[Chem. Pharm. Bull. 23(9)1996—2000(1975)]

UDC 547.597.04 : 547.92.057

# Conversion of Dehydroabietic Acid into a Steroid Skeleton: Formation of the A-Ring. II[1]

Akira Tahara,[2a] Yoshihiro Harigaya and Masayuki Onda[2b]

*Rikagaku Kenkyusho (The Institute of Physical and Chemical Research)[2a] and School of Pharmaceutical Sciences, Kitasato University[2b]*

(Received December 26, 1974)

Conversion of dehydroabietic acid (**1**) to a steroid skeleton was attempted. The oxo ester (**3**), an important intermediate in the synthesis of **4**, was synthesized from **7** having a double bond in the A ring. It was confirmed that the oxo ester (**3**) has the α configuration at the 5-position.

We have been attempting the conversion of abietic acid, a representative resin acid, to a steroid skeleton, and had succeeded in the conversion of dehydroabietic acid (**1**) to the 3-oxo compound (**4**), possessing a steroid-type A ring, *via* the oxo ester (**3**), which was described in our preceding paper.[3] In the present series of work, the oxo ester (**3**), which may be regarded as an important intermediate in the synthesis of **4**, was synthesized by another route with reliable configuration of the 5-position.

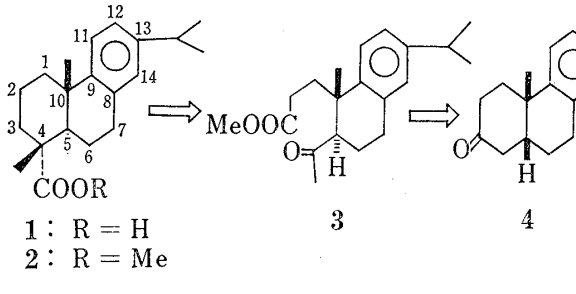


Chart 1

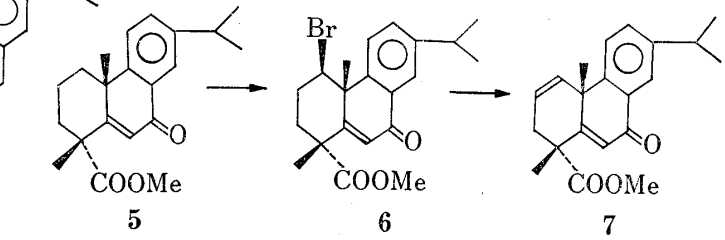


Chart 2

For the starting material, the compound (**7**) possessing a double bond in the A ring, whose synthesis was reported previously,[4] was used. This compound (**7**) can be obtained by dehydrobromination of the 1-bromide (**6**) formed by the use of the rearrangement reaction of the benzonilidene compound (**5**). Oxidation of the 3-position in **7**, corresponding to the allyl position, was attempted with chromium trioxide or N-bromosuccinimide or lead tetraacetate but either the starting material was recovered or complex products were formed. Oxidation

1) This paper constitutes Part XXXIII of "Diterpenoids" series by A. Tahara and co-workers. Part XXXII: A. Tahara, Y. Harigaya, and M. Onda, *Chem. Pharm. Bull.* (Tokyo), **23**, 1989 (1975).
Melting points were determined on a micro hot-stage and were uncorrected. Infrared (IR) spectra ($\nu_{max}$ $cm^{-1}$) were recorded on a JASCO IR-G. Nuclear magnetic resonance (NMR) spectra ($\delta$) were measured at 60 MHz in $CCl_4$ unless otherwise specified (5—10% solution *vs.* tetramethylsilane as internal reference) with a Varian T-60. Mass spectra were taken on a JEOL JMS-OlS. Circular dichroism (CD) curve was measured in MeOH with a JASCO J-20. Every thin-layer chromatography (TLC) was carried out on Silica gel G plates and shown by *Rf* values and preparative TLC (pre TLC) was carried out with Silica gel G–Silica gel $PF_{254}$ (2 : 1) as adsorbent. Gas–liquid chromatography (GLC) (1.5% OV-17 on Shimalite W (80—100 mesh), 2 m×4 mm) was shown by $t_R$ values.
2) Location: *a) Wakō-shi, Saitama, 351, Japan; b) Minato-ku, Tokyo, 108, Japan.* To whom inquiries regarding this report should be addressed.
3) A. Tahara, Y. Harigaya, and M. Onda, *Chem. Pharm. Bull.* (Tokyo), **23**, 1989 (1975).
4) A. Tahara and H. Mizuno, *Tetrahedron Letters*, **1974**, 523.

of **7** with N-bromosuccinimide–lead tetraacetate[5] resulted in the substitution of an acetoxyl group into the methine of the 13-isopropyl group to form **8**. Finally, oxidation of **7** with selenium oxide gave the objective 3-oxo compound (**11**), mp 162—165°, in 30% yield.

