[Chem. Pharm. Bull. 23(10)2329—2338(1975)]

UDC 547.914.2.04 : 547.913.6.057

Diterpenoids. XXXVI. Synthesis of *d*-Kaurene and *d*-Phyllocladene from *l*-Abietic Acid[1]

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(Received March 10, 1975)

d-Kaurene (XXXVI) and *d*-phyllocladene (XXXVII) were synthesized from *l*-abietic acid (I) *via* intramolecular carbenoid reaction of diazoketones and subsequent cleavage of the resulting cyclopropyl ring with Li-liq. NH_3. Methyl dehydroabietate (XVI) and dehydroabietane (V) introduced from I were used as the starting materials. The improved synthesis of V was also described.

Chemical conversion of *l*-abietic acid (I) to tetracyclic diterpenoids by using the carbon unit of the isopropyl group attracts our attention. This objective has been achieved *via* the intramolecular carbenoid reaction of diazoketones and subsequent cleavage of the resulting cyclopropyl ring to form the bicyclo[3.2.1]octane system.

Yoshikoshi and his co-workers[3] reported the direct formation of this system by carbenoid reaction of the diazoketone in the synthesis of a diterpene. Beames'[4] and Ghatak's[5b] groups also succeeded by intramolecular alkylation of the diazoketones with phenoxyl or anisyl groups through a π-bond participation. Beames and his co-workers,[6] on the other hand, obtained the products from conjugated cyclopropyl ketones by retrograde Michael-type reaction, while Ghatak's[5] and Beames'[4] groups achieved this objective by opening the bond at the benzylic position.

We aimed to examine the opening pattern of cyclopropyl ketones (i) prepared from *l*-abietic acid (I). The cyclopropyl ketones (i) would not be expected to undergo a bond cleavage as mentioned above. Norin[7] reported, however, that the conjugated cyclopropyl bond which was cleaved by Li-liq. NH_3 is the one possessing the maximum overlap with the π-orbital of the carbonyl group. According to his hypothesis, it is expected that ii would be more likely to be obtained than iii.

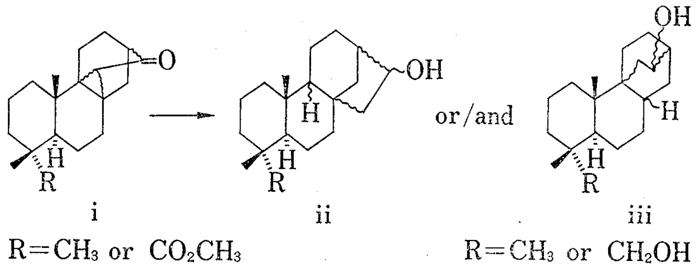

Chart 1

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[1] A part of this work was presented at the 93rd Annual Meeting of the Pharmaceutical Society of Japan at Tokyo, April 1973 (Meeting Abstracts, Part II, p. 161) and published as preliminary communication: A. Tahara, M. Shimagaki, S. Ohara, and T. Nakata, *Tetrahedron Letters*, **1973**, 1701; Part XXXV: T. Nakata and A. Tahara (the late), *Chem. Pharm. Bull.* (Tokyo), 23, 2323 (1975), Dr. Akira Tahara passed away suddenly on January 2, 1975.

[2] Location: *Wako, Saitama.*

[3] M. Kitadani, K. Ito, and A. Yoshikoshi, *Bull. Chem. Soc. Japan*, **44**, 3431 (1971).

[4] D.J. Beames, T.R. Klose, and L.N. Mander, *Chem. Commun.*, **1971**, 773.

[5] *a*) S.K. Dasgupta, R. Dasgupta, S.R. Ghosh, and U.R. Ghatak, *Chem. Commun.*, **1969**, 1253; *b*) P.N. Chakrabortty, R. Dasgupta, S.K. Dasgupta, S.R. Ghosh, and U.R. Ghatak, *Tetrahedron*, **28**, 4653 (1972).

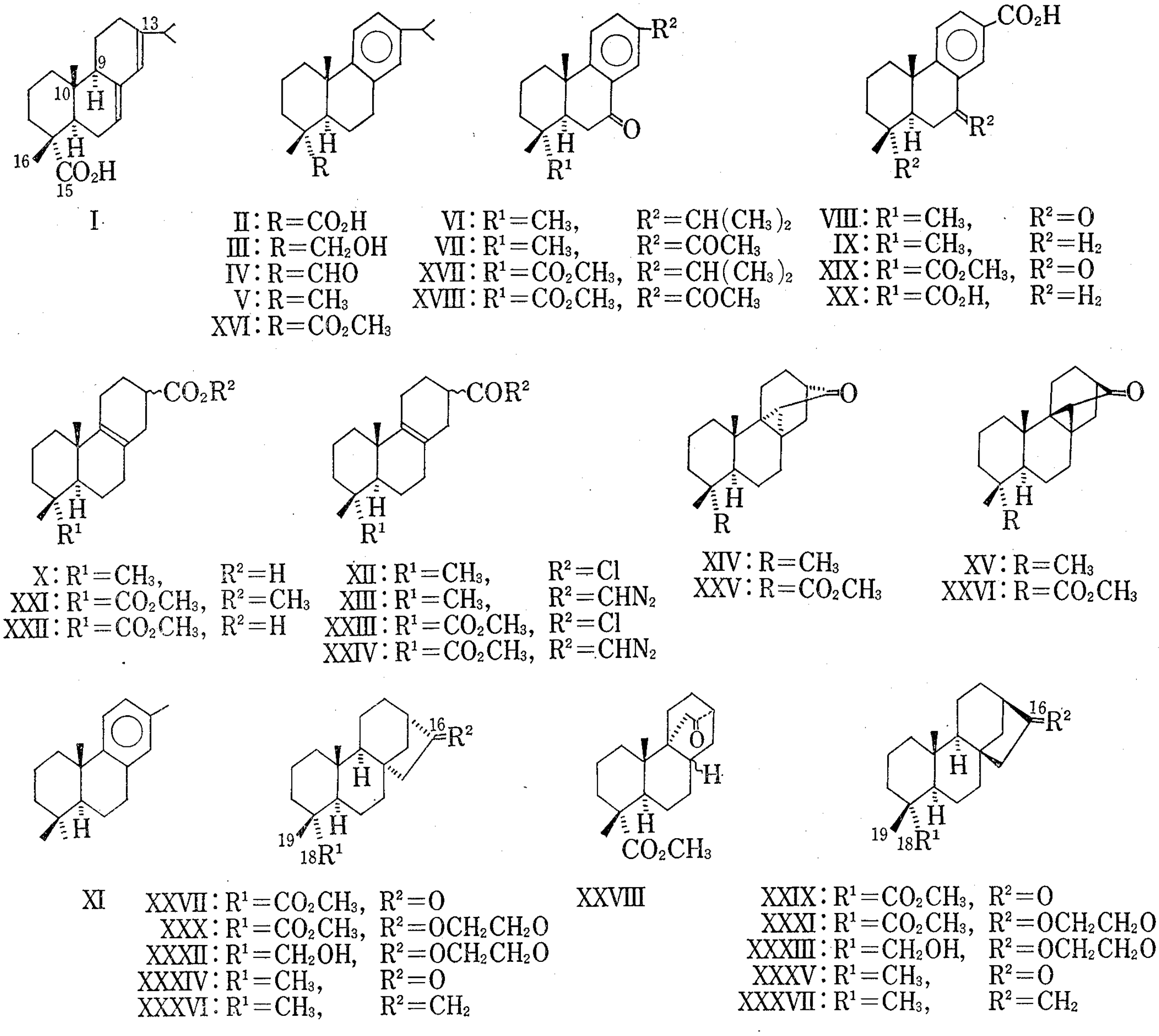
[6] D.J. Beames and L.N. Mander, *Chem. Commun.*, **1969**, 498; D.J. Beames, J.A. Halleday, and L.N. Mander, *Aust. J. Chem.*, **25**, 137 (1972).

[7] T. Norin, *Acta Chem. Scand.*, **19**, 1289 (1965).

First of all, dehydroabietane (V) was used for this objective, but there was the difficulty of purification of cyclopropyl ketones. Methyl dehydroabietate (XVI) was then used. Type ii and iii compounds were obtained in proportion of 5:1 from α-cyclopropyl keto ester (XXV). On the other hand, only type ii compound was obtained from β-cyclopropyl keto ester (XXVI).

