[Chem. Pharm. Bull. 33(1) 121—126 (1985)]

Stereoselective Reactions. VII.[1] Synthesis of Racemic and Optically Pure Stegane, Isostegane, Picrostegane, and Isopicrostegane *via* Highly Selective Isomerization[2]

KIYOSHI TOMIOKA, HIDEMICHI MIZUGUCHI, TSUNEO ISHIGURO, and KENJI KOGA*

Faculty of Pharmaceutical Sciences, University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan

(Received May 10, 1984)

Novel isomerizations of isostegane (**6**) into the three other possible isomers, namely, isopicrostegane (**7**), picrostegane (**8**), and stegane (**9**) are described. All the possible enantiomers were synthesized.

Keywords——isomerization; dibenzocyclooctadiene; antitumor lignan lactone; atropisomerization; enantiomer; asymmetric synthesis; steganacin; ^{13}C-NMR

The dibenzo[4,5 : 6,7]cycloocta[1,2-*c*]furanone system is found in the carbon skeleton of a novel type of liganan lactones including steganacin (**1**), steganangin (**2**), steganol (**3**), and steganone (**4**).[3,4] Steganacin and steganangin are known to be endowed with remarkable antitumor activity.[3] Since the initial report by Kupchan on the isolation of **1**—**4**, considerable efforts have been expended on the total syntheses of these antitumor lignan lactones.[1,4-9] Schlessinger *et al.* have reported that oxidation of (±)-deoxypodorhizon ((±)-**5**) resulted in the stereoselective formation of (±)-isostegane ((±)-**6**), whose structure was established by X-ray analysis.[10] Brown and Robin have also reported the syntheses of (±)-isostegane ((±)-**6**), (±)-isopicrostegane ((±)-**7**), and (±)-pictrostegane ((±)-**8**).[11] Although three among the four possible isomers of the steganacin type lignan skeleton have been synthesized in racemic forms as described above, stegane ((±)-**9**), the parent skeleton of steganacin (**1**), has remained unknown. During our studies aimed at the asymmetric total synthesis of the antitumor lignan lactone steganacin (**1**),[1] we found a novel isomerization reaction of (±)-isostegane ((±)-**6**) into (±)-stegane ((±)-**9**), (±)-picrostegane ((±)-**8**), and (±)-isopicrostegane ((±)-**7**). In this paper we describe the novel and highly selective isomerization of these stegane isomers and, further, their application to the synthesis of all of the possible enantiomers.

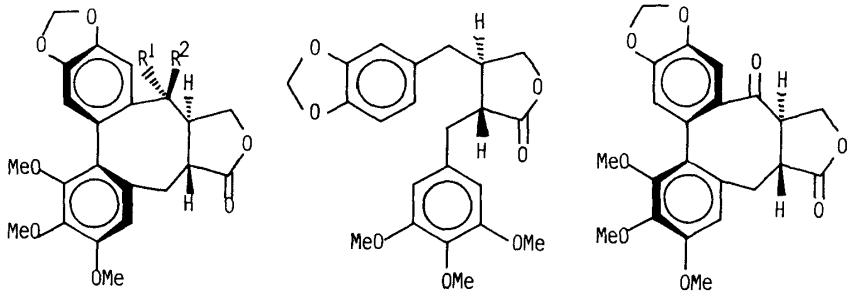


Fig. 1

Isomerization of (±)-Isostegane ((±)-6). First Synthesis of (±)-Stegane ((±)-9)

The four possible isomers bearing the steganacin skeleton are related as follows. Rotational isomerization of a bond joining two aromatic rings of isostegane (**6**) leads to stegane (**9**). In the same way, isopicrostegane (**7**) is correlated to picrostegane (**8**). On the other hand, isomerization at the α-position of lactone carbonyl of isostegane (**6**) leads to isopicrostegane (**7**), and that in the case of stegane (**9**) leads to picrostegane (**8**). These relations are shown in Chart 1.[12]

