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STEREOCHEMISTRY OF cis-CLERODANE DITERPENES

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Abstract - To piscicidal solidagolactones [IV, V, VII and VIII (1 ~ 4, cis-clerodane diterpenes)] isolated from Solidago altissima, a non-steroidal conformation was assigned on the basis of chemical and physicochemical evidence. ^{13}C NMR chemical shifts of methyl groups proved useful for determining stereochemistry of the A/B ring junction in clerodanes. For clerodanes having an epoxide, ^{1}H NMR data and the Tori equation were useful for assigning the epoxide configuration. Cremer's puckering parameters were used to express the conformation of the solidagolactones.

Introduction

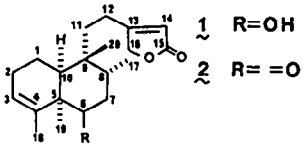
Some erroneous assignments have been reported for absolute configurations[1], stereochemistry of the A/B ring junction[2] and epoxide configurations[3] in clerodane diterpenes.

We have isolated solidaoglactones IV(1), V(2), VII(3) and VIII(4) (all cis-clerodane diterpenes) from Solidago altissima L. (Compositae) as piscicidal constituents, and determined their absolute configurations, as reported in short communications[3,4]. In this paper, we wish to describe structure determination of 1 ~ 4 in detail, and also to demonstrate the usefulness of ^{13}C NMR chemical shifts of methyl groups, Cremer's puckering parameters and one of the Tori equations for determining stereochemistry of A/B ring junction, precise molecular conformation and epoxide configuration, respectively. The epoxide configurations of several cis-clerodanes are corrected in this study.

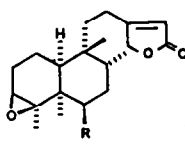
Isolation and Structures of Solidagolactones

By monitoring the piscicidal activity for killifish, we isolated piscicidal compounds 1 ~ 4 from the methanol (MeOH) extract of S. altissima by column chromatographies and recrystallization (1 ~ 3) (Scheme 1).

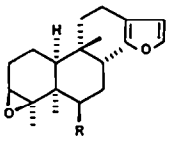
Compounds 1 ~ 3 were the known solidagolactones IV, V and VII[2], respectively. ^{1}H NMR spectrum of 4, a new compound named as solidagolactone VIII, quite resembled to that of 3 except for protons on the C6 substituent [δ 1.81 (3H, dm, J=6.8 Hz, 1.89 (3H, m) and 6.90 (1H, qq, J=1.2 and 6.8 Hz)], which was assigned to tygloyloxyl moiety. The C6 protons (H6) showed a triplet in 1 (δ 3.71) or double doublets in 3 (δ 5.44) and 4 (δ 5.40) signals, all of which possessing small J values (2.50 ~ 2.80 Hz). This means that the H6 in these compounds is in equatorial position.



1 R=OH
2 R= =O



3 R=OCO
4 R=OCO
16 R=OCO—Br



5 R=OCO
6 R=OCO
7 R=OH

With diisobutylaluminum hydride (DIBAL) in tetrahydrofuran (THF) (-35° → -20°C, 3.5 hr), 3 and 4 converted into furano-compounds 5 and 6, respectively, both of which showed the presence of a β-substituted furan ring in IR (ν_{max} 880 cm^{-1}) and ^{1}H NMR [δ 6.25 (1H, m), 7.21 (1H, m) and 7.35 (1H, t, J=1.5 Hz)] spectra. Both 5 and 6 gave identical

furano-alcohol (7) [IR: ν_{max}(film) 3480 cm^{-1}; ^1H NMR: 4.13 (1H, t, J=2.6 Hz, H6)] on treatment with lithiumaluminium hydride (LAH) (THF, 0°→15°C, 3 hr). The OH proton of 7 resonated at very low field [δ5.44 (1H, bs)]. On treatment with m-chloroperbenzoic acid (CH_2Cl_2, room temperature, 1 hr), 1 gave two epoxides 8 and 9 (ratio 1.7:1). According to usual epoxidation mechanism of homoallylic alcohol[5], the major product 8 was expected to have a β-epoxide ring (Fig. 1-A). Acetate (10) yielded only α-epoxide 11 (identified by acetylation of 9) under the same epoxidation condition as performed for 1 (Fig. 1-B). From these observations, a non-steroidal conformation is assigned to 1.

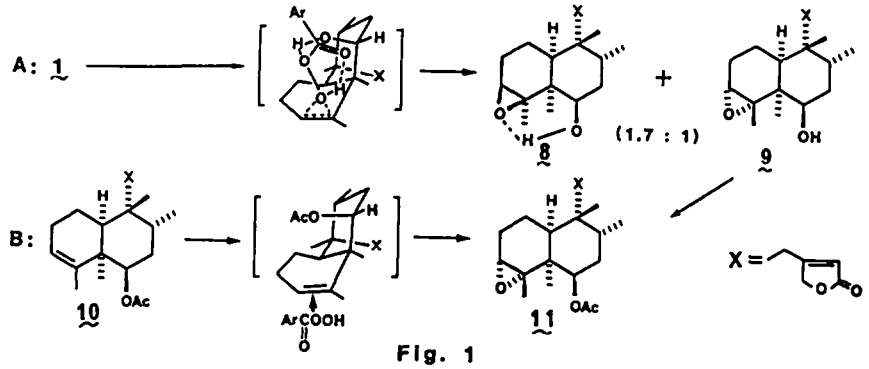
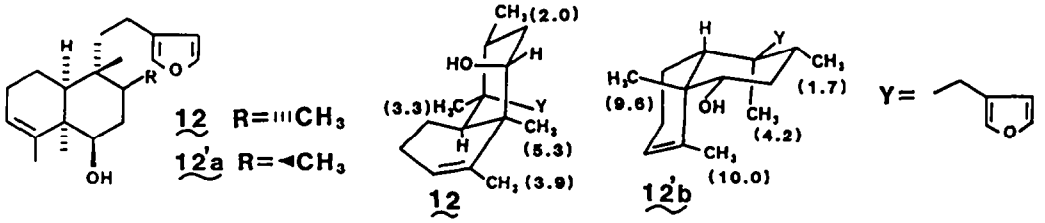


Fig. 1

In 8, an intramolecular hydrogen bond exists based on ^1H NMR signal at δ5.41 and IR ($CHCl_3$) band at 3470 cm^{-1} which was unaffected upon dilution. On the other hand, 9 showed a strong band at 3600 cm^{-1} and a weak band at 3475 cm^{-1} (disappeared upon dilution) in IR ($CHCl_3$), and a multiplet signal at much higher field (δ1.8) in ^1H NMR. Therefore, an intramolecular hydrogen bond exists between the β-C6-OH and the β-C3-C4 epoxide oxygen in 8 which afforded 7 on reaction with DIBAL (THF, -35°→-25°C, 3.5 hr). Thus, we assigned β-configuration to the epoxide ring of solidagolactone VII(3) and VIII(4). The former was previously reported as the α-epoxide compound[2].

McCrindle et al.[6] added $Eu(dpm)_3$ in the ^1H NMR measurement of 12'b (antipode of 12'a), and gave a normalized ratio of 10 : 9.6 : 1.7 : 4.2 in the induced shifts of protons of C18, C19, C17 and C20 methyls, respectively. They gave a steroid-like conformation to 12'b (see below). We measured ^1H NMR of 12 (C8 epimer of 12'a), which was a DIBAL reduction product of 1, in the presence of $Eu(dpm)_3$. A normalized ratio for the C18, C19, C17 and C20 methyl protons was 3.9 : 5.3 : 2.0 : 3.3, respectively. The value of 5.3 of C19 methyl indicates an anti-trans relation to the axial C6-OH group. Our normalized ratio is consistent only with non-steroidal conformation, which also agrees with the above epoxidation results.



