[Chem. Pharm. Bull. 25(5) 974—980 (1977)]

UDC 547.913.6.04 : 546.214.04

Diterpenoids. XLV.[1] Ozonolysis of Phenolic Dehydroabietic Acid Derivatives

Hiroyuki Akita,[2a] Kazuhiko Mori,[2b] and Akira Tahara (the late)[2]

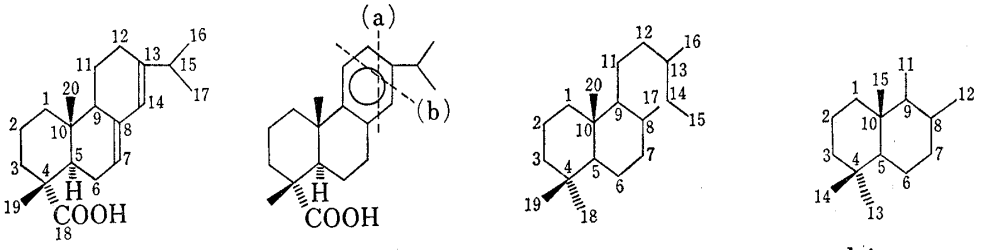
Rikagaku Kenkyusho (The Institute of Physical and Chemical Research[2])

(Received August 2, 1976)

Ozonolysis of phenolic dehydroabietic acid derivatives with an isopropyl group at 13-position was investigated and the direction of cleavage of the aromatic ring by means of ozonolysis was found to be affected by the substitution pattern of hydroxyl group in the aromatic ring. Ozonolysis of the 12-hydroxy ester (**12**) afforded the pentanorlabdane type compounds, (**13**), (**14**), and (**15**), while ozonolysis of the 14-hydroxy ester (**17**) and (**18**) gave the drimane type products, (**19**) and (**20**).

Keywords——diterpenoid; ozonolysis; phenol; selective cleavage of aromatic ring; sesquiterpenoid

In the studies of the new utilization of pine rosin, chemical conversion of its major component, *l*-abietic acid (**1**), to labdane type diterpenoids and drimane type sesquiterpenoids has aroused our interest. The most important problem in the earlier stage of this conversion is the partial cleavage of the aromatic C-ring of dehydroabietic (**2**), easily obtained from **1**, at the desired direction. The cleavage at (a)-direction may enable conversion into labdane type diterpenoids while the cleavage at (b)-direction would lead to drimane type sesquiterpenoids.

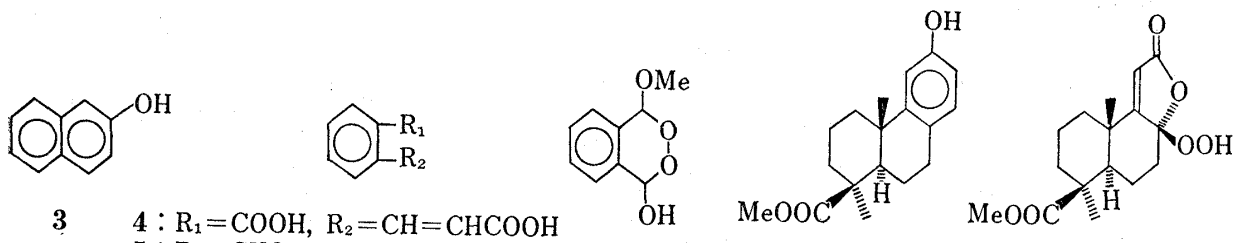


1 **2** labdane drimane

Chart 1

In general, ozonolysis of phenols has been of little use in synthetic organic chemistry because random cleavage is observed. On the other hand, product distribution of ozonolysis of polycyclic phenols depends on the solvent used. For example, 2-naphthol (**3**) affords a complex mixture of **4**, **5**, **6**, **7**, and **8** in nonhydroxylic solvents,[3] while ozonolysis in methanol results in the formation of the single product, 4-methxoy-2,3-benzodioxan-1-ol (**9**).[4] In the field of diterpenoid chemistry, one example has been reported on this partial cleavage.[5] Low temperature ozonolysis of methyl podocarpate (**10**) in methanol-methylene chloride results in the formation of the hydroperoxy γ-lactone (**11**) in high yield.