Finally, XXVII and XXIX derived from type ii compounds were correlated, *via* the corresponding norketones (XXXIV and XXXV)[8] with *d*-kaurene (XXXVI) and d-phyllocladene (XXXVII),[9] respectively, and accordingly, XXXVI and XXXVII were synthesized from *l*-abietic acid (I).

At first, dehydroabietic acid (II) derived from *l*-abietic acid (I) was converted to dehydroabietane (V). Although the synthesis of V was reported by Campbell's[10] and Wenkert's[11]



I

II: $R=CO_2H$
III: $R=CH_2OH$
IV: $R=CHO$
V: $R=CH_3$
XVI: $R=CO_2CH_3$

VI: $R^1=CH_3$, $R^2=CH(CH_3)_2$
VII: $R^1=CH_3$, $R^2=COCH_3$
XVII: $R^1=CO_2CH_3$, $R^2=CH(CH_3)_2$
XVIII: $R^1=CO_2CH_3$, $R^2=COCH_3$

VIII: $R^1=CH_3$, $R^2=O$
IX: $R^1=CH_3$, $R^2=H_2$
XIX: $R^1=CO_2CH_3$, $R^2=O$
XX: $R^1=CO_2H$, $R^2=H_2$

X: $R^1=CH_3$, $R^2=H$
XXI: $R^1=CO_2CH_3$, $R^2=CH_3$
XXII: $R^1=CO_2CH_3$, $R^2=H$

XII: $R^1=CH_3$, $R^2=Cl$
XIII: $R^1=CH_3$, $R^2=CHN_2$
XXIII: $R^1=CO_2CH_3$, $R^2=Cl$
XXIV: $R^1=CO_2CH_3$, $R^2=CHN_2$

XIV: $R=CH_3$
XXV: $R=CO_2CH_3$

XV: $R=CH_3$
XXVI: $R=CO_2CH_3$

XI

XXVII: $R^1=CO_2CH_3$, $R^2=O$
XXX: $R^1=CO_2CH_3$, $R^2=OCH_2CH_2O$
XXXII: $R^1=CH_2OH$, $R^2=OCH_2CH_2O$
XXXIV: $R^1=CH_3$, $R^2=O$
XXXVI: $R^1=CH_3$, $R^2=CH_2$

XXVIII

XXIX: $R^1=CO_2CH_3$, $R^2=O$
XXXI: $R^1=CO_2CH_3$, $R^2=OCH_2CH_2O$
XXXIII: $R^1=CH_2OH$, $R^2=OCH_2CH_2O$
XXXV: $R^1=CH_3$, $R^2=O$
XXXVII: $R^1=CH_3$, $R^2=CH_2$

Chart 2

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[8] From *d*-kaurene: L.H. Briggs, B.F. Cain, R.C. Cambie, B.R. Davis, P.S. Rutledge, and J.K. Wilmshurst, *J. Chem. Soc.*, **1963**, 1345. From *l*-kaurene: R.A. Appleton, P.A. Gunn, and R. McCrindle, *J. Chem. Soc.* (*C*), **1970**, 1148. From *d*-phyllocladene: W. Bottomley, A.R.H. Cole, and D.E. White, *J. Chem. Soc.*, **1955**, 2624; R.A. Appleton, P.A. Gunn, and R. McCrindle, *J. Chem. Soc.* (*C*), **1970**, 1148.

[9] *dl*-kaurene: R.A. Bell and R.E. Ireland, *Tetrahedron Letters*, **1963**, 269; R.A. Bell, R.E. Ireland, and R. A. Partyka, *J. Org. Chem.*, **31**, 2530 (1966). *dl*-phyllocladene: R. B. Turner, K. H. Gänshirt, P. E. Shaw, and J.D. Tauber, *J. Am. Chem. Soc.*, **88**, 1776 (1966).

[10] W.P. Campbell and D. Todd, *J. Am. Chem. Soc.*, **64**, 928 (1942).

[11] E. Wenkert, P. Beak, R.W.J. Carney, J.W. Chamberlin, D.B.R. Johnson, C.D. Roth, and A. Tahara, *Can. J. Chem.*, **41**, 1924 (1963).

groups and Kanno,[12] the yield was relatively low, and improved synthesis was achieved as follows: Dehydroabietinol (III) ($\nu_{\text{max}}^{\text{CCl}_4}$: 3650 cm^{-1}) derived from II by $LiAlH_4$-reduction was oxidized with CrO_3–pyridine in CH_2Cl_2 to dehydroabietinal (IV) ($\nu_{\text{max}}^{\text{CCl}_4}$: 2800, 2700, 1730 cm^{-1}). The aldehyde (IV) was converted to V by the modified Wolff-Kishner reduction; slow addition of an ether solution of IV to stirred diethylene glycol with hydrazine hydrate at 100° in one hour and then the usual manner after addition of KOH. Dehydroabietane (V) was identical with the authentic sample[10] and the overall yield from II to V was 79%.

In order to make a foothold for the bridge-formation, the isopropyl side chain of V was converted to a carboxylic acid. Dehydroabietane (V) was oxidized with CrO_3 in AcOH and Ac_2O to give 7-oxodehydroabietane (VI) ($\nu_{\text{max}}^{\text{CCl}_4}$: 1680 cm^{-1}, δ (CCl_4): 1.27 (d, J=7 Hz, isopropyl)) in 3.1% yield and 13-acylpodocarpa-8,11,13-trien-7-one (VII)[11] in 42.5% yield. The acyl derivative (VII) was changed to podocarpa-8,11,13-trien-13-oic acid (IX)[11] *via* 7-oxopodocarpa-8,11,13-trien-13-oic acid (VIII).

The bridge-formation was furnished by the carbenoid reaction *via* reduction of the C-ring. The carboxylic acid (IX) was treated with Li-liq. NH_3 to give acidic and neutral products. The acidic product shows the bands at $\nu_{\text{max}}^{\text{CCl}_4}$: 1690 cm^{-1} for non-conjugated carboxyl group in its infrared (IR) spectrum and the signals at δ (CCl_4): 10.20 (b.s) for a carboxyl group and 0.95, 0.88 and 0.86 for three methyl groups and no signal for vinyl protons in its NMR spectrum. Its esterification with CH_2N_2 shows two main peaks of about the same ratio by gas-liquid chromatography (GLC) and both of them give m/e at 290 (M^+) by gas chromatography–mass spectrometry (GC–MS). These results give the structure as an epimeric mixture of substituent at 13-position and therefore the acidic product was about 1:1 mixture of podocarp-8-en-13α-oic acid and podocarp-8-en-13β-oic acid (X). The mixture (X) was not further purified or separated because of its instability. The neutral product shows no remarkable bands in its IR spectrum, the signals at 7.08 (d, J=7 Hz, C_{11}–H), 6.81 (q, J=2 and 7 Hz, C_{12}–H) and 6.76 (d, J=2 Hz, C_{14}–H) for three benzenoid protons, 2.23 (s, C_{13}–CH_3) for methyl group substituted at the benzenoid ring and 1.19, 0.97 and 0.97 for three methyl groups in its NMR spectrum and m/e at 242.2045 (M^+) (Calcd. for $C_{18}H_{26}$: 242.2031) by high resolution mass spectrometry (high-MS). These results give the structure as 13-methylpodocarpa-8,11,13-triene (XI), which was derived from IX by reduction of 13-carboxyl to methyl group.

The 13-epimeric mixture (X) was treated with $SOCl_2$ to give a mixture of podocarp-8-en-13α-oic chloride and podocarp-8-en-13β-oic chloride (XII) ($\nu_{\text{max}}^{\text{CCl}_4}$: 1795, 1765 (weak) cm^{-1} (the latter band would be derived from a contaminated mixture of acid anhydrides by a side reaction)), which was treated with CH_2N_2 to give a mixture of podocarp-8-en-13α-diazomethyl ketone and podocarp-8-en-13β-diazomethyl ketone (XIII) ($\nu_{\text{max}}^{\text{CCl}_4}$: 2100, 1645 cm^{-1}). The mixture of diazoketones (XIII) was treated with $CuSO_4$ in refluxing cyclohexane and the product was chromatographed on alumina, but only α-cyclopropyl ketone (XIV) was isolated in 3.8% yield from IX. The ketone (XIV) shows the band at $\nu_{\text{max}}^{\text{CCl}_4}$: 1720 cm^{-1} for carbonyl group in its IR spectrum, the signals at 0.97, 0.93 and 0.92 for three methyl groups in its NMR spectrum, a strong positive Cotton effect in its ORD and m/e at 272.2137 (M^+) (Calcd. for $C_{19}H_{28}O$: 272.2139) by high-MS.

