,8b*S**)- and (±)-(3a*R**,4*S**,8b*S**)-4-Hydroxy-8,8-dimethyl-3,3a,4,5,6,7,8,8b-octahydroindeno[1,2-*b*]furan-2-one [(±)-18 and (±)-19]:** To a stirred solution of the α,β-unsaturated ketone (±)-**17** (119 mg, 0.54 mmol) in ethanol (4 mL) was added $CeCl_3 \cdot 7\ H_2O$ (201 mg, 0.54 mmol) followed by slow addition of sodium tetrahydroborate (21 mg, 0.54 mmol). After stirring for 30 min, the reaction mixture was quenched by dropwise addition of 1 N HCl and then extracted with CH_2Cl_2. The organic layer was washed with brine and dried with $MgSO_4$. Evaporation of the solvent gave a crude product, which was chromatographed on silica gel (hexane/ethyl acetate = 4:1) to afford first 95 mg (79%) of (±)-

18 (R_f = 0.24, hexane/ethyl acetate = 1:1) as colorless columns and then 6 mg (5%) of (±)-**19** (R_f = 0.16, hexane/ethyl acetate = 1:1) as a pale yellowish paste. The stereostructures of (±)-**18** and (±)-**19** were determined by the X-ray analysis of (±)-**18**. − **(±)-18:** M.p. 79−80°C (hexane/diethyl ether). − IR (KBr): $\tilde{\nu}$ = 3445 cm^{-1} (s, O−H), 1745 (s, C=O), 1195 (s, C−O), 1005 (m, C−O). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.09 (s, 3 H, 8-Me), 1.13 (s, 3 H, 8-Me), 1.38 (dd, 1 H, J = 13.5, J' = 6.4 Hz, 7-H), 1.51 (dt, 1 H, J = 13.5, J' = 5.0 Hz, 7-H′), 1.71 (m, 2 H, 6-CH_2), 1.96 (m, 1 H, 5-H), 2.02 (m, 1 H, OH), 2.26 (dt, 1 H, J = 17.9, J' = 5.4 Hz, 5-H′), 2.51 (dd, 1 H, J = 18.5, J' = 10.9 Hz, 3-H), 2.86 (dd, 1 H, J = 18.5, J' = 5.2 Hz, 3-H′), 3.12 (dtd, 1 H, J = 10.9, J' = 7.3, J'' = 5.2 Hz, 3a-H), 4.54 (dd, 1 H, J = 7.0, J' = 6.9 Hz, 4-H), 5.26 (dd, 1 H, J = 7.2, 1.8 Hz, 8b-H). − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 19.1, 23.7, 27.7, 28.1, 28.4, 32.0, 38.8, 40.2, 75.9, 86.3, 143.0, 143.6, 177.7. − $C_{13}H_{18}O_3$ (222.3): calcd. C 70.24, H 8.16; found C 70.16, H 8.30. − **(±)-19:** n_D^{24} = 1.5187. − IR (film): $\tilde{\nu}$ = 3580−3200 cm^{-1} (s, O−H), 2940 (s, C−H), 1760 (s, C=O), 1340 (m, O−H), 1325 (m, O−H), 1175 (s, C−O), 1030 (s, C−O), 1005 (s, C−O). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.11 (s, 3 H, 8-Me), 1.12 (s, 3 H, 8-Me), 1.47 (m, 2 H, 7-CH_2), 1.72 (m, 2 H, 6-CH_2), 1.98 (dt, 1 H, J = 17.9, J' = 5.5 Hz, 5-H), 2.17 (dtd, 1 H, J = 17.9, J' = 6.9, J'' = 2.0 Hz, 5-H′), 2.44 (m, 1 H 3-H), 2.78−2.93 (m, 2 H, 3-H′ and 3a-H), 2.85 (dd, 1 H, J = 23.1, J' = 10.7 Hz, 3-H′), 4.45 (s, 1 H, 4-H), 5.56 (dd, 1 H, J = 3.9, 2.3 Hz, 8b-H). − HRMS calcd. for $C_{13}H_{18}O_2$ 222.1256; found 222.1267. − MS (EI, 70 eV); m/z = 222 [M^+], 207, 189, 147, 138, 119, 105, 95, 70, 55.