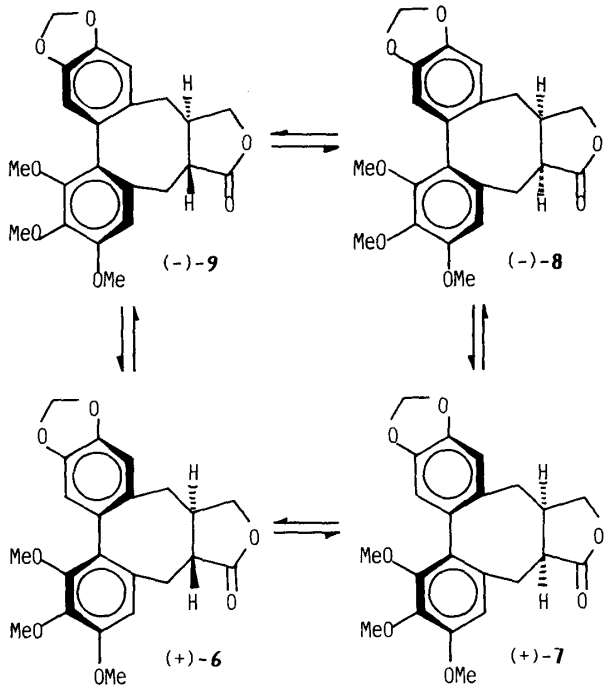


Chart 1

Isomerization of (±)-isostegane ((±)-**6**), prepared from (±)-**5** according to the Schlessinger procedure,[10] was first attempted using the similar condition (KOH, EtOH, reflux) to that described by Kende *et al.* for the isomerization of (±)-isosteganone ((±)-**10**) to (±)-steganone ((±)-**4**).[5b] However, (±)-**6** was recovered unchanged. Then (±)-**6** was treated with AcOK (10 eq) in AcOH at reflux for 22 h.[13] Careful purification of the crude products by medium pressure liquid chromatography on silica gel afforded all four possible isomers, (±)-**6** (14% recovery), (±)-**7** (38%), (±)-**8** (19%), and (±)-**9** (1%), as shown in Table I (entry 1). Proton nuclear magnetic resonance (^{1}H-NMR) and infrared (IR) spectra and melting points of (±)-**6**, (±)-**7**, and (±)-**8** agreed well with those reported.[10,11] The fourth compound was assigned as (±)-stegane ((±)-**9**) based on the spectral data and isomerization studies. ^{13}C-NMR (Table II) and mass spectra (MS) of (±)-**9** confirmed that this compound was an isomer bearing the same carbon framework. The results of isomerization studies with the racemic and optically active forms are summarized in Table I.[14]

Isomerization of (−)-stegane ((−)-**9**) with NaOH in aq. EtOH afforded, after acidification with aq. HCl for relactonization, (−)-**9** and (−)-**8** in 50 and 45% isolated yields, respectively (entry 2). However, (±)-**8** was recovered unchanged from the attempted isomerization of (±)-**8** under the same condition as described above (entry 4). This seems to imply that isomerization at the α-position of the lactone carbonyl and opening of the lactone ring are the competitive processes, and picrostegane (**8**) is the more stable product in the isomerization. This was confirmed by the isomerization with *tert*-BuOK in *tert*-BuOH, under the condition such that hydrolysis of the lactone ring is minimized. In fact (−)-**9** was

TABLE I. Isomerizations of **6**, **7**, **8**, and **9**[a]

Entry	Conditions	Isostegane (**6**) (%)	Isopicrostegane (**7**) (%)	Picrostegane (**8**) (%)	Stegane (**9**) (%)
1	AcOK–AcOH 120 °C, 22 h	14[d]	38	19	1
2[b,c]	NaOH–aq. EtOH r.t., 24 h	0	0	45	50[d]
3[c]	*tert*-BuOK–*tert*-BuOH 70 °C, 24 h	0	0	51	5[d]
4[b]	NaOH–aq. EtOH r.t., 24 h	0	0	99[d]	0
5[c]	*tert*-BuOK–*tert*-BuOH 70 °C, 48 h	0	0	81[d]	6
6[b]	NaOH–aq. EtOH r.t., 24 h	99[d]	0	0	0
7	*tert*-BuOK–*tert*-BuOH 70 °C, 24 h	99[d]	0	0	0
8	Neat, 195 °C 3.5 h	61[d]	0	0	39
9	Neat, 195 °C 2 h	59	0	0	41[d]
10[c]	Neat, 190 °C 10 min	0	60	40[d]	0

a) Isolated yields. *b*) Aqueous HCl was added to relactonize the products.
c) In optically active form. *d*) Starting material.

converted to a mixture of (−)-**8** and (−)-**9**, consisting mainly of (−)-**8** with the preference of 10 : 1 (entry 3). Picrostegane (−)-**8** was also isomerized to the mixture of (−)-**8** and (−)-**9**, consisting mainly of (−)-**8** with preference of 14 : 1 (entry 5).