Finally, the structure of XIV was decided by converting it to 17-norkauran-16-one (XXXIV). The ketone (XIV) was reduced with Li-liq. NH_3 and successively oxidized with CrO_3–pyridine in CH_2Cl_2[13] *via* type ii compound to XXXIV in 25% yield. The norketone (XXXIV) was identical with the authentic sample[8] synthesized from d-kaurene (XXXVI).

Methyl dehydroabietate (XVI) was treated by nearly the same procedures as described above because of difficulty of purification of the products from V and non-isolation of

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[12] H. Kanno, *Tokyo Gakugei Daigaku Kenkyu Hokoku, 3-ba, Shizen Kagaku*, **12**, 37 (1961) [*Chem. Abstr.* **60**, 12061 (1964)].

[13] R. Ratcliffe and R. Rodehorst, *J. Org. Chem.*, **35**, 4000 (1970).

β-cyclopropyl ketone (XV). The methyl ester (XVI) prepared from II was converted to methyl 7-oxodehydroabietate (XVII)[14] in 4.2% yield and methyl 13-acyl-7-oxopodocarpa-8,11,13-trien-15-oate (XVIII)[15] in 29% yield, in the same manner as in the oxidation of V. The acyl derivative (XVIII) was changed to podocarpa-8,11,13-triene-13,15-dioic acid (XX)[16] *via* methyl 13-carboxy-7-oxopodocarpa-8,11,13-trien-15-oate (XIX). The diacid (XX) was treated with Li-liq. NH_3 and then with CH_2N_2 to give products in 4: 4: 1 ratio as determined by GLC. The mixture of the first two peaks after separation by alumina chromatography shows the band at $\nu_{max}^{CCl_4}$: 1725 cm^{-1} for non-conjugated ester in its IR spectrum, the signals at δ (CCl_4): 3.60 for two methoxycarbonyl groups, 1.13 and 0.96 for two methyl groups and no signal for vinyl protons in its NMR spectrum and *m/e* at 334.2132 (M^+) (Calcd. for $C_{20}H_{30}O_4$: 334.2144) by high-MS. Both of them give *m/e* at 334 (M^+) by GC–MS. These results give the structures as an epimeric mixture at 13-position, a mixture of dimethyl podocarp-8-en-13α,15-dioate and dimethyl podocarp-8-en-13β,15-dioate (XXI) and, therefore, the yield was 18.3% from XX. The last peak after separation by alumina chromatography gave a lot of products in contrast with the ratio of GLC and shows the signals for two vinyl and many methoxycarbonyl groups in its NMR spectrum. When XXI was left on alumina, it gradually changed to the products of the last peak in GLC. These results give the structures of the last peak as a mixture of double bond isomers of XXI. The following reactions were performed without further purification. The 13-epimeric mixture (XXI) was partially hydrolyzed with KOH–MeOH–H_2O to give a mixture of methyl 13α-carboxypodocarp-8-en-15-oate and methyl 13β-carboxypodocarp-8-en-15-oate (XXII) in 91% yield. The mixture of the half esters (XXII) was treated by the same procedure as for X *via* a mixture of acid chlorides (XXIII) ($\nu_{max}^{CCl_4}$: 1800, 1730 cm^{-1}) and that of diazoketones (XXIV) ($\nu_{max}^{CCl_4}$: 2110, 1650 cm^{-1}) and the product was chromatographed on alumina to give α-cyclopropyl keto ester (XXV) in 7.5% yield, β-cyclopropyl keto ester (XXVI) in 8.6% yield and a mixture of XXV and XXVI in 17.8% overall yield from XXII. The cyclopropyl keto ester (XXV) shows the band at $\nu_{max}^{CCl_4}$: 1725 cm^{-1} for carbonyl groups in its IR spectrum, the signals at δ (CCl_4): 3.60 for methoxycarbonyl group, 1.18 and 1.12 for methyl groups in its NMR spectrum, *m/e* at 316.2066 (M^+) (Calcd. for $C_{20}H_{28}O_3$: 316.2037) by high-MS and a strong positive Cotton effect in its ORD. The cyclopropyl keto ester (XXVI) shows the band at $\nu_{max}^{CCl_4}$: 1725 cm^{-1} for carbonyl groups in its IR spectrum, the signals at δ (CCl_4): 3.62 for methoxycarbonyl group and 1.07 and 1.06 for methyl groups in its NMR spectrum, *m/e* at 316.2031 (M^+) (Calcd. for $C_{20}H_{28}O_3$: 316.2037) by high-MS and a strong negative Cotton effect in its ORD.

The stereochemistry and the mode of cleavage of cyclopropyl ketones attracted our attention. The respective cyclopropyl keto esters (XXV and XXVI) were treated with Li-liq. NH_3 and successively with Jones reagent, followed with CH_2N_2 to give a mixture of methyl 16-oxo-17-norkauran-18-oate (XXVII) and α-keto ester (XXVIII) in 41.3 and 8.1% yields and only methyl 16-oxo-17-norphyllocladan-18-oate (XXIX) in 62% yield. The keto ester (XXVII) shows the bands at $\nu_{max}^{CCl_4}$: 1745 and 1730 cm^{-1} for carbonyl and methoxycarbonyl groups, respectively, in its IR spectrum, the signals at δ (CCl_4): 3.61 for methoxycarbonyl group and 1.13 for two methyl groups in its NMR spectrum, *m/e* at 318.2192 (M^+) (Calcd. for $C_{20}H_{30}O_3$: 318.2195) by high-MS and a strong negative Cotton effect in its ORD. The keto ester (XXVIII) shows the band at $\nu_{max}^{CCl_4}$: 1725 cm^{-1} for carbonyl groups in its IR spectrum, the signals at δ (CCl_4): 3.62 for methoxycarbonyl group and 1.18 and 1.03 for methyl groups, *m/e* at 318.2192 (M^+) (Calcd. for $C_{20}H_{30}O_3$: 318.2195) by high-MS and a positive background rotation in its ORD. The keto ester (XXIX) shows the bands at $\nu_{max}^{CCl_4}$: 1745 and 1730 cm^{-1} for carbonyl and methoxycarbonyl groups, respectively, in its IR spectrum, the signals at

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[14] P.F. Ritchie, T.F. Sanderson, and L.F. McBurney, *J. Am. Chem. Soc.*, **76**, 723 (1954).

[15] T.F. Sanderson, U.S. Patent 2750368 (1956) [*Chem. Abstr.*, **51**, 1278 (1957)].

[16] M. Ohta, *Pharm. Bull. Japan*, **4**, 273 (1956).

δ (CCl_4): 3.62 for methoxycarbonyl group, 1.12 and 0.94 for methyl groups in its NMR spectrum *m/e* at 318.2192 (M^+) (Calcd. for $C_{20}H_{30}O_3$: 318.2195) by high-MS and a strong positive Cotton effect in its ORD.

IR spectra show that XXVII and XXIX have a five-membered and XXVIII has a six-membered ring ketone. The stereochemistry of the five-membered ring of XXVII and XXIX was assumed by comparison of their ORD with those of 17-norkauran-16-one (XXXIV) and 17-norphyllocladan-16-one (XXXV).

