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On the Constituents of *Linaria japonica* Miq. IV.[1] Chemical Correlation of *cis*-Clerodane Diterpenes with *trans*-Clerodane Diterpenes

Isao Kitagawa, Toshiyuki Kamigauchi, Kazuto Yonetani, and Minoru Yoshihara

Faculty of Pharmaceutical Sciences, Osaka University[2]

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The chemical correlation between 5α-methyl-*trans*-clerodane diterpenes and 5β-methyl-*cis*-clerodane diterpenes was investigated. Attempts to correlate a *trans*-clerodane [*e.g.* methyl kolavenate (**1**)] with a *cis*-clerodane by virtue of i) photoisomerization of a 19-nor-4-keto derivative (**6**) of **1** and ii) photoisomerization of a related *trans*-hydrindanone derivative (**14**=**18**), were unsuccessful. However, an interrelation, by virtue of photolysis of a 19-nor-4-keto derivative (**26**) of *cis*-clerodane [*e.g.* linaridial (**19**)] leading to **6**, was successful. This is the first report of a chemical correlation between *cis*- and *trans*-clerodane diterpenes. The stereochemical course of the photoisomerization observed for *cis*-19-nor-4-ketone (**26**) leading to its *trans* isomer (**6**) is discussed.

Keywords——*cis*-clerodane diterpenes; *trans*-clerodane diterpenes; photoisomerization; linaridial; methyl kolavenate; decalone; hydrindanone

Among naturally occurring clerodane-type diterpenes, two types of carbon skeletons having a 5α-methyl-*trans*-decalin moiety (*e.g.* **iv**) and a 5β-methyl-*cis*-decalin moiety (*e.g.* **v**) are known. They have been considered to be biosynthesized from geranylgeranyl pyrophosphate (**i**) *via* an *ent*-labdane intermediate (**ii**) and a carbonium cation (**iii**), from which route **a** provides **iv** while route **b** leads to **v**, as shown in Chart 1.[3]

Although increasing numbers of *trans*- and *cis*-clerodane diterpenes have been isolated from nature and their structures elucidated, no work has been reported on the chemical correlation between these two groups. As a part of our studies on the chemical transformations of terpenoids,[4] we have attempted to chemically correlate the *trans*- and *cis*-clerodanes. This paper deals with our studies on the chemical correlation.[5]

In order to interrelate a 5α-methyl-*trans*-clerodane with a 5β-methyl-*cis*-clerodane (or *vice versa*), inversion of the angular 5-methyl configuration is essential. For this purpose, the photochemical isomerization undertaken between estrone (**vi**) and lumiestrone (**vii**)[6] seemed relevant, and the 4-keto derivatives (**viii** and **ix**) of 19-nor-*trans*- and 19-nor-*cis*-clerodanes and allied compounds were therefore prepared and their photochemical behavior was investigated.

Attempted Conversion from *trans*-Clerodane to *cis*-Clerodane

The desired 19-nor-4-keto derivative (**6**) of 5α-methyl-*trans*-clerodane was prepared from methyl kolavenate (**1**), which is readily available from the root of *Solidago altissima* L. (Compositae). Lithium aluminum hydride ($LiAlH_4$) reduction of methyl kolavenate (**1**) gave

1) Part III: I. Kitagawa, M. Yoshihara, and T. Kamigauchi, *Chem. Pharm. Bull.*, **26**, 79 (1978).
2) Location: *133-1, Yamada-kami, Suita, Osaka 565, Japan.*
3) R. Misra, R.C. Pandey, and S. Dev, *Tetrahedron Lett.*, **1964**, 3751.
4) *a*) I. Kitagawa, K. Kitazawa, K. Aoyama, M. Asanuma, and I. Yosioka, *Tetrahedron*, **28**, 923 (1972); *b*) I. Kitagawa, H. Shibuya, and H. Fujioka, *Chem. Pharm. Bull.*, **25**, 2718 (1977), and references cited therein.
5) Presented at the 23rd TEAC Annual Meeting (Tottori, Oct. 3—5, 1979). Symposium Papers, p. 246.
6) A. Butenandt, A. Wolff, and P. Karison, *Chem. Ber.*, **74**, 1308 (1941).

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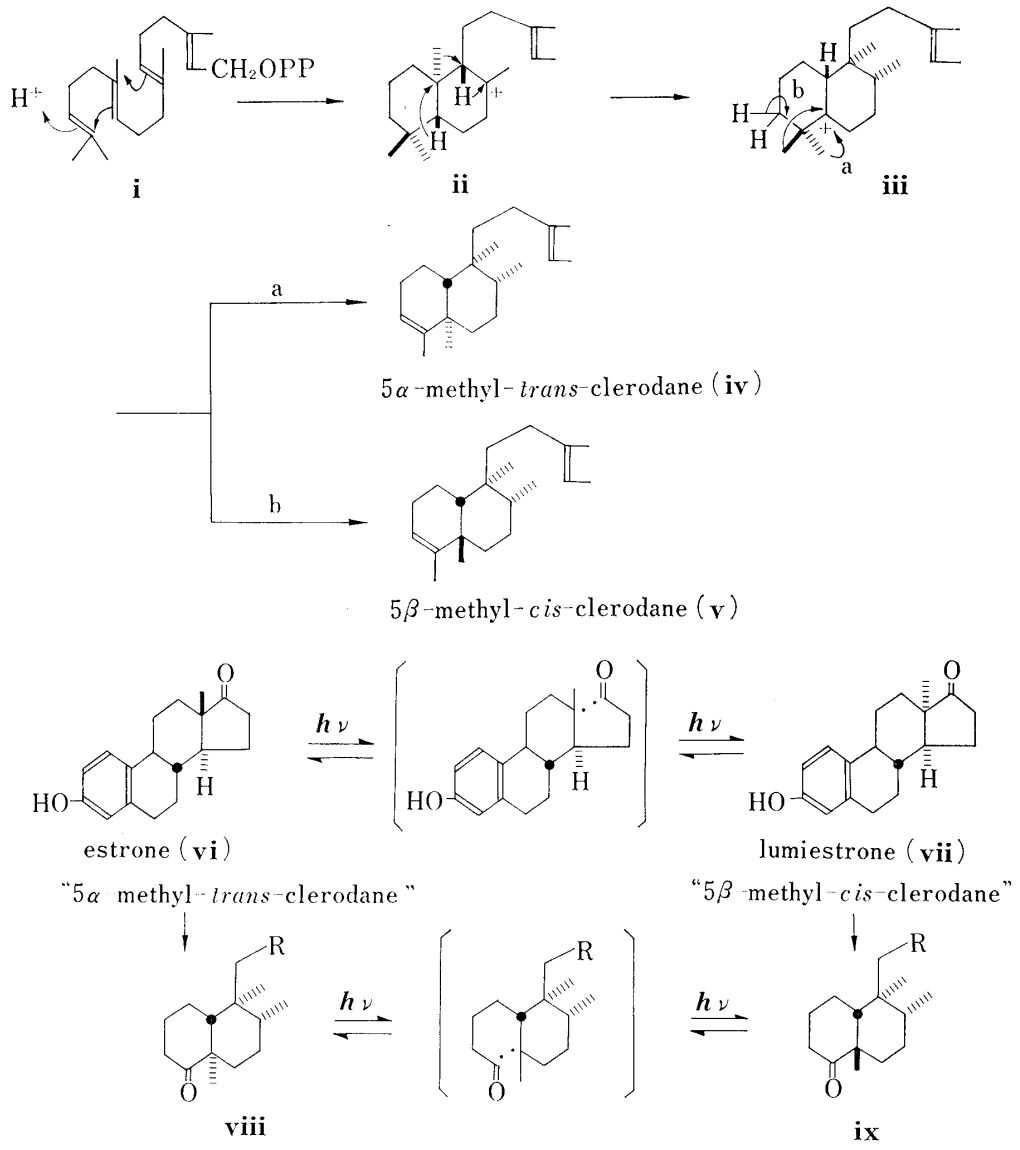

Chart 1

kolavenol (**2**),[7] which, on selective reduction with Raney nickel (Ni), was converted to dihydrokolavenol (**3**), an epimeric mixture at C-13.[8] The proton magnetic resonance (^{1}H-NMR) spectrum of **3** indicates retension of the 3(4) double bond (3H broad singlet at δ 1.53 for 4-CH_3 and 1H multiplet at δ 5.07 for 3-H). Photosensitized isomerization[9] of the acetate (**4**) furnished dihydroisokolavenol acetate (**5**) which possesses an exomethylene moiety, as shown by its infrared (IR) spectrum (1637, 897 cm^{-1}) and ^{1}H-NMR spectrum (δ 4.45, 2H, s). In order to synthesize the norketone (**6**), we initially attempted ozone oxidation of **5** in methylene chloride (CH_2Cl_2), but found that the product was an undesired lactone (**5a**).