1) Part XLIV: H. Mizuno, T. Ohsawa, and A. Tahara (the late), *Chem. Pharm. Bull.* (Tokyo), **24**, 1527 (1976).
2) Location: *Hirosawa, Wako-shi, Saitama-ken, 351, Japan*; *a*) To whom inquiries regarding this paper should be addressed; *b*) Present address: *Science University of Tokyo, 12, Ichigaya Funakawara-machi, Shinjuku-ku, Tokyo, 162, Japan.*
3) E. Bernatek and C. Frengen, *Acta. Chem. Scand.*, **16**, 2421 (1962).
4) P.S. Bailey, S.S. Bath, F. Dobinson, F.J. Garcia-Sharp, and C.D. Johnson, *J. Org. Chem.*, **29**, 697 (1964).
5) R.A. Bell and M.B. Gravestock, *Can. J. Chem.*, **48**, 1105 (1970). *cf*) R.C. Cambie and R.C. Hayward, *Aust. J. Chem.*, **28**, 225 (1975).



3 4 : R_1=COOH, R_2=CH=CHCOOH
5 : R_1=CHO , R_2=CH=CHCOOH
6 : R_1=CHO , R_2=CHO
7 : R_1=CHO , R_2=COOH
8 : R_1=COOH, R_2=COOH

9 10 11

Chart 2

We have studied ozonolysis of phenolic dehydroabietic acid derivatives with isopropyl group at 13-position and found that the direction of the cleavage was affected significantly by the substitution pattern on the aromatic ring.

At first, 12-hydroxy ester (**12**)[6] was ozonolized in methanol–methylene chloride under dry ice-acetone cooling. Catalytic hydrogenation of the ozonolized products at ordinary temperature and pressure over 10 % palladium–charcoal, followed by methylation with diazomethane, gave the hydroxy-γ-lactone (**13**), colorless needles, mp 187—190° (14 %) and the keto-diester (**14**), colorless prisms, mp 94.5—95° (22 %). Catalytic hydrogenation of **13** in methanol over 10 % palladium–charcoal and the subsequent methylation with diazomethane gave the keto-diester (**14**). Reduction of **13** with sodium borohydride in 50 % aqueous ethanol afforded the unsaturated lactone (**15**), colorless prisms, mp 153.5—155°. Direct reduction of the ozonolized products with sodium borohydride in 50 % aqueous ethanol afforded **15** ,which was consistent with the above observation, while reduction with aqueous sodium sulfite and zinc in acetic acid followed by methylation afforded **13** and **14** respectively. The $\Delta^{9,11}$ double bond was found to be reduced only by catalytic hydrogenation and zinc in acetic acid.

It was found that the above three compounds possess the same pentanorlabdane skeleton and an oxygen function at 8-position, because the keto-diester (**14**) was identical to the authentic sample (**14**) prepared by ozonolysis and subsequent methylation from

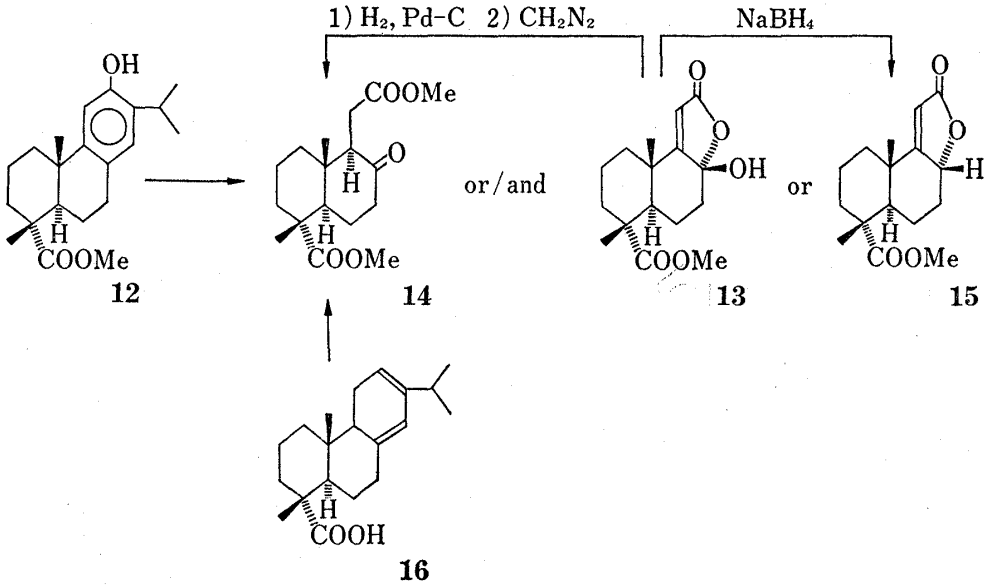


Chart 3

6) R.C. Cambie and R.A. Franich, *Aust. J. Chem.*, **24**, 117 (1971).