The keto ester (XXVII and XXIX) were derived respectively from XXV and XXVI (type i compounds) *via* type ii compounds by the opening of the maximum overlapping bond of the cyclopropyl ring with the π-orbital of the carbonyl group and XXVIII from XXV (type i compound) *via* type iii compound by the opening at the second overlapping one,[7,17] *i.e.* type ii and iii compounds were obtained from XXV and only type ii compound was obtained from XXVI by the Li-liq. NH_3-reduction. From a consideration of molecular models of XXV and XXVI, there is no difference of the environment between the cyclopropyl ring and the carbonyl group. Although an elucidation of the mechanistic details of these results must await further studies, the 10-methyl group may participate in these differences.[18]

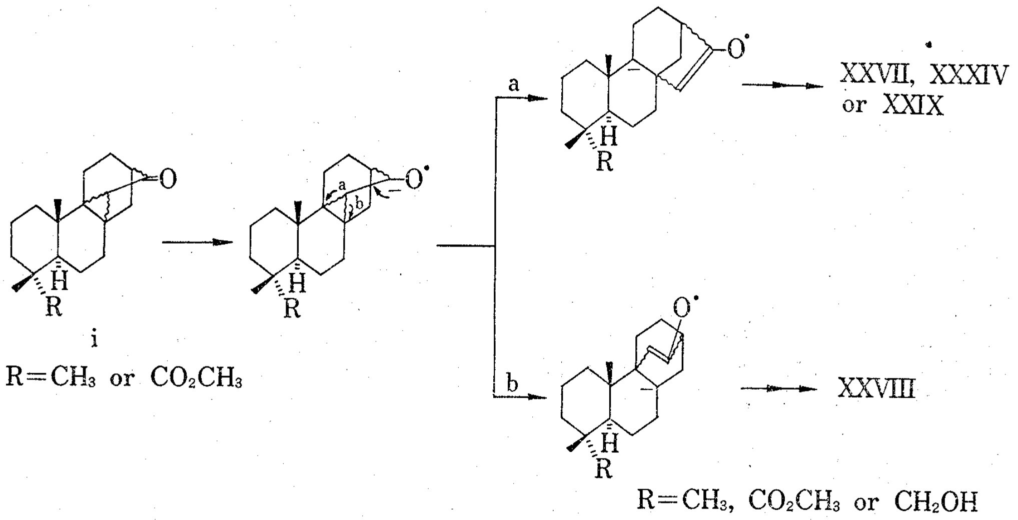

Chart 3

In order to ascertain the structural assumption including the configuration at the 9-position,[19] the keto esters (XXVII and XXIX) were converted to the respective natural products, *d*-kaurene (XXXVI) and *d*-phyllocladene (XXXVII) having a rigid structure. The carbonyl groups of XXVII and XXIX were protected as the respective ketals, (XXX) ($\nu_{max}^{CCl_4}$: 1725 cm^{-1}, δ (CCl_4): 3.77 and 3.73 (OCH_2CH_2O)) and (XXXI) ($\nu_{max}^{CCl_4}$: 1725 cm^{-1}, δ (CCl_4): 3.74 and 3.71 (OCH_2CH_2O)). The ketal esters (XXX and XXXI) were reduced with $LiAlH_4$ to the respective ketal alcohols, (XXXII) ($\nu_{max}^{CCl_4}$: 3660 cm^{-1}) and (XXXIII) ($\nu_{max}^{CCl_4}$: 3660 cm^{-1}). The ketal alcohols (XXXII and XXXIII) were treated with CrO_3-pyridine in CH_2Cl_2,[12] Wolff-Kishner condition and successively with HCl to give 17-norkauran-16-one (XXXIV) and 17-norphyllocladan-16-one (XXXV), respectively. Mixed melting points and their IR and NMR spectra were completely identical with those of the authentic samples[8]

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[17] An opposite mechanistic suggestion was reported [S.A. Monti, D.J. Bucheck, and J.C. Shepard, *J. Org. Chem.*, 34, 3080 (1969)].

[18] In highly strained systems, it was reported that the mode of cleavage was affected by the distortion of the ring systems [Reference 7. Also see H.O. House, S.G. Boots, and V.K. Jones, *J. Org. Chem.*, 30, 2519 (1965); W.G. Dauben and E.J. Deviny, *ibid.*, 31, 3794 (1966)].

[19] The octant rule was not applied to bicyclo[3.2.1]octan-6-one systems [W. Klyne, *Tetrahedron*, 13, 29 (1961)].

synthesized from the natural *d*-kaurene (XXXVI) and *d*-phyllocladene (XXXVII), respectively. Then it was confirmed that hydrogen at the 9-position possesses the α-configuration. In the formation of XXVII and XXXIV from respective XXV and XIV, the transfer of hydrogen (either a hydrogen atom or a proton) occurred with retention at the 9-carbon atom. On the other hand, in the formation of XXIX from XXVI, the transfer of hydrogen occurred with inversion at the 9-carbon atom. These results show that the more stable products were formed in these all cases by the Li-liq. NH_3-reduction.[20)]

Since the syntheses of the natural products (XXXVI and XXXVII) from the respective norketones (XXXIV and XXXV) had been published,[9)] a chemical conversion from *l*-abietic acid (I) to XXXVI and XXXVII and, accordingly, their total synthesis have been accomplished.

Experimental

All melting points were measured on a micro hot-stage and were uncorrected. Boiling point was also uncorrected. Nuclear magnetic resonance (NMR) spectra were measured at 60 MHz, when not mentioned, in CCl_4 or $CDCl_3$ *vs*. Me_4Si as internal reference. High-resolution mass spectra (high-MS) were taken with a JEOL JMS-OlSG spectrometer. Retention times (t_R) of gas-liquid chromatography (GLC) were detected by using a glass column (1.5% OV-17 on Shimalite W (80—100 mesh), 4 mm × 2.0 m) and N_2 as carrier gas. Gas chromatography–mass spectra (GC–MS) were taken with a Hitachi model 063 (GLC) and RMS-4 (MS) spectrometer. Optical rotatory dispersions (ORD) were taken with a JASCO MODEL ORD/UV-5 spectrometer.

Dehydroabietinol (III)——A solution of dehydroabietic acid (II) (40.0 g) in abs. ether (200 ml) was added portionwise to a stirred suspension of $LiAlH_4$ (11.0 g) in abs. ether (600 ml) at room temperature. After the mixture was stirred overnight at room temperature, ice was added cautiously to decompose excess $LiAlH_4$, which was acidified with conc. HCl. The organic layer was separated, and the residue was extracted with ether. The combined ethereal layer was washed with brine and dried over Na_2SO_4. Removal of the solvent gave III (38.1 g),[12)] IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3650. NMR $\delta(CCl_4)$: 7.12 (d, $J=8$ Hz, 1H, C_{11}-H), 6.87 (d,d, $J=2$ and 8 Hz, 1H, C_{12}-H), 6.78 (d, $J=2$ Hz, 1H, C_{14}-H), 3.44, 3.07 (q,q, $J=11$ Hz, 2H, $C\underline{H}_2OH$), 1.35 (s, 1H, $CH_2O\underline{H}$), 1.21 (d, $J=7$ Hz, 6H, isopropyl), 1.19, 0.85 (each s, 3H × 2, C_4,C_{10}-CH_3).

Dehydroabietane (V) *via* Dehydroabietinal (IV)——To KOH-dried pyridine (350 ml) was added CrO_3 (100 g) with stirring at 10—20°, and the mixture was stirred at room temperature for one hr. Petr. ether (100 ml) was added, and the solvent mixture was decantäted. The residue was washed five times with petr. ether (each 100 ml). The precipitate was dissolved in $CaCl_2$-dried CH_2Cl_2 (700 ml) to make a solution of CrO_3-pyridine complex in $CaCl_2$-dried CH_2Cl_2. A solution of III (38.1 g) in $CaCl_2$-dried CH_2Cl_2 (100 ml) was added in one portion to the solution of the complex with stirring at room temperature. After stirring the solution for 30 min, it was poured onto alumina column and eluted with ether (1.5 liter). Removal of the solvent gave IV (36.2 g), GLC: one peak ($t_R=2.90$ min, 200°). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 2800, 2700, 1730. NMR δ (CCl_4): 9.12 (s, 1H, CHO), 7.04 (d. $J=8$ Hz, 1H, C_{11}-H), 6.82 (q, $J=2$ and 8 Hz, 1H, C_{12}-H), 6.75 (d, $J=2$ Hz, 1H, C_{14}-H), 1.19 (d, $J=7$ Hz, 6H, isopropyl), 1.21, 1.15 (each s, 3H × 2, C_4,C_{10}-CH_3). The aldehyde (IV) was used without further purification to the following reaction.