The structure of **5a** was supported by its IR: 1744, 1730 cm^{-1} (lactone, acetate), ^{1}H-NMR: δ 1.44 (3H, s, 5-CH_3), and circular dichroism (CD) spectrum: $[\theta]_{234}$ −1000 (neg. max.). However, when the ozone oxidation was carried out in CH_2Cl_2 containing pyridine (50: 1),[10] the

7) S. Kusumoto, T. Okazaki, A. Ohsuka, and M. Kotake, *Bull. Chem. Soc. Jpn.* **42**, 812 (1969).
8) Separation of the epimers could not be achieved by thin-layer or gas-liquid chromatography (TLC, GLC) under various conditions.
9) J.A. Marshall and A.R. Hochstetler, *J. Am. Chem. Soc.*, **91**, 648 (1969).
10) G. Slomp, Jr. and J.L. Johnson, *J. Am. Chem. Soc.*, **80**, 915 (1958).

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desired norketone (**6**), IR: 1714 cm^{-1}; $[\theta]_{294}$ −13000 (neg. max.), was obtained in high yield. This unusual formation of lactone (**5a**) is presumably attributable to the strongly electron-releasing character[11] of C-5 toward C-4 in **5** (there is a probable zwitterion intermediate: *cf.* **x**). When pyridine was added to the oxidation medium, nucleophilic association of pyridine with the zwitterion intermediate (*cf.* **xi** and/or **xii**)[10] would occur and subsequent decomposition (*cf.* **xiii** and **xii**) would provide **6** and pyridine N-oxide, although formation of the latter in the reaction mixture was not confirmed (Chart 2).

Irradiation of **6** dissolved in various solvents (dioxane, cyclohexane, benzene, toluene, *etc.*) in a quartz vessel always yielded a mixture of unsaturated aldehydes (**7**) (approximately 1:1 mixture of $\Delta^{5(10)}$ and $\Delta^{5(18)}$), IR: 2715, 1747, 886 cm^{-1} and the desired photoisomerized *cis* product was not detected.

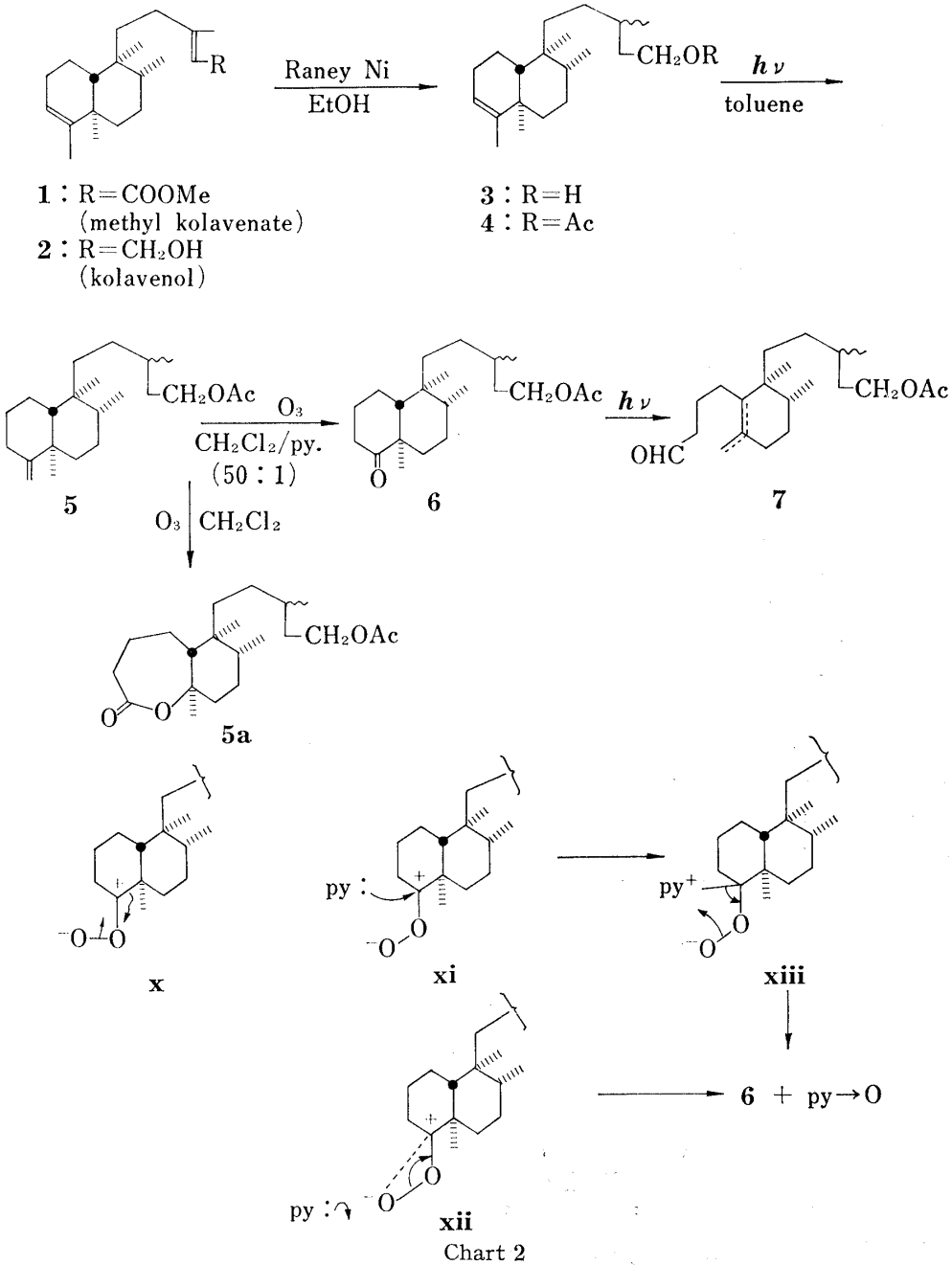

Chart 2

11) W.G. Young, A.C. McKinnis, D. Webb, and J.D. Roberts, *J. Am. Chem. Soc.*, **68**, 293 (1946).

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At this stage, the different photolytic behavior of **6**, as compared with the photoisomerization between estrone (**vi**) and lumiestrone (**vii**), was considered ascribable to the fact that the moieties concerned in the photoisomerization in **vi** and **vii** are hydrindanones while **6** is a decalone derivative. We next attempted to induce the *trans-cis* isomerization of **viii** and **ix** by way of photoisomerization of *trans-cis* hydrindanones (**xiv**, **xv**).

A *trans*-hydrindanone (**14**) was synthesized from dihydrokolavenol acetate (**4**). Photosensitized oxygenation of **4** in isopropanol containing rose bengal followed by sodium borohydride ($NaBH_4$) reduction furnished an exomethylene allyl alcohol (**8**), IR: 3600, 3440 (br), 903 cm^{-1}; ^1H-NMR: δ 4.88, 5.51 (both 1H, br. s), which, on chromium trioxide oxidation, was converted to an exomethylene enone (**9**), IR: 1698, 1610 cm^{-1}. Since **9** was a fairly unstable oil, it was immediately transformed to a ketal (**10**). Ozone oxidation of **10** in methanol gave a ketal-ketone (**11**), IR: 1727 cm^{-1}, which, upon irradiation in cyclohexane under a nitrogen atmosphere, was converted to a mixture of A-nor-ketal (**12**) and A-seco-ketal (**13**), although both yields were unsatisfactory. To facilitate isolation of the products, the total reaction mixture was subjected to deketalization with acid to give the desired A-nor-ketone (**14**), IR: 1747 cm^{-1}, and A-seco-aldehyde (**15**), a mixture of $\Delta^{5(10)}$ and $\Delta^{5(18)}$ (*vide infra*), IR: 2720, 1747 cm^{-1}. In order to confirm the 5α-methyl configuration in **14** and to procure a sufficient amount of **14**, another synthetic route from **8** leading to **14** was pursued.

Ozone oxidation of **8** in methanol gave an α-ketol (**16**), IR: 3460, 1747, 1713 cm^{-1}, which on chromium trioxide oxidation followed by methylation, was transformed to a diester (**17**), IR: 1745 cm^{-1}; ^1H-NMR: δ 3.60, 3.62 (both 3H, s). Dieckman condensation of **17** with sodium in refluxing toluene followed by acid treatment yielded A-nor-*trans*-ketone (**18**), which was found to be identical with the A-nor-ketone (**14**) obtained above in many respects (TLC, IR, GLC, $[\alpha]_D$, and CD). It follows therefore that the 5α-methyl configuration in **11** has been preserved during the photolytic A-ring contraction (giving **12**).