Table I

Starting material	Reductant	Product (%)
12	H_2, 10% Pd-C, CH_2N_2[a]	**13**; 14% **14**; 22%
12	aq. Na_2SO_3	**13**; 20%
12	$NaBH_4$ in 50% EtOH-H_2O	**15**; 65%
12	Zn–AcOH, CH_2N_2[a]	**14**; 50%

a) For the purification, reduction products were methylated with diazomethane.

levopimaric acid (**16**) in the same manner as described by Pelletier.[7] The butenolide structure of **15** follows from the presence of one proton doublet (J=1.5 Hz) at δ 5.49 (olefinic proton) and one proton octet (J=1.5, 7.2, and 9.6 Hz) at δ 4.85 (proton adjacent to the lactone oxygen) in the nuclear magnetic resonance (NMR) spectrum and a band characteristic of an unsaturated lactone at 1750 and 1640 cm^{-1} in the infrared (IR) spectrum. The ultraviolet (UV) spectrum, which showed λ_{max}^{EtOH} 209 nm (log ε=4.09), was also in agreement with the presence of an unsaturated lactone. Further, a nuclear Overhauser effect (NOE) was distinctly observed on 8-hydrogen by irradiation at 10-methyl group; 10.4% increases were noticed by irradiation at δ 1.25. Therefore, the 8-hydrogen must be on the same side of the molecule with the 10-methyl group possessing a β-configuration. On the other hand, the compound (**13**) was proved to have a hydroxy-unsaturated lactone moiety since the absorption in IR at 1750 and 1645 cm^{-1} showed the presence of an unsaturated lactone and the absorption at 3400 cm^{-1}, a hydroxy group. Additional evidence for the structure of **13** was derived from the absorption at λ_{max}^{EtOH} 209 nm (log ε=4.09) and one proton singlet at δ 5.58