Catalytic reduction of **11** over 10% palladium-carbon in acetic acid–conc. sulfuric acid resulted in the reduction of double bonds at 1—2 and 5—6 positions, and of the 7-oxo group, and two isomers of the 5-position, **12**, mp 108—109.5°, and oily **13**, were obtained. Formation ratio of **12** and **13** in the reduction was irregular, sometimes giving only **12**. In the NMR spectrum,[6] the chemical shift of the ester-methyl appeared at $\delta$ 3.69 in **12** but shifted to $\delta$ 3.1 in **13** due to the anisotropic effect of the benzene ring. The product formed by the Clemmensen reduction of **12** was identical with methyl dehydroabietate (**2**) having A/B *trans* ring juncture, the starting material for the series of these reactions. These facts indicate that **12** has 5$\alpha$-H (A/B *trans*) and **13** has 5$\beta$-H (A/B *cis*).

In another catalytic reduction of **11** over 10% palladium-carbon in methanol–acetic acid, the two double bonds were reduced and the 7-oxo group was reduced to a hydroxyl group, forming **14**. Jones' oxidation of **14** gave the 3,7-dioxo ester (**15**), mp 141—142°. Configuration of the 5-position in **14** was considered to be 5$\alpha$-H (A/B *trans*) since the chemical shift of the ester-methyl appeared at $\delta$ 3.6, same as in **12**, in the NMR spectrum of **14**, differing entirely from that of $\delta$ 3.1 in **13** having 5$\beta$-H.

In order to remove the ester group in 4-position, $\beta$-oxo esters (**12** and **13**) were hydrolysed with 5% potassium hydroxide–methanol at 50°. The 5$\alpha$-H compound (**12**) underwent ketone decomposition quantitatively to give the 3-oxo compound (**18**)[7] but the 5$\beta$-H compound (**13**) was hardly affected under these conditions. Under a more drastic condition of refluxing in 20% potassium hydroxide–methanol, **12** gave a ketone decomposition product (**18**) and an acid decomposition product (the corresponding acid to **16**) in *ca.* 1:1 ratio. The carboxylic acid compound was methylated with diazomethane to the diester (**16**). Under this drastic condition, **13** underwent acid decomposition alone quantitatively to give the dicarboxylic acid compound (the corresponding acid to **17**) which was methylated with diazomethane to the diester (**17**).

This difference in the reactivity of **12** (5$\alpha$-H) and **13** (5$\beta$-H) to alkaline hydrolysis is probably due to the spatial position of the ester group which in **13** is under the benzene ring and will be difficult to be hydrolyzed, which made it difficult for ketone decomposition to take place and only the acid decomposition occurred in **13**.

In order to cleave the A ring, the 3-oxo compound (**18**) was submitted to the Baeyer-Villiger reaction of treating with *m*-chloroperbenzoic acid to form the lactone (**19**) which was hydrolyzed with 10% potassium hydroxide–methanol, and the acid product (**20**) was methylated with diazomethane giving a hydroxy ester (**21**) with cleavage between 3- and 4-positions. Since the separation of **12** and **13**, the reduction products of **11**, was difficult by column chromatography, the mixture of **12** and **13** was submitted to the hydrolysis and the Baeter-Villiger reaction, and separation and purification were made on the lactone (**19**). Jones' oxidation of the hydroxy ester (**21**) afforded the 5$\alpha$-oxo ester (**3**), which was identified with the 5$\alpha$-oxo ester obtained previously.[3]

The 5$\alpha$-oxo ester (**3**) was also obtained in the following way. Dehydroabietic acid (**1**) was derived to the olefin (**22**) by the method of Huffman and Arapakos.[8] This mixture was directly oxidized with ozone, followed by oxidation of its product with potassium permanganate, and the acid product was methylated with diazomethane. Separation and purification

5) D.H.R. Barton, E.F. Lier, and J.F. McGhie, *J. Chem. Soc.* (*C*), **1968**, 1031.
6) N.S. Bhacca and D.H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day Inc., San Fransisco, 1964.
7) R.C. Cambie and R.A. Franich, *Aust. J. Chem.*, **23**, 93 (1970); J.W. Huffman, *J. Org. Chem.*, **37**, 17 (1972).
8) J.W. Huffman and P.G. Arapakos, *J. Org. Chem.*, **30**, 1604 (1965).