Photochemical isomerization of **14** was examined under various conditions: in cyclohexane, dioxane, or benzene as a solvent and with a Pyrex or a quartz tube as a reaction vessel. However, no *trans-cis* isomerization product was obtained, but instead a mixture ($\Delta^{5(10)}$: $\Delta^{5(18)}$ = *ca.* 4:1) of unsaturated aldehydes was formed, IR: 2720, 1747, 1738 (sh), 1648 (w), 891 (w); ^1H-NMR: δ 1.60 (2.4H, s, 5-CH_3 in a major isomer), 4.42, 4.82 (both 0.2H, br. s, 18-H_2 in a minor isomer), 9.92 (1H, narrow m). The mixture obtained here was found to be very similar to a mixture (**15**) obtained above through photolysis of **11** followed by acid treatment.

Thus, our examinations of the photochemical behavior of 5α-methyl-*trans*-norketones (**6**, **14**) failed to achieve photoisomerizations from *trans* (**viii**, **xiv**) to *cis* isomers (**ix**, **xv**), but photolytic ring-opening occurred to give a mixture of unsaturated aldehydic products (**7**, **15**).

Next, we examined the photochemical behavior of 5β-methyl-*cis*-norketone (**26**), anticipating that *cis-trans* photoisomerization might occur.

Transformation from *cis*-Clerodane to *trans*-Clerodane

The substrate (**26**), a 19-nor-4-keto derivative of 5β-methyl-*cis*-clerodane, was synthesized for photoisomerization studies from linaridial (**19**),[12] which was obtained from the fresh subterranean part of *Linaria japonica* Miq. (Scrophulariaceae).

An ester aldehyde (**20**),[12] which was prepared from linaridial (**19**) by chromium trioxide oxidation followed by methylation, was subjected to thioketalization to afford an ester-thicketal (**21**), IR: 1734, 785 cm^{-1}; ^1H-NMR: δ 3.00—3.29 (6H, m, 14-H_2 and ethylene thioketal protons). Treatment of **21** with Raney Ni in ethanol brought about concomitant reductive dethioketalization and selective reduction of the 12(13) double bond to furnish an ester (**22**), an epimeric mixture at C-13,[8] IR: 1747 cm^{-1}; ^1H-NMR: δ 0.93 (3H, d, J=6, 13-CH_3),

12) I. Kitagawa, M. Yoshihara, T. Tani, and I. Yosioka, *Chem. Pharm. Bull.*, **24**, 294 (1976).

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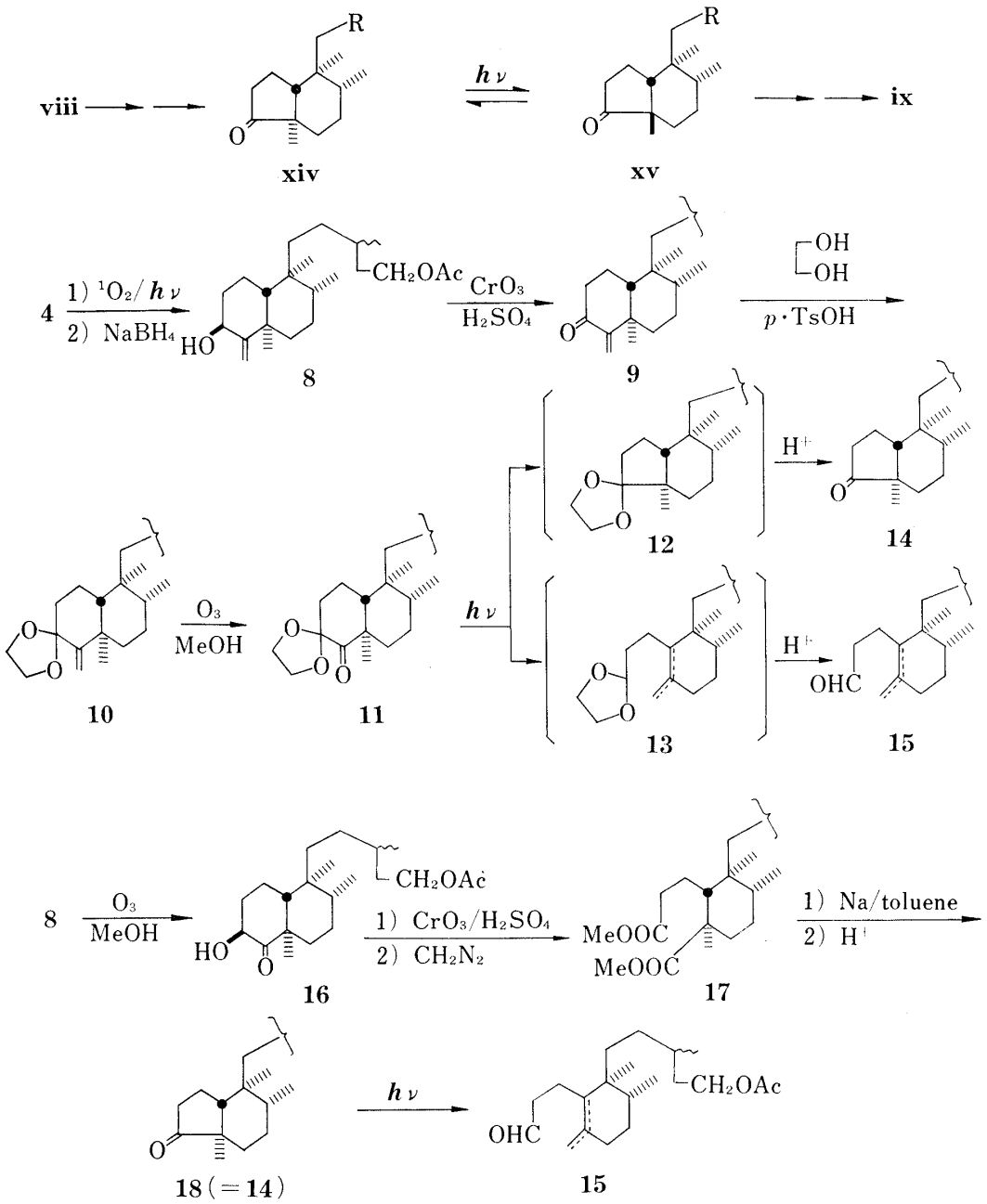

Chart 3

1.66 (3H, d, J=2, 4-CH_3), 5.22 (1H, br.s, 3-H). $LiAlH_4$ reduction of **22** gave an alcohol (**23**), IR: 3640 cm^{-1}; ^{1}H-NMR: δ 3.57 (2H, t, J=6, 15-H_2). Irradiation of the acetate (**24**) in toluene yielded an isomerization product (**25**), which possesses an exomethylene moiety as shown by IR: 1636, 894 cm^{-1} and ^{1}H-NMR: δ 4.60—4.72 (2H, narrow m). Ruthenium tetroxide oxidation of **25** gave the desired *cis*-4-norketone (**26**), IR: 1709 cm^{-1}; ^{1}H-NMR: δ 1.23 (3H, s, 5-CH_3), 4.01 (2H, t, J=6, 15-H_2), $[\theta]_{295}$ −5400 (neg. max.).

Finally, irradiation of **26** in cyclohexane for 35 minutes furnished in low yield an isomeric norketone (**27**) and a mixture of unsaturated aldehydes (**7**) in high yield together with a major amount of recovered norketone (**26**). The isomeric norketone (**27**) obtained here was found to be identical with the *trans*-4-norketone (**6**) prepared above from methyl kolavenate (**1**) in many respects (TLC, GLC, IR, ^{1}H-NMR, and CD), thus accomplishing a conversion from *cis*-4-nor-ketone (**26**) to *trans*-4-norketone (**6**). As for the aldehydic mixture, the ^{1}H-NMR and IR spectra were very similar to those of **7**, although the precise composition was not