A direct confirmation to the stereochemistry of the solidagolactones was obtained by chemical reactions. 1 was treated with N-bromosuccinimide (NBS) (THF, room temperature, 45 min) to give an oxetane 13 in quantitative yield (attack of β-OH to C4). ^1H NMR spectrum of 13 showed a singlet signal of C18 methyl protons (expressed as H_3C18) at δ 1.66 and two double doublet signals at δ4.09 (J=3.9 and 5.6 Hz) and 4.46 (J= 2.6 and 3.3 Hz)(H3 and H6 respectively). ^{13}C NMR signals of 13 at δ59.55 (d, C3), 79.81 (d, C6) and 84.62 (s, C4) supported the structure 13.

If a compound having an ether bond between C3 and C6 (14) was isolated, it should

prove the cis-A/B ring junction and non-steroidal conformation. Indeed, on treatment of **13** with p-toluenesulfonic acid, **14** was obtained as a minor product (21%) together with a major product **15** (36%). ^{1}H NMR of **14** showed signals at δ1.82 (3H, s, H_3C18), 3.75 (1H, dd, J=2.2 and 3.1 Hz, H6) and 4.02 (1H, dd, J=1.7 and 3.0 Hz, H3). ^{13}C NMR signals at δ74.66 (s), 76.77(d) and 81.63(d) were assigned to C4, C3 and C6, respectively. If C4-O bond cleaves in preference to the C6-O bond, generating a carbenium ion on C4, the carbenium ion will collapse with the bromine atom at C3, forming a bromonium cation. Then, attack by the oxygen atom at C3 gives **14** (Fig. 2). **15** can be considered as originating from an intermediate **13'**.

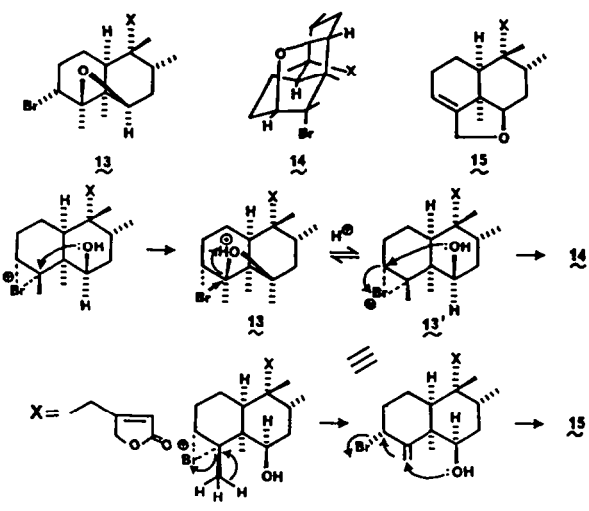


Fig. 2

We conclude the 5α,10α-cis-clerodane skeleton with β-C6-OH for the solidagolactones. The absolute configurations of the solidagolactones were determined by X-ray analyses[3] and the CD benzoate method[4] using p-bromobenzoate derivative (**16**). It is noted that there is no essential conformational change in **16** between solution and crystal.

Utilization of ^{13}C NMR Chemical Shifts of Pendant Methyls to Assign Stereochemistry of A/B Ring Junction of Clerodane Diterpenes

The X-ray analysis of tricyclosolidagolactone[7] revised the stereochemistry of A/B ring junction of solidagolactones II ~ VII from trans to cis. The ^{13}C chemical shifts of some pendant methyl groups of clerodane diterpenes is discussed here in relation to the stereochemistry of ring junction.

As shown in Table 1, ^{13}C chemical shifts of C11 methyl of decalins and C19 methyl of steroids reflect stereochemistry of A/B ring junction. The methyl carbon atoms in cis resonate in a region of about 12 ppm higher field than those in trans. Similarly, C19's of our clerodanes resonate in a region higher than δ20, in particular around δ25. The corresponding carbon atoms of other cis-clerodanes also resonate in the same region, whereas C19's in trans-clerodanes appear at δ11 ~ 19. In cis-clerodanes, C20 resonates also at lower field (δ21 ~ 29) than that in trans-clerodanes (δ17 ~ 19).

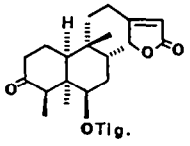
^{13}C chemical shift of a carbon atom is influenced by the shielding effect from carbon atoms with γ-gauche relationship[15,16]. In trans-clerodanes, the number of carbon atoms having γ-gauche interaction with C19 is larger than that in cis-clerodanes. The chemical shifts of C20 indicate axial orientation in trans-clerodanes and equatorial in cis-clerodanes. C17 carbon atoms are generally possess constant chemical shifts (around δ15) because this methyl is equatorial in both cis- and trans-clerodanes.

^{13}C chemical shifts of methyls, especially C19, are thus useful to distinguish between cis and trans ring junction in clerodane diterpenes.

Cremer's Ring Puckering Parameters for cis-Clerodane Diterpenes

For a quantitative conformational analysis for cyclopentanes, cyclohexanes and heterocyclic rings, Cremer and Pople[17] have proposed a generalized set of puckering coordinate, which is composed of three parameters, Q[total puckering amplitude: length (Å)], θ[magnitude of distortion from complete chair conformation: angle (degree)] and φ[magnitude in change of conformation: angle (degree)]. Calculation of Cremer's parameters needs Cartesian coordinate of the skeletal atoms[17], which is derived from cell

Table 1 ^{13}C Chemical Shifts of Pendant Methyl Groups in ^{13}C NMR
(δppm in $CDCl_3$, unless otherwise stated)

	Compound	C11			Reference
	cis-10-Methyldecalin	24.1[a]			8
	trans-10-Methyldecalin	12.1[a]			8
		C19			
	5β-Androstane	24.1[b]			8
	5α-Androstane	12.0[b]			8
	Coprostane	24.1[c]			8
	Chorestane	12.5[c]			8
		C17	C19	C20	
cis	Tricyclosolidagolactone[d]	-[e]	21.2	23.8	7
	1	15.40	24.18	28.34	
	2	15.17	21.55	24.24	
	3	15.75	26.64	27.46	
	4	15.75	26.53	27.46	
	5	15.75	26.53	28.05	
	6	15.81	26.47	28.05	
	7	15.58	25.24	28.58	
	8	15.52	25.24	28.34	
	9	15.28	22.37	28.87	
	10	15.28	24.54	28.11	
	11	15.05	21.90	28.69	
	12	15.46	24.13	28.58	
	13	15.17	26.29	24.54	
	14	14.58	27.46	28.28	
	15	14.29	21.73	29.28	
		15.23	28.46	26.66	9
trans	2-Oxokolavenic acid	15.8	19.5	17.8	10
	Deacetylajugarin-II	15.5	*[f]	17.6	11
	Teumassilin	15.6	*	17.6	11
	6,19-Diacetylteumassilin	15.5	*	17.3	11
	Ajugarin-I	15.3	*	17.3	12
	Ajugarin-IV	15.4	10.6	17.8	13
	Eremone	7.8	18.5[g] / 18.8 / 18.9	18.5[g] / 18.8 / 18.9	14

a: Taken with neat liquid with TMS. b: Taken in a $CDCl_3$ solution and originally shown in shift values upfield from CS_2. Values converted to the TMS scale are shown here. c: Taken in a CH_2Cl_2, CH_2Cl-$CDCl_3$ or CH_2Cl_2-dioxane solution. The chemical shifts were originally referenced to CH_2Cl_2 as internal standard and converted to the CS_2 scale. Values in this table are reconverted from the CS_2 scale to the TMS scale. d: The reported shift values were assigned by us. e: This carbon is included in the cyclic structure. f: Substituents are not methyl group. g: These assignments may be reversed.