Isomerization of (±)-isostegane ((±)-**6**) into (±)-isopicrostegane ((±)-**7**) was not observed under the basic conditions described above (entry 6 and 7), though (±)-**7** is known to isomerize into (±)-**6**.[11]

Thermal isomerization by rotation of the pivot bond was also examined.[15] On being heated without solvent at 195 °C for 3.5 h, (±)-**6** gave a mixture of (±)-**6** (61%) and (±)-stegane ((±)-**9**) (39%) as described in the synthesis of (−)-**9** from (+)-**6**[1] (entry 8). A mixture of (±)-**9** (41%) and (±)-**6** (59%) was obtained from (±)-**9** (entry 9). (−)-Picrostegane ((−)-**8**) was converted to a mixture of (−)-**8** (40%) and (+)-**7** (60%) (entry 10).[11]

These findings supported the structure of newly found stegane (**9**) in racemic and optically active forms. The isomerization of (±)-**6** into a mixture of all four possible isomers with AcOK in refluxing AcOH may be attributed to the sum of the rotational isomerization and isomerization at the α-position of the lactone carbonyl.

As a result of these highly selective isomerizations, all four possible isomers in racemic modifications are now available. ^{13}C-NMR data for these four isomers are presented in Table II.

Synthesis of Optically Pure Isostegane (6), Isopicrostegane (7), Picrostegane (8), and Stegane (9)

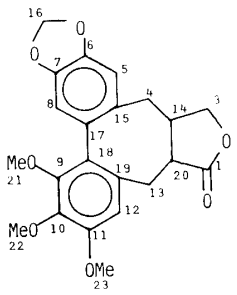
In previous papers,[1,4b,c,16] we have presented highly efficient asymmetric syntheses of optically pure (−)- and (+)-deoxypodorhizon ((−)-**5** and (+)-**5**). Syntheses of optically pure stegane isomers were carried out starting from (−)-**5** and (+)-**5**.

Nonphenolic oxidative coupling of (−)-**5** gave (+)-isostegane ((+)-**6**) of $[\alpha]_D^{23}$ +154°

TABLE II. ^{13}C-NMR of **6**, **7**, **8**, and **9**[a]

Carbon[b]	Isostegane (**6**)	Isopicrostegane (**7**)	Picrostegane (**8**)	Stegane (**9**)
C-13	32.1 t	29.3 t	30.1 t	32.3 t
C-4	33.8 t	35.7 t	30.6 t	33.6 t
C-20	46.7 d	40.3 d	37.1 d	39.8 d
C-14	49.8 d	42.4 d	44.7 d	43.0 d
C-23	55.8 q	55.9 q	56.1 q	55.8 q
C-22	60.4 q	60.7 q	60.7 q	60.5 q
C-21	60.6 q	60.9 q	61.0 q	60.7 q
C-3	69.7 t	72.9 t	69.3 t	70.8 t
C-16	100.9 t	101.0 t	101.2 t	101.0 t
C-12	107.4 d	108.4 d	107.6 d	108.9 d
C-8	108.5 d	110.0 d	110.2 d	110.1 d
C-5	111.5 d	111.9 d	110.9 d	111.4 d
C-19	126.2 s	126.9 s	126.9 s	127.5 s
C-18	128.1 s	129.4 s	128.9 s	129.8 s
C-17	132.3 s	131.7 s	130.0 s	130.6 s
C-15	135.8 s	132.2 s	133.7 s	133.4 s
C-10	140.6 s	141.1 s	141.0 s	140.8 s
C-7	145.6 s	145.7 s	146.2 s	146.1 s
C-6	147.4 s	147.4 s	147.4 s	146.9 s
C-9	151.6 s	150.3 s	150.8 s	151.3 s
C-11	153.1 s	152.1 s	153.4 s	152.5 s
C-1	176.2 s	177.1 s	179.1 s	178.3 s

a) Taken in $CDCl_3$ using TMS as an internal standard. The figures after numbers are the multiplicities in the case of off-resonance. s, singlet; d, doublet; t, triplet; q, quartet.
b) Assignment in parentheses may be interchanged.