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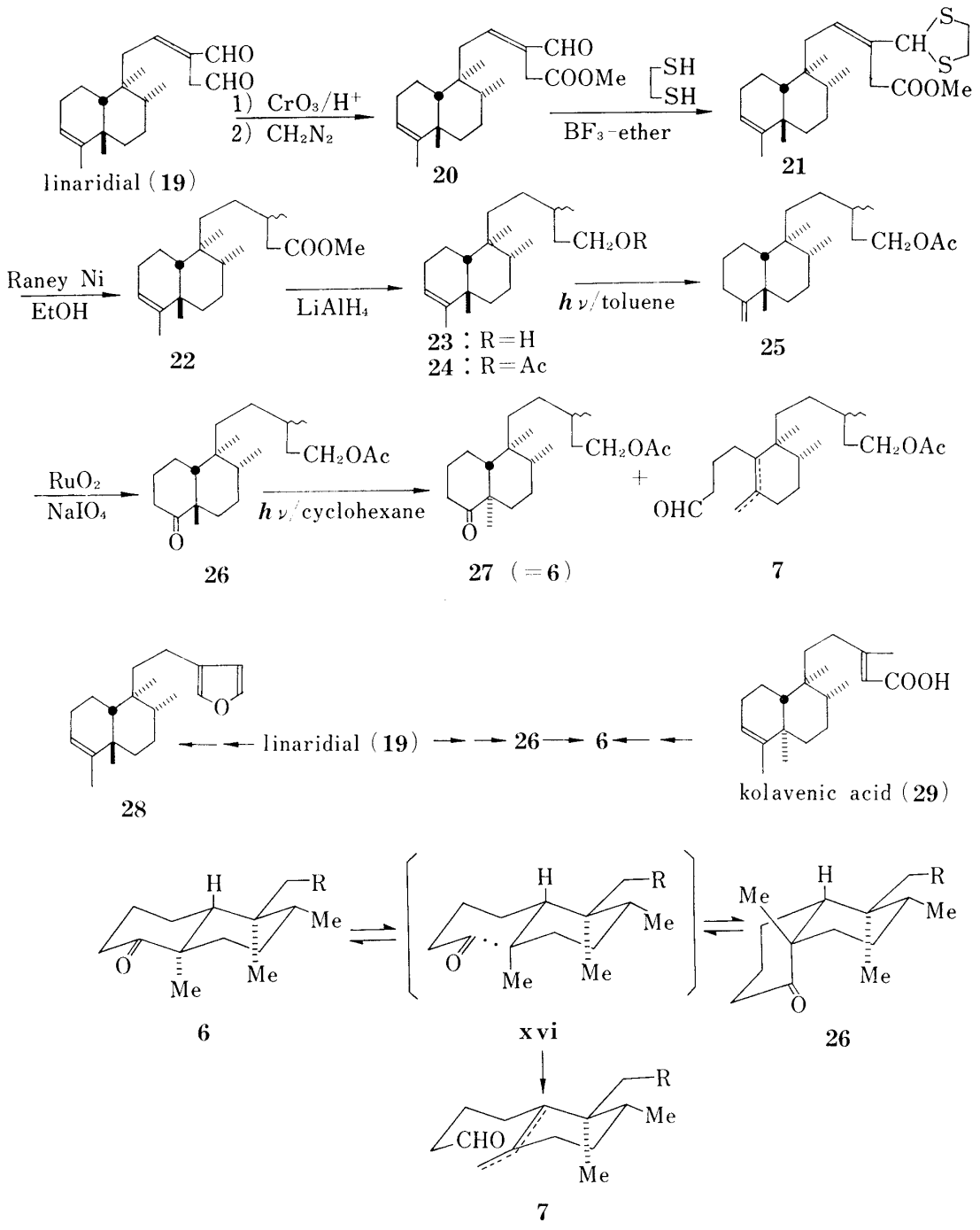

Chart 4

determined.

The present conversion (from **26** to **6**) is interesting in that it involves a direct inversion of absolute configuration at a quaternary carbon which is adjacent to a carbonyl group by way of photochemical ring opening and ring closure. This conversion also constitutes a successful chemical interrelation between kolavenic acid (**29**), a 5α-methyl-*trans*-clerodane whose absolute stereostructure was established by virtue of CD and ORD analyses,[7] and linaridial (**19**), a 5β-methyl-*cis*-clerodane whose absolute stereostructure was chemically correlated with that of an X-ray analyzed furan (**28**).[13]

13) G. Ferguson, W.C. Marsh, R. McCrindle, and E. Nakamura, *J. Chem. Soc. Chem. Commun.*, **1975**, 299.

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As for the photoepimerization at C-13 of 17-keto steroids (**vi** ⇄ **vii**),[6] it has been shown that i) the photoepimerization is a reversible reaction and ii) the final photochemically equilibrated mixture contains more of the thermodynamically favorable 13α-methyl (*cis*) isomer.[14]

In the present photoisomerization of 19-nor-4-keto derivatives of clerodanes (**6**, **26**), if the provisional biradical intermediate (**xvi**) recombines from the equatorial side, *trans*-4-norketone (**6**) would be formed, while if the recombination occurs from the axial side, *cis*-4-norketone (**26**) would be formed. On the other hand, if the biradical (**xvi**) abstracts hydrogen from C-10 and C-18, a mixture of unsaturated aldehydes (**7**) would be produced.

In a photochemical study of 9-methyl-1-decalones, Yang and Chen reported that a biradical intermediate (*cf.* **xvi**) preferentially gave a *cis*-ketone by way of an axial ring closure.[15] In our case, an equatorial ring closure (giving **6**) is preferred to an axial ring closure (giving **26**) and the results appear to be inconsistent with the reported evidence. However, the finding that the *cis*-4-norketone (**26**) gave *trans*-4-norketone (**6**), although in low yield, but not *vice versa*, may be rationalized by assuming that i) the *cis*-isomer (**26**) is thermodynamically less favored as compared with the *trans*-isomer (**6**), and ii) the axial ring closure from **xvi** is less favored than the equatorial ring closure because of steric hindrance caused by the axial 9α-methyl.

It should be noted in connection with the photolysis of **11** that a *trans*-hydrindanone ketal (**12**) was selectively formed *via* preferential equatorial recombination of the biradical intermediate. This result may be rationalized in an analogous manner.

Experimental[16]

Isolation of Methyl Kolavenate (**1**)——Methyl kolavenate (**1**) was isolated by the following modification of the reported procedure.[7] Rhizomes (23 kg) of *Solidago altissima* (collected in March, air-dried for one day and cut) were immersed in benzene (100 l) for one month. The extract (260 g) obtained by removal of the benzene under reduced pressure was extracted with aq. 2 N KOH. The alkali-soluble portion was separated, acidified with aq. 4 N H_2SO_4, and extracted with ether. The ether extract was washed with water, dried over $MgSO_4$, and concentrated to give a residue (225 g), which was dissolved in ether again and methylated with diazomethane. After usual work-up, a brown oily product (225 g) was obtained. A part of the product (90 g) was subjected to column chromatography (SiO_2 1.8 kg, *n*-hexane–benzene=10: 1→1: 1) to afford methyl kolavenate (**1**) (27 g, 26% from benzene ext., 0.3% from air-dried rhizome). Methyl kolavenate thus obtained was identical with an authentic sample[7] as judged by TLC, IR, $[\alpha]_D$, and ^{1}H-NMR.

Reduction of 1 giving Kolavenol (**2**)——Kolavenol (**2**) was prepared from methyl kolavenate (**1**) by a slight modification of the reported method.[7] A solution of **1** (2.43 g) in dry ether (40 ml) was added dropwise to a suspension of $LiAlH_4$ (1.32 g) in dry ether (50 ml), and the total reaction mixture was stirred at room temp. (25°) for 1.5 hr. After treatment with aq. ether and aq. 5% H_2SO_4 as usual, the reaction mixture was extracted with ether and the ether extract was worked up in a usual manner to furnish kolavenol (**2**) (2.21 g, 99%). Colorless oil, $[\alpha]_D^{20}$ −54° (*c*=1.25, $CHCl_3$) (lit.[7] $[\alpha]_D$ −57°). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600, 3350 (br), 1664, 995. ^{1}H-NMR (CCl_4) δ: 0.70 (3H, s, 9-CH_3), 0.82 (3H, d, *J*=6, 8-CH_3), 0.98 (3H, s, 5-CH_3), 1.54 (3H, d, *J*=1, 4-CH_3, changed to s on irr. at δ 5.09), 1.65 (3H, br.s, 13-CH_3, changed to s on irr. at δ 5.30), 4.01 (2H, d, *J*=7, 14-CH_2OH, changed to s on irr. at δ 5.30), 5.09 (1H, m, $W_{h/2}$=8, 3-H, changed to t on irr. at δ 1.54), 5.30 (1H, t-like, 14-H, changed to t, *J*=7 on irr. at δ 1.65). MS (*m/e*, %): 290 (M^+, 12), 95 (100).