Table 2. Cartesian Coordinates (Å) for Decalin Skeleton of 16

			X	Y	Z				X	Y	Z
A-ring	origin at C1	C1	0	1.3988	-0.3792	B-ring	origin at C9	C5	1.0366	-0.7478	0.1287
		C2	1.2759	0.7734	0.2159			C6	-0.0697	-1.2160	-0.1680
		C3	1.2645	-0.7149	0.0383			C7	-1.0720	-0.5923	0.2179
		C4	0.0359	-1.4641	-0.1296			C8	-0.9941	0.7025	-0.2288
		C5	-1.3550	-0.7648	-0.0337			C9	0	1.2536	0.1895
		C10	-1.2216	0.7714	0.2879			C10	1.0990	0.5996	-0.1895

coordinates induced from X-ray data.

In clerodane diterpenes, Eguren et al.[18] have reported Cremer's puckering parameters for neo- and norneo-clerodanes having trans A/B ring junction. For cis-clerodanes, however, none of the parameters has been reported yet.

The cell coordinates in the X-ray data for the skeletal carbons of p-bromobenzoate (16) were transformed to Cartesian coordinates (Table 2). In this case, C1 and C9 were

chosen as origins of the A- and B-ring, respectively[18]. Q, θ and φ values were evaluated to be Q_A = 0.541 Å and Q_B = 0.447Å, θ_A = 124.4° and θ_B = 11.8°, and, ϕ_A = 170.7° and ϕ_B =281.9°. These values imply that the A-ring takes an envelope conformation flapping at C1, and the B-ring a slightly deformed chair conformation flattening at C5 (Fig. 3-A). The tortion around the C5–C10 axis is shown by dihedral angles of C4–C5–C10–C1 (35.60°) and C8–C5–C10–C9 (43.02°)(Fig. 3-B).

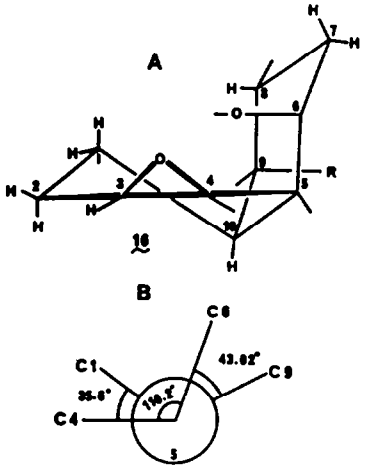


Fig. 3

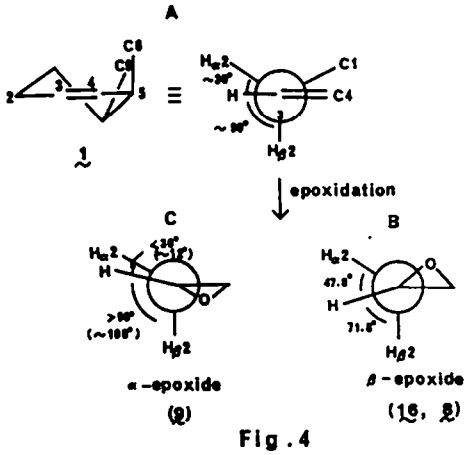


Fig. 4

Utilization of the Tori Equation to Assign Epoxide Configuration on Clerodane Skeleton

Table 3 compiles ^{1}H NMR data of the epoxide proton (H3) and C19 methyl protons (H_3C19) of clerodane diterpenes possessing a C3–C4 epoxide.

In our compounds, coupling patterns and/or coupling constants of H3 signals showed clear differences between α- and β-epoxides, despite no significant difference in their chemical shifts. Singlet or doublet signals having small J values (1.5 ~ 2.4 Hz) were observed in the β-epoxides, while doublet signals have a large value (J=5.1 Hz) in the α-epoxides. C19 methyl protons resonated at a lower field (δ1.19 ~ 1.27) in the β-epoxides than in the α-epoxides (δ1.16). According to these observations, the previous epoxide configurations should be revised as indicated in Table 3.

Tori *et al.*[19] have proposed an equation, J=5.1 $\cos^2\theta$, to correlate coupling constants of epoxide protons with dihedral angles in the >C–CH(O)–CH–C< system of steroidal epoxides (episulfides). We wish to show here that the equation is useful for the confiurational assignment of epoxides in clerodane diterpenes.

From the X-ray data of **16**, the dihedral angles of H3–C3–C2–H_α2 and H3–C3–C2–H_β2 are 47.80° and 71.80°, respectively (Fig. 4-B), which respectively corresponds to $J_{3,2\alpha}$ = 0.50 and $J_{3,2\beta}$ = 2.30 Hz by the Tori equation. These J values agree with the observed values, $J_{3,2\alpha}$ = ~0 and $J_{3,2\beta}$ = 1.5 Hz in **16**; $J_{3,2\alpha}$ = ~0 and $J_{3,2\beta}$ = 2.40 Hz in **7** and **8**.

The A-ring of **1** is expected to have dihedral angles of ca. 30° and ca. 90° at H3–C3–C2–H_α2 and H3–C3–C3–H_β2, respectively (Fig. 4-A). This means that the change of ca. 18° occurs in these dihedral angles between **1** and the β-epoxide **8**. In α-epoxide (**9**), the change of also ca. 18° is expected for these dihedral angles, namely, ca. 12° for H3–C3–C2–H_α2 and ca. 108° for H3–C3–C2–H_β2 (Fig. 4-C). The values, $J_{3,2\alpha}$ = 4.88 (12°) and $J_{3,2\beta}$ = 0.49 Hz (108°), calculated from the Tori equation agreed with the observed values ($J_{2,3\alpha}$ = 5.1 and $J_{3,2\beta}$ =~0 Hz).

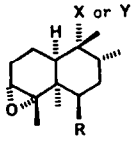
EXPERIMENTAL

Melting points were uncorrected. Specific rotations were measured in ethanol (EtOH), unless otherwise stated, at 25°C with a Union automatic polarimeter PM-201. UV spectra were recorded in EtOH on a Cary 17 UV spectrometer. CD curves were run in EtOH

Table 3. ^{1}H NMR Data of H3 and $H_3$19 of α- and β-Epoxide in Clerodane Diterpenes

(Taken in $CDCl_3$ and TMS, unless otherwise stated)

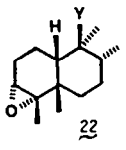
Compound	Original assignment to α-epoxide					Compound	Original assignment to β-epoxide				
	H3		H_3C19	Reference	Revision of epoxide configuration		H3		H_3C19	Reference	Revision of epoxide configuration
	δppm	J(Hz)	δppm				δppm	J(Hz)	δppm		
9	3.11	5.1	1.16	this work	-	3	2.75	bs	1.22	this work	-
11	3.04	5.1	1.16	"	-	4	2.75	bs	1.22	"	-
17[a]	-	-	1.22	2,20	→β	5	2.75	bs	1.27	"	-
18	2.72	s	1.22	2	→β(3)[b]	6	2.75	bs	1.27	"	-
18	2.74	br	1.22	9	→β(3)	7	3.01	2.4	1.19	"	-
19	2.70	s	1.26	2	→β(5)	16	2.75	1.5	1.26	"	-
20	2.75	br	1.22	9	→β(4)	23	3.04	4	1.14	9	→α
21	2.99	2	1.20	6	→β	24	3.04	4	1.16	9	→α
22[c]	2.77	W½5	1.27	6	→β	25	2.99	5.0	1.08	6	→α
						26[d]	2.89	5.0	1.17	6	→α