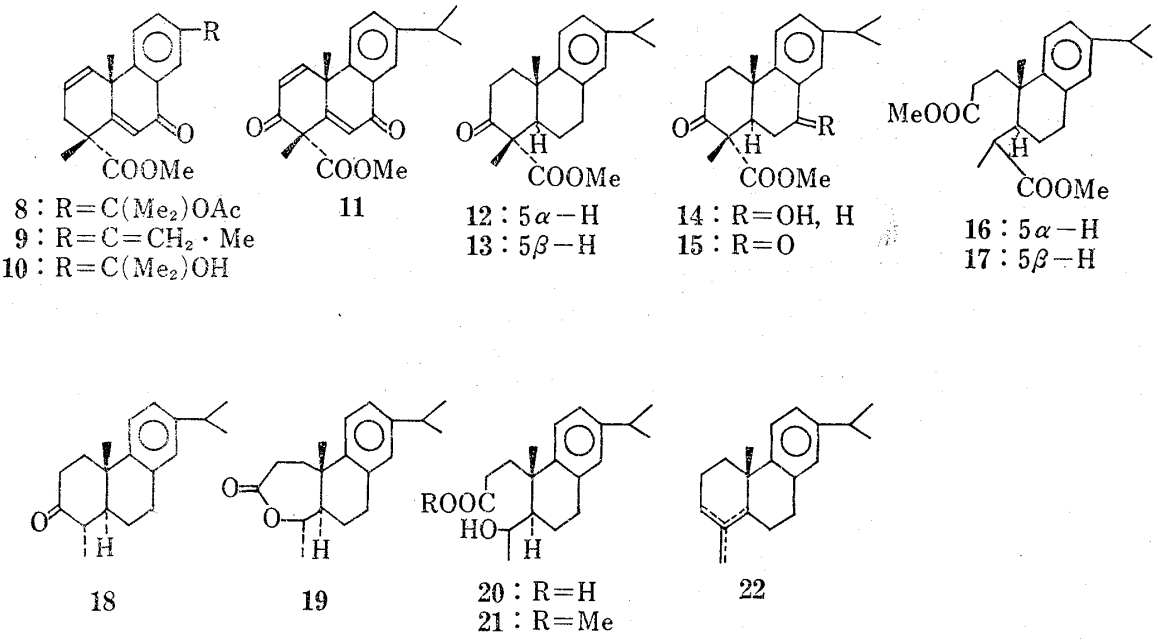


Chart 3

of the product through column chromatography afforded the 5α-oxo ester (3) in *ca.* 10% yield from **1**.

As was stated in our preceding paper,[3] the oxo ester (3) is an important intermediate in the synthesis of **4**, possessing a steroid-type A ring, and the synthesis of **4** should become easier by the preparation of this intermediate ester (3) by the reliable method for retention of the configuration at 5-position.

## Experimental

**Allylic Oxidation of 7 with $Pb(OAc)_4$-NBS**——To a solution of oxo ester (**7**) (54 mg) in dry benzene (4 ml) were added $Pb(OAc)_4$ (30 mg) and NBS (20 mg) under nitrogen stream. After refluxed for 17 hr. the reaction mixture was washed with $H_2O$, 5% KOH aq. and sat. NaCl aq. The work-up gave light yellow oil (63 mg), which gave two components by TLC; $Rf$=0.65, 0.42 (benzene:AcOEt=6: 0.5). They were separated by pre TLC (benzene:AcOEt=9: 1) to give two fractions; colorless oil (**7**) (32 mg) ($Rf$=0.65), which was identical with the starting material by comparison of $Rf$ values and IR spectra, and colorless oil (**8**) (14 mg) ($Rf$=0.42). Mass Spectrum: Calcd. for $C_{33}H_{26}O_5$ ($M^+$, $m/e$): 382.1780. Found: 382.1761. IR ($CCl_4$): 1735, 1660, 1237. NMR: 1.54, 1.77 (each 3H, s; 4- and 10-Me), 1.70 (6H, d, $J$=7 Hz; $CMe_2$), 3.68 (3H, s; COOMe), 5.66—6.40 (1H, m; 2-H), 6.09 (1H, s; 6-H), 6.33 (1H, d, $J$=10 Hz; 1-H), 7.46 (2H, bs, $W_{h/2}$=3 Hz; 11-, and 12-H), 7.85 (1H, bs, $W_{h/2}$=5 Hz; 14-H).