Catalytic Hydrogenation of 2 giving Dihydrokolavenol (**3**)——A solution of **2** (3.51 g) in dry EtOH (25 ml) was treated with a suspension of Raney Ni (W-2) in EtOH (80 ml) and heated under reflux for 2 hr. After cooling, the catalyst was removed by filtration. The filtrate was concentrated under reduced pressure to give a residue (3.45 g) which was purified by column chromatography (SiO_2 60 g, benzene–AcOEt=5: 1) to furnish dihydrokolavenol (**3**) (3.09 g, 88%). Colorless oil, $[\alpha]_D^{20}$ −36° (*c*=1.20, $CHCl_3$). High resolution MS (*m/e*): Calcd for $C_{20}H_{36}O$: 292.279; Found: 292.277. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3625, 3300 (br), 1055. ^{1}H-NMR

14) H. Wehrli and K. Schaffner, *Helv. Chim. Acta*, **45**, 385 (1962).
15) N.C. Yang and R.H.-K. Chen, *J. Am. Chem. Soc.*, **93**, 530 (1971).
16) The instruments used to obtain physical data, and the experimental conditions for chromatography were the same as in our previous paper[1] unless otherwise specified. Specific rotations were measured with JASCO DIP-181 digital polarimeter (l=5 cm). For column chromatography on SiO_2 impregnated with $AgNO_3$, the adsorbent was prepared by extensive mixing of SiO_2 and $AgNO_3$ (10: 1) with the aid of water followed by drying at 100° for 3 days.

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(CCl_4) δ: 0.69 (3H, s, 9-CH_3), 0.75, 0.88 (both 3H, d, J=6, 8-CH_3), 13-CH_3), 0.96 (3H, s, 5-CH_3), 1.53 (3H, br.s, 4-CH_3, changed to s on irr. at δ 5.07), 3.56 (2H, t, J=6, 14-CH_2OH), 5.07 (1H, m, $W_{h/2}$=8, 3-H, changed to t, J=3 on irr. at δ 1.53). MS (*m/e*, %): 292 (M^+, 7), 191 (58), 107 (58), 95 (100).

Acetylation of 3 giving Dihydrokolavenol Acetate (4)——A solution of **3** (2.73 g) in pyridine (3 ml) was treated with Ac_2O (3 ml) and stirred at room temp. (28°) for 1.5 hr. The reaction mixture was poured into ice-water and extracted with AcOEt. The AcOEt extract was then washed successively with aq. 5% HCl, aq. sat. $NaHCO_3$, and water, and worked up in the usual manner to give dihydrokolavenol acetate (**4**) (2.81 g, 90%). Colorless oil, $[\alpha]_D^{20}$ −75° (c=1.20, $CHCl_3$), High resolution MS (*m/e*): Calcd for $C_{22}H_{38}O_2$: 334.287; Found: 334.287. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1747, 1235, 1037. ^{1}H-NMR (CCl_4) δ: 0.69 (3H, s, 9-CH_3), 0.78, 0.92 (both 3H, d, J=6, 8-CH_3, 13-CH_3), 0.95 (3H, s, 5-CH_3), 1.55 (3H, br.s, 4-CH_3), 1.95 (3H, s, OAc), 4.03 (2H, t, J=6, 14-CH_2OAc), 5.05 (1H, m, $W_{h/2}$=8, 3-H). MS (*m/e*, %): 334 (M^+, 6), 191 (88), 95 (100).

Photosensitized Isomerization of 4 giving Dihydroisokolavenol Acetate (5)——Dihydrokolavenol acetate (**4**) (312 mg) was dissolved in dry toluene (45 ml), previously deaerated by flushing with nitrogen for one hour. The solution was put in a Vycor tube and irradiated with a 500 W high pressure mercury lamp (Eikosha PIH-500) under a nitrogen atmosphere for 4 hr. After removal of the solvent under reduced pressure, a brown oily product (333 mg) was purified by column chromatography ($AgNO_3$ 1.5 g, SiO_2 15 g, benzene–ether=50: 1→10: 1) to furnish dihydroisokolavenol acetate (**5**) (208 mg, 67%). Colorless oil, $[\alpha]_D^{15}$ +33° (c=1.19, $CHCl_3$). High resolution MS (*m/e*): Calcd for $C_{22}H_{38}O_2$: 334.287; Found: 334.288. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3085, 1748, 1637, 1234, 1042, 897. ^{1}H-NMR (CCl_4) δ: 0.72 (3H, s, 9-CH_3), 0.77, 0.89 (both 3H, d, J=6, 8-CH_3, 13-CH_3), 1.02 (3H, s, 5-CH_3), 1.97 (3H, s, OAc), 4.02 (2H, t, J=6, 14-CH_2OAc), 4.45 (2H, s, 4=CH_2). MS (*m/e*, %): 334 (M^+, 11), 191 (76), 95 (100).

Ozone Oxidation of 5 in CH_2Cl_2 giving the Lactone (5a)——A cooled solution (−78°, with dry ice–acetone) of **5** (218 mg) in CH_2Cl_2 (10 ml) was treated with ozonized oxygen for one hour. The cooled (−78°) reaction mixture was then flushed with nitrogen to remove excess ozone and treated with NaI (75 mg) with stirring. After allowing the temperature of the reaction mixture to rise gradually to room temp., the reaction mixture was treated with aq. $Na_2S_2O_3$ and extracted with AcOEt. Usual work-up of the AcOEt extract gave a brown product (210 mg) which was purified by column chromatography (SiO_2 25 g, benzene–AcOEt=20: 1) to furnish the lactone (**5a**) (77 mg). Colorless oil, $[\alpha]_D^{15}$ +31° (c=1.69, $CHCl_3$). High resolution MS (*m/e*): Calcd for $C_{21}H_{36}O_4$: 352.261; Found: 352.261. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1744, 1730, 1238, 1089, 1041. CD (c=0.588, MeOH): $[\theta]_{218}$ 0, $[\theta]_{234}$ −1000 (neg. max.), $[\theta]_{266}$ 0. ^{1}H-NMR (CCl_4) δ: 0.67 (3H, s, 9-CH_3), 0.81, 0.89 (both 3H, d, J=6, 8-CH_3, 13-CH_3), 1.44 (3H, s, 5-CH_3), 1.97 (3H, s, OAc), 4.04 (2H, t, J=6, 14-CH_2OAc). MS (*m/e*, %): 352 (M^+, 2), 209 (86), 43 (100).

Ozone Oxidation of 5 in CH_2Cl_2–Pyridine giving the Norketone (6)——A cooled (−78°) solution of **5** (113 mg) in CH_2Cl_2 (10 ml)–pyridine (0.2 ml) was treated with ozonized oxygen for one hour. After removing excess ozone by flushing with nitrogen and treatment with NaI (35 mg) as above, the cooled reaction mixture (−78°) was allowed to warm up gradually to room temp. (27°), treated with aq. $Na_2S_2O_3$, and extracted with AcOEt. Usual work-up of the AcOEt extract gave a brown product (110 mg), which was purified by column chromatography (SiO_2 15 g, benzene–AcOEt=10: 1) to furnish the norketone (**6**) (101 mg, 89%). Colorless oil, $[\alpha]_D^{15}$ −10° (c=0.90, $CHCl_3$). High resolution MS (*m/e*): Calcd for $C_{21}H_{36}O_3$: 336.266; Found: 336.266. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1749, 1714, 1235. ^{1}H-NMR (CCl_4) δ: 0.78 (3H, s, 9-CH_3), 0.79, 0.90 (both 3H, d, J=6, 8-CH_3, 13-CH_3), 1.08 (3H, s, 5-CH_3), 1.95 (3H, s, OAc), 4.00 (2H, t, J=6, 14-CH_2OAc). MS (*m/e*, %): 336 (M^+, 8), 193 (100). CD (c=0.490, MeOH): $[\theta]_{248}$ 0, $[\theta]_{294}$ −13000 (neg. max.), $[\theta]_{324}$ 0.

Photolysis of 6 giving Unsaturated Aldehydes (7)——A solution of **6** (97 mg) in dioxane (12 ml) was put in a quartz tube and irradiated under nitrogen atmosphere with a 100 W high pressure mercury lamp (Eikosha PIH-100) for 40 min. After removal of the solvent under reduced pressure, a brown oily product (97 mg) was subjected to preparative (p-) TLC (benzene–ether=10: 1) to furnish a mixture ($\Delta^{5(10)}$: $\Delta^{5(18)}$=1: 1) of unsaturated aldehydes (**7**) (26 mg) and a mixture (25 mg) of **6** and **7**. **7**, colorless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3075 (w), 2715, 1747, 1643, 1234, 886. ^{1}H-NMR (CCl_4) δ: 0.80—0.91 (9H, m, 8-CH_3, 9-CH_3, 13-CH_3), 1.62 (1.5H, s, 5-CH_3), 1.96 (3H, s, OAc), 4.00 (2H, m, 14-CH_2OAc), 4.51, 4.81 (both 0.5H, br.s, $W_{h/2}$=4, 5=CH_2), 9.89 (1H, narrow m, 3-CHO). MS (*m/e*, %): 336 (M^+, 3), 193 (100).