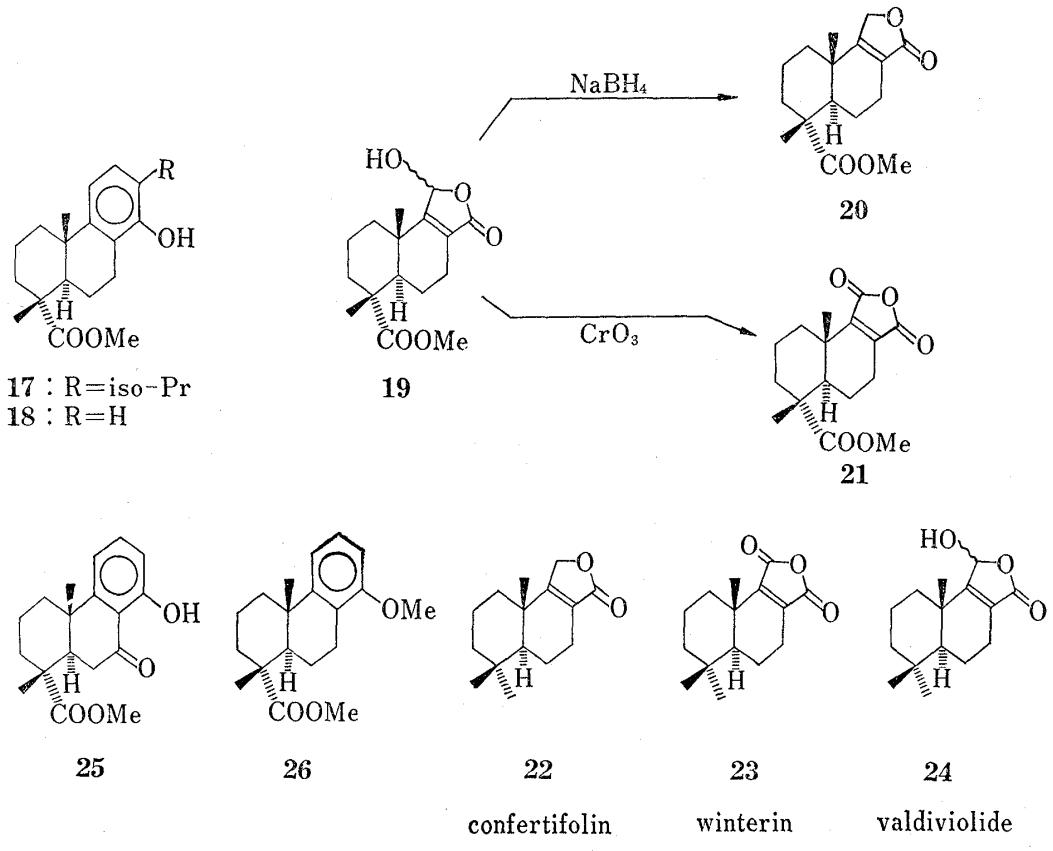


Chart 4

7) S.W. Pelletier, L.B. Hawley, Jr., and K.W. Gopinath, *Chem. Commun.*, **1967**, 96.

due to 11-hydrogen and a broad singlet due to the hydroxyl group at δ 4.73 ($W_{h/2}$=5 Hz). Furthermore, 10-methyl protons of **13** appear in a slightly lower field than the corresponding protons of **15**. This indicates that the 8-hydroxyl group of **13** is in the same side of 10-methyl group and thus must be in β-configuration.

Next, 14-hydroxy ester (**17**)[8] was ozonolized in the same manner as for the 12-hydroxy ester (**12**) and catalytic hydrogenation of the ozonolized products over 10% palladium-charcoal gave the hydroxy-lactone (**19**), colorless prisms, mp 195—196° (15 %). The reduction of **19** with sodium borohydride in 50 % aqueous ethanol gave the unsaturated lactone (**20**) as an oil. Jones oxidation of **19** afforded the maleic anhydride derivative (**21**) as an oil. **21** was also obtained by autoxidation of **20** in air at room temperature. It was also found that when the reducing reagents were properly selected, desired products would be produced.

TABLE II

Starting material	Reductant	Product (%)
17	H_2, Pd–C	**19**; 15
17	aq. Na_2SO_3	**19**; 16
17	$NaBH_4$ in 50% EtOH–H_2O	**20**; 49
18	aq. Na_2SO_3	**19**; 25
18	$NaBH_4$ in 50% EtOH–H_2O	**20**; 48

The oily two compounds (**20**) and (**21**) have the molecular formula, $C_{16}H_{22}O_4$ and $C_{16}H_{20}O_5$ respectively, as determined by high-resolution mass spectroscopy. The infrared band of **20** at 1769 cm^{-1} may be ascribed to the α,β-unsaturated γ-lactone and the band at 1680 cm^{-1}, to the conjugated double bond. In the UV region, it has the absorption at λ_{max}^{EtOH} 215 nm (log ε=4.19). The NMR spectrum of **20** showed the signals due to two allylic protons adjacent to the lactone oxygen as a multiplet (δ 4.55—4.70) and no absorption was observed in the olefinic region. These spectroscopic properties are closely resembling to those of confertifolin (**22**)[9] and indicate the presence of α,β-disubstituted butenolide moiety, that is drim-8-en-11,12-olide structure. Jones oxidation product (**21**) was found to possess a maleic anhydride moiety by its IR spectrum [$\nu_{max}^{CCl_4}$ 1850, 1770 (anhydride carbonyl) and 1668 (conjugated olefinic linkage) cm^{-1}] and UV spectrum [λ_{max}^{EtOH} 251 nm (log ε=3.85)]. These spectroscopic properties are almost the same with those of winterin (**23**)[10] of known structure. Thus, the structure of **20** and **21** were unequivocally established.

As mentioned above, **19** afforded **20** on sodium borohydride reduction and **21** on Jones oxidation. Now that the structures of **20** and **21** were established, the structure of **19** was confirmed. Furthermore, closely resembling spectral data of **19** to those of valdiviolide (**24**)[10] supports this conclusion. In the NMR spectrum of **19**, there were observed two signals due to ester methyl in 3:2 ratio, which indicates that **19** is an epimeric mixture of hydroxyl group at 11-position.