A solution of IV (36.2 g) in ether (100 ml) was added at 100° in one hr to a stirred solution of hydrazine hydrate (36 ml) in diethylene glycol (470 ml) without cooler. After the mixture was stirred under the same condition for one hr, KOH (36 g) was added. The temperature was raised gradually to 210° with removal of excess hydrazine hydrate and it was heated at 210° for 2 hr. After cooling, water was added, and it was extracted with ether. The extract was washed with brine and dried over Na_2SO_4. Removal of the solvent gave an oil (33.0 g), which was chromatographed on alumina (600 g) with *n*-hexane as eluant to give V (28.2 g; 79% from II), [11)] IR: no remarkable band. NMR $\delta(CDCl_3)$: 7.15 (d, $J=8$ Hz, 1H, C_{11}-H), 6.94 (q, $J=2$ and 8 Hz, 1H, C_{12}-H), 6.87 (d, $J=2$ Hz, 1H, C_{14}-H), 1.23 (d, $J=7$ Hz, 6H, isopropyl), 1.17 (s, 3H, CH_3), 0.94 (s, 6H, CH_3 × 2). These physical constants were identical with those of the authentic samples synthesized by the method of Campbell's[10)] group.

7-Oxodehydroabietane (VI) and 13-Acylpodocarpa-8,11,13-trien-7-one (VII)——To a stirred solution of V (10.8 g) in AcOH (440 ml) and Ac_2O (26.5 ml) was added CrO_3 (26.0 g) devided into several portions under ice cooling. The mixture was stirred under water cooling for 2 hr and at room temperature for 21.5 hr. To the reaction mixture was added MeOH to decompose excess CrO_3 and the solvent mixture was evaporated. After addition of water to the residue, it was extracted with ether. The extract was washed with

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[20)] *cf.* H.O. House and C.J. Blankley, *J. Org. Chem.*, 33, 47 (1968); E. Piers and P.M. Worster, *J. Am. Chem. Soc.*, 94, 2895 (1972).

sat. $NaHCO_3$ solution and brine and dried over Na_2SO_4. Removal of the solvent gave an oil (7.4 g), which was chromatographed on alumina (150 g) with petr. ether–ether (9: 1) as eluant to give VI (0.35 g; 3.1%), mp 91—92° (MeOH). IR $\nu_{\max}^{\mathrm{CCl_4}}$ $\mathrm{cm^{-1}}$: 1680. NMR $\delta(\mathrm{CCl_4})$: 7.76 (d, $J=2$ Hz, 1H, C_{14}–H), 7.23 (m, 2H, C_{11},-C_{12}–H), 1.27 (d, $J=7$ Hz, 6H, isopropyl), 1.24, 1.04, 0.98 (each s, $3H\times3$, C_{4ax},C_{4eq},C_{10}–CH_3). *Anal.* Calcd. for $C_{20}H_{28}O$: C, 84.44; H, 9.94. Found: C, 84.45; H, 9.92., and then with petr. ether–ether (4: 1) to give VII (4.81 g; 42.5%),[11] mp 136—137° ($MeOH$–H_2O). IR $\nu_{\max}^{\mathrm{CCl_4}}$ $\mathrm{cm^{-1}}$: 1680. NMR $\delta(\mathrm{CCl_4})$: 8.49 (d, $J=2$ Hz, 1H, C_{14}–H), 8.12 (q, $J=2$ and 8 Hz, 1H, C_{12}–H), 7.48 d, $J=8$ Hz, 1H, C_{11}–H), 2.61 (s, 3H, $COCH_3$), 1.27, 1.05, 1.02 (each s, $3H\times3$, C_{4ax},C_{4eq},C_{10}–CH_3). *Anal.* Calcd. for $C_{19}H_{24}O_2$: C, 80.49; H, 8.45. Found: C, 80.24: H, 8.51.

Podocarpa-8,11,13-trien-13-oic Acid (IX) *via* 7-Oxopodocarpa-8,11,13-trien-13-oic Acid (VIII)——According to Wenkert's group,[11] VII was converted to IX *via* VIII.

α-Cyclopropyl Ketone (XIV) *via* a Mixture of Podocarp-8-en-13α-oic Acid and Podocarp-8-en-13β-oic Acid (X), a Mixture of Podocarp-8-en-13α-oic Chloride and Podocarp-8-en-13β-oic Chloride (XII) and a Mixture of Podocarp-8-en-13α-diazomethyl Ketone and Podocarp-8-en-13β-diazomethyl Ketone (XIII), and 13-Methylpodocarpa-8,11,13-triene (XI)——To a stirred solution of IX (2.50 g) in abs. tetrahydrofuran (100 ml) was added liq. NH_3 (250 ml) under dry ice–acetone cooling, and then small pieces of Li (2.50 g) in 75 min under the same conditions. After stirring under dry ice–acetone cooling for 105 min, abs. EtOH was added cautiously until blue color faded (it needed 28 ml of EtOH). After removal of NH_3 at room temperature under atmospheric pressure and then under reduced one, small portion of water was added. The mixture was acidified with conc. HCl and extracted with ether. The extract was washed with brine and dried over Na_2SO_4. The solvent was removed, but the reaction was not completed. The residue was treated again as the same procedure mentioned above (though the reaction was examined in several conditions, it was not completed by a single run). To the residue was added water, and it was washed with ether. The water layer was acidified with conc. HCl and extracted with ether. The extract was washed with brine and dried over Na_2SO_4. Removal of the solvent gave crude X (2.38 g), IR $\nu_{\max}^{\mathrm{CCl_4}}$ $\mathrm{cm^{-1}}$: 1690. NMR $\delta(\mathrm{CCl_4})$: 10.20 (b.s, 1H, CO_2H), 0.95, 0.88, 0.86 (each s, $3H\times3$, C_{4ax},C_{4eq},C_{10}–CH_3).

A part of the crude X was esterified with CH_2N_2, which gave two main peaks of about 1: 1 ratio by GLC ($t_R=3.5$ and 3.6 min, respectively, 220°), a mixture of methyl podocarp-8-en-13α-oate and methyl podocarp-8-en-13β-oate. GC–MS Calcd. for $C_{19}H_{30}O_2$ (both peaks, M^+; *m/e*): 290. Found: 290. The mixture was not further purified because of its instability.

The ethereal washing was washed with brine and dried over Na_2SO_4. Removal of the solvent gave XI (0.29 g; 11%), IR: no remarkable band. NMR δ ($\mathrm{CCl_4}$): 7.08 (d, $J=7$ Hz, 1H, C_{11}–H), 6.81 (q, $J=2$ and 7 Hz, 1H, C_{12}–H), 6.76 (d, $J=2$ Hz, 1H, C_{14}–H), 2.23 (s, 3H, C_{13}–CH_3), 1.19 (s, 3H, CH_3), 0.97 (s, 6H, $CH_3\times2$). *Anal.* high-MS. Calcd. for $C_{18}H_{26}$ (M^+; *m/e*): 242.2031. Found: 242.2045.

A solution of the crude X (2.38 g) and $SOCl_2$ (2.22 ml) in abs. C_6H_6 (25 ml) was refluxed for 2 hr. Removal of the solvent and the residual $SOCl_2$ gave crude XII (2.57 g), IR $\nu_{\max}^{\mathrm{CCl_4}}$ $\mathrm{cm^{-1}}$: 1795, 1765 (weak) (the latter band would be derived from a contaminated mixture of acid anhydrides by a side reaction). NMR δ ($\mathrm{CCl_4}$): 0.96, 0.90, 0.86 (each s, $3H\times3$, C_{4ax},C_{4eq},C_{10}–CH_3).

A solution of the crude XII (2.57 g) in abs. ether was added with stirring to a KOH-dried ethereal CH_2N_2 solution prepared from nitrosomethyl urea (7.5 g) at room temperature and the stirring was continued at room temperature for 2 hr. Removal of the solvent gave crude XIII (2.52 g), IR $\nu_{\max}^{\mathrm{CCl_4}}$ $\mathrm{cm^{-1}}$: 2100, 1645. NMR δ ($\mathrm{CCl_4}$): 0.95, 0.89, 0.85 (each s, $3H\times3$, C_{4ax},C_{4eq},C_{10}–CH_3).