17 R=O·Ac, X (11)[b] 20 R=O·Tig., X

18 R=O·Ang., X 21 R=H, Y

19 R=O·Ang., Y



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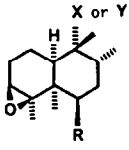
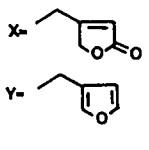


23 R=O·Ang., X (3)

24 R=O·Tig., X (4)

25 R=H, Y

26 R=H, X



a, No ^{1}H NMR data in reference 2, but only H_3C19 in reference 20. b, Compounds in parentheses indicate our compounds.

c, Taken in CCl_4. d, The ^{1}H NMR data was presented by Anthonsen et al. (Acta Chem Scand, 1971, 25, 1924).

on a JASCO J-40A spectropolarimeter. IR spectra were recorded on a Hitachi Model 260-50 IR spectrometer. ^{1}H NMR and ^{13}C NMR spectra were taken in $CDCl_3$ and TMS with a JEOL FX90Q spectrometer at 89.55 MHz and 22.50 MHz, respectively. Mass spectra (MS) were measured with a Shimadzu GCMS-7000 mass spectrometer using a direct inlet system. Exact MS were obtained with a JEOL JMS-01SC mass spectrometer. E. Merck silica gel (60, particle size 0.063-0.2 mm) and Wako alumina activated (200 mesh) were used for column chromatographies. The above silica gel impregnated with 10% (w/w) $AgNO_3$ was also used for column chromatography. Preparative thin layer chromatography (TLC) was performed on 2mm x 20cm x 20cm E. Merck precoated silica gel plates (60F-254) or E. Merck precoated aluminum oxide plates (150F-254, type T).

Isolation of piscicidal solidagolactones.

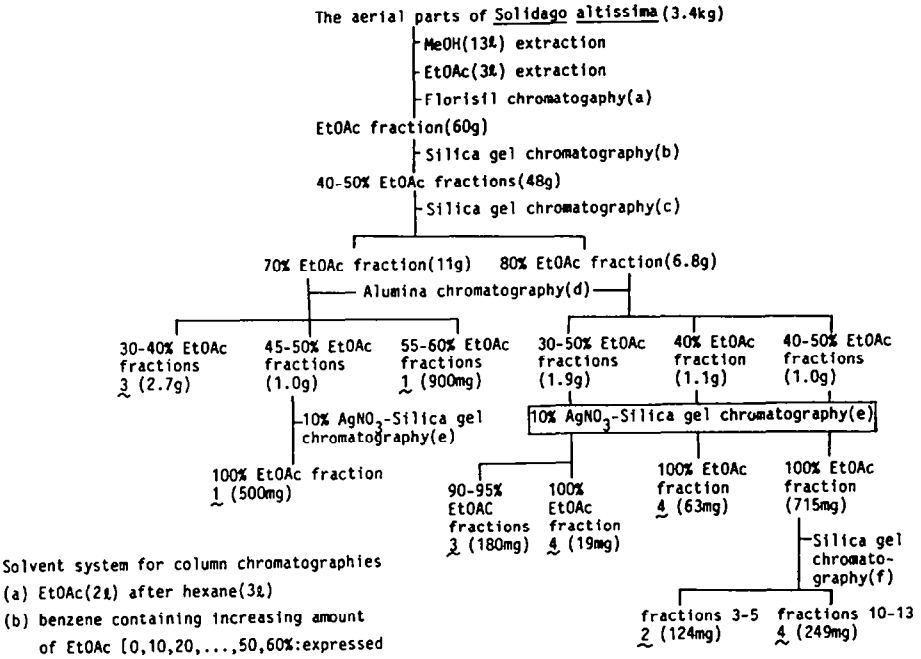
Isolation procedure is shown in Scheme 1.

^{13}C NMR data of solidagolactones

Physical data other than ^{13}C NMR are reported in a previous paper[3] for solidagolactones (1~4) isolated.

Solidagolactone IV [(5R, 6R, 8R, 9R, 10S)-6-Hydroxy-cis-cleroda-3,13-diene-15,16-olide (1)], ^{13}C NMR, δppm : 15.40 (q, C17), 18.33 (q, C18), 22.55 (t, C2), 23.25 (t, C11), 24.18 (q, C19), 26.35 (t, C1), 28.34 (q, C20), 30.63 (d, C8), 32.91 (t, C7), 33.67 (t, C12), 38.65 (s, C9), 44.21 (s, C5), 44.21 (d, C10), 71.27 (d, C6), 73.02 (t, C16), 115.13 (d, C14), 128.77 (d, C3), 137.03 (s, C4), 171.10 (s, C13), 173.86 (s, C15).

Solidagolactone V [(5R, 8R, 9R, 10S)-6-Keto-cis-3,13-diene-15.16-olide(2)] ^{13}C NMR, δppm : 15.17 (q, C17), 19.56 (t, C2), 20.26 (q, C18), 21.55 (q, C19), 22.78 (t, C1), 23.54 (t, C11), 24.24 (t, C20), 34.84 (t, C12), 38.00 (d, C8), 38.82 (s, C9), 44.15 (t, C7), 46.32 (d, C10), 52.29 (s, C5), 72.96 (t, C16), 115.30 (d, C14), 124.96 (d, C3), 134.27 (s, C4), 170.52 (s, C13), 173.68 (s, C15), 215.08 (s, C6). Solidagolactone VII [(3S, 4R, 5R, 6R, 8R, 9R, 10S)-3,4-Epoxy-6-angeloyloxy-cis-cleroda-13-ene-15,16-olide) (3)] ^{13}C NMR, δppm : 15.75 (q, C17 and, C4' or C5'), 19.03 (t, C2), 20.73 (q, C4' or C5'), 21.73 (q, C18), 23.42 (t, C11), 26.64 (q, C19), 27.64 (q, C20), 27.76 (t, C1), 32.56 (t, C7), 32.91 (d, C8), 34.49 (t, C12), 38.30 (s, C9), 40.41 (s, C5), 45.21 (d, C10), 57,27 (d, C3), 61.66 (s, C4), 75.50 (d, C6), 72.96 (t, C16), 115.30 (d, C14), 128.65 (s, C2'), 137.73 (d, C3'), 167.01, (s, C1'), 170.64 (s, C13), 173.68 (s, C15). Solidagolactone VIII [(3S, 4R, 5R, 6R, 8R, 9R, 10S)-3,4-Epoxy-6-tygloyloxy-cis-cleroda-13-ene-15,16-olide] (4) ^{13}C NMR, δppm : 12.18 (q, C4' or C5'), 14.41 (q, C4' or C5'), 15.75 (q, C17), 19.15 (t, C2), 21.61 (q, C18), 23.42 (t, C11), 26.53 (q, C19), 27.46 (q, C20), 27.70 (t, C1), 32.38 (t, C7),



Solvent system for column chromatographies
(a) EtOAc(2ℓ) after hexane(3ℓ)
(b) benzene containing increasing amount of EtOAc [0,10,20,...,50,60%:expressed as 10% stepwise (0→60%)]
(c) hexane-EtOAc, 10% stepwise (0→100%)
(d) benzene-EtOAc, 10% stepwise (0→100%)
(e) hexane-EtOAc, 5% stepwise (0→100%)
(f) hexane-EtOAc (4:1)

Total yield
1 (1.40g): mp. 137-138°C (hexane-EtOAc); $[\alpha]_D^{25}$+3.58° (c 0.921, EtOH)
2 (124mg): mp. 106.5°-107°C (hexane); $[\alpha]_D^{25}$+125.2° (c 1.15, EtOH)
3 (2.88g): mp. 119-120°C (hexane-EtOAc); $[\alpha]_D^{25}$-28.4° (c 1.29, EtOH)
4 (331mg): oil; $[\alpha]_D^{25}$-27.4° (c 0.341, EtOH)

Scheme 1

32.73 (d, C8), 34.43 (t, C12), 38.30 (s, C9), 40.41 (s, C5), 45.15 (d, C10), 57.33 (d, C3), 61.66 (s, C4), 72.96 (t, C16), 73.20 (d, C6), 115.24 (d, C14), 129.42 (s, C2'), 136.68 (d, C3'), 167.41 (s, C1'), 170.69 (s, C13), 173.68 (s, C15).