($CHCl_3$). Thermal isomerization of (+)-**6** gave (−)-stegane ((−)-**9**) of $[\alpha]_D^{23}$ −196° ($CHCl_3$). Isomerization of (−)-**9** with NaOH in aq. EtOH gave (−)-picrostegane ((−)-**8**) of $[\alpha]_D^{23}$ −57.2° ($CHCl_3$). (−)-**8** was converted to (+)-isopicrostegane ((+)-**7**) of $[\alpha]_D^{23}$ +155° ($CHCl_3$). The absolute stereochemistries of these isomers are shown in Chart 1. The optical antipodes of these isomers were also synthesized from (+)-**5**.

The usefulness of the present isomerization reactions, especially the synthesis of (−)-stegane ((−)-**9**), was demonstrated in the successful asymmetric total synthesis of the natural antitumor lignan lactone steganacin (**1**).[1,4b]

Experimental[17]

(−)-Isostegane ((−)-6)——(−)-Isostegane was synthesized by the same procedure as used for the synthesis of (+)-**6**[1] starting from (+)-deoxypodorhizon ((+)-**5**)[1,4b,16] of $[\alpha]_D^{25}$ +25.3° (*c* = 0.400, $CHCl_3$) in 41% yield. Colorless prisms of mp 169—170 °C[18] (from MeOH). $[\alpha]_D^{23}$ −161° (*c* = 0.668, $CHCl_3$). *Anal.* Calcd for $C_{22}H_{22}O_7$: C, 66.32; H, 5.57. Found: C, 66.04; H, 5.56. Spectral data (^{1}H-NMR, IR ($CHCl_3$)) and thin layer chromatography (TLC) behavior were identical with those of (+)-isostegane ((+)-**6**).[1] The present crytalline (−)-isostegane was considered

to be dimorphous with respect to (+)-**6**,[1] showing different mp and IR spectrum (KBr).

(±)-Isostegane ((±)-6)——(±)-Isostegane of mp 172—174.5 °C (from ether) was synthesized from (±)-**5** by the same procedure. Spectral data and melting point were identical with those reported.[10,11]

(+)-Stegane ((+)-9)——(+)-Stegane was synthesized by the thermal atropisomerization of (−)-isostegane ((−)-**6**) according to the procedure described for the synthesis of (−)-**9**.[1] Mp 179 °C (from MeOH). $[\alpha]_D^{23}$ +196° (c=0.520, $CHCl_3$). *Anal.* Calcd for $C_{22}H_{22}O_7$: C, 66.32; H, 5.57. Found: C, 66.06; H, 5.61. Spectral and TLC behavior were identical with those of (−)-**9**.[1]

(±)-Stegane ((±)-9) (Entry 8)——(±)-Stegane was synthesized by the same procedure starting from (±)-isostegane ((±)-**6**). Colorless prisms of mp 130.5—133 °C (from MeOH). IR ν_{max}^{KBr} cm^{-1}: 1767 (lactone). *Anal.* Calcd for $C_{22}H_{22}O_7$: C, 66.32; H, 5.57. Found: C, 66.06; H, 5.64.