After this compound was allowed to stand at room temperature for 6 months, the reaction mixture was purified by pre TLC (benzene:AcOEt=9: 1) to separate two compound; **9** ($Rf$=0.60), Mass Spectrum: Calcd. for $C_{21}H_{22}O_3$ ($M^+$, $m/e$): 322.1569. Found: 322.1595. IR ($CCl_4$): 1737, 1663, 1620, and **10** ($Rf$=0.05). Mass Spectrum: Calcd. for $C_{21}H_{24}O_4$ ($M^+$, $m/e$): 340.1645. Found: 340.1708. IR ($CCl_4$): 3600, 3450, 1735, 1660.

**Methyl 13-Isopropyl-3,7-dioxo-podocarpa-1,5,8,11,13-pentaen-15-oate (11)**——After a solution of oxo ester (**7**) (390 mg) and $SeO_2$ (200 mg) in dioxane (40 ml) was refluxed for 19 hr, the precipitates were filtered off and the filtrate was evaporated under reduced pressure. The residue was dissolved in ether and insoluble parts were filtered off, and then the filtrate was washed with 5% KOH aq. and sat. NaCl aq. The ether layer was treated by Mackenzie's method[9] to give light yellow oil (320 mg), which was recrystallized from hexane–benzene to give small prisms (**11**) (140 mg), mp 162—165°. $t_R$=12.45 (227°). $Rf$=0.42 (benzene: AcOEt=6: 0.3). *Anal.* Calcd. for $C_{21}H_{22}O_4$: C, 74.55; H, 6.55. Found: C, 74.61; H, 6.52. IR ($CCl_4$): 1755, 1693, 1665, 1628. NMR: 1.30 (6H, d, $J$=7 Hz; $CHMe_2$), 1.69, 1.79 (each 3H, s; 4- and 10-Me), 3.63 (3H, s; COOMe), 6.19 (1H, s; 6-H), 6.23 (1H, d, $J$=10 Hz; 2-H), 7.46 (1H, d, $J$=10 Hz; 1-H), 7.50 (2H, bs, $W_{h/2}$=2.5 Hz; 11- and 12-H), 7.96 (1H, bs, $W_{h/2}$=3 Hz; 14-H).

9) B.F. Mackenzie, V.R. Mattox, L.X. Engel, and E.C. Kendall, *J. Biol. Chem.*, **173**, 271 (1948).

**Catalytic Reduction of 11 to 12 and 13**——a) A solution of **11** (230 mg), conc. $H_2SO_4$ (3 drops) in AcOH (15 ml) was shaken in the presence of 10% Pd-C (120 mg) under 5 atm of hydrogen at room temperature. The work-up in the usual way gave colorless semi-solid (250 mg). $Rf$=0.45, 0.39 (benzene:AcOEt=6: 0.2). $t_R$=3.8, 6.0 (1: 1) (230°).

Pre TLC ($CHCl_3$) of 5$\alpha$- and 5$\beta$-oxo ester mixture gave two fractions; colorless oil (**13**), $Rf$=0.45. Mass Spectrum: Calcd. for $C_{21}H_{28}O_3$ ($M^+$, $m/e$): 328.2039. Found: 328.2055. IR ($CCl_4$): 1735, 1718 (sh), 1712. NMR: 1.23 (6H, d, $J$=7 Hz; $CHMe_2$), 1.23, 1.35 (each 3H, s; 4- and 10-Me). 3.10 (3H, s; COOMe), 6.83—7.20 (3H, m; 11-, 12-, and 14-H), and colorless prisms (**12**) ($Rf$=0.39), mp 108—109.5° (hexane–ether). *Anal.* Calcd. for $C_{21}H_{28}O_3$: C, 76.79; H, 8.59. Found: C, 76.84; H, 8.46. IR ($CCl_4$): 1745, 1712. NMR: 1.22 (6H, d, $J$=7 Hz; $CHMe_2$), 1.13, 1.38 (each 3H, s,; 4- and 10-Me), 3.69 (3H, s; COOMe), 6.81—7.18 (3H, m; 11-, 12-, and 14-H).