It should be mentioned that 14-hydroxy-7-oxo ester (**25**)[11] was not cleaved under the same ozonolysis conditions as applied to **12** and **17**, while 14-methoxy ester (**26**)[8] afforded a complex mixture under the same conditions.

In conclusion, the direction of cleavage of the aromatic ring by means of ozonolysis is subtly affected by the substitution pattern of hydroxyl group in the aromatic ring. For instance, ozonolysis of the 12-hydroxyl ester (**12**) with an isopropyl group at 13-position

8) A. Tahara and H. Akita, *Chem. Pharm. Bull.* (Tokyo), **23**, 1976 (1975).
9) H.H. Appel, J.D. Connolly, K.H. Overton, and (in part) R.P.M. Bond, *J. Chem. Soc.*, **1960**, 4685.
10) H.H. Appel, R.P.M. Bond, and K.H. Overton, *Tetrahedron*, **19**, 635 (1963).
11) A. Tahara and H. Akita, *Chem. Pharm. Bull.* (Tokyo), **23**, 1984 (1975).

afforded pentanorlabdane type compounds, while ozonolysis of the 14-hydroxy ester (**17**) with an isopropyl group at 13-position and **18**[8] having no substituent on this position gave drimane type products. Both reaction products are considered to be useful intermediates for synthesis of natural labdane type diterpenoids and drimane type sesquiterpenoids. The experiments are bering continued in this direction.

Experimental[12]

Ozonolysis of Methyl 12-Hydroxy Dehydroabietate (12) to 8,8-Dihydroxy-(13→17)-pentanorlabd-9(11)-en-12,18-dioic Acid 18-Methyl Ester 8α→12-Lactone (13) and 8-Oxo-(13→17)-pentanorlabdan-12,18-dioic Acid 12,18-Dimethyl Ester (14)——Ozone was passed through a solution of **12** (5.000 g) in 100 ml of 1: 1 methanol–methylene chloride under dry ice-acetone cooling for 3 hr. The ozonolized products were hydrogenated at ordinary temperature and pressure over 10% Pd-C (1 g). After hydrogen absorption had ceased, the catalyst was filtered off and the filtrate was evaporated under reduced pressure. The resulting residue was dissolved in ether and washed with 10% KOH aq., sat. NaCl aq. and dried over Na_2SO_4. Removal of the solvent gave 1.754 g of an oil (neutral fraction), which was the complex mixture by means of gas–liquid chromatographic (GLC) analysis. The above alkaline washings were acidified with 10% HCl aq. and extracted with $CHCl_3$. The $CHCl_3$ extract was washed with sat. NaCl aq. and then dried over Na_2SO_4. Removal of $CHCl_3$ gave an oil, which was methylated with diazomethane–ether solution to give 3.368 g of a brown oil (acidic fraction). It was chromatographed on silica gel (100 g) to be separated into two fractions. The first fraction (1.051 g; 22% yield) eluted with petr. ether–ether (2: 1) was recrystallized from *n*-hexane to give **14** (835 mg), colorless prisms, mp 94.5—95°. *Anal.* Calcd. for $C_{17}H_{26}O_5$: C, 65.78; H, 8.44. Found: C, 65.83; H, 8.37. IR ν_{max}^{KBr} cm^{-1}: 1740, 1725, 1715. NMR δ: 0.74 (3H, s; 10-Me), 1.18 (3H, s; 4-Me), 3.62, 3.68 (each 3H, s; 4-COOMe, 9-CH_2COOMe). The first fraction (**14**) was identical (mixed mp 94—95°, IR, NMR, and GLC) to the authentic sample (**14**) prepared from levopimaric acid (**16**) in the same manner as described by Pelletier.[7] The second fraction eluted with ether was recrystallized from ethyl acetate–*n*-hexane to give **13** (618 mg; 14% yield), colorless needles, mp 187—190°. *Anal.* Calcd. for $C_{16}H_{22}O_5$: C, 65.29; H, 7.53. Found: C, 65.51; H, 7.61. IR ν_{max}^{KBr} cm^{-1}: 3400, 1750, 1716, 1645. NMR δ: 1.23 (3H, s; 4-Me), 1.33 (3H, s; 10-Me), 3.67 (3H, s; COOMe), 4.63—4.83 (4.73) (1H, br.s, $W_{h/2}$=5 Hz; 8-OH), 5.58 (1H, s; 11-H), UV λ_{max}^{EtOH} nm (log ε): 209 (4.09).