(−)-Picrostegane ((−)-8) (Entry 2)——A solution of 2 N aq. NaOH (1.5 ml, 3 mmol) was added to a solution of (−)-stegane ((−)-**9**)[1] (150 mg, 0.376 mmol) of $[\alpha]_D^{23}$ −196° (c=0.500, $CHCl_3$) in EtOH (10 ml) and the whole was stirred at room temperature for 24 h. A solution of 10% aq. HCl (6 ml) was added and the whole was stirred for an additional 24 h. The mixture was made alkaline with satd. aq. $NaHCO_3$ and extracted with AcOEt (100 ml × 3). The combined extracts were washed with satd. aq. NaCl and dried over $MgSO_4$. Concentration *in vacuo* afforded a colorless foam (160 mg). Purification by silica gel TLC (benzene–AcOEt (10:1)) gave (−)-stegane ((−)-**9**) (74.4 mg, 50% recovery) and (−)-picrostegane ((−)-**8**) (66.9 mg, 45%) as colorless pillars of mp 181—181.5 °C (from MeOH). $[\alpha]_D^{23}$ −57.2° (c=0.690, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 1782 (lactone), 1598 (aromatic). ^{1}H-NMR (C_6D_6) δ: 1.8—2.5 (5H, m), 2.6—2.8 (1H, m), 3.32 (3H, s, $OC\underline{H}_3$), 3.44 (3H, s, $OC\underline{H}_3$), 3.79 (3H, s, $OC\underline{H}_3$), 3.6—3.8 (2H, m), 5.35 (1H, d of ABq, J_{AB}=1 Hz, $OC\underline{H}_2O$), 5.43 (1H, d of ABq, J_{AB}=1 Hz, $OC\underline{H}_2O$), 6.18 (1H, s, aromatic H), 6.41 (1H, s, aromatic $\underline{H}$), 6.82 (1H, s, aromatic $\underline{H}$). MS m/z: 398 (M^+), 367, 353, 329. *Anal.* Calcd for $C_{22}H_{22}O_7$: C, 66.32; H, 5.57. Found: C, 66.04; H, 5.51.

(+)-Picrostegane ((+)-8)——(+)-Picrostegane was synthesized by the same procedure as used for (−)-**8** starting from (+)-stegane ((+)-**9**)[1] of $[\alpha]_D^{23}$ +196° (c=0.520, $CHCl_3$). Colorless pillars of mp 180—182 °C (from MeOH). $[\alpha]_D^{23}$ +59.5° (c=0.672, $CHCl_3$). *Anal.* Calcd for $C_{22}H_{22}O_7$: C, 66.32; H, 5.57. Found: C, 66.40; H, 5.62. Spectral data were identical with those of (−)-**8**.

(±)-Picrostegane ((±)-8)——(±)-Picrostegane was synthesized by the same procedure as used for (−)-**8** starting from (±)-stegane ((±)-**9**). Colorless needles of mp 182—184 °C (from $CHCl_3$–ether). IR ν_{max}^{Nujol} cm^{-1}: 1760 (lactone). Spectral data (^{1}H-NMR, MS) and TLC behavior were identical with those of (+)- and (−)-picrostegane.

(+)-Isopicrostegane ((±)-7) (Entry 10)——(−)-Picrostegane ((−)-**8**) (22.4 mg, 0.056 mmol) of $[\alpha]_D^{23}$ −57.2° (c=0.690, $CHCl_3$) was heated to melt at 190 °C for 10 min under argon. Purification by silica gel TLC (benzene–AcOEt (7:1)) gave (−)-picrostegane ((−)-**8**) (8.9 mg, 40% recovery) and (+)-isopicrostegane ((+)-**7**) (13.5 mg, 60%) as colorless plates of mp 194—195 °C (from MeOH). $[\alpha]_D^{23}$ +155° (c=0.220, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 1760 (lactone), 1594 (aromatic). ^{1}H-NMR (C_6D_6) δ: 1.6—2.0 (2H, m), 2.1—2.5 (3H, m), 2.9—3.1 (1Hm m), 3.2—3.4 (1H, m), 3.5—3.7 (1H, m), 3.48 (3H, s, $OC\underline{H}_3$), 3.63 (3H, s, $OC\underline{H}_3$), 3.81 (3H, s, $OC\underline{H}_3$), 5.40 (1H, d of ABq, J_{AB}=1 Hz, $OC\underline{H}_2O$), 5.44 (1H, d of ABq, J_{AB}=1 Hz, OCH_2O), 6.44 (1H, s, aromatic H), 6.92 (1H, s, aromatic H), 7.31 (1H, s, aromatic H). MS m/z: 398 (M^+), 383, 368, 353. *Anal.* Calcd for $C_{22}H_{22}O_7$: C, 66.32; H, 5.57. Found: C, 66.04; H, 5.48.