To a solution of the crude XIII (2.52 g) in abs. cyclohexane (840 ml) was added $CuSO_4$ (3.36 g), and it was refluxed for 62 hr until the aliquot gave no CON_2-band in its IR spectrum. The mixture was filtered and the filtrate was concentrated under reduced pressure to give an oil (2.40 g), which was chromatographed on alumina (70 g) with petr. ether–ether (15: 1) as eluant to give XIV (98 mg; 3.8% from IX), bp 75—80° (bath, 0.04 mmHg). IR $\nu_{\max}^{\mathrm{CCl_4}}$ $\mathrm{cm^{-1}}$: 1720. NMR δ ($\mathrm{CCl_4}$): 0.97, 0.93, 0.92 (each s, $3H\times3$, C_{4ax},C_{4eq},C_{10}–CH_3). ORD ($c=0.00107$, dioxane) (mμ): +3170° (305) (peak), 0° (291), −3320° (269) (trough). *Anal.* Calcd. for $C_{19}H_{28}O$: C, 83.77; H, 10.36. Found: C, 83.78; H, 10.31. High-MS. Calcd. (M^+; *m/e*): 272.2139. Found: 272.2137.

17-Norkauran-16-one (XXXIV) from XIV——To a stirred solution of XIV (10.5 mg) in abs. tetrahydrofuran (0.25 ml) and *t*-BuOH (0.02 ml) was added liq. NH_3 (3.6 ml) under dry ice–acetone cooling, and then slowly added small pieces of Li (70.5 mg). After stirring under the same condition for 2 hr, abs. EtOH was added cautiously until blue color faded. After removal of NH_3 at room temperature, small portion of water was added. The mixture was extracted with ether, and the extract was washed with brine and dried over Na_2SO_4. Removal of the solvent gave an oil (11.9 mg). One half of the CrO_3–pyridine complex solution prepared from CrO_3 (100 mg), KOH-dried pyridine (158 mg) and CH_2Cl_2 (6ml)[13] was added to the oil (11.9 mg), and the mixture was stirred at room temperature for 30 min. The reaction mixture was poured onto alumina (0.5 g) column and eluted with ether (30 ml). Removal of the solvent gave an oil (9.5 mg), which was chromatographed on alumina (1.0 g) with petr. ether–ether (50: 1) as eluant to give XXXIV (2.6 mg; 25%), IR $\nu_{\max}^{\mathrm{CCl_4}}$ $\mathrm{cm^{-1}}$: 1740. GLC: $t_R=5.6$ min (180°). MS Calcd. for $C_{19}H_{30}O$: 274. Found: 274. The retention time of GLC and the IR and MS spectra were identical with those of the authentic sample[8] synthesized from *d*-kaurene (XXXVI).

Methyl 7-Oxodehydroabietate (XVII) and Methyl 13-Acyl-7-oxopodocarpa-8,11,13-trien-15-oate (XVIII)——A mixture of methyl dehydroabietate (XVI) (50.0 g), CrO_3 (100.0 g), AcOH (2.0 liter) and Ac_2O (103 ml) was treated as the same procedure mentioned in the formation of VI and VII. Chromatography on alumina (600 g) gave XVII[14] (2.18 g; 4.2%) by elution with petr. ether–ether (3: 1) and XVIII[15] (15.00 g; 29%) with petr. ether–ether (2: 1—1: 1).

Podocarpa-8,11,13-triene-13,15-dioic Acid (XX) *via* Methyl 13-Carboxy-7-oxopodocarpa-8,11,13-trien-15-oate (XIX)——According to Ohta,[16] XVIII was converted to XX *via* XIX.

A Mixture of Dimethyl Podocarp-8-ene-13α,15-dioate and Dimethyl Podocarp-8-ene-13β,15-dioate (XXI)——To a stirred solution of XX (3.11 g) in abs. EtOH (70 ml) was added liq. NH_3 (300 ml) under dry ice–acetone cooling, and then small pieces of Li (3.50 g) in 10 min. The stirring and cooling was continued until blue color faded (*ca.* 20 min). After removal of NH_3 at room temperature, small portion of water was added. The mixture was acidified with 10% HCl solution and extracted with ether. The extract was washed with brine and dried over Na_2SO_4. Removal of the solvent gave a solid (2.63g), which was esterified with CH_2N_2 to give a mixture of 4: 4: 1 ratio by GLC (t_R=7.7, 8.8 and 14.6 min, respectively, 220°). The mixture was chromatographed on alumina (250 g) with petr. ether–ether (10: 1) as eluant to give XXI (0.63 g; 18.3%: the first two peaks by GLC), IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1725. NMR δ (CCl_4): 3.60 (s, 3H, CO_2CH_3), 1.13, 0.96 (each s, 3H × 2, C_4,C_{10}–CH_3). *Anal.* high-MS. Calcd. for $C_{20}H_{30}O_4$ (M^+; *m/e*): 334.2144. Found: 334.2132. GC–MS Calcd. (both peaks, M^+; *m/e*): 334. Found: 334., and a mixture of double bond isomers of XXI (1.64 g; 48%: the last peak by GLC), IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1725, 1720 (shoulder). NMR δ (CCl_4): 6.53, 4.75 (each b.s, 0.5 H × 2, vinyl-H), 3.77, 3.58, 3.57 (each s, 6H, $CO_2CH_3 \times 2$).

When XXI was left on alumina or neutral alumina, it gradually changed to the isomers (the last peak by GLC).

Although the 4: 4: 1 mixture did not changed on silica gel, it could not be separated by the chromatography.

A Mixture of Methyl 13α-Carboxypodocarp-8-en-15-oate and Methyl 13β-Carboxypodocarp-8-en-15-oate (XXII)——To a solution of XXI (0.622 g) in EtOH (8 ml) was added 0.5% KOH solution (21.4 ml), and the mixture was refluxed for 4.5 hr. After removal of most of the solvent, the residue was acidified with dil. HCl solution and extracted with ether. The ethereal layer was extracted with 5% KOH solution. The alkaline extract was acidified with conc. HCl and extracted with ether. The extract was washed with brine and dried over Na_2SO_4. Removal of the solvent gave XXII (0.543 g; 91%), IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1725, 1700. NMR δ (CCl_4): 11.65 (b.s, 1H, CO_2H), 3.62 (s, 3H, CO_2CH_3), 1.14, 0.97 (each s, 3H × 2, C_4,C_{10}–CH_3).

The residual ethereal layer by extraction with 5% KOH solution was washed with brine and dried over Na_2SO_4. Removal of the solvent recovered XXI (0.039 g; 6.3%).

α-Cyclopropyl Keto Ester (XXV) and β-Cyclopropyl Keto Ester (XXVI) *via* a Mixture of Acid Chlorides (XXIII) and a Mixture of Diazoketones (XXIV)——The half ester (XXII) (0.543 g) and $SOCl_2$ (0.42 ml) in abs. C_6H_6 (5 ml) was treated as the same procedure mentioned in the formation of XII to give XXIII, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1800, 1730.

The acid chlorides (XXIII) in abs. ether and KOH-dried ethereal CH_2N_2 prepared from nitrosomethyl urea (5.0 g) was treated as the same procedure mentioned in the formation of XIII to give XXIV, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 2110, 1650.

The diazoketones (XXIV) and $CuSO_4$ (104 mg) in abs. cyclohexane (70 ml) was treated as the same procedure mentioned in the formation of XIV, except for the change of the reaction time to 28 hr, to give an oil (0.563 g). Chromatography on alumina (50 g) with petr. ether–ether (10: 1) as eluant gave XXVI (46.0 mg; 8.6% from XXII), mp 161—163° (*n*-hexane). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1725. NMR δ (100 MHz, CCl_4): 3.62 (s, 3H, CO_2CH_3), 1.07, 1.06 (each s, 3H × 2, C_4,C_{10}–CH_3). ORD (*c*=0.0015, dioxane) $[\alpha]^{34}$ (mμ): −4425° (306.5) (trough), 0° (292), +4975° (270.5) (peak). *Anal.* Calcd. for $C_{20}H_{28}O_3$: C, 75.91; H, 8.92. Found: C, 75.69; H, 8.94. High-MS. Calcd. (M^+; *m/e*): 316.2037. Found: 316.2031., the mixture of XXV and XXVI (95.5 mg; 17.8% from XXII) and XXV (40.0 mg; 7.5% from XXII), mp 114—116° (*n*-hexane). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1725. NMR δ (100 MHz, CCl_4): 3.60 (s, 3H, CO_2CH_3), 1.18, 1.12 (each s, C_4,C_{10}–CH_3). ORD (*c*=0.00173, dioxane) $[\alpha]^{23}$ (mμ): +4350° (306) (peak), 0° (291), −3870° (270) (trough). *Anal.* Calcd. for $C_{20}H_{28}O_3$: C, 75.91; H, 8.92. Found: C, 75.79; H, 8.94. High-MS. Calcd. (M^+; *m/e*): 316.2037. Found: 316.2066.