b) Oxo ester (**11**) (50 mg) was catalytically hydrogenated in AcOH (5 ml) in the presence of 10% Pd-C (25 mg), conc. $H_2SO_4$ (2 drops) under hydrogen stream for 16 hr at room temperature. The reaction mixture was treated in the usual way to give colorless oil (51 mg), whose component (**12**: **13** in ratio 1: 2) were shown by peak area in GLC.

**Reduction of 11 with 10% Pd-C in MeOH-AcOH**——A solution of dioxo ester (**11**) (52 mg) in MeOH (6 ml) was shaken in the presence of 10% Pd-C (20 mg) and AcOH (2 drops) under hydrogen stream for 40 min at room temperature. The work-up in the usual way gave colorless oil (52 mg). $t_R$=6.3, 13.0 (1: 4.5) (227°). Separation was carried out by pre TLC (benzene:AcOEt=12: 1) to give 5$\alpha$-oxo ester (**12**) (5.5 mg) as first fraction ($Rf$=0.56; benzene:AcOEt=6: 0.2), which was identified with **12** by comparison of physical constants ($Rf$, $t_R$, IR and NMR spectra), and colorless oil (**14**) (24 mg) ($Rf$=0.11; benzene:AcOEt=6: 0.2). Mass Spectrum: Calcd. for $C_{21}H_{28}O_4$ ($M^+$, $m/e$): 344.1988. Found: 344.2005. IR ($CCl_4$): 3600, 1745, 1710. NMR: 1.23 (6H, d, $J$=7 Hz; $CHMe_2$), 1.31, 1.39 (each 3H, s; 4- and 10-Me), 2.53 (1H,[10] bs, $W_{h/2}$=5 Hz; 7-OH), 3.65 (3H, s; COOMe), 4.69 (1H, t, $J$=8 Hz; 7-H), 7.02 (2H, s; 11- and 12-H), 7.32 (1H, s; 14-H). The latter (**14**) (11.5 mg) in acetone (2 ml) was oxidized with Jones' reagent in the usual way to give a colorless oil (9.5 mg). The oil was crystallized from hexane–ether to give colorless prisms (**15**), mp 141—142°. Mass Spectrum: Calcd. for $C_{21}H_{26}O_4$ ($M^+$, $m/e$): 342.1831. Found: 342.1821. IR ($CCl_4$): 1745, 1718, 1690. NMR: 1.28 (6H, d, $J$=7 Hz; $CHMe_2$), 1.42, 1.45 (each 3H, s; 4- and 10-Me), 3.69 (3H, s; COOMe), 7.28 (2H, bs, $W_{h/2}$=3 Hz; 11- and 12-H), 7.79 (1H, b, $W_{h/2}$=4 Hz; 14-H).

**Clemmensen Reduction of 5$\alpha$-Oxo Ester (12)**——A solution of 5$\alpha$-oxo ester (**12**) (80 mg) in benzene (3 ml) was added to a mixture of Zn–Hg (prepared from Zn (1.2 g), $HgCl_2$ (130 mg), 10% HCl aq. (2.1 ml)) in 11% HCl aq. (2.6 ml). After reaction mixture was refluxed for 15 hr, the work-up in the usual way gave colorless oil (80 mg). The oil was purified by pre TLC (hexane:$CHCl_3$=1: 2) to give colorless oil (32 mg, $Rf$=0.76; hexane:$CHCl_3$=1: 2), and colorless crystals (35 mg, $Rf$=0.09; hexane:$CHCl_3$=1: 2). The latter crystals were identical with unreacted starting material. The former oil was crystallized from MeOH to give colorless needles (**2**), mp 62°, which were identical with methyl dehydroabietate (**2**) by comparison of melting points (mixed mp) and IR spectra.