DIBAL reduction of 3 and 4. To a THF (15 ml) solution of 3 (245 mg), 1M THF solution of DIBAL (0.66 ml) was added dropwise at -35°C in argon atmosphere. After stirring for 3.5 hr (-35°→-20°C) 10% H_2SO_4 (aq. soln.) (0.5 ml) was added to the reaction mixture, and the mixture was further stirred for 20 min. at -20°→-25°C. After addition of water (5.0 ml), the reaction mixture was extracted with EtOAc. The EtOAc layer was evaporated to give a residue. Silica gel preparative TLC (benzene - EtOAc, 4 : 1) of the residue gave 5 (106.3 mg : conversion yield, 63%) and unchanged 3 (70.0 mg). Similarly, 6 (58.0 mg, conversion yield 57%) was given from 4 (138 mg). 5, $[\alpha]_D$ -23.6° (c 1.10). ν_{max}^{film}, cm^{-1} : 1712, 1650, 1238, 878. ^1H NMR, δppm : 0.86 (3H, d, J = 6.4 Hz, H_3C17), 1.03 (3H, s, H_3C20), 1.27 (3H, s, H_3C19), 1.31 (3H, s, H_3C18), 1.99 (3H, m, H_3C5'), 2.04 (3H, dm, J = 6.8 Hz, H_3C4'), 2.75 (1H, bs, H3'), 5.44 (1H, dd, J = 2.2 and 3.5 Hz, H6), 6.06 (1H, qq, J = 1.1 and 6.8 Hz, H3'), 6.25 (1H, m, H of furan), 7.21 (1H, m, H of furan), 7.35 (1H, t, J = 1.6 Hz, H of furan). ^{13}C NMR, δppm : 15.75 (q, C17 and C4' or C5'), 19.09 (t, C2), 19.32 (t, C11), 20 79 (q, C4' or C5'), 21.67 (q, C18), 26.53 (q, C19), 27.82, (t, C1), 28.05 (q, C20), 32.62 (t, C7), 32.85 (d, C8), 37.36 (t, C12), 38.30 (s, C9), 40.35 (s, C5), 44.74 (d, C10), 57.39 (d, C3), 61.90 (s, C4), 72.73 (d, C6), 110.91 (d, C14), 125.56 (s, C13), 128.83 (s, C2'), 137.44 (d, C3'), 138.43 (d, C16), 142.77 (d, C15), 167.07 (s, C1'). MS, m/z : 400 (M^+, $C_{25}H_{36}O_4$), 382 (M^+-H_2O), 317 ($M^+-CH_3(H)C{=}C(CH_3)CO$), 301 ($M^+-CH_3(H)C{=}C(CH_3)CO_2$), 300 ($M^+-CH_3(H)C{=}C(CH_3)CO_2H$). 6, mp. 84.5°-86°C (hexane-EtOAc). $[\alpha]_D$ -31.9°(c 0.345). ν_{max}^{film}, cm^{-1} : 1710, 1655, 1270, 880. ^1H NMR, δppm : 0.85 (3H, d, J = 6.6 Hz, H_3C17), 1.04 (3H, s, H_3C20), 1.27 (3H, s, H_3C19), 1.29 (3H, s, H_3C18), 1.80 (3H, dm, J = 6.8 Hz, H_3C4'), 1.90 (3H, m, H_3C5'), 2.75 (1H, bs, H3), 5.41 (1H, dd, J = 2.4 and 3.5 Hz, H6), 6.26 (1H, m, H of furan), 6.91 (1H, qq, J = 1.2 and 6.8 Hz, H3'), 7.21 (1H, m, H of furan), 7.35 (1H, t, J = 1.5 Hz, H of furan). ^{13}C NMR, δppm : 12.24 (q, C4' or C5'), 14.41 (q, C41 or C51), 15.81 (q, C17), 19.27 (t, C2), 19.38 (t, C11), 21.55 (q, C18), 26.47 (q, C19), 27.82 (t, C1), 28.05 (q, C20), 32.50 (d, C8), 32.73 (t, C7), 37.36 (t, C12), 38.30 (s, C9), 40.41 (s, C5), 44.80 (d, C10), 57.45 (d, C3), 61.96 (s, C4), 73.49 (d, C6), 110.91 (d, C14), 125.55 (s, C13), 129.59 (s, C2'), 136.50 (d, C4'), 138.43 (d, C16), 142.77 (d, C15), 167.53 (s, C1'). MS, m/z : 400 (M^+, $C_{25}H_{36}O_4$), 385 (M^+-CH_3), 382 (M^+-H_2O), 317 ($M^+-CH_3(H)C{=}C(CH_3)C$),301 ($M^+-CH_3(H)C{=}C(CH_3)CO_2$), 300 ($M^+-CH_3(H)C{=}C(CH_3)CO_2H$). Anal. Calcd. for $C_{25}H_{36}O_4$: C, 74.96;

H, 9.06. Found : C, 75.17; H, 9.21.

LiAlH$_4$ reduction of **5** and **6**. To a mixture of LiAlH$_4$ (20 mg) and THF (2 ml), a THF (1 ml) solution of **5** or **6** (30 mg) was added dropwise in argon atmosphere under ice-cooling, and the reaction mixture was stirred for 3 hr at 15°C. After a small amount of an aqueous solution of potassium sodium tartrate was added to the mixture under ice-cooling, and then the mixture was filtered. The filtrate was concentrated to give a residue which was chromatographed on silica gel (benzene-EtOAc, 4 : 1). The obtained **7** (18.4 mg, 77%) was a colorless oil. **7**, $[\alpha]_D$ -28.0° (c 0.900). ν_{max}^{film}, cm^{-1} : 3480, 875. ^{1}H NMR, δppm : 0.85 (3H, d, J = 7.0 Hz, H$_3$C17), 1.02 (3H, s, H$_3$C20)1.19 (3H, s, H$_3$C19), 1.37 (3H, s, H$_3$C18), 3.01 (1H, d, J = 2.4 Hz, H3), 4.13 (1H, t, J = 2.6 Hz, H6), 5.44 (1H, bs, OH), 6.25 (1H, m, H of furan), 7.20 (1H, m, H of furan), 7.35 (1H, t, J = 1.5 Hz, H of furan). ^{13}C NMR, δppm : 15.58 (q, C17), 19.38 (t, C11), 19.91 (t, C2), 21.78 (q, C18), 25.24 (q, C19), 27.46 (t, C1), 28.58 (q, C20), 30.98 (d, C8), 33.85 (t, C7), 37.42 (t, C12), 38.47 (s, C9), 39.70 (s, C5), 43.57 (d, C10), 59.91 (d, C3), 65.70 (s, C4), 74.43 (d, C6), 110.91 (d, C14), 125.61 (s, C13),138.43 (d, C16), 142.76 (d, C15). MS, m/z : 318 (M$^+$, C$_{20}$H$_{30}$O$_3$), 300 (M$^+$-H$_2$O), 285 (M$^+$-H$_2$O-CH$_3$). Exact MS, m/z : 318.2192 (Calcd. for C$_{20}$H$_{30}$O$_3$, 318.2195).