Photosensitized Oxygenation of 4 giving Allyl Alcohol (8)——An ice-cooled solution of **4** (110 mg) in isopropanol (2.5 ml) in a Pyrex tube was treated with rose bengal (50 mg) and irradiated with a 500 W high pressure mercury lamp (Eikosha PIH-500) for 2 hr while introducing a stream of oxygen. The reaction mixture was poured dropwise into a suspension of $NaBH_4$ (125 mg) in isopropanol (3 ml) and the whole was stirred at room temp. (26°) for 1.5 hr. After slow addition of aq. 5% HCl, the solvent was removed under reduced pressure and the residue was extracted with AcOEt. The AcOEt extract was washed with aq. sat. NaCl and dried over $MgSO_4$. Removal of the solvent by evaporation gave an oily product (110 mg) which was purified by p-TLC (double development with benzene–AcOEt=6: 1) to furnish the exomethylene allyl alcohol (**8**) (53 mg, 46%). Amorphous, $[\alpha]_D^{15}$ +35° (c=1.05, $CHCl_3$). *Anal.* Calcd for $C_{22}H_{38}O_3$: C, 75.38; H, 10.93. Found: C, 75.06; H, 10.84. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600, 3440 (br), 3075, 1743, 1639, 1233, 903. ^{1}H-NMR (CCl_4) δ: 0.70 (3H, s, 9-CH_3), 0.79, 0.90 (both 3H, d, J=6, 8-CH_3, 13-CH_3), 1.01 (3H, s, 5-CH_3), 1.96 (3H, s, OAc), 3.89—4.29 (3H, m, 3-H, 14-CH_2OAc), 4.61, 4.84 (both 1H, br.s, $W_{h/2}$=4, 4=CH_2); (d_5-pyridine) δ: 0.70 (3H, s, 9-CH_3), 0.77, 0.84 (both 3H, d, J=6, 8-CH_3, 13-CH_3), 1.04 (3H, s, 5-CH_3), 1.98 (3H, s, OAc),

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4.13 (2H, t, $J=6$, 14-CH_2OAc), 4.38—4.64 (1H, m, 3-H), 4.88, 5.51 (both 1H, br.s, $W_{h/2}=4$, $4=CH_2$). MS (*m/e*, %): 350 (M^+, 7), 189 (100).

Chromium Trioxide Oxidation of 8 giving Enone (9)——An ice-cooled solution of **8** (50 mg) in acetone (2 ml) was treated dropwise with Jones reagent [prepared from CrO_3 (7 g), conc. H_2SO_4 (11.2 g), and H_2O (30 ml)] and stirred for 30 min. The reaction mixture was poured into ice-water and extracted with AcOEt. Usual work-up of the AcOEt extract gave a product (42 mg) which was purified by p-TLC (Merck PF_{254}, benzene–AcOEt=10: 1) to furnish an unstable enone (**9**) (22 mg, 44%). Colorless oil, $[\alpha]_D^{26}$ +31° ($c=0.94$, $CHCl_3$), IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1745, 1698, 1610, 1233. UV λ_{max}^{EtOH} nm (ε): 226 (3800). ^{1}H-NMR (CCl_4) δ: 0.78 (3H, s, 9-CH_3), 0.80—0.90 (6H, m, 8-CH_3, 13-CH_3), 1.01 (3H, s, 5-CH_3), 1.94 (3H, s, OAc), 4.03 (2H, t, $J=6$, 14-CH_2OAc), 4.91, 5.46 (both 1H, d, $J=2$, $4=CH_2$). MS (*m/e*, %): 348 (M^+, 8.5), 205 (59), 43 (100).

Ketalization of 9 giving the Ketal (10)——A solution of **9** (38 mg) in dry benzene (2 ml) was treated with ethylene glycol (0.3 ml) and *p*-TsOH·H_2O (1 microspatulafull) and heated for 2 hr. During this period, dry benzene (4 ml) was added slowly to the reaction mixture while removing benzene and water azeotropically. After cooling, the reaction mixture was diluted with water and extracted with AcOEt. Usual work-up of the AcOEt extract gave a product (40 mg) which was purified by p-TLC (benzene–ether=10: 1) to furnish the ketal (**10**) (17 mg, 36%). Colorless oil, $[\alpha]_D^{24}$ −5° ($c=1.22$, $CHCl_3$). High resolution MS (*m/e*): Calcd for $C_{24}H_{40}O_4$: 392.292; Found: 392.294. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1743, 1631, 1232, 1069, 921. ^{1}H-NMR (CCl_4) δ: 0.73 (3H, s, 9-CH_3), 0.78, 0.89 (both 3H, d, $J=6$, 8-CH_3, 13-CH_3), 1.07 (3H, s, 5-CH_3), 1.95 (3H, s, OAc), 3.67—4.11 (6H, m, $-OCH_2-CH_2O-$, 14-CH_2OAc), 4.73, 5.05 (both 1H, d, $J=2$, $4=CH_2$); (d_6-benzene) δ: 0.72 (3H, s, 9-CH_3), 0.72—0.82 (6H, m, 8-CH_3, 13-CH_3), 1.24 (3H, s, 5-CH_3), 1.75 (3H, s, OAc), 3.49—3.76 (4H, m, $-OCH_2-CH_2O-$), 4.01 (2H, t, $J=6$, 14-CH_2OAc), 4.88, 5.25 (both 1H, d, $J=2$, $4=CH_2$). MS (*m/e*, %): 392 (M^+, 57), 377 (78), 249 (39), 99 (100).

Ozone Oxidation of 10 giving the Ketal-ketone (11)——A cooled solution (−78°, with dry ice-acetone) of **10** (111 mg) in MeOH (36 ml) was treated with a stream of ozonized oxygen for 1.5 hr then flushed with nitrogen to remove excess ozone. After allowing the temp. of the reaction mixture to rise gradually to room temp. (26°), the reaction mixture was concentrated under reduced pressure to give a product (121 mg). Column chromatography (SiO_2 5 g, benzene–AcOEt=10: 1) of the product furnished the ketal-ketone (**11**) (80 mg, 72%). Colorless needles (from MeOH) of mp 92—93.5°, $[\alpha]_D^{26}$ −33° ($c=0.77$, $CHCl_3$). *Anal.* Calcd for $C_{23}H_{38}O_5$: C, 70.01; H, 9.71. Found: C, 70.09; H, 9.73. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1748, 1727, 1237, 1037. ^{1}H-NMR (CCl_4) δ: 0.78 (3H, s, 9-CH_3), 0.79, 0.90 (both 3H, d, $J=6$, 8-CH_3, 13-CH_3), 1.13 (3H, s, 5-CH_3), 1.96 (3H, s, OAc), 3.78—4.22 (6H, m, $-OCH_2-CH_2O-$, 14-CH_2OAc). MS (*m/e*, %): 366 (M^+-28, 3), 99 (100). CD ($c=0.138$, MeOH): $[\theta]_{279}$ 0, $[\theta]_{320}$ −900 (neg. max.), $[\theta]_{349}$ 0.

Photolysis of 11 followed by Deketalization giving the Bisnorketone (14) and Seco-aldehyde (15)——A solution of **11** (180 mg) in cyclohexane (14 ml) in a quartz tube was irradiated under a nitrogen atmosphere with a 30 W low pressure mercury lamp (Eikosha PIL-30) for 22 hr. Removal of the solvent under reduced pressure yielded a product which was purified by p-TLC (benzene–AcOEt=9: 1) to give **11** (30 mg, recovered) and a mixture (25 mg) of **12** and **13**. The latter mixture was dissolved in acetone (1.5 ml) and the solution was treated with *p*-TsOH·H_2O (13 mg) then stirred at room temp. (29°) for 1.5 hr. Purification of the product by column chromatography (SiO_2 15 g, benzene–AcOEt=10: 1) furnished **14** (6 mg) and **15** (5 mg). **14**, colorless oil, $[\alpha]_D^{26}$ −64° ($c=0.18$, $CHCl_3$). High resolution MS (*m/e*): Calcd for $C_{20}H_{34}O_3$: 322.251; Found: 322.251. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1747, 1235. ^{1}H-NMR (CCl_4) δ: 0.79 (3H, s, 9-CH_3), 0.80, 0.91 (both 3H, d, $J=6$, 8-CH_3, 13-CH_3), 0.91 (3H, s, 5-CH_3), 1.96 (3H, s, OAc), 4.01 (2H, t-like, 14-CH_2OAc). MS (*m/e*, %): 322 (M^+, 9), 178 (100). CD ($c=0.129$, MeOH): $[\theta]_{240}$ 0, $[\theta]_{296}$ −10000 (neg. max.), $[\theta]_{329}$ 0. **15**, colorless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 2720, 1747, 1235. ^{1}H-NMR (CCl_4) δ: 0.82 (3H, s, 9-CH_3), 0.86, 0.92 (both 3H, d, $J=6$, 8-CH_3, 13-CH_3), 1.60 (3H, s, 5-CH_3), 1.96 (3H, s, OAc), 4.02 (2H, t, $J=6$, 14-CH_2OAc), 9.80 (1H, s, CHO). MS (*m/e*, %): 322 (M^+, 2), 179 (100).