Conversion of 13 by Means of Catalytic Hydrogenation and the Subsequent Methylation to 14——A solution of **13** (607 mg) in MeOH (20 ml) was hydrogenated at ordinary temperature and pressure over 10% Pd-C (300 mg). After hydrogen absorption had ceased, the catalyst was filtered off and the filtrate was evaporated. The resulting residue was methylated with diazomethane–ether solution to give an oil, which was recrystallized from *n*-hexane to afford **14** (551 mg). It was identical (mixed mp 94—95°, IR, NMR, and GLC) to the authentic sample (**14**).

Reduction of 13 with Sodium Borohydride to 8α-Hydroxy-(13→17)-pentanorlabd-9(11)-en-12,18-dioic Acid 18-Methyl Ester 8α→12-Lactone (15)——An ice-cooled solution of **13** (150 mg) and $NaBH_4$ (200 mg) in 50% (v/v) EtOH–H_2O (5 ml) was stirred for 30 min. The reaction mixture was diluted with H_2O and extracted with ether. The extract was washed with sat. NaCl aq. and then dried over Na_2SO_4. Removal of the solvent gave crystals, which were recrystallized from ethyl acetate–*n*-hexane to give **15** (119 mg), colorless prisms, mp 153.5—155°. *Anal.* Calcd. for $C_{16}H_{22}O_4$: C, 69.04; H, 7.97. Found: C, 69.04; H, 7.87. IR λ_{max}^{KBr} cm^{-1}: 1750, 1720, 1640. NMR δ: 1.20 (3H, s; 4-Me), 1.25 (3H, s; 10-Me), 3.62 (3H, s; COOMe), 4.85 (1H, octet, J=1.5, 7.2, 9.6 Hz; 8-βH), 5.49 (1H, d, J=1.5 Hz; 11-H). NOE (100 MHz): Irradiation at δ 1.25 increased the area of peak due to 8-H by 10.4%. UV λ_{max}^{EtOH} nm (log ε): 209 (4.09).

Ozonolysis of 12 and the Subsequent Reduction with Another Reductant to 13 or 14 or 15——1) Sodium Sulfite Reduction: A solution of above ozonolized products (from **12** (1.000 g)) and Na_2SO_3 (2 g) in H_2O (40 ml) was stirred for 12 hr at room temperature. The reaction mixture was acidified with 10% HCl aq. and extracted with $CHCl_3$. The extract was washed with sat. NaCl aq. and then dried over Na_2SO_4. Removal of $CHCl_3$ gave 962 mg of an oil, which was chromatographed on silica gel (30 g) by ether elution to give an oil. It was recrystallized from ethyl acetate–*n*-hexane to afford **13** (180 mg; 20% yield), which was identical (mixed mp 186—190°, IR, and NMR) to the authentic sample (**13**).

2) Zinc in Acetic Acid Reduction: A mixture of above ozonolized products (from **12** (1.000 g)) and Zn dust (10 g) in AcOH (20 ml) was stirred for 2.5 hr at room temperature. The precipitate was filtered off and the filtrate was evaporated under reduced pressure. The resulting residue was treated as in the case of ozonolysis of **12** and the subsequent catalytic hydrogenation. Ether extract (274 mg; neutral fraction)

12) All melting points were measured on the Kofler block and were uncorrected. NMR spectra were measured (δ) at 60 MHz in $CDCl_3$ *vs.* Me_4Si as internal reference. High-resolution mass spectra were taken with JMS-01SG spectrometer. GLC was measured under the column condition (2 m×4 mm, 1.5% OV-17 on Shimalite W (80—100 mesh)).

was the complex mixture by means of GLC analysis. $CHCl_3$ extract (702 mg; acidic fraction) was chromatographed on silica gel (50 g) by petr. ether–ether (2: 1) to give **14** (465 mg; 50% yield). It was recrystallized from *n*-hexane to afford the colorless prism **14** (397 mg), which was identical (mixed mp 92—93.5°, IR, NMR, and GLC) to the authentic sample (**14**).