Epoxidation of **1**. To a CH_2Cl_2 solution of 1 (400 mg), solid $NaHCO_3$ (330 mg) and m-chloroperbenzoic acid (326 mg) were successively added and stirred for 1 hr at room temperature. To consume exess peracid, dimethylsulfide (0.2 ml) was added to the reaction mixture and followed by the addition of water (10 ml). After extraction of reaction mixture with CH_2Cl_2 (30 ml x 4), the CH_2Cl_2 extract was chromatographed on silica gel (hexane-EtOAc, 2 : 1) to give **8** (237 mg, 56.4%) and **9** (137 mg, 32.6%) (**8** : **9** = 1.7 : 1) as colorless oils. **8**, $[\alpha]_D$ -27.2° (c 1.14). ν_{max}^{film}, cm^{-1} : 3475, 1780, 1745, 1638; $\nu_{max}^{CHCl_3}$, cm^{-1} : 3470, 1785, 1750, 1640. ^{1}H NMR, δ ppm : 0.87 (3H, d, J = 6.8 Hz, H$_3$C17), 1.00 (3H, s, H$_3$C20), 1.14 (3H, s, H$_3$C19), 1.37 (3H, s, H$_3$C18), 3.02 (1H, d, J = 2.4 Hz, H3), 4.13 (1H, bt, J = 2.7 Hz, H6), 4.75 (2H, d, J = 1.8 Hz, H16), 5.41 (1H, bs,OH), 5.83 (1H, tt, J = 1.5 and 1.8 Hz, H14). ^{13}C NMR, δppm : 15.52 (q, C17), 19.91 (t, C2), 21.73 (q, C18), 23.42 (t, C11), 25.24 (q, C19), 27.29 (t, C1), 28.34 (q, C20), 30.86 (d, C8), 33.73 (t, C7), 34.43 (t, C12), 38.41 (s, C9), 39.64 (s, C5) 43.86 (d, C10), 59.73 (d, C3), 65.53 (s. C4), 72.96 (t, C16), 74.14 (d, C6), 115.18 (d, C14), 170.76 (s, C13), 173.68 (s, C15). MS, m/z : 334 (M$^+$, C$_{20}$H$_{30}$O$_4$), 316 (M$^+$-H$_2$O). Exact MS, m/z : 334.2145 (Calcd. for C$_{20}$H$_{30}$O$_4$, 334.2144). **9**, $[\alpha]_D$ - 17.1° (c 1.29). ν_{max}^{film}, cm^{-1} : 3460, 1780, 1745, 1638; $\nu_{max}^{CHCl_3}$, cm^{-1} : 3600, 3475, 1785, 1750, 1640. ^{1}H NMR, δppm : 0.87 (3H, d, J = 6.4 Hz, H$_3$C17), 0.97 (3H, s, H$_3$C20), 1.16 (3H, s, H$_3$C19), 1.40 (3H, s, H$_3$C18), around 1.8 (1H, OH), 3.11 (1H, s, J = 5.1 Hz, H3), 3.82 (1H, bt, J = 2.6 Hz, H6), 4.73 (2H, d, J = 1.8 Hz, H16), 5.82 (1H, tt, J = 1.5 and 1.8 Hz, H14). ^{13}C NMR, δppm : 15.28 (q, C17), 19.32 (q, C18), 20.55 (t, C2), 22.37 (q, C19), 23.13 (t, C1 and C11), 28.87 (q, C20), 30.51 (d, C8), 33.38 (t, C12), 35.60 (t, C7), 38.53 (s, C9), 40.46 (d, C10), 41.75 (s, C5), 62.77 (d, C3), 65.06 (s, C4), 73.08 (d, C6), 73.08 (t, C16), 114.95 (d, C14), 171.34 (s, C13), 174.04 (s, C15). MS, m/z : 334 (M$^+$, C$_{20}$H$_{30}$O$_4$), 319 (M$^+$-CH$_3$), 316 (M$^+$-H$_2$O). Exact MS, m/z : 334.2138 (Calcd. for C$_{20}$H$_{30}$O$_4$, 334.2144).

Acetylation of **1**. To a solution of 1 (92.6 mg) in CH_2Cl_2 (1.5 ml), N,N-dimethyl-4-aminopyridine (214 mg) and acetic anhydride (0.13 ml) were added at room temperature, and stirred for 3 hr at room temperature. After the addition of 1N-HCl (aq. soln.) (12.8 ml), the reaction mixture was extracted with ether (40 ml + 15 ml). Removal of the solvent from the ether layer gave a residue which was subjected to preparative silica gel TLC (henzene-EtOAc, 2 : 1) to afford **10** (99.4 mg, 94.8%), $[\alpha]_D$ + 22.5° (c 1.04). λ_{max}, nm : 203.5 (ε 18400). ν_{max}^{film}, cm^{-1} : 1778, 1740, 1720, (sh.), 1638, 1245. ^{1}H NMR, δ ppm : 0.87 (3H, d, J = 6.4 Hz, H$_3$C17), 1.06 (3H, s, H$_3$C20), 1.19 (3H, s, H$_3$C19), 1.56 (3H, bs, H$_3$C18), 1.99 (3H, s, CH$_3$CO), 4.76 (2H, d, J = 1.8 Hz, H16), 4.96 (1H, dd, J = 2.2 and 3.1 Hz, H6), 5.52 (1H, m, H3), 5.84 (1H, tt, J = 1.5 and 1.8 Hz, H14). ^{13}C NMR, δppm : 15.28 (q, C17), 18.39 (q, C18), 21.26 (q, COCH$_3$), 21.78 (t, C2), 23.19 (t, C11), 24.54 (q, C19), 26.47 (t, C1), 28.11 (q, C20), 31.62 (t, C7), 31.91 (d, C8), 33.79 (t, C12), 38.53 (s, C9), 42.81 (s, C5), 44.74 (d, C10), 72.96 (t, C16), 74.02 (d, C6), 115.18 (d, C14), 124.79 (d, C3), 137.55 (s, C4), 169.82 (s, COCH$_3$), 170.87 (s, C13), 173.74 (s, C15). MS, m/z : 360 (M$^+$, C$_{22}$H$_{32}$O$_4$), 318 (M$^+$-CH$_2$O), 317 (M$^+$-CH$_3$CO), 300 (M$^+$-CH$_3$CO$_2$H). Exact MS, m/z : 300.2091 (Calcd. for C$_{22}$H$_{32}$O$_4$-CH$_3$CO$_2$H, 300.2089).

Epoxidaiton of **10**. Using **10** (48.0 mg), a crude epoxide **11** was obtained by the same procedure as performed in the epoxidation of 1 [m-CPBA (28 mg), for 40 min at room temperature, $(CH_3)_2S$(0.05 ml)]. The crude **11** was purified by a preparative silica gel TLC (benzene-EtOAc, 3 : 2) to give pure **11** (46.7 mg, 93.2%), $[\alpha]_D$ -13.0° (c 0.920). λ_{max}, nm : 204.1 (ε 16300). ν_{max}^{film}, cm^{-1} : 1780, 1745, 1640, 1243. ^{1}H NMR, δ ppm : 0.85 (3H, d, J = 6.0 Hz, H$_3$C17), 0.98 (3H, s, H$_3$C20), 1.16 (3H, s, H$_3$C19), 1.24 (3H, s,

H_3C18), 2.07 (3H, s, CH_3CO), 3.04 (1H, d, J = 5.1 Hz, H3), 4.74 (2H, d, J = 1.8 Hz, H16), 4.84 (1H, t, J = 2.9 Hz, H6), 5.82 (1H, tt, J = 1.5 and 1.8 Hz, H14). ^{13}C NMR, δppm : 15.05 (q, C17), 18.68 (q, C18), 19.91 (t, C2), 21.43 (q, $COCH_3$), 21.90 (q, C19), 23.13 (t, C1 or C11), 24.30 (t, C1 or C11), 28.69 (q, C20), 31.27 (t, C7), 31.27 (d, C8), 33.38 (t, C12), 38.41 (s, C9), 40.17 (d, C10), 40.93 (s, C5), 62.31 (d, C3), 64.24 (s, C5), 72.96 (t, C16), 75.89 (d, C6), 115.13 (d, C14), 169.82 (s, $COCH_3$), 170.76 (s, C13), 173.74 (s, C15). MS, m/z : 376 (M^+, $C_{22}H_{32}O_5$), 361 (M^+-CH_3), 334 (M^+-CH_2O), 317 ($M^+-CH_3CO_2$), 316 ($M^+-CH_3CO_2H$). Exact MS, m/z : 376.2268 (Calcd. for $C_{22}H_{32}O_5$, 376.2249).