Ozone Oxidation of 8 giving the α-Ketol (16)——A cooled solution (−78°, with dry ice-acetone) of **8** (220 mg) in MeOH (14 ml) was treated with ozonized oxygen for one hour and worked up as described after the ozone oxidation of **10**. Purification of the product (219 mg) by column chromatography (SiO_2 30 g, benzene–AcOEt=7: 1) furnished the α-ketol (**16**) (165 mg, 75%). Colorless oil, $[\alpha]_D^{25}$ +21° ($c=2.81$, $CHCl_3$). High resolution MS (*m/e*): Calcd for $C_{21}H_{36}O_4$: 352.261; Found: 352.261. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3460, 1747, 1713, 1235. ^{1}H-NMR (CCl_4) δ: 0.78 (3H, s, 9-CH_3), 0.79, 0.89 (both 3H, d, $J=6$, 8-CH_3, 13-CH_3), 1.11 (3H, s, 5-CH_3), 1.95 (3H, s, OAc), 3.28 (1H, br.s, OH, disappeared on addition of D_2O), 4.00 (2H, t, $J=6$, 14-CH_2OAc), 4.22 (1H, d.d, $J=7$, 11, 3-H). MS (*m/e*, %): 352 (M^+, 14), 163 (100).

Chromium Trioxide Oxidation of 16 followed by Methylation giving the Diester (17)——A solution of **16** (126 mg) in acetone (5 ml) was treated dropwise with Jones reagent (0.6 ml) and stirred at room temp. (27°) for 30 min. After dilution with water, the reaction mixture was concentrated under reduced pressure to give a residue which was extracted with AcOEt. The AcOEt extract was washed with water and then extracted with aq. sat. $NaHCO_3$. The bicarbonate layer was separated, acidified slowly with conc. HCl and extracted with AcOEt. The AcOEt extract was washed with aq. NaCl and dried over $MgSO_4$. Removal of the solvent under reduced pressure gave a product (109 mg). A solution of the product in ether was treated overnight with ethereal diazomethane. After removal of the ether by evaporation, the product was purified by column chromatography (SiO_2 10 g, benzene –AcOEt=10: 1) to furnish the diester (**17**) (66 mg, 45%).

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Colorless oil, $[\alpha]_D^{16}$ +6° (c=1.22, $CHCl_3$). High resolution MS (m/e): Calcd for $C_{23}H_{40}O_6$: 412.282; Found: 412.281. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1745, 1240. ^{1}H-NMR (CCl_4) δ: 0.77 (3H, s, 9-CH_3), 0.80, 0.92 (both 3H, d, J=6, 8-CH_3, 13-CH_3), 1.18 (3H, s, 5-CH_3), 1.96 (3H, s, OAc), 3.60, 3.62 (both 3H, s, $COOCH_3$), 4.06 (2H, t, J=6, 14-CH_2OAc). MS (m/e, %): 412 (M^+, 1.5), 43 (100).

Dieckman Condensation of 17 followed by Acid Treatment giving the Bisnorketone (18=14)——A solution of **17** (300 mg) in dry toluene (4 ml) was added dropwise over a period of 30 min to a stirred mixture of sodium (60 mg) in dry toluene (3 ml) under reflux. The reaction mixture was stirred under reflux for further 13 hr. After cooling, the mixture was acidified with aq. 10% AcOH and extracted with AcOEt. Concentration of the AcOEt extract under reduced pressure gave a residue which was dissolved in AcOH (5 ml), treated with aq. 18% HCl (1 ml) and heated under reflux for 19 hr. After dilution with water, the reaction mixture was concentrated under reduced pressure to remove AcOH and then extracted with AcOEt. Usual work-up of the AcOEt extract gave a product (280 mg) which was purified by column chromatography (SiO_2 20 g, benzene–AcOEt=10: 1) to furnish the bisnorketone (**18**) (80 mg, 34%). Colorless oil, $[\alpha]_D^{28}$ −61° (c=1.42, $CHCl_3$). High resolution MS (m/e): Calcd for $C_{20}H_{34}O_3$: 322.250; Found: 322.251. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1747, 1235. ^{1}H-NMR (CCl_4) δ: 0.79 (3H, s, 9-CH_3), 0.80, 0.91 (both 3H, d, J=6, 8-CH_3, 13-CH_3), 0.91 (3H, s, 5-CH_3), 2.00 (3H, s, OAc), 4.02 (2H, t-like, 14-CH_2OAc). MS (m/e, %): 322 (M^+, 14), 179 (100). CD (c= 0.463, MeOH): $[\theta]_{238}$ 0, $[\theta]_{296}$ −11000 (neg. max.), $[\theta]_{330}$ 0. The bisnorketone (**18**) was identical with the bisnorketone (**14**) as judged by TLC, $[\alpha]_D$, IR, ^{1}H-NMR, CD, and GLC: i) 10% SE-30 (1 m×3 mm), N_2 flow rate 30 ml/min, C.T. 230°, t_R=5′28″; ii) Hitachi Golay column Z (45 m×0.5 mm), N_2 1 ml/min, C.T. 230°, t_R=6′18″.

Photolysis of 18 giving the Seco-aldehyde (15)——A solution of **18** (50 mg) in dioxane (12 ml) in a quartz tube was irradiated under a nitrogen atmosphere with a 100 W high pressure mercury lamp (Eikosha PIH-100) for 40 min. A residue, obtained by removal of the solvent under reduced pressure, was purified by column chromatography (SiO_2 15 g, benzene–AcOEt=15: 1) to furnish **15** (20 mg, 40%). Colorless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 2720, 1747, 1738 (sh), 1648 (w), 1239, 891 (w). ^{1}H-NMR (CCl_4) δ: 0.81 (3H, s, 9-CH_3), 0.83, 0.90 (both 3H, d, J=6, 8-CH_3, 13-CH_3), 1.60 (2.4H, s, 5-CH_3), 1.96 (3H, s, OAc), 4.01 (2H, t, J=6, 14-CH_2OAc), 4.42, 4.82 (both 0.2H, br.s, $W_{h/2}$=4, 5=CH_2), 9.92 (1H, narrow m, CHO). MS (m/e, %): 322 (M^+, 2), 179 (100).

Thioketalization of the Ester-aldehyde (20) giving the Ester-thioketal (21)——An ice-cooled solution of **20** (312 mg)[12] in dry ether (3 ml) was treated with 1,2-ethanedithiol (0.5 ml) and BF_3-ether (0.5 ml) and the whole was stirred under a nitrogen atmosphere for 1.5 hr. After dilution with ether, the reaction mixture was washed successively with water, aq. 1 N NaOH, and aq. sat. NaCl, then dried over $MgSO_4$. Removal of the solvent gave a product (375 mg) which was purified by column chromatography (SiO_2 40 g, benzene) to furnish **21** (302 mg, 79%). Colorless oil, $[\alpha]_D^{21}$ +27° (c=1.34, $CHCl_3$). High resolution MS (m/e): Calcd for $C_{23}H_{36}O_2S_2$: 408.218; Found: 408.216. IR ν_{max}^{film} cm^{-1}: 1734, 1191, 1153, 785. ^{1}H-NMR (CCl_4) δ: 0.77 (3H, d, J=6, 8-CH_3), 0.82 (3H, s, 9-CH_3), 1.02 (3H, s, 5-CH_3), 1.64 (3H, d, J=2, 4-CH_3, changed to s on irr. at δ 5.22), 3.00—3.29 (6H, m, 14-CH_2COOCH_3, -SCH_2-CH_2S-), 3.61 (3H, s, $COOCH_3$), 5.19 (1H, s, 15-H), 5.22 (1H, br.s, 3-H, deformed on irr. at δ 1.64), 5.75 (1H, t, J=7, 12-H). MS (m/e, %): 408 (M^+, 5), 191 (48), 95 (100).

Reduction of 21 giving the Ester (22)——A solution of **21** (272 mg) in abs. EtOH (5 ml) was treated with a suspension of Raney Ni (W-2) in EtOH (20 ml) and heated under reflux for 2 hr. After cooling, the reaction mixture was filtered to remove the catalyst and the filtrate was concentrated under reduced pressure to give a product (185 mg). Purification of the product by column chromatography (SiO_2 30 g, benzene) furnished **22** (197 mg, 92%). Colorless oil, $[\alpha]_D^{20}$ +32° (c=1.79, $CHCl_3$). High resolution MS (m/e): Calcd for $C_{21}H_{36}O_2$: 320.271; Found: 320.271. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1747, 1200, 1173. ^{1}H-NMR (CCl_4) δ: 0.74 (3H, d, J=6, 8-CH_3), 0.78 (3H, s, 9-CH_3), 0.93 (3H, d, J=6, 13-CH_3), 1.02 (3H, s, 5-CH_3), 1.66 (3H, d, J=2, 4-CH_3, changed to s on irr. at δ 5.22), 3.60 (3H, s, $COOCH_3$), 5.22 (1H, br.s, $W_{h/2}$=8, 3-H, deformed on irr. at δ 1.66). MS (m/e, %): 320 (M^+, 12), 191 (100).