(−)-Isopicrostegane ((−)-7)——(−)-Isopicrostegane was synthesized by the same procedure as described above for (+)-isopicrostegane ((+)-**7**) starting from (+)-picrostegane ((+)-**8**) of $[\alpha]_D^{23}$ +59.5° (c=0.672, $CHCl_3$). Colorless pillars of $[\alpha]_D^{23}$ −158° (c=0.662, $CHCl_3$). *Anal.* Calcd for $C_{22}H_{22}O_7$: C, 66.32; H, 5.57. Found: C, 66.20; H, 5.63. Spectral data and TLC behavior were identical with those of (+)-isopicrostegane ((+)-**7**).

(±)-Isopicrostegane ((±)-7)——(±)-Isopicrostegane was synthesized by the same procedure as described above starting from (±)-picrostegane ((±)-**8**). Colorless prisms of mp 179—181 °C (from $CHCl_3$–ether). IR ν_{max}^{Nujol} cm^{-1}: 1780 (lactone). Spectral data and TLC behavior were identical with those of (+)- and (−)-isopicrostegane and those reported.[11]

Theraml Isomerization of (±)-Stegane ((±)-9) to (±)-Isostegane ((±)-6) (Entry 9)——(±)-Stegane ((±)-**9**) (100 mg, 0.25 mmol) was heated to melt at 195 °C for 2 h. Purification by silica gel column chromatography (benzene–AcOEt (10:1)) gave (±)-stegane ((±)-**9**) (41 mg, 41% recovery) and (±)-isostegane ((±)-**6**) (59 mg, 59%).

Isomerization of (−)-Picrostegane ((−)-8) to (∓)-Stegane ((−)-9) (Entry 5)——A solution of (−)-picrostegane ((−)-**8**) (25 mg, 0.063 mmol) and *tert*-BuOK (1 mg, 0.01 mmol) in *tert*-BuOH (2 ml) was heated at 70 °C for 48 h, then diluted with AcOEt (100 ml). The whole was washed successively with 10% aq. HCl (10 ml), water (10 ml), satd. aq. $NaHCO_3$ (10 ml), water (10 ml × 3), and satd. aq. NaCl (10 ml), then dried over $MgSO_4$. Concentration *in vacuo* afforded colorless needles (22 mg). Purification by silica gel TLC (benzene–AcOEt (10:1)) gave (−)-picrostegane ((−)-**8**) (20.2 mg, 81% recovery) and (−)-stegane ((−)-**9**) (1.5 mg, 6%).

Isomerization of (±)-Isostegane ((±)-6) to the Other Three Isomers ((±)-7, (±)-8, and (±)-9) (Entry 1)——A solution of (±)-isostegane ((±)-**6**) (1.0 g, 3.5 mmol) and AcOK (2.5 g, 25 mmol) in AcOH (30 ml) was heated to reflux for 22 h. The mixture was concentrated *in vacuo*. The residue was diluted with $CHCl_3$ (100 ml) and washed with satd. aq. $NaHCO_3$ (30 ml) and satd. aq. NaCl (30 ml). After being dreid over $MgSO_4$, the whole was concentrated *in vacuo* afforded a colorless oil. Purification by silica gel column chromatography (CH_2Cl_2–ether (10:1)) gave a solid (150 mg) from the first fraction and a solid (700 mg) from the second fraction.

The solid obtained from the first fraction was purified by silica gel column chromatography (benzene–ether (10 : 1)) to give (±)-stegane ((±)-**9**) (6 mg, 0.6%) and (±)-isostegane ((±)-**6**) (143 mg, 14% recovery).

The solid obtained from the second fraction was purified by silica gel column chromatography (benzene–ether (10 : 1)) to give (±)-picrostegane ((±)-**8**) (190 mg, 19%) and (±)-isopicrostegane ((±)-**7**) (379 mg, 38%).