3) Sodium Borohydride Reduction: A solution of above ozonolized products (from **12** (1.000 g)) and $NaBH_4$ (800 mg) in 50% (v/v) EtOH–H_2O (10 ml) was stirred for 30 min at room temperature. The reaction mixture was treated as in the case of reduction of **13** with $NaBH_4$ to give 808 mg of an oil, which was recrystallized from ethyl acetate–*n*-hexane to give **15** (546 mg; 65% yield). It was identical (mixed mp 152—154°, IR, NMR, and GLC) to the authentic sample (**15**).

Ozonolysis of Methyl 14-Hydroxy Dehydroabietate (17) to 11,11-Dihydroxy-drim-8-en-12,13-dioic Acid 13-Methyl Ester 11→12-Lactone (19)——Ozone was passed through a solution of **17** (2.009 g) in 40 ml of 1: 1 methanol–methylene chloride under dry ice-acetone cooling for 3 hr. After the ozonolized products were hydrogenated at ordinary temperature and pressure over 10% Pd-C (700 mg), the reaction mixture was treated as in the case of ozonolysis of **12** and the subsequent catalytic hydrogenation. Ether extract (594 mg; neutral fraction) was the complex mixture by means of GLC analysis. $CHCl_3$ extract (1.243 g; acidic fraction) was chromatographed on silica gel (80 g) by ether elution to give an oil, which was recrystallized from ether–*n*-hexane to afford **19** (271 mg; 15% yield), colorless prisms, mp 195—196°. *Anal.* Calcd. for $C_{16}H_{22}O_5$: C, 65.29; H, 7.53. Found: C, 65.37; H, 7.41. IR ν_{max}^{KBr} cm^{-1}: 3430, 1767, 1705. NMR (100 MHz)[13] δ: 1.22, 1.26 (each 3H, s; 4-, 10-Me), 1.26, 1.30 (each 3H, s; 4-, 10-Me), 3.69, 3.70 (each 3H, s; COOMe), 5.24, 5.26 (each 1H, br. s; 11-OH, disappeared with D_2O), 6.12, 6.16 (each 1H, br. s; 11-H). UV λ_{max}^{EtOH} nm (log ε): 208 (4.34).

Reduction of 19 with Sodium Borohydride to 11-Hydroxy-drim-8-en-12,13-dioic Acid 13-Methyl Ester 11→12-Lactone (20)——An ice-cooled solution of **19** (179 mg) and $NaBH_4$ (200 mg) in 50% (v/v) EtOH–H_2O (5 ml) was stirred for 30 min. The reaction mixture was treated as in the case of reduction of **13** with $NaBH_4$ to give **20** (100 mg), a homogeneous oil. *Anal.* High-resolution mass spectrum. Calcd. for $C_{16}H_{22}O_4$ (M^+; *m/e*): 278.1517. Found: 278.1514. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1769, 1732, 1680. NMR δ: 1.20, 1.26 (each 3H, s, 4-, 10-Me), 3.63 (3H, s; COOMe), 4.60—4.75 (2H, m; 11-H_2). UV λ_{max}^{EtOH} nm (log ε): 215 (4.19).

Oxidation of 19 with Jones Reagent to Drim-8-en-11,12,13-trioic Acid 13-Methyl Ester 11,12-dioic Acid Anhydride (21)——A mxiture of **19** (150 mg) and Jones reagent (0.5 ml) in acetone (10 ml) was stirred for 15 min at room temperature. After MeOH (2 ml) was added and stirred for 15 min, the reaction mixture was evaporated. The resulting residue was diluted with H_2O and extracted with ether. The ether extract was washed with sat. NaCl aq. and dried over Na_2SO_4. Removal of the solvent gave 139 mg of an oil, which was chromatographed on silica gel (15 g) by petr. ether–ether (4: 1) elution to give **21** (87 mg), a homogeneous oil. *Anal.* High-resolution mass spectrum. Calcd. for $C_{16}H_{20}O_5$ (M^+; *m/e*): 292.1310. Found: 292.1342. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1850, 1770, 1730, 1688. NMR δ: 1.24 (6H, s; 4-, 10-Me), 2.32—2.62 (2H, m; 7-H_2), 3.65 (3H, s; COOMe). UV λ_{max}^{EtOH} nm (log ε): 251 (3.85).

Autoxidation of 20 to 21——After **20** (779 mg) was left standing for 90 days at room temperature, the mixture was chromatographed on silica gel (50 g) by petr. ether–ether (4: 1) elution to give **21** (48 mg). It was identical (IR, NMR, and GLC) to the authentic sample (**21**).