Reduction of 22 giving Alcohol (23)——A solution of **22** (190 mg) in dry ether (5 ml) was added dropwise at room temp. (20°) to a stirred suspension of $LiAlH_4$ (68 mg) in dry ether (3 ml). After 30 min, the reaction mixture was treated with aq. ether in small portions and acidified with dil. HCl. The total mixture was extracted with ether and the ether extract was worked up as usual to furnish **23** (168 mg, 98%). Colorless oil, $[\alpha]_D^{16}$ +32° (c=1.14, $CHCl_3$). High resolution MS (m/e): Calcd for $C_{20}H_{36}O$: 292.276; Found: 292.275. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3630. ^{1}H-NMR (CCl_4) δ: 0.74 (3H, d, J=6, 8-CH_3), 0.79 (3H, s, 9-CH_3), 0.91 (3H, d, J=6, 13-CH_3), 1.03 (3H, s, 5-CH_3), 1.66 (3H, d, J=2, 4-CH_3, changed to s on irr. at δ 5.22), 3.07 (1H, s, OH, disappeared on addition of D_2O), 3.57 (2H, t, J=6, 14-CH_2OH), 5.22 (1H, br.s, $W_{h/2}$=8, 3-H, deformed on irr. at δ 1.66). MS (m/e, %): 292 (M^+, 18), 191 (100), 95 (75).

Acetylation of 23 giving the Acetate (24)——A solution of **23** (180 mg) in dry pyridine (1 ml) was treated with Ac_2O (1 ml) at room temp. (17°) and stirred for one hour. The reaction mixture was poured into ice-water and extracted with AcOEt. Usual work-up of the extract furnished **24** (200 mg, 97%). Colorless oil, $[\alpha]_D^{16}$ +31° (c=1.16, $CHCl_3$). High resolution MS (m/e): Calcd for $C_{22}H_{38}O_2$: 334.287; Found: 334.286. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1747, 1369, 1225. ^{1}H-NMR (CCl_4) δ: 0.74 (3H, d, J=6, 8-CH_3), 0.80 (3H, s, 9-CH_3), 0.93 (3H, d, J=6, 13-CH_3), 1.02 (3H, s, 5-CH_3), 1.66 (3H, d, J=2, 4-CH_3, changed to s on irr. at δ 5.22), 1.97 (3H, s, OAc), 4.02 (2H, t, J=6, 14-CH_2OAc), 5.22 (1H, br.s, $W_{h/2}$=8, 3-H, deformed on irr. at δ 1.66). MS

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(*m/e*, %): 334 (M^+, 7), 191 (100), 95 (67).

Photosensitized Isomerization of 24 giving 25——A solution of **24** (69 mg) in dry toluene (5 ml) in a Vycor tube, which had previously been deaerated by flushing with nitrogen for one hour, was irradiated under nitrogen atmosphere with a 500 W high pressure mercury lamp (Eikosha PIH-500) for one hour. Removal of the solvent under reduced pressure gave a product which was purified by column chromatography ($AgNO_3$ 2 g and SiO_2 20 g, *n*-hexane–benzene=1: 5→1: 10) to furnish **25** (40 mg, 87% from consumed **24**) and **24** (23 mg, recovered). **25**, colorless oil, $[\alpha]_D^{20}$ −21° (*c*=1.15, $CHCl_3$). High resolution MS (*m/e*): Calcd for $C_{22}H_{38}O_2$: 334.287; Found: 334.289. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3090, 1749, 1636, 1370, 1236, 894. ^{1}H-NMR (CCl_4) δ: 0.74 (3H, d, *J*=6, 8-CH_3), 0.82 (3H, s, 9-CH_3), 0.91 (3H, d, *J*=6, 13-CH_3) 1.13 (3H, s, 5-CH_3), 1.96 (3H, s, OAc), 4.01 (2H, t, *J*=6, 14-CH_2OAc), 4.60—4.72 (2H, narrow m, 4=CH_2). MS (*m/e*, %): 334 (M^+, 70), 191 (100), 95 (66).

Ruthenium Tetroxide Oxidation of 25 giving the Ketone (26)——i) Preparation of RuO_4 solution: A solution of $NaIO_4$ (120 mg) in water (2 ml) was treated with a suspension of $RuO_2 \cdot xH_2O$ (Alfa Co., 20 mg) in acetone (2 ml), and the total mixture was vigorously stirred at room temp. (17°) for 25 min to yield a yellowish green RuO_4 solution.

ii) A stirred solution of **25** (60 mg) in acetone (4 ml) was treated with the above RuO_4 solution; the reaction mixture turned black immediately. The stirred reaction mixture was then treated twice with a solution of $NaIO_4$ (80 mg) in water (1 ml), firstly after 5 min and secondly after 15 min. After a total of 35 min stirring, the reaction was quenched by addition of isopropanol, and the reaction mixture was filtered. Concentration of the filtrate under reduced pressure gave a residue which was extracted with AcOEt. The AcOEt extract was washed with aq. sat. NaCl and worked up as usual. Purification of the product (58 mg) by column chromatography (SiO_2 30 g, *n*-hexane–AcOEt=5: 1) furnished **26** (45 mg, 75%). Colorless oil, $[\alpha]_D^{16}$ −47° (*c*=1.13, $CHCl_3$). High resolution MS (*m/e*): Calcd for $C_{21}H_{36}O_3$: 336.266; Found: 336.265. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1744, 1709, 1368, 1233. ^{1}H-NMR (CCl_4) δ: 0.68 (3H, s, 9-CH_3), 0.74 (3H, d, *J*=6, 8-CH_3), 0.92 (3H, d, *J*=6, 13-CH_3), 1.23 (3H, s, 5-CH_3), 1.97 (3H, s, OAc), 4.01 (2H, t, *J*=6, 14-CH_2OAc). MS (*m/e*, %): 336 (M^+, 7), 193 (69), 111 (100). CD (*c*=0.581, MeOH): $[\theta]_{240}$ 0, $[\theta]_{295}$ −5400 (neg. max.), $[\theta]_{330}$ 0.

Photoisomerization of 26 giving the Isomeric Norketone (27=6) and Unsaturated Aldehydes (7)——A solution of **26** (30 mg) in cyclohexane (14 ml) in a Pyrex tube was irradiated under a nitrogen atmosphere with a 100 W high pressure mercury lamp (Eikosha PIH-100) for 35 min. Concentration of the reaction mixture under reduced pressure gave a product (34 mg) which was purified by repeated column chromatography (SiO_2 15 g, benzene–ether=30: 1) to furnish **27** (1.5 mg, 7.5% from consumed **26**), **26** (10 mg recovered), and **7** (7 mg, 35%). The isomeric norketone (**27**) obtained here was identical with **6** prepared above from **1** as judged by TLC, IR, ^{1}H-NMR [the spectrum of **27** was taken on an Anelva NV-21 (90 MHz) ^{1}H-NMR spectrometer; No. of scans, 30; data points, 8192], GLC [3% SE-30 (2 m×3 mm), N_2 flow rate 30 ml/min, C.T. 250°, t_R=7′24″ (*cf.* **26**, t_R=6′12″)], and CD (*c*=0.0485, MeOH): $[\theta]_{250}$ 0, $[\theta]_{294}$ −10000 (neg. max.), $[\theta]_{324}$ 0. ^{1}H-NMR ($CDCl_3$) δ: **27**: 0.79 (3H, s, 9-CH_3), 0.78, 0.90 (both 3H, d, *J*=6, 8-CH_3, 13-CH_3), 1.13 (3H, s, 5-CH_3), 2.03 (3H, s, OAc), 4.08 (2H, t, *J*=6, 14-CH_2OAc); **6**: 0.80 (3H, s), 0.78, 0.90 (both 3H, d, *J*=6), 1.13 (3H, s), 2.03 (3H, s), 4.07 (2H, t, *J*=6); **26**: 0.68 (3H, s), 0.73, 0.91 (both 3H, d, *J*=6), 1.25 (3H, s), 2.03 (3H, s), 4.09 (2H, t, *J*=6). The unsaturated aldehydes obtained here gave IR and ^{1}H-NMR spectra similar to those of **7** obtained above from **6**. The precise composition was not examined in this case since the amount of material available was insufficient.

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