**13-Isopropyl-3-oxo-16-nor-podocarpa-8,11,13-triene (18)**——A solution of 5$\alpha$-oxo ester (**12**) (110mg) in 5% KOH–MeOH (5 ml) was heated at 50° for 2.5 hr. The work-up in the usual way gave neutral light yellow oil (90 mg), whose pre TLC ($CHCl_3$) gave colorless oil (**18**) (63 mg). Mass Spectrum: Calcd. for $C_{19}H_{26}O$ ($M^+$, $m/e$): 270.1984. Found: 270.2004. IR ($CCl_4$): 1713. NMR: 1.05 (3H, d, $J$=6 Hz; 4-Me), 1.21 (6H, d, $J$=7 Hz; $CHMe_2$), 1.33 (3H, s; 10-H), 6.79—7.00 (3H, m; 11-, 12- and 14-H).

**Hydrolysis of 5$\alpha$-Oxo Ester (12) with 20% KOH-MeOH**——A solution of 5$\alpha$-oxo ester (**12**) (35 mg) in 20% KOH–MeOH (2 ml) was refluxed for 3 hr. The usual work-up gave neutral colorless oil (13.5 mg), which was purified by pre TLC ($CHCl_3$), $Rf$=0.54 ($CHCl_3$). The oily compound was identical with **18** by comparison of $Rf$, $t_R$ and IR spectra.

The acidic fraction gave colorless oil (12 mg), which was methylated with $CH_2N_2$–ether in the usual way to give colorless oil (14 mg). The methylated oil (**16**) was purified by pre TLC ($CHCl_3$), $Rf$=0.45 ($CHCl_3$). Mass Spectrum: Calcd. for $C_{22}H_{32}O_4$ ($M^+$, $m/e$): 360.2301. Found: 360.2325. IR ($CCl_4$): 1738. NMR: 1.18 (3H, s; 10-Me), 1.20 (3H, d, $J$=7 Hz; 4-Me), 1.20 (6H, d, $J$=7 Hz; $CHMe_2$), 3.50, 3.60 (each 3H, s; 3- and 15-COOMe), 6.80—7.17 (3H, m; 11-, 12- and 14-H).

**Hydrolysis of 5$\beta$-Oxo Ester (13) with 20% KOH-MeOH**——A solution of 5$\beta$-oxo ester (**13**) (65 mg) in 20% KOH–MeOH (5 ml) was refluxed for 4 hr. The usual work-up gave acidic colorless oil (62 mg), which was methylated with $CH_2N_2$–ether to give colorless oil (64 mg). The oil (**17**) was purified by pre TLC ($CHCl_3$; $Rf$=0.58, $CHCl_3$). Mass Spectrum: Calcd. for $C_{22}H_{32}O_4$ ($M^+$, $m/e$): 360.2309. Found: 360.2301. IR ($CCl_4$): 1738. NMR: 1.20 (3H, d, $J$=7 Hz; 4-Me), 1.24 (6H, d, $J$=7 Hz; $CHMe_2$), 1.34 (3H, s; 10-Me), 3.59, 3.69 (each 3H, s; 3- and 15-COOMe), 6.86—7.21 (3H, m; 11-, 12-, and 14-H).

**4-Hydroxyl-13-isopropyl-3,4-seco-16-nor-podocarpa-8,11,13-trien-3-oic Acid 3,4-Lactone (19)**——A solution of **18** (750 mg), *m*-$ClC_6H_4CO_3H$ (500 mg) in $CHCl_3$ (20 ml) was allowed to stand in the presence

10) On addition of $D_2O$ this signal was disappeared.

of 10% $H_2SO_4$–AcOH solution (0.2 ml) for 23 hr at room temperature. After the reaction mixture was diluted with ether, the work-up in the usual way gave a light yellow oil (**19**) (560 mg), which was pure enough for the further experiment. A part of the oil (**19**) was purified by pre TLC (benzene:AcOEt=90:5), *Rf*=0.46 (benzene:AcOEt=6:0.5). Mass Spectrum: Calcd. for $C_{19}H_{26}O_2$ ($M^+$, *m/e*): 286.1933. Found: 286.1946. IR ($CCl_4$): 1740. NMR: 1.21 (6H, d, *J*=7 Hz; $CHMe_2$), 1.26 (3H, s; 10-Me), 1.35 (3H, d, *J*=6 Hz; 4-Me), 4.60 (1H, t, *J*=6 Hz; 4-H), 6.78—7.19 (3H, m; 11-, 12-, and 14-H).