DIBAL reduction of **8**. By the same method as described in "DIBAL reduction of 3 and 4", **8** (94 mg) was reacted with DIBAL [1M THF soln. (0.62 ml) of DIBAL] and finally gave a residue which was purified by preparative silica gel TLC (benzene–EtOAc, 3 : 1. The TLC afforded unchanged **8** (13.4 mg)and desired **7** (45.2 mg, conversion yield, 58.9%).

Compund **12**. The same DIBAL reduction method as described above was performed for **1**. **1** (170 mg) and 1M THF solution (1.3 ml) of DIBAL finally gave unchanged **1** (37 mg) and **12** (68 mg, conversion yield, 53.7%) by purification on preparative silica gel TLC (benzene–EtOAc, 4 : 1). **12**, $[\alpha]_D$ + 12.6° (c 0.950). ν_{max}^{film}, cm^{-1} : 3560, 3470 (sh.), 878. ^1H NMR, δ ppm : 0.86 (3H, d, J = 6.6 Hz, H_3C17), 1.05 (3H, s, H_3C20), 1.21 (3H, s, H_3C19), 1.70 (3H, bs, H_3C18), 3.69 (1H, t, J = 2.5 Hz, H6), 5.83 (1H, m, H3), 6.25 (1H, m, H of furan), 7.19 (1H, m, H of furan), 7.33 (1H, t, J = 1.5 Hz, H of furan). δppm [with 0.84 mol. equiv. of Eu(dpm)$_3$] : 2.73 (3H, d, J = 6.6 Hz, H_3C17), 4.20 (3H, s, H_3C20), 5.36 (3H, bs, H_3C18), 6.22 (3H, s, H_3C19); Normarized ratio : 2.0 : 3.3 : 3.9 : 5.3, respectively. ^{13}C NMR, δppm : 15.46 (q, C17), 18.33 (q, C18), 19.09 (t, C11), 22.60 (t, C2), 24.13 (q, C19), 26.41 (t, C1), 28.58 (q, C20), 30.68 (d, C8), 33.03 (t, C7), 36.66 (t, C7), 36.66 (t, C12), 38.71 (s, C9), 43.92 (d, C10), 44.33 (s, C5), 71.56 (d, C6), 110.97 (d, C14), 125.84 (s, C13), 128.77 (d, C3), 137.32 (s, C4), 138.43 (d, C16), 142.65 (d, C15). MS, m/z : 302 (M^+,$C_{20}H_{30}O_2$), 287 (M^+-CH_3), 284 (M^+-H_2O). Exact MS, m/z : 302.2235 (Calcd. for $C_{20}H_{30}O_2$, 302.2245).

Compound **13**. To a THF (2.0 ml) solution of **1** (86 mg), NBS (96 mg) was added, and stirred for 1.5 hr at room temperature. After the addition of sodium thiosulfate ($Na_2S_2O_3$, $5H_2O$) and water (5.0 ml), the reaction mixture was extracted with ether (20 ml x 3). The ether layer was concentrated to give a residue which was purified by preparative silica gel TLC ($CHCl_3$–EtOAc, 4 : 1) to afford **13** (102 mg, 95.2%), $[\alpha]_D$ −42.2° (c 0.900). ν_{max}^{film}, cm^{-1} : 1780, 1745, 1640. ^1H NMR, δppm : 0.86 (3H, J = 6.8 Hz, H_3C17), 0,97 (3H, s, H_3C20), 1.16 (3H, s, H_3C19), 1.66 (3H, s, H_3C18), 4.09 (1H, dd, J = 3.9 and 5.6 Hz, H6 or H3), 4.46 (1H, dd, J = 2.6 and 3.3 Hz, H3 or H6), 4.75 (2H, d, J = 1.8 Hz, H16), 5.82 (1H, qq, J = 1.5 and 1.8 Hz, H14). ^{13}C NMR, δppm : 15.17 (q, C17), 20.20 (t, C2), 22.84 (t, C11), 24.54 (q, C20), 24.83 (q, C18), 26.29 (q, C19), 29.34 (t, C1), 29.87 (t, C7), 30.10 (d, C8), 34.20 (t, C12), 37.59 (s, C9), 40.70 (d, C10), 41.99 (s, C5), 59.55 (d, C3), 34.20 (t, C12), 37.59 (s, C9), 40.70 (d, C10), 41.99 (s, C5), 59.55 (d, C3), 72.96 (t, C16), 79.81 (d, C6), 84.62 (s, C4), 115.24 (d, C14), 170.46 (s, C13), 173.57 (s, C15). MS, m/z : 398 (M^+ + 2)/396 (M^+, $C_{20}H_{29}O_3Br$) (1 : 1), 317 (M^+-Br), 316 (M^+-HBr). Exact MS, m/z : 317.2131 (Calcd. for $C_{20}H_{29}O_3Br$-Br, 317.2116), 316.2053 (Calcd. for $C_{20}H_{29}O_3Br$-HBr, 316.2038).

Compounds **14** and **15**. Compound **13** (60.0 mg) was dissolved in CH_2Cl_2 (3 ml). To the solution, p-toluenesulfonic acid (5 mg) was added and stirred for 7 hr at room temperature. To the reaction mixture, saturated $NaHCO_3$ was added and extracted with $CHCl_3$ (15 ml x 3). The $CHCl_3$ extract was subjected to a preparative silica gel TLC (hexane–EtOAc, 2 : 1) to give two fractions, one of which contained **14** and, another of which **15**. Either fraction was purified by HPLC [Lichrosorb SI-60 (5 μm; column, 4.6 mm x 250 mm); hexane–EtOAc, 1 : 3; flow rate, 1.5 ml/min] to give **14** (12.6 mg, 21.0%) and **15** (17.3 mg, 36.3%). **14**, $[\alpha]_D$ −63.9° (c 0.360). ν_{max}^{film}, cm^{-1} : 1780, 1745, 1640. ^1H NMR, δppm : 0.88 (3H, d, J = 6.8 Hz, H_3C17), 1.00 (3H, s, H_3C20), 1.14 (3H, s, H_3C19), 1.82 (3H, s, H_3C18), 3.75 (1H, dd, J = 2.2 and 3.1 Hz, H6 or H3), 4.02 (1H, dd, J = 1.7 and 3.0 Hz, H3 or H6), 4.76 (2H, d, J = 1.8 Hz, H16), 5.84 (1H, tt, J = 1.5 and 1.8 Hz, H14). ^{13}C NMR, δppm : 14.58 (q, C17), 16.63 (t, C2), 17.33 (q, C18), 22.90 (t, C11), 27.46 (q, C19), 28.28 (q, C20), 29.87 (d, C8), 31.33 (t, C1, C7 or C12), 32.21 (t, C1, C7 or C12), 32.91 (t, C1, C7 or C12), 39.94 (s, C9), 43.57 (d, C10), 45.91 (s, C5), 72.96 (t, C16), 74.66 (s, C4), 76.77 (d, C3), 81.63 (d, C6), 115.24 (d, C14), 170.52 (s, C13), 173.68 (s, C15). MS, m/z : 398 (M^+ + 2)/396 (M^+, $C_{20}H_{29}O_3Br$) (1 : 1), 317 (M^+-Br), 299 (M^+-Br-H_2O). Exact MS, m/z : 317.2122 (Calcd. for $C_{20}H_{29}O_3Br$-Br, 317.2116). **15**, $[\alpha]_D$ −56.6° (c 0.530). ν_{max}^{film}, cm^{-1} : 1780, 1745, 1640. ^1H NMR, δppm : 0.91 (3H, d, J = 7.0 Hz, H_3C17), 1.06 (3H, s, H_3C20), 1.22 (3H, s, H_3C19), 4.08 (1H, dd, J = 8.1 and 9.5 Hz, H6), 4.29 (1H, dm, J = 13.0 Hz, H18), 4.50 (1H, dm, J = 13.0 Hz, H18), 4.76 (2H, d, J = 1.8 Hz, H16), 5.45 (1H, bt, J = 3.1 Hz, H3), 5.85 (1H, tt, J = 1.5 and 1.8 Hz, H14). ^{13}C NMR, δppm : 14.29 (q, C17),