The mixture was separated by preparative thin-layer chromatography (TLC) (alumina [Merck PF_{254}], 20 cm × 20 cm × 0.5 mm) by four-time elution with C_6H_6–$CHCl_3$ (3: 1).

The reactions of XX (5.00 g) were participated without purification to the last stage to give XXVI (0.235 g; 4.5% overall), a mixture of XXV and XXVI (0.152 g; 2.9% overall) and XXV (0.302 g; 5.8% overall).

Methyl 16-Oxo-17-norkauran-18-oate (XXVII) and α-Keto Ester (XXVIII)——To a stirred solution of XXV (0.370 g) in abs. tetrahydrofuran (8.7 ml) and *t*-BuOH (0.78 ml) was added liq. NH_3 (34 ml) under dry ice–acetone cooling, and then slowly small pieces of Li (2.48 g). After stirring under the same condition for 90 min, abs. EtOH was added cautiously until blue color faded. After removal of NH_3 at room temperature, small portion of water was added. The mixture was extracted with ether, and the extract was washed with brine and dried over Na_2SO_4. Removal of the solvent gave an oil (0.343 g). To the solution of the oil (0.343 g) in acetone (38 ml) was added Jones reagent (1.9 ml), which was stirred at room temperature for 15 hr. To the reaction mixture was added MeOH to decompose excess $H_2Cr_2O_7$ and the solvent was evaporated under reduced pressure. Water was added to the residue, and it was extracted with ether. The ethereal layer was extracted with 10% KOH solution. The alkaline solution was acidified with conc. HCl and extracted with ether. The extract was washed with brine and dried over Na_2SO_4. After removal of the solvent, the residue was treated with CH_2N_2 to give an oil (0.325 g). The oil was chromatographed on alumina (33 g) with petr. ether–ether (3: 1) as eluant to give XXVII (0.154 g; 41.3%), mp 138—141° (*n*-hexane). IR $\nu_{\max}^{\mathrm{CCl_4}}$ cm^{-1}: 1745, 1730. NMR δ (CCl_4): 3.61 (s, 3H, CO_2CH_3), 1.13 (s, 6H, C_4,C_{10}–CH_3). ORD (c=0.001, dioxane) $[\alpha]^{34}$ (mμ): −1150° (324) (trough), −435° (315) (peak), −500° (312) (trough), 0° (308), +1700° (280) (peak). *Anal.* Calcd. for $C_{20}H_{30}O_3$: C, 75.43; H, 9.50. Found: C, 75.60; H, 9.50. High-MS. Calcd. (M^+; *m/e*): 318.2195. Found: 318.2192., and XXVIII (0.030 g; 8.1%), mp 133—135° (MeOH). IR $\nu_{\max}^{\mathrm{CCl_4}}$ cm^{-1}: 1725. NMR δ (CCl_4): 3.62 (s, 3H, CO_2CH_3), 1.18, 1.03 (each s, 3H × 2, C_4,C_{10}–CH_3). ORD (dioxane): a positive background rotation. *Anal.* Calcd. for $C_{20}H_{30}O_3$: C, 75.43; H, 9.50. Found: C, 75.31; H, 9.61. High-MS. Calcd. (M^+; *m/e*): 318.2195. Found: 318.2192.

Methyl 16-Oxo-17-norphyllocladan-18-oate (XXIX)——Treatment of XXVI (81.4 mg), *t*-BuOH (0.17 ml), Li (545 mg), tetrahydrofuran (1.9 ml) and liq. NH_3 (7.5 ml) as the same procedure mentioned in the formation of XXVII and XXVIII gave an oil (77.0 mg). Treatment of the oil (77.0 mg), Jones reagent (0.425 ml) and acetone (8.5 ml) gave a crystal (73.0 mg). The crystal was chromatographed on alumina (10 g) with petr. ether–ether (8: 1—5: 1) as eluant to give XXIX (50.8 mg; 62%), mp 170—171° (*n*-hexane). IR $\nu_{\max}^{\mathrm{CCl_4}}$ cm^{-1}: 1745, 1730. NMR δ (CCl_4): 3.62 (s, 3H, CO_2CH_3), 1.12, 0.94 (each s, 3H × 2, C_4,C_{10}–CH_3). ORD (c=0.00085, dioxane) $[\alpha]^{34}$ (mμ): +2000° (321) (peak), +1130° (313) (trough), +1250° (309) (peak), 0° (304), −2050° (280) (trough). *Anal.* Calcd. for $C_{20}H_{30}O_3$: C, 75.43; H, 9.50. Found: C, 75.45; H, 9.51. High-MS. Calcd. (M^+; *m/e*): 318.2195. Found: 318.2192.

Methyl 16-Ethylenedioxy-17-norkauran-18-oate (XXX)——A solution of XXVII (27.6 mg), ethylene glycol (56.0 mg) and *p*-TsOH (trance) in abs. C_6H_6 (8.0 ml) was refluxed for 6 hr using a Dean-Stark water separator. The reaction mixture was diluted with ether and washed with 10% KOH solution and successively with brine and dried over Na_2SO_4. Removal of the solvent gave XXX (quantitative), mp 139—140° (abs. MeOH). IR $\nu_{\max}^{\mathrm{CCl_4}}$ cm^{-1}: 1725, 1170, 1135, 1110, 1095, 1065. NMR δ (CCl_4): 3.77, 3.73 (each s, 2H × 2, OCH_2CH_2O), 3.57 (s, 3H, CO_2CH_3), 1.09, 1.05 (each s, 3H × 2, C_4,C_{10}–CH_3). *Anal.* Calcd. for $C_{22}H_{34}O_4$: C, 72.89; H, 9.45. Found: C, 72.89; H, 9.57.

Methyl 16-Ethylenedioxy-17-norphyllocladan-18-oate (XXXI)——Treatment of XXIX (50.0 mg), ethylene glycol (105.6 mg) and *p*-TsOH (trace) in abs. C_6H_6 (15 ml) as the same procedure mentioned in the formation of XXX gave XXXI (quantitative), mp 136—137° (abs. MeOH). IR $\nu_{\max}^{\mathrm{CCl_4}}$ cm^{-1}: 1725, 1155, 1135, 1105, 1075, 1040. NMR δ(CCl_4): 3.74, 3.71 (each s, 2H × 2, OCH_2CH_2O), 3.57 (s, 3H, CO_2CH_3), 1.09, 0.92 (each s, 3H × 2, C_4,C_{10}–CH_3). *Anal.* Calcd. for $C_{22}H_{34}O_4$: C, 72.86; H, 9.45. Found: C, 72.85; H, 9.55.

16-Ethylenedioxy-17-norkauran-18-ol (XXXII)——To a solution of XXX (43.6 mg) in abs. ether (8.5 ml) was added $LiAlH_4$ (45.0 mg), which was stirred overnight at room temperature. Water was added to the mixture, which was alkalined with 50% KOH solution. The mixture was extracted with ether. The extract was washed with brine and dried over Na_2SO_4. Removal of the solvent gave XXXII (quantitative), mp 111.5—113° (*n*-hexane). IR $\nu_{\max}^{\mathrm{CCl_4}}$ cm^{-1}: 3660, 3400 (b), 1180, 1110, 1065, 1040. NMR δ(CCl_4): 3.79 (b.s, 4H, OCH_2CH_2O), 3.33, 2.92 (d.d, J=11 Hz, 2H, $C\underline{H_2}OH$), 1.06, 0.73 (each s, 3H × 2, C_4,C_{10}–CH_3). *Anal.* Calcd. for $C_{21}H_{34}O_3$: C, 75.40; H, 10.25. Found: C, 75.27; H, 10.33. High-MS. Calcd. (M^+; *m/e*): 334.2508. Found: 334.2498.