**Methyl 4-Hydroxyl-13-isopropyl-3,4-seco-16-nor-podocarpa-8,11,13-trien-3-oate** (**21**)——A solution of lactone (**19**) (65 mg) in 10% KOH–MeOH (2 ml) was allowed to stand for 1 hr at room temperature. The work-up in the usual way gave the acidic colorless powder (68 mg), which was recrystallized from hexane–ether to give colorless plates (**20**), mp 134—135.5°. *Anal.* for $C_{19}H_{28}O_3$: C, 74.96; H, 9.27. Found: C, 74.76; H, 9.28. IR ($CCl_4$): 3600, 3500—2400, 1710 (broad). NMR ($CDCl_3$): 1.26 (6H, d, *J*=7 Hz; $CHMe_2$), 1.28 (3H, d, *J*=4 Hz; 4-Me), 1.33 (3H, s; 10-Me), 4.20 (1H, q, *J*=5 and 11 Hz; 4-H), 6.89 (3H,[11] bs, $W_{h/2}$=4 Hz; 4-OH, COOH and one of aromatic protons), 7.10—7.16 (2H, m; aromatic protons).

Hydroxy acid (**20**) (29 mg) was methylated with $CH_2N_2$–ether in the usual way to give colorless oil (**21**) (30 mg), which was purified by pre TLC ($CHCl_3$:MeOH=100:1). *Rf*=0.3 ($CHCl_3$:MeOH=100:1). Mass Spectrum; Calcd. for $C_{20}H_{30}O_3$ ($M^+$, *m/e*): 318.2195. Found: 318.2201. IR ($CCl_4$): 3600, 3500, 1738, 1730 (sh). NMR: 1.28 (6H, d, *J*=6 Hz; $CHMe_2$), 1.30 (3H, d, *J*=4 Hz; 4-Me), 1.30 (3H, s; 10-Me), 2.16 (1H,[10] bs, $W_{h/2}$=6 Hz; 4-OH), 3.55 (3H, s; COOMe), 4.0 (1H, b, $W_{h/2}$=22 Hz; 4-H), 6.85—7.18 (3H, m; 11-, 12-, and 14-H).

**Methyl 13-Isopropyl-4-oxo-16-nor-5α-podocarpa-8,11,13-trien-15-oate** (**3**)——A solution of hydroxy ester (**21**) (70 mg) in acetone (2 ml) was oxidized with Jones' reagent under ice-cooling as usual way to give colorless oil (58 mg). Purification by pre TLC (benzene:AcOEt=90:0.5) gave colorless oil (**3**) (50 mg), *Rf*=0.53 (benzene:AcOEt=6:1). $t_R$=4.25 (222°). Mass Spectrum: Calcd. for $C_{20}H_{28}O_3$ ($M^+$, *m/e*): 316.2039. Found: C, 316.2038. IR ($CCl_4$): 1740, 1735 (sh), 1710, 1700 (sh). NMR: 1.23 (6H, d, *J*=7 Hz; $CHMe_2$), 1.25 (3H, s; 10-Me), 2.17 (3H, s; 4-Me), 3.53 (3H, s; COOMe), 6.76—7.18 (3H, m; 11-, 12-, and 14-H).

**5α-Oxo Ester** (**3**) **from Dehydroabietic Acid** (**1**) ***via*** **Olefin Mixture** (**22**)——Dehydroabietic acid (**1**) (10 g) was decarboxylated with $Pb(OAc)_4$, successively ozonized as reported by Huffman and Arapakos.[6] The resulting oil (6.5 g) was dissolved in acetone (200 ml) and oxidized with $KMnO_4$ aq. under ice-cooling as usual way. The work-up gave acidic colorless oil (2.2 g), which was methylated with $CH_2N_2$–ether as usual to give colorless oil (2.2 g). The oil was chromatographed on silica gel (130 g) to give colorless oil (1.1 g) in benzene:AcOEt (100:1) eluate. The resulting oil was identical with 5α-oxo ester (**3**) by comparison of *Rf*, $t_R$, IR, and NMR spectra.

11) On addition of $D_2O$ two of them were disappeared.