17.74 (t, C2), 21.73 (q, C19), 22.19 (t, C1), 23.54 (t, C11), 29.28 (q, C20), 30.80 (t, C7), 36.60 (d, C9), 37.48 (t, C12), 38.00 (s, C9), 41.39 (s, C5), 42.75 (d, C10), 67.75 (t, C18), 72.96 (t, C16), 115.18 (d, C14), 115,95 (d, C3), 143.29 (s, C4), 170.87 (s, C13), 173.80 (s, C15). MS, m/z : 316 (M^+, $C_{20}H_{28}O_3$), 301 (M^+-CH_3), 283 (M^+-CH_3-H_2O). Exact MS, m/z : 316.1672 (Calcd. for $C_{20}H_{28}O_3$, 316.2038), 301, 1793 (Calcd. for $C_{20}H_{28}O_3$-CH_3, 301.1803).

p-Bromobenzoate (**16**). To a solution of 1 (40.0 mg) in pyridine (1.5 ml), N, N-dimethyl-4-aminopyridine (130 mg) and p-bromobenzoyl chloride (170 mg) were added, and stirred for 6 hr at 65°C. After the addition of 2N NaOH aq. soln. (7 ml), the reaction mixture was extracted with ether (20 ml + 10 ml + 10 ml). The ether layer was concentrated to give a residue which was purified by preparative silica gel TLC (hexane-EtOAc, 1 : 1) to give a crude **16**. The crude **16** was further purified by preparative aluminum oxide TLC (hexane-EtOAc, 1 : 1) to give **16** (38.3 mg, 62.0%), mp. 192.5°-194°C (hexane-EtOAc). $[\alpha]_D$ -10.7° (c 0.466). λmax, nm : 242.9 (ε 17200). CD : λ_{ext}, nm : 248.3 ($\Delta\varepsilon$ + 3.97), 229.0 (0.0), 213.0 (-4.14). ν_{max}^{KBr}, cm^{-1} : 1790, 1750, 1715, 1645, 1598, 1490. ^1H NMR, δppm : 0.89 (3H, d, J = 6.6 Hz, H_3C17), 1.07 (3H, s, H_3C20), 1.26 (3H, s, H_3C19), 1.30 (3H, s, H_3C18), 2.75 (1H, d, J = 1.5 Hz, H3), 4.76 (2H, d, J = 1.8 Hz, H16), 5.57 (1H, dd, J = 2.4 and 3.5 Hz, H6), 5.86 (1H, tt, J = 1.5 and 1.8 Hz, H14), 7.58 (2H, dm, J = 8.7 Hz, benzene ring protons), 7.97 (2H, dm, J = 8.7 Hz, benzene ring protons). MS, m/z : 518 (M^+ + 2)/516 (M^+, $C_{27}H_{33}O_5Br$) (1 : 1), 503 (M^+ + 2-CH_3)/501 (M^+-CH_3) (1 : 1), 333 (M^+ -$BrC_6H_4CO_2$), 316 (M^+-$BrC_6H_4CO_2H$). Anal. Calcd. for $C_{27}H_{33}O_5Br$: C, 62.67; H, 6.43; Br, 15.44. Found : C, 62.75; H, 6.31; Br, 15.50.

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REFERENCES

1. M. Morita, Y. Kojima, N. Kato, K. Miwa, I. Tanaka, T. Yamane and T. Ashida, Tetrahedron Lett., 1983, **24**, 5631, and references cited therein.
2. M. Niwa and S. Yamamura, Tetrahedron Lett., 1981, **22**, 2789.
3. C. Nishino, S. Manabe, M. Kazui and T. Matsuzaki, Tetrahedron Lett., 1984, **25**, 2809.
4. S. Manabe, N. Enoki and C. Nishino, Tetrahedron Lett., 1985, **26**, 2213.
5. E. W. Colvin, S. M. Malchenko, R. A. Ralphael and J. S. Roberts, J. Chem. Soc. Perkin I, **1973**, 1989.
6. R. McCrindle, E. Nakamura and A. B. Anderson, J. Chem. Soc. Perkin I, **1976**, 1590.
7. S. Yamamura, M. Ito, M. Niwa, I. Hasegawa, S. Ohba and Y. Saito, Tetrahedron Lett., 1981, **22**, 739.
8. E. Breitmaier and W. Voelter, ^{13}C NMR Spectroscopy, Chapter 5 : ^{13}CNMR of Natural Products, pp 219-299, Werlag Chemie, Weinheim, New York, 1978.
9. A. Goswami, R. N. Barua, R. P. Sharma, J. N, Baruah, P. Kulanthaivel and W. Herz, Phytochemistry, 1984, **23**, 837.
10. C. H. Hasan, T. M. Healey and P. G. Waterman, Phytochemistry, 1982, **21**, 1365.
11. G. Savona, M. Bruno, F. Piozzi, O. Servettaz and B. Rodriguez, Phytochemistry, 1984, **23**, 849.
12. I. Kubo, Y-W. Lee, V. Balogh-Nair, K. Nakanishi and A. Chapya, J. Chem. Soc. Chem. Comm.,**1976**, 949.
13. I. Kubo, J. A. Klocke, I. Miura and Y. Fukuyama, J. Chem. Soc. Chem. Comm., **1982**, 618.
14. S. D. Jolad, J. J. Hoffmann, K. H. Schram and J. R. Cole, J. Org. Chem., 1982, **47**, 1356.
15. J. L. Gough, J. P. Guthrie and J. B. Stothers, J. Chem. Soc. Chem. Comm., **1972**, 979.
16. D. K. Dalling and D. M. Grant, J. Amer,. Chem. Soc., 1972, **94**, 5318.
17. D. Cremer and J. A. Pople, J. Amer. Chem. Soc., 1975, **97**, 1354.
18. L. Eguren, A. Perales, J. Fayos, B. Rodriguez, G. Savona and F. Piozzi, J. Org. Chem., 1982, **47**, 4157.
19. K. Tori, T. Komeno and T. Nakagawa, J. Org. Chem., 1964, **29**, 1136.
20. T. Anthonsen and R. McCrindle, Acta Chem. Scand., 1969, **23**, 1068.