Conversion of (±)-18 to (±)-19 Utilizing Mitsunobu Inversion: In the same manner as described for (±)-**14**, esterification of the alcohol (±)-**18** (64 mg, 0.29 mmol) and subsequent hydrolysis gave the epimerized alcohol (±)-**19** (63 mg, 98%) as a pale yellowish paste, which was employed in the next step without further purification.

(±)-(3a*R,4*S**,8b*S**,2′*R**)- and (±)-(3a*R**,4*S**,8b*S**,2′*S**)-3-[(*E*)-2′,5′-Dihydro-4′-methyl-5′-oxo-2′-furanyloxymethylene]-4-hydroxy-8,8-dimethyl-3,3a,4,5,6,7,8,8b-octahydroindeno[1,2-*b*]furan-2-one [(±)-5a and (±)-5b]:** In the same manner as described for (±)-**4a** and (±)-**4b**, the hydroxylactone (±)-**19** (27 mg, 0.12 mmol) was converted to (±)-**5a** [16 mg, 38%, R_f = 0.32 (hexane/ethyl acetate = 1:4), colorless crystals] and (±)-**5b** [13 mg, 31%, R_f = 0.26 (hexane/ethyl acetate = 1:4), colorless needles]. The structures of (±)-**5a** and (±)-**5b** were determined by the X-ray analysis of (±)-**5b**. − **(±)-5a:** M.p. 170−172°C (hexane/ethyl acetate). − IR (KBr): $\tilde{\nu}$ = 3600−3300 cm^{-1} (w, O−H), 1790 (s, C=O), 1735 (s, C=O), 1725 (s, C=C), 1675 (s, C=C), 1345 (m, O−H), 1180 (s, C−O), 1095 (s, C−O), 1015 (s, C−O), 955 (s). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.13 (s, 3 H, 8-Me), 1.14 (s, 3 H, 8-Me), 1.39−1.52 (m, 2 H, 7-CH_2), 1.71 (m, 2 H, 6-CH_2), 1.87 (d, 1 H, J = 6.2 Hz, OH), 1.96 (dt, 1 H, J = 17.8, J' = 5.4 Hz, 5-H), 2.04 (t, 3 H, J = 1.5 Hz, 4′-Me), 2.18 (tdt, 1 H, J = 17.8, J' = 7.4, J'' = 2.1 Hz, 5-H′), 3.42 (ddd, 1 H, J = 7.3, J' = 2.5, J'' = 1.9 Hz, 3a-H), 4.58 (d, 1 H, J = 6.2 Hz, 4-H), 5.61 (d, 1 H, J = 7.3 Hz, 8b-H), 6.21 (s, 1 H, 2′-H), 6.95 (t, 1 H, J = 1.5 Hz, 3′-H), 7.48 (d, 1 H, J = 2.7 Hz, 9-H). − $C_{19}H_{22}O_6$ (346.2): calcd. C 65.88, H 6.40; found C 65.80, H 6.41. − **(±)-5b:** M.p. 200−201°C (hexane/ethyl acetate). − IR (film): $\tilde{\nu}$ = 3465 cm^{-1} (w, O−H), 2955 (m, C−H), 1790 (s, C=O), 1725 (s, C=O), 1680 (s, C=C), 1345 (s, O−H), 1240 (m, C−O), 1190 (s, C−O), 1100 (s, C−O), 1020 (s, C−O), 980 (s), 955 (s). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.13 (s, 3 H, 8-Me), 1.14 (s, 3 H, 8-Me), 1.38−1.52 (m, 2 H, 7-CH_2), 1.70 (m, 2 H, 6-CH_2), 1.91 (d, 1 H, J = 6.2 Hz, OH), 1.96 (dt, 1 H, J = 17.8, J' = 5.4 Hz, 5-H), 2.03 (t, 3 H, J = 1.5 Hz, 4′-Me), 2.16 (dtd, 1 H, J = 17.8, J' = 7.7, J'' = 2.3 Hz, 5-H′), 3.41 (ddd, 1 H, J = 7.3, J' = 2.7, J'' = 1.7 Hz, 3a-H), 4.56 (d, 1 H, J = 6.2 Hz, 4-H), 5.61 (d, 1 H, J = 7.3 Hz, 8b-H), 6.18 (t, 1 H, J = 1.5 Hz, 2′-H), 6.97 (t, 1 H, J = 1.6 Hz, 3′-H), 7.52 (d, 1 H, J = 2.7 Hz, 9-H). − ^{13}C NMR (100.4 MHz, $CDCl_3$): δ = 10.8, 18.9, 23.6, 27.4, 27.9, 32.1, 38.8, 48.2, 83.0, 85.9, 100.6, 111.2, 136.1, 141.1, 143.0, 144.2, 151.1, 170.1, 170.9. − HRMS calcd. for $C_{19}H_{22}O_6$ 346.1415; found 346.1415. − $C_{19}H_{22}O_6$ (346.2): calcd. C 65.88, H 6.40; found C 65.75, H 6.56.