Ozonolysis of 17 and the Subsequent Reduction with Another Reductant to 19 or 20——1) Sodium Sulfite Reduction: A solution of above ozonolized products (from **17** (1.144 g)) and Na_2SO_3 (4 g) in H_2O (80 ml) was stirred for 2 hr at room temperature. The reaction mixture was treated as in the case of ozonolysis of **12** and the subsequent reduction with Na_2SO_3 aq. to give 952 mg of an oil, which was chromatographed on silica gel (50 g) by ether elution to give an oil. It was recrystallized from ether–*n*-hexane to give **19** (168 mg; 16% yield), which was identical (IR and NMR) to the authentic sample (**19**).

2) Sodium Borohydride Reduction: A solution of above ozonolized products (from **17** (1.087 g)) and $NaBH_4$ (800 mg) in 50% (v/v) EtOH–H_2O (10 ml) was stirred for 30 min at room temperature. The reaction mixture was treated as in the case of reduction of **13** with $NaBH_4$ to give 787 mg of an oil, which was chromatographed on silica gel (50 g) by petr. ether–ether (2: 1) elution to give **20** (446 mg; 49% yield). It was identical (IR, NMR, and GLC) to the authentic sample (**20**).

Ozonolysis of Methyl 14-Hydroxy Deisopropyldehydroabietate (18) and the Subsequent Reduction to 19 or 20——1) Sodium Sulfite Reduction: Ozone was passed through a solution of **18** (500 mg) in 10 ml of 1: 1 methanol-methylene chloride under dry ice-acetone cooling for 2 hr. A solution of the ozonolized products and Na_2SO_3 (2 g) in H_2O (40 ml) was stirred for 2 hr at room temperature. The reaction mixture was treated as in the case of ozonolysis of **12** and the subsequent reduction with Na_2SO_3 aq. to give 484 mg of an oil, which was chromatographed on silica gel (30 g) by petr. ether–ether (1: 1) elution to give an oil. It was recrystallized from ether–*n*-hexane to afford **19** (127 mg; 25% yield), which was identical (IR and NMR) to the authentic sample (**19**).

2) Sodium Borohydride Reduction: A solution of above ozonolized products (from **18** (500 mg)) and $NaBH_4$ (400 mg) in 50% (v/v) EtOH–H_2O (5 ml) was stirred for 30 min at room temperature. The reaction

13) As **19** is a mixture of stereoisomers with respect to the 11-hydroxyl group in 3: 2 ratio, each chemical shift is given.

mixture was treated as in the case of reduction of **13** with $NaBH_4$ to give 300 mg of an oil, which was chromatographed on silica gel (30 g) by petr. ether–ether (2: 1) elution to afford **20** (233 mg; 48% yield). It was identical (IR, NMR, and GLC) to the authentic sample (**20**).

Attempted Ozonolysis of Methyl 14-Hydroxy-7-oxo Deisopropropyldehydroabietate (**25**)——Ozone was passed through a solution of **25** (685 mg) in 14 ml of 1: 1 methanol–methylene chloride under dry ice-acetone cooling for 1 hr. The ozonolized products were hydrogenated at ordinary temperature and pressure over 10% Pd-C (200 mg). After hydrogen absorption had ceased, the catalyst was filtered off and the filtrate was evaporated under reduced pressure to give an oil. It was recrystallized from MeOH to give the colorless prisms (**18**), which was identical (IR, NMR, and GLC) to the authentic sample (**18**).

Attempted Ozonolysis of Methyl 14-Methoxy Deisopyldehydroabietate (**26**)——Ozone was passed through a solution of **26** (813 mg) in 18 ml of 1: 1 methanol–methylene chloride under dry ice-acetone cooling for 2 hr. A solution of the ozonolized products and $NaBH_4$ (800 mg) in 50% (v/v) EtOH–H_2O (10 ml) was stirred for 30 min at room temperature. The reaction mixture was treated as in the case of **13** with $NaBH_4$ to give an oil, which was a complex mixture by means of GLC and was not purified by silica gel chromatography.

Acknowledgement One of the authors (H.A.) wishes to thank Dr. T. Oishi, Chief of Laboratory of this Institute, for his helpful suggestions in preparation and critical reading of the manuscript.