16-Ethylenedioxy-17-norphyllocladan-15-ol (XXXIII)——Treatment of XXXI (34.4 mg) and $LiAlH_4$ (35.0 mg) in abs. ether (7.0 ml) as the same procedure mentioned in the formation of XXXII gave XXXIII (quantitative), mp 128.5—129.5° (*n*-hexane). IR $\nu_{\max}^{\mathrm{CCl_4}}$ cm^{-1}: 3660, 3400 (b), 1155, 1115, 1075, 1040. NMR δ (CCl_4): 3.76, 3.73 (each s, 2H × 2, OCH_2CH_2O), 3.31, 2.93 (d.d, J=10 Hz, 2H, $C\underline{H_2}OH$), 0.93, 0.72 (each s, 3H × 2, C_4,C_{10}–CH_3). *Anal.* High-MS. Calcd. for $C_{21}H_{34}O_3$ (M^+; *m/e*): 334.2508. Found: 334.2498.

17-Norkauran-16-one (XXXIV) from XXXII——The α-ketal alcohol (XXXII) (84.9 mg) in CH_2Cl_2 (5 ml) was added to the CrO_3–pyridine complex solution prepared from CrO_3 (193.5 mg), KOH-dried pyridine (306 mg) and CH_2Cl_2 (5 ml),[12] which was stirred at room temperature for 30 min. The reaction mixture was poured onto alumina (2.5 g) column and eluted with ether and the elute was concentrated to give a crude aldehyde (79.6 mg), IR $\nu_{\max}^{\mathrm{CCl_4}}$ cm^{-1}: 2800, 2690, 1725, 1185, 1110, 1070.

A solution of the crude aldehyde (79.6 mg) in ether (5 ml) was added slowly at 100° to a stirred solution of hydrazine hydrate (250 μl) in diethylene glycol (3 ml) without cooler. After the mixture was stirred under the same condition for 2 hr, KOH (340 mg) was added. The temperature was raised gradually to 200° with removal of excess hydrazine hydrate, and it was heated at 200° for 2 hr. After cooling, water was added, and it was extracted with ether. The extract was washed with brine and dried over Na_2SO_4. Removal of the solvent gave a crude ketal of 17-norkauran-16-one (76.6 mg), IR $\nu_{\max}^{\mathrm{CCl_4}}$ cm^{-1}: 1180, 1110, 1070, 1040.

The ketal (76.6 mg) in acetone (12 ml) was refluxed with addition of 10% HCl solution (one drop) for 2 hr. After evaporation of the solvent, the residue was dissolved in ether, which was washed with brine and dried over Na_2SO_4. Removal of the solvent gave a crystal (61.6 mg). The crystal was chromatographed on alumina (2 g) with petr. ether–ether (30: 1) as eluant to give XXXIV (19.7 mg; 28.3% from XXXII), mp 114—115° (sintered at 113°) (MeOH–H_2O), mixed mp 114—115°.[8] IR ν_{max}^{KBr} cm^{-1}: 1746. NMR δ ($CDCl_3$): 1.08, 0.87, 0.83 (each s, 3H×3, C_{4ax},C_{4eq},C_{10}–CH_3). *Anal.* High-MS. Calcd. for $C_{19}H_{30}O$ (M^+; *m/e*): 274.2296. Found: 274.2301. The mixed melting point and the IR and NMR spectra were identical with those of the authentic sample[8] synthesized from the natural *d*-kaurene (XXXVI).

17-Norphyllocladan-16-one (XXXV) from XXXIII——Treatment of a solution of XXXIII (49.0 mg) in CH_2Cl_2 (5 ml) and a solution of CrO_3 (190 mg) and pyridine (300 mg) in CH_2Cl_2 (5 ml) as the same procedure mentioned in the formation of XXXIV gave a crude aldehyde (52.2 mg), IR $\nu_{max}^{CCl_4}$ cm^{-1}: 2810, 2700, 1725, 1185, 1150, 1110, 1080, 1040.

Treatment of the aldehyde (52.2 mg) in ether (5 ml), hydrazine hydrate (170 µl), diethylene glycol (2 ml) and KOH (200 mg) gave a crude ketal of 17-norphyllocladan-16-one (45.3 mg), IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1150, 1110, 1070, 1035. NMR δ(CCl_4): 3.73 (b.s, 4H, OCH_2CH_2O), 0.89, 0.84, 0.79 (each s, 3H×3, C_{4ax},C_{4eq},C_{10}–CH_3).

Treatment of the ketal of the norketone (45.3 mg) and 10% HCl solution (one drop) in acetone (8.0 ml) gave a crystal (39.7 mg). The crystal was chromatographed on alumina (2 g) with petr. ether–ether (40: 1) as eluant to give XXXV (25.3 mg; 63.1% from XXXIII), mp 91.5—97° (MeOH-H_2O), mixed mp 90—96.5°. IR ν_{max}^{KBr} cm^{-1}: 1744. NMR δ ($CDCl_3$): 0.87 (s, 6H, CH_3×2), 0.81 (s, 3H, CH_3). *Anal.* High-MS. Calcd. for $C_{19}H_{30}O$ (M^+; *m/e*): 274.2296. Found: 274.2276. The mixed melting point and the IR and NMR spectra were identical with those of the authentic sample[8] synthesized from the natural *d*-phyllocladene (XXXVII).

17-Norkauran-16-one (XXXIV) from XXXVI——To a solution of XXXVI (49.9 mg) in ether (4.0 ml) was added OsO_4 (50.0 mg), which was left standing under dark at room temperature for 2 days. The solution was saturated with H_2S and filtered. Evaporation of the filtrate gave a crystal (51.0 mg), which was dissolved in EtOH (26 ml) and a solution of H_5IO_6 (292 mg) in water (4 ml) was added. After stirring at room temperature for 26 hr, it was neutralized with sat. $Ba(OH)_2$ solution. The solution was extracted with ether, and the extract was washed with brine and dried over Na_2SO_4. Evaporation of the solvent gave a crystal (44.4 mg), which was chromatographed on alumina (2.5 g) with petr. ether–ether (20: 1) as eluant to give XXXIV (10.0 mg; 19.9%), mp 114—115° (sintered at 113°) (MeOH–H_2O). IR ν_{max}^{KBr} cm^{-1}: 1746. NMR δ ($CDCl_3$): 1.08, 0.87, 0.83 (each s, 3H×3, C_{4ax},C_{4eq},C_{10}–CH_3). *Anal.* High-MS. Calcd. for $C_{19}H_{30}O$ (M^+; *m/e*): 274.2296. Found: 274.2320.

17-Norphyllocladan-16-one (XXXV) from XXXVII——To a solution of XXXVII (35.0 mg) in ether (3 ml) was added OsO_4 (35.0 mg), which was left standing under dark at room temperature for 2 days. The solution was saturated with H_2S and filtered. Evaporation of the filtrate gave an oil (35.7 mg), which was dissolved in EtOH (26 ml) and a solution of H_5IO_6 (200 mg) in water (5 ml) was added. After stirring at room temperature for 40 hr, it was neutralized with sat. $Ba(OH)_2$ solution. The solution was extracted with ether, and the extract was washed with brine and dried over Na_2SO_4. Evaporation of the solvent gave a crystal (34.4 mg), which was sublimed at 90—95° under 1 mmHg to give a crystal (18.2 mg). The crystal was chromatographed on alumina (2.0 g) with petr. ether–ether (40: 1) as eluant to give XXXV (8.9 mg; 25.3%), mp 91—96.5° (MeOH–H_2O). IR ν_{max}^{KBr} cm^{-1}: 1744. NMR δ ($CDCl_3$): 0.87 (s, 6H, CH_3×2), 0.81 (s, 3H, CH_3). *Anal.* High-MS. Calcd. for $C_{19}H_{30}O$ (M^+; *m/e*): 274.2296. Found: 274.2285.

Acknowledgement Authors thank Prof. A. Yoshikoshi, Tohoku University, and Prof. M. Kitadani, Kobe University, for the donation of the valuable samples of XXXVI and XXXVII.