X-ray Analysis of (±)-4a: The crystal used for data collection was a colorless prism with the approximate dimensions 0.5 × 0.3 × 0.3 mm. All the data were obtained with a Rigaku AFC-5S automated four-circle diffractometer with graphite-monochromated Mo-K_α radiation. Unit cell parameters were determined by least-squares refinement of the optimized setting angles of 25 reflections in the range 10.1° < θ < 16.8°. Crystal data: $C_{19}H_{22}O_6$, M_r = 346.38, triclinic, space group $P\bar{1}$, a = 9.822(7), b = 12.247(3), c = 8.979(2) Å, α = 97.94(2), β = 115.40(2), γ = 108.10(3)°, V = 879.8(8) Å^3, Z = 2, D_C = 1.307 g cm^{-3}, F(000) = 368 and μ(Mo-K_α) = 0.968 cm^{-1}. The intensities were measured using ω/2θ scans up to 50°. Three standard reflections were monitored every 150 measurements. The data were corrected for Lorentz and polarization factors. Absorption correction was applied. Of the 3116 independent reflections collected, 2305 reflections with I > 3.0 σ(I) were used for the structure determination and refinement. The structure was solved by direct method using TEXSAN crystallographic software package.[21] All non-H atoms were found in Fourier map. The refinement of atomic parameters were carried out by the full matrix least-squares refinement, using anisotropically temperature factors for all non-H atoms. H atoms were placed geometrically and not refined, except that of hydroxy group, which was located in difference map and refined isotropically. The final refinement converged with R = 0.045 and R_w = 0.047 for 230 parameters. The minimum and maximum peaks in the final difference Fourier map were −0.30 and 0.32 e Å^{-3}. Atomic scattering factors were taken from "International Tables for X-ray Crystallography".[22] The supplementary material includes the lists of atomic coordinates for the non-H atoms, the bond lengths and angles of (±)-**4a** with their e.s.d.s in parentheses.[23]

X-ray Analysis of (±)-18: The crystal used for data collection was a colorless column with the approximate dimensions 0.8 × 0.6 × 0.5 mm. All the data were obtained with a Rigaku AFC-5S automated four-circle diffractometer with graphite-monochromated Mo-K_α radiation. Unit cell parameters were determined by least-squares refinement of the optimized setting angles of 25 reflections in the range 12.1° < θ < 16.5°. Crystal data: $C_{13}H_{18}O_3$, M_r = 222.28, monoclinic, space group $P2_1/a$, a = 13.595(4), b = 5.946(8), c = 16.379(3) Å, β = 114.16(1)°, V = 1208(2) Å^3, Z = 4, D_C = 1.222 g cm^{-3}, F(000) = 480 and μ(Mo-K_α) = 0.661 cm^{-1}. The intensities were measured using ω/2θ scans up to 50°. Three standard reflections were monitored every 150 measurements. The data were corrected for Lorentz and polarization factors. Absorption correction was applied and decay correction was not applied. Of the 2367 independent reflections collected, 1447 reflections with I > 2.0 σ(I) were used for the structure determination and refinement. The structure was solved by direct method using TEXSAN crystallographic software package.[21] All non-H atoms were found in Fourier map. The refinement of atomic parameters were carried out by the full-matrix least-squares refinement, using anisotropically temperature factors for all non-H atoms. All H atoms except for one attached to O of the hydroxy group were located geometrically and not refined. The H atom attached to O of the hydroxy group was located from difference Fourier map, and refined isotropically. The final refinement converged