References and Notes

1) Part VI: K. Tomioka, T. Ishiguro, Y. Iitaka, and K. Koga, *Tetrahedron*, **40**, 1303 (1984).
2) A part of this work has been reported. K. Tomioka, H. Mizuguchi, and K. Koga, *Tetrahedron Lett.*, **1979**, 1409.
3) S. M. Kupchan, R. W. Britton, M. F. Ziegler, C. J. Gilmore, R. J. Restivo, and R. F. Bryan, *J. Am. Chem. Soc.*, **95**, 1335 (1973).
4) The absolute configuration of natural steganacin was corrected to **1** as a result of two independent asymmetric syntheses. *a*) J. P. Robin, O. Gringore, and E. Brown, *Tetrahedron Lett.*, **21**, 2709 (1980); *b*) K. Tomioka, T. Ishiguro, and K. Koga, *Tetrahedron Lett.*, **21**, 2973 (1980); *c*) See ref. 1.
5) *a*) A. S. Kende and L. S. Liebeskind, *J. Am. Chem. Soc.*, **98**, 267 (1976); *b*) A. S. Kende, L. S. Liebeskind, C. Kubiak, and R. Eisenberg, *ibid.*, **98**, 6389 (1976).
6) *a*) D. Becker, L. R. Hughes, and R. A. Raphael, *J. Chem. Soc., Perkin Trans. 1*, **1977**, 1674; *b*) E. R. Larson and R. A. Raphael, *Tetrahedron Lett.*, **1979**, 5041; *c*) E. R. Larson and R. A. Raphael, *J. Chem. Soc., Perkin Trans. 1*, **1982**, 521.
7) F. E. Ziegler, I. Chliwner, K. W. Fowler, S. J. Kanfer, S. J. Kuo, and N. D. Sinha, *J. Am. Chem. Soc.*, **102**, 790 (1980), and references cited therein.
8) G. R. Krow, K. M. Damodaran, E. Michener, R. Wolf, and J. Guare, *J. Org. Chem.*, **43**, 3950 (1978).
9) M. Mervic, Y. Ben-David, and E. Ghera, *Tetrahedron Lett.*, **22**, 5091 (1981).
10) R. E. Damon, R. H. Schlessinger, and J. F. Blount, *J. Org. Chem.*, **41**, 3772 (1976).
11) E. Brown and J. P. Robin, *Tetrahedron Lett.*, **1978**, 3613.
12) For simplicity, the structures of (+)-isostegane ((+)-**6**), (+)-isopicrostegane ((+)-**7**), (−)-picrostegane ((−)-**8**), and (−)-stegane ((−)-**9**) are drawn. These compounds are stereochemically related with each other.
13) We fortuitously found the present conditions during an oxidation study of **6** with DDQ-AcOK in AcOH.
14) In the communication[2] we reported that isomerization of **6** could be achieved in refluxing AcOH distilled from $KMnO_4$. However the isomerization of **6** could not be reproduced when we used AcOH obtained by the simple distillation. The reason for this is unclear.
15) *a*) K. Mislow and A. J. Gordon, *J. Am. Chem. Soc.*, **85**, 3521 (1963); *b*) D. R. Mckelvey, R. P. Kraig, K. Zimmerman, A. Ault, and R. Perfetti, *J. Org. Chem.*, **38**, 3610 (1973); *c*) M. Mervic and E. Ghera, *J. Chem. Soc., Chem. Commun.*, **1979**, 12.
16) *a*) K. Tomioka, H. Mizuguchi, and K. Koga, *Tetrahedron Lett.*, **1978**, 4687; *b*) K. Tomioka and K. Koga, *ibid.*, **1979**, 3315; *c*) K. Tomioka, T. Ishiguro, and K. Koga, *J. Chem. Soc., Chem. Commun.*, **1979**, 652; *d*) K. Tomioka, H. Mizuguchi, and K. Koga, *Chem. Pharm. Bull.*, **30**, 4304 (1982).
17) Melting points were measured using a Büchi 510 melting point apparatus and are not corrected. Optical rotations were taken with a JASCO DIP-181 automatic polarimetrimeter. IR spectra were taken with a JASCO Infrared Spectrometer Model DS-402 G and a JASCO IRA-1 Grating Infrared Spectrometer. ^{1}H-NMR spectra were taken with a JNM-PS 100 Spectrometer, with a JEOL-FX 100 Spectrometer at 100 MHz, or with a Hitachi R-24 Spectrometer at 60 MHz. ^{13}C-NMR spectra were taken with a JEOL FX-100 Spectrometer at 25 MHz. Chemical shift values are expressed in ppm relative to internal tetramethylsilane. Abbreviations are as follows: s, singlet; d, doublet; t, triplet; m, multiplet. MS spectra were taken with a JEOL-01, SG-2 Mass Spectrometer.