[Chem. Pharm. Bull. 24(4) 705—715 (1976)]

UDC 547.914.2.04 : 547.292-931.04

Diterpenoids. XL. Acid Catalyzed Rearrangement of Dehydroabietic Acid Derivatives[1]

Tomihiko Ohsawa,[2] Hiromitsu Mizuno,[2a] Toshio Takizawa,[2b] Masayoshi Itoh, Shigeo Saito,[2c] and Akira Tahara (the late)

Rikagaku Kenkyusho (The Institute of Physical and Chemical Research)[3]

(Received July 4, 1975)

Acid treatment in acetic anhydride of blocked cyclohexadienone derivatives (**6a**) and (**6b**) obtained from *l*-abietic acid (**1**) gave **14** and **16**, respectively, through Wagner-Meerwein rearrangement of the angular methyl group. On the other hand, under similar conditions, **6c** and **6d** were transformed into **18** and **20**, respectively, as the result of an abnormal dienone phenol rearrangement, namely, aromatization of the B-ring with concomitant cleavage of C–C bond.

In the study of the conversion of *l*-abietic acid (**1**) from pine rosin into diterpene alkaloids,[4] autoxidation of styrene derivative (**3**) of **1** to phenacylidene compound[5] (**4**) was observed.[6] The product with vinylogous 1,3-ketol system, gave a naphthoic compound (**5**) smoothly and quantitatively under a weakly basic condition as the result of aromatization of dienone system accompanied by C-C bond cleavage to eliminate formaldehyde moiety as is shown in Chart 1.

This phenomenon stimulated the authors' interest in the study of the reactivity, for example, the aromatization aptitude, of the phenacylidene system of dehydroabietic acid derivatives.

Phenacylidene derivatives of dehydroabietic acid (**2**) with an angular methyl group in place of hydroxy methyl group at C_{10} position would be blocked to realize an aromatic ring through a dienone phenol rearrangement. The situation resembles what was experienced by Huffman.[7] In their study of blocked dienone system, compound (**8**) was chosen as a model of a blocked cyclohexadienone system and treated with sulfuric acid in acetic anhydride, or polyphosphoric acid, to be recovered unchanged.

In order to examine the possibility of migration or, if any, the migratory aptitude of the bonds in the possible intermediate (**7**) generated from phenacylidene compounds by the enolization of the enone system under an acidic condition, **6a**, **6b**, **6c**, and **6d** were synthesized from dehydroabietic acid (**2**) and were treated with acids in acetic anhydride. Variation of the substituent at C_4 and the configuration of the angular methyl group at C_{10} should affect the fate of the intermediate carbonium ion at C_5.

1) Previous communications: A. Tahara, H. Mizuno, and T. Ohsawa, *Chemistry Letters*, **1972**, 1163; A. Tahara, H. Akita, T. Takizawa, and H. Mizuno, *Tetrahedron Letters*, **1974**, 2837; Part XXXIX: A. Tahara, Y. Harigaya, and M. Onda, *Chem. Pharm. Bull.* (Tokyo), **24**, 427 (1976).

2) To whom inquiries regarding this paper should be addressed. Present address: *a*) *Nichiban Co. Ltd., Hidaka-cho, Iruma-gun, Saitama*; *b*) *Meiji Seika Co. Ltd., Horikawa, Saiwai-ku, Kawasaki-shi, Kanagawa*; *c*) *Showa Kobunshi Co. Ltd., Ikegami, Ohta-ku, Tokyo.*