with $R = 0.050$ and $R_w = 0.057$ for 149 parameters. The minimum and maximum peaks in the final difference Fourier map were −0.19 and 0.13 eÅ^{-3}. Atomic scattering factors were taken from "International Tables for X-ray Crystallography".[22] The supplementary material includes the lists of atomic coordinates for the non-H atoms, the bond lengths and angles of (±)-**18** with their e.s.d.s in parentheses.[23]

X-ray Analysis of (±)-5b: The crystal used for data collection was a colorless needle with the approximate dimensions 0.5 × 0.2 × 0.2 mm. All the data were obtained with a Rigaku AFC-5S automated four-circle diffractometer with graphite-monochromated Mo-K_α radiation. Unit cell parameters were determined by least-squares refinement of the optimized setting angles of 25 reflections in the range $7.9° < \theta < 10.0°$. Crystal data: $C_{19}H_{22}O_6$, $M_r = 346.38$, monoclinic, space group $P2_1/n$, $a = 7.799(10)$, $b = 10.337(6)$, $c = 21.240(5)$ Å, $\beta = 95.77(4)°$, $V = 1704(2)$ Å^3, $Z = 4$, $D_C = 1.350$ g cm^{-3}, $F(000) = 736$ and μ(Mo-K_α) = 1.001 cm^{-1}. The intensities were measured using ω/2θ scan up to 50°. Three standard reflections were monitored every 150 measurements. The data were corrected for Lorentz and polarization factors. Absorption correction was applied and decay correction was not applied. Of the 3216 independent reflections collected, 1674 reflections with $I > 2.0\ \sigma(I)$ were used for the structure determination and refinement. The structure was solved by direct method using TEXSAN crystallographic software package.[21] All non-H atoms were found in Fourier map. The refinement of atomic parameters were carried out by the full-matrix least-squares refinement, using anisotropically temperature factors for all non-H atoms. All H atoms except for one attached to O of the hydroxy group were located geometrically and not refined. The H atom attached to O of the hydroxy group was located from difference Fourier map, and refined isotropically. The final refinement converged with $R = 0.078$ and $R_w = 0.089$ for 230 parameters. The minimum and maximum peaks in the final difference Fourier map were −0.29 and 0.45 eÅ^{-3}. Atomic scattering factors were taken from "International Tables for X-ray Crystallography".[22] The supplementary material includes the lists of atomic coordinates for the non-H atoms, the bond lengths and angles of (±)-**5b** with their e.s.d.s in parentheses.[23]

Bioassay Using *Orobanche minor* Seeds:[18] Seeds of *Orobanche minor* (clover broomrape) were harvested at the riverside of Watarase river in Tochigi, Japan, dried and stored in a refrigerator. Compounds to be tested were dissolved in 10^{-4} M gibberelin A_3 solution. For preconditioning, seeds were spread on a glass fiber filter paper (5 mm diameter) wet with 10^{-4} M gibberelin A_3 solution and stored in the dark for 10 d at room temperature. The seeds were then treated with test solutions of (±)-**4a**−(±)-**4h**, (±)-**5a** and (±)-**5b**. After incubation in the dark for 3 d, germination rates were determined under a microscope. In each test series, 10^{-4} M gibberelin A_3 solution was used as negative control and (±)-strigol was used as positive control. Tests were replicated 3 times.

Bioassay Using *Striga asiatica* Seeds:[19] Seeds of *Striga asiatica* (witchweed) were obtained from the USDA Methods Development Laboratory, Whiteville, N.C., USA. For preconditioning, seeds were spread on a glass fiber filter paper (5 mm diameter) wetted with water and stored in the dark for 7 d at room temperature. The seeds were then treated with test solutions of (±)-**4a**−(±)-**4h**, (±)-**5a** and (±)-**5b**. After incubation in the dark for 1 d, germination rates were determined under a microscope. In each test series, water was used as negative control and (±)-strigol was used as positive control. Tests were replicated 3 times.

GC-MS Analysis of TMS Ethers:[11] GC-MS analysis (ionization voltage = 70 eV) was conducted on a short DB-5 capillary column (4 m × 0.25 mm) using He as carrier gas at a flow rate of 1 mL/min. Samples were introduced in a splitless mode. To analyze TMS ethers which were prepared by reacting the samples with *N*-methyl-*N*-(trimethylsilyl)trifluoroacetamide at room temperature for 10 min, the column temperature was kept at 130°C for the first 1.5 min, elevated to 220°C by 32°C/min gradient, then to 270°C by 16°C/min gradient and finally kept at 270°C for 5 min. − **TMS-(±)-4a ($C_{22}H_{30}O_6Si$):** t_R = 4′42″; MS (EI, 70 eV); *m/z*: 418 [M$^+$], 403, 362, 321, 303, 293, 281, 265, 247, 231, 210, 195, 175, 105, 97, 75, 69. − **TMS-(±)-4b ($C_{22}H_{30}O_6Si$):** t_R = 4′42″; MS (EI, 70 eV); *m/z*: 418 [M$^+$], 403, 362, 321, 303, 293, 281, 265, 247, 231, 210, 195, 185, 175, 105, 97, 75. − **TMS-(±)-4c ($C_{22}H_{30}O_6Si$):** t_R = 4′57″; MS (EI, 70 eV); *m/z*: 418 [M$^+$], 403, 362, 321, 303, 293, 265, 247, 210, 195, 182, 175, 97, 73. − **TMS-(±)-4d ($C_{22}H_{30}O_6Si$):** t_R = 4′52″; MS (EI, 70 eV); *m/z*: 418 [M$^+$], 403, 385, 362, 328, 321, 293, 265, 247, 210, 195, 182, 147, 97, 73. − **TMS-(±)-4e ($C_{22}H_{30}O_6Si$):** t_R = 4′40″; MS (EI, 70 eV); *m/z*: 418 [M$^+$], 403, 362, 349, 321, 303, 293, 265, 247, 231, 213, 195, 185, 163, 131, 105, 97, 75. − **TMS-(±)-4f ($C_{22}H_{30}O_6Si$):** t_R = 4′46″; MS (EI, 70 eV); *m/z*: 418 [M$^+$], 403, 362, 349, 321, 303, 293, 265, 247, 231, 213, 195, 185, 147, 97, 75. − **TMS-(±)-4g ($C_{22}H_{30}O_6Si$):** t_R = 4′56″; MS (EI, 70 eV); *m/z*: 418 [M$^+$], 403, 362, 349, 321, 303, 293, 265, 247, 231, 210, 195, 185, 170, 97, 73. − **TMS-(±)-4h ($C_{22}H_{30}O_6Si$):** t_R = 4′49″; MS (EI, 70 eV); *m/z*: 418 [M$^+$], 403, 362, 349, 321, 303, 293, 265, 247, 231, 210, 195, 185, 175, 143, 97, 73. − **TMS-(±)-5a ($C_{22}H_{30}O_6Si$):** t_R = 4′45″; MS (EI, 70 eV); *m/z*: 418 [M$^+$], 403, 371, 349, 321, 309, 299, 285, 275, 231, 210, 203, 187, 170, 97, 95, 73. − **TMS-(±)-5b ($C_{22}H_{30}O_6Si$):** t_R = 4′42″; MS (EI, 70 eV); *m/z*: 418 [M$^+$], 403, 371, 349, 321, 309, 299, 285, 275, 231, 210, 203, 187, 175, 97, 75, 73. − **TMS-(±)-Strigol ($C_{22}H_{30}O_6Si$):** t_R = 4′55″; MS (EI, 70 eV); *m/z*: 418 [M$^+$], 403, 362, 321, 309, 303, 293, 265, 247, 231, 210, 195, 185, 175, 105, 97, 75, 73. − **TMS-Orobanchol ($C_{22}H_{30}O_6Si$):** t_R = 4′45″; MS (EI, 70 eV); *m/z*: 418 [M$^+$], 403, 349, 321, 300, 299, 285, 275, 231, 210, 203, 187, 170, 97, 73.

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