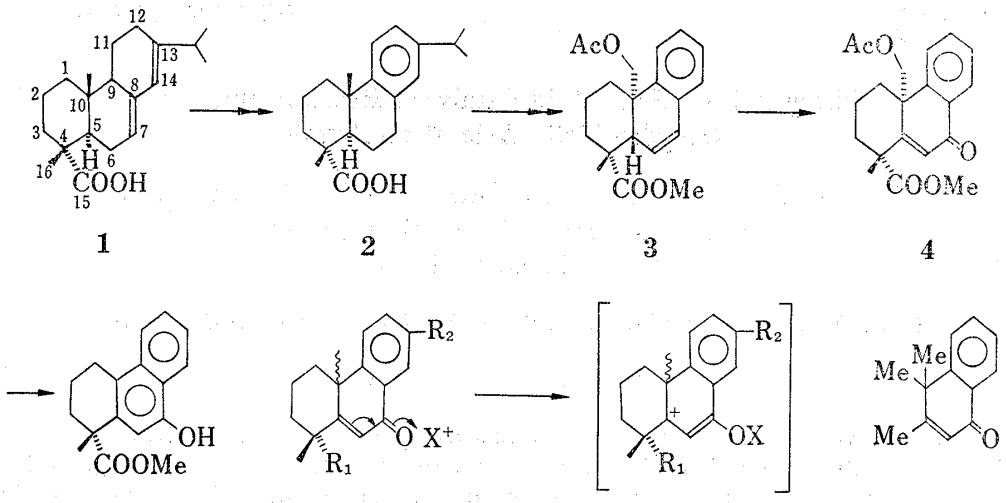
3) Location: *Hirosawa, Wako-shi, Saitama.*

4) A. Tahara, K. Hirao, and Y. Hamazaki, *Tetrahedron*, **21**, 2133 (1965); *idem*, *Chem. Ind.*, **1965**, 850; *idem*, *Chem. Pharm. Bull.* (Tokyo), **15**, 1785 (1967); A. Tahara and K. Hirao, *Tetrahedron Letters*, **1966**, 1453; *idem*, *Chem. Pharm. Bull.* (Tokyo), **15**, 1934 (1967).

5) In the previous communications, the term "benzonilidene" was used for phenyl vinyl ketone, or naphthalenone, system, but it will be replaced by "phenacylidene" from now on following the IUPAC rule of nomenclature.

6) T. Ohsawa, M. Kawahara, and A. Tahara, *Chem. Pharm. Bull.* (Tokyo), **21**, 487 (1973).

7) J.W. Huffman and T.W. Bethea, *J. Org. Chem.*, **30**, 2956 (1965).

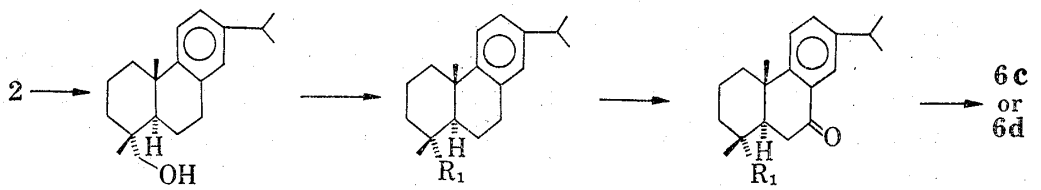


1 2 3 4

5 7 8

6a: R_1=COOMe, R_2=iso-Pr, $C_{10}\beta$·Me
6b: R_1=COOMe, R_2=H, $C_{10}\alpha$·Me
6c: R_1=Me, R_2=iso-Pr, $C_{10}\beta$·Me
6d: R_1=CH_2OAc, R_2=iso-Pr, $C_{10}\beta$·Me

Chart 1



9

10: R_1=Me
11: R_1=CH_2OAc

12: R_1=Me
13: R_1=CH_2OAc

Chart 2

Among these four, C_4-methoxycarbonyl derivatives (**6a**) and (**6b**) were synthesized by the methods of Wenkert[8] and Ohta,[9] respectively.

As for **6c**, dehydroabietane (**10**)[10] was oxidized with chromium trioxide in aqueous acetic acid to the oxo compound (**12**) in 67% yield, which was recrystallized from methanol to colorless needles, mp 91—92°; IR cm^{-1}: 1678. Then **12** was dehydrogenated by refluxing with selenium dioxide in acetic acid to **6c** in 73% yield, which was recrystallized from *n*-hexane to colorless prisms, mp 50—53°; IR cm^{-1}: 1695. Similarly, 15-acetoxy derivative (**11**)[9] was oxidized to 7-oxo compound (**13**) as an oil in 65% yield; IR cm^{-1}: 1740, 1681. Successively it was dehydrogenated to **6d** as an oil in 46% yield; IR cm^{-1}; 1740, 1648.

As a condition for acid treatment of phenacylidene compounds, the most commonly employed, namely, acetic anhydride containing sulfuric acid was chosen.[11] First of all, **6a** was left standing at room temperature in 0.03% (v/v) sulfuric acid in acetic anhydride for 4 hr. After dilution with water followed by the ether extraction, column chromatography on silica gel gave the following two products: colorless oil in 64% yield, and colorless crystals in 24% yield which was recrystallized from methanol to colorless prisms, mp 86—87°. The structure for these products were determined as **14** and **15**, respectively, as the products

8) E. Wenkert, R.W.T. Carney, and C. Kaneko, *J. Am. Chem. Soc.*, **83**, 4440 (1961).
9) M. Ohta and L. Ohmori, *Pharm. Bull.* (Japan), **5**, 96 (1957).
10) The late A. Tahara, M. Shimagaki, S. Ohara, T. Tanaka, and T. Nakata, *Chem. Pharm. Bull.* (Tokyo), **23**, 2329 (1975).
11) (ed.) B.S. Thyagarajan, "Mechanisms of Molecular Migrations," Vol. 1, Interscience Publishers, New York, N.Y., p. 275.

resulting from Wagner-Meerwein rearrangement of C_{10}-angular methyl group to C_5 position as is shown in Chart 3. The former was hydrolysed to the latter in 88% or 70% yield by treating at room temperature with 12% potassium hydroxide in ethanol for 30 min, or 1.2% hydrochloric acid in ethanol for 2 hr, respectively.

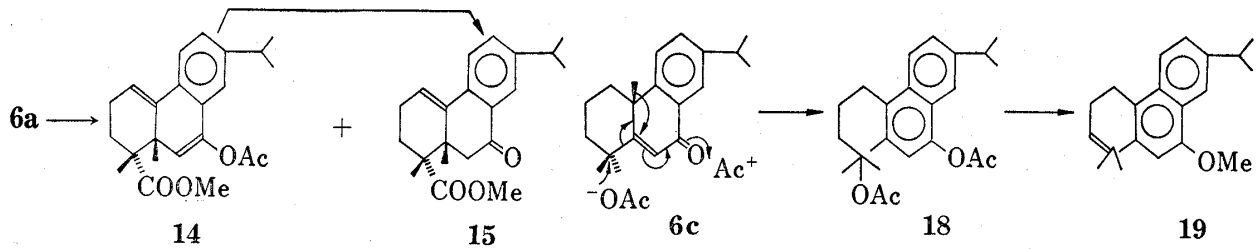
Other acids such as phosphoric acid or *p*-toluene sulfonic acid were found to be effective for the same rearrangement.

The structure of the enol acetate (**14**) and oxo ester (**15**) were determined as follows. The formation of the enol acetate group was confirmed by the molecular formula, $C_{23}H_{30}O_4$, obtained by the elemental analysis, by the appearance of the infrared (IR) absorption at 1776 cm^{-1} ascribable to an enol acetate group, and by the existence of an acetyl methyl signal at δ 2.25 in the nuclear magnetic resonance (NMR) spectrum. The IR absorption at 1721 cm^{-1} and a methyl signal at δ 3.55 in the NMR spectrum show the retention of the methoxycarbonyl group. Also the aromatic C-ring was unchanged, giving the signals of C_{14}-, C_{12}- and C_{11}–H at δ 6.76 (doublet, J=2 Hz), 6.95 (quartet, J=2 and 7 Hz) and 7.32 (doublet, J=7 Hz), respectively. These aromatic protons, as a whole, appear in the higher field than those of the starting compound (**6a**), because of the enolization of the carbonyl group that caused the paramagnetic shift by conjugating with aromatic ring. Especially, C_{14}–H, which appeared at δ 7.96 in **6a** is observed at δ 6.76 in **14**. This remarkable diamagnetic shift will be interpreted by the cancel of the paramagnetic effect of 7-carbonyl group. In the region of olefinic proton, a singlet (one proton) and a quartet (J=J'=4 Hz, one proton) are observed. As the former can be assigned to C_6–H on the enol acetate structure, the latter must be attached to a new olefinic bond and that tri-substituted olefin. All of these data are best explained by the enol acetate structure (**14**). That is, the enol acetylation of the phenacylidene carbonyl group was accompanied by the C_{10}-methyl migration to C_5, resulting in the formation of a tri-substituted olefin between C_1 and C_{10}. Moreover the fact that the hydrolysis of the enol acetate (**14**) to the corresponding oxo ester (**15**) wiped off the singlet at δ 5.68, leaving the quartet at δ 6.26, can be reasonably explained by these structures. The structure of the oxo ester (**15**) is characterized by the IR absorption at 1681 cm^{-1} ascribable to a benzylic carbonyl. The existence of an olefinic proton at C_1 position in **15**, therefore in **14**, is confirmed by the observation of the nuclear Overhauser effect. That is, the irradiation of C_{11}–H at δ 7.43 causes an increase of 20% of the intensity of the former. Thus the location of the olefinic proton at C_1 position is reasonable.

The second substrate, **6b**, for the acid treatment also has α-methoxycarbonyl group at C_4 position, but with α-angular methyl group at C_{10} position. Under a similar condition as above, compound **6b** was recovered unchanged even after a prolonged time (20 hr). So, the reaction temperature was elevated to 100°. After 5 hr the reaction mixture was treated in the same manner as before to give an oil product, which was submitted to column chromatography on silica gel. In the benzene–*n*-hexane (7: 3) eluate, the enol acetate (**16**) was obtained in 36% yield, which was recrystallized from aqueous methanol to give colorless needles, mp 111—112°. Its structure was determined by the comparison of the following physical data of it with that of the enol acetate (**14**): IR cm^{-1}: 1768, 1188; molecular formula $C_{20}H_{22}O_4$; NMR δ 2.25 (singlet, AcO), 5.94 (quartet, J=3 and 4 Hz, one proton), 6.08 (singlet, one proton). This enol acetate (**16**) was also hydrolysed to the corresponding oxo ester (**17**) quantitatively by treating with 12% potassium hydroxide in ethanol at room temperature for 30 min: IR cm^{-1}: 1730, 1691; molecular formula, $C_{18}H_{20}O_3$.

Thus, it was shown that two phenacylidene compounds with α-COOMe at C_4, irrespective of the configuration of the angular C_{10}-methyl group, give enol acetates with concomitant Wagner-Meerwein rearrangement of C_{10}-methyl group under the most common condition for dienone-phenol rearrangements, namely, treatment with acetic anhydride containing a little sulfuric acid.

On the other hand, the phenacylidene compound (**6c**) and (**6d**) with α-methyl or α-acetoxymethyl at C_4, respectively, turned out to be quite different from the former two phenacylidene



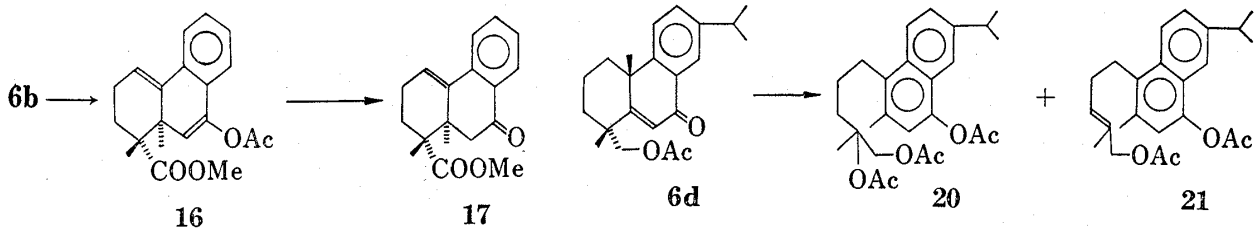


Chart 3

Chart 4

compounds in their reactivity. At first, the acid treatment of the compound (**6c**) in acetic anhydride containing 0.03% sulfuric acid was done at room temperature for 2 hr, but gas–liquid chromatography (GLC) tracing revealed more than one products and the pattern was simplified in less reaction time. So, the temperature of the reaction was lowered to 0° and after 2 hr, it was treated in the same manner as before. The resulting oil was chromatographed on silica gel column to afford a major product as an oil in 82% in the *n*-hexane–ether (10: 1) eluate. The feature of the IR spectrum resembles those of the former two enol acetates. A band at 1770 cm^{-1} ascribable to an enol acetate or phenol acetate and another at 1725 cm^{-1} ascribable to an ordinary ester are observed. However the molecular formula obtained by high resolution mass spectrometry is $C_{24}H_{32}O_4$, which means the addition of a molecule of acetic anhydride ($C_4H_6O_3$), in place of C_2H_2O moiety as in the previous cases, to the starting material. The NMR spectrum of it shows seven singlet methyl signals including the two at δ 1.87 and 2.37 ascribable to the introduced two acetyl methyls. This assignment was further supported by the disappearance of these signals during the hydrolysis-methylation reaction to be stated below. Another methyl signal at δ 2.45 is ascribable to an aromatic methyl group. In the region of the aromatic protons, C_{11}-, C_{12}- and C_{14}–H appeared at δ 7.92 (doublet, J=9 Hz), 7.39 (quartet, J=2 and 9 Hz) and 7.57 (doublet, J=2 Hz), respectively. Beside these signals, new additional singlet appeared with the intensity of a proton at δ 7.01, which can be reasonably interpreted only by assuming an additional aromatic ring in the molecule. Furthermore, the pattern of the following absorption maxima in the ultraviolet (UV) spectrum in ethanol suggests a naphthalene skeleton; nm (log ε): 285 (3.78), 314 (3.24), 322 (3.03) and 329 (3.32).

Conclusively, the structure (**18**) for this compound and the mechanism for the formation of it can be presumed as is shown in Chart 4. That is, the enone group in the B-ring of the starting compound (**6c**) is enol-acetylated with concomitant migration of C_{10}-methyl to C_5 position followed by the cleavage of C_4–C_5 bond to form an carbonium ion at C_4-carbon, which is attacked by an acetate ion. Thus, a naphthyl acetate derivative is formed as the result of an abnormal dienone-phenol rearrangement reaction. This structure satisfies all the physical data.

Moreover, hydrolysis-methylation reaction of **18** was carried out by refluxing with dimethyl sulfate and potassium carbonate in methyl ethyl ketone for 3 hr. The resulting oil product was chromatographed on silica gel column to give a major product (**19**) in 28% yield in the *n*-hexane–chloroform (5: 1) eluate. The methyl ether (**19**) is characterized by the molecular formula, $C_{21}H_{28}O$, obtained from the high resolution mass spectrometry, by the disappearance of the two acetyl methyl groups in the NMR spectrum and by the appearance of a new methoxy methyl signal at δ3.97, an olefinic proton as multiplet at δ5.28, two methyls of the isopropylidene

group at δ 1.59 and 1.71, and singlet aromatic C_6–H at δ 6.50. Furthermore, nuclear Overhauser effect was observed and supports the validity of the relative location of the methyl and methoxy *ortho* to C_6–H as in the structure (**19**). The irradiation of C_6–H at δ 6.50 caused an increase of the signal of C_5-methyl at δ 2.45 and the methoxy methyl at δ 3.97 by 25% and 27%, respectively.

Finally, acetoxymethyl derivative (**6d**) was treated in 0.2% (v/v) sulfuric acid in acetic anhydride at room temperature for 2 hr. The treatment in the same manner as the preceding experiments gave an oil, which was chromatographed on silica gel to give triacetate (**20**) as an oil in 10% yield in the early part of the *n*-hexane–ether (5: 1) eluate, and diacetate (**21**) as an oil in 27% yield in the later part of the same eluate. The former has a molecular formula $C_{26}H_{34}O_6$ determined by the elemental analysis and the high resolution mass spectrometry. This means the formal addition of a molecule of acetic anhydride ($C_4H_6O_3$) to the starting compound (**6d**). The IR spectrum reveals three carbonyls at 1765, 1740 and 1735 cm^{-1}. It is consistent with the addition of a molecule of acetic anhydride, therefore two carbonyl groups, to the remaining 15-acetoxy group. One of these three, the absorption at 1765 cm^{-1} is ascribable to a phenolic acetate. Thus, the same reaction as in the formation of **18** seems to occur in this case too. So, the structure for this product can be presumed to be **20**. This structure reasonably explains the following NMR data of it. Two methyl signals at δ 1.91 and 1.95 are ascribable to aliphatic acetoxy groups, and that at δ 2.44 to an aromatic C_5-methyl. The C_{15}-methylene signal appeared as broad singlet at δ 4.18, and aromatic C_6–H at δ 6.98 as singlet. Three protons at δ 7.35 (quartet, J=2 and 9 Hz), 7.54 (doublet, J=2 Hz) and 7.86 (doublet, J=9 Hz) are assigned to C_{12}-, C_{14}- and C_{11}–H respectively.

On the other hand, the elemental analysis and the high resolution mass spectrometry of the major product gave a molecular formula $C_{24}H_{30}O_4$ corresponding to a product from an elimination of a molecule of acetic acid from **20**. The IR spectrum supports this assumption, showing only one aliphatic acetoxyl group at 1735 cm^{-1} beside a phenolic acetoxyl group at 1765 cm^{-1}. In the NMR spectrum this phenolic acetoxyl methyl appears at δ 2.35 and another one is observed at δ 1.97, which is ascribable to C_{15}-acetoxy group considering two protons as a broad singlet at δ 4.35 assignable to the C_{15}-methylene. Thus the structure (**21**), formally resulting from the elimination of the C_4-acetoxy group and C_3–H of **20** is the most probable. Based on this structure, a methyl signal at δ 2.43, proton signals at δ 7.30 (quartet, J=2 and 9 Hz), 7.53 (doublet, J=2 Hz) and 7.87 (doublet, J=9 Hz) can be ascribed to C_5-methyl, C_{12}-, C_{14}- and C_{11}–H, respectively. The additional aromatic C_6–H as a singlet at δ 6.96 as in the previous case and a new olefinic proton as a quartet (J=6 and 9 Hz) at δ 5.53 are observed.

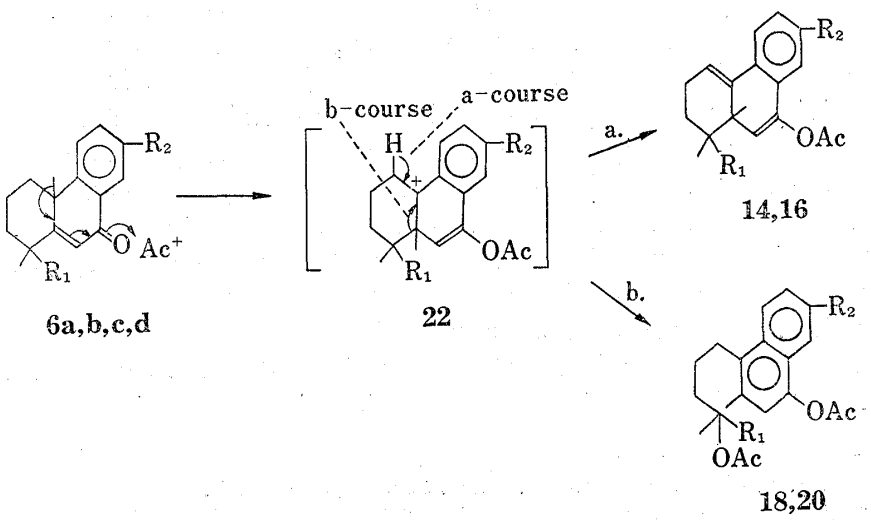


Chart 5

From the acid rearrangement reaction of the four phenacylidene derivatives of *l*-abietic acid, it is concluded that a pair of the phenacylidene (**6a**) and (**6b**), with α-methoxycarbonyl group at C_4 give the enol acetate (**14**) and (**16**) through a simple Wagner-Meerwein rearrangement of the angular methyl group at C_{10} to C_5, irrespective of its configuration, but on the contrary, another pair of the phenacylidene (**6c**) and (**6d**) with α-methyl or α-acetoxy methyl group at C_4 undergo a dienone-phenol type rearrangement with concomitant cleavage of the C_4–C_5 bond, in acetic anhydride containing a little sulfuric acid. However, both types of the rearrangement seem to share the common intermediate (**22**), resulting from the 1,2-shift of the angular methyl groups at C_{10} to C_5 induced by the enolization of the enone group. As for this first step of the reactions, strong preference was observed for the migration of the angular methyl at C_{10} over other five groups on the carbons (C_4, C_{10}) adjacent to the cationic center (C_5), irrespective of the configuration of the migrating methyl or type of the functionality at C_4. In this regard, the assistance of the π-electron of the aromatic C-ring for pushing the axial C_{10}-methyl and the stabilization of the cation at the benzylic C_{10} seems to be most responsible. At the second step, the fate of the intermediate cation (**22**) relies upon the character of the functionality at C_4 position. Strongly electron-withdrawing group, as methoxycarbonyl in **6a** and **6b**, will be unfavorable for the formation of a carbonium cation at C_4, and the reaction will take a-course to result in the elimination of C_1–H to **14** and **16**. On the other hand, a methyl or an acetoxy-methyl group at C_4 will be favorable or not too unfavorable and it will take b-course, to accept an acetate anion at C_4 to give **18** and **20**, or to form an olefinic bond between C_3 and C_4 as in **21**. This is, so far, the most probable explanation for this remarkable contrast.

Afterward it was disclosed that this Wagner-Meerwein rearrangement observed on **6a** and **6b** could be reversed by treating the rearrangement product from the above compounds in concentrated sulfuric acid at room temperature as in the reported conversion of pimaric acid and isopimaric acid into abietic acid.[12] The rearrangement product (**14**) and (**15**) were dissolved in concentrated sulfuric acid and left standing at room temperature for 6 or 2 hr, respectively, followed by dilution with ice water and extraction with ether. From the ethereal extract the phenacylidene compound (**6a**) was obtained almost quantitatively in both cases. The identification was done by GLC, IR and NMR spectra. Furthermore, 2,4-dinitrophenylhydrazone of the obtained phenacylidene compound was synthesized and recrystallized from aqueous ethanol to give yellow needles, mp 155—156°. This sample did not depress the melting point of the authentic 2,4-dinitrophenylhydrazone of **6a**. In the same manner, **16** and **17** were transformed into **6b** in 75% yield in concentrated sulfuric acid at room temperature for 2 hr.

This reversed methyl migration reaction of **14** and **15** was tried by using neat boron trifluoride ether complex as acid at room temperature, but the starting material was recovered unchanged. Lewis acid itself without proton or co-catalyst might be ineffective for this reaction. The inactivity of pure anhydrous Lewis acid in certain Friedel-Crafts reaction, polymerization, isomerization and disproportionation, and the necessity of co-catalysts are reported.[13] Thus, above enol acetate (**14**) was treated with 10% (v/v) boron trifluoride ether complex in methanol at room temperature for 4 hr, to recover the enol acetate unchanged. Nevertheless, when the concentration of boron trifluoride ether complex was raised to 91%, the resulting product was found to be composed of the oxo ester (**15**) and the phenacylidene compound (**6a**) in a ratio of 6.3: 1 (GLC). Furthermore, boron trifluoride ether complex containing a little lithium chloride could transform **15** to a mixture of **15** and **6a** in a ratio of 3: 1 (GLC) at room temperature for 24 hr. When **15** was left in 50% boron trifluoride acetic acid complex in acetic acid

12) E. Wenkert and J.W. Chamberlin, *J. Am. Chem. Soc.*, **81**, 688 (1959).
13) G.A. Olah, "Friedel-Crafts and Related Reactions," Vol. 1, Interscience Publishers, Inc., New York, 1963—1964, p. 205.

at room temperature for 24 hr, the reaction mixture contained **15** and **6a** in a ratio of 1:2. Finally quantitative conversion of **15** to **6a** was successfully carried out by treating it in neat boron trifluoride acetic acid complex at room temperature for 24 hr.

This reversed methyl migration by cationic species stimulated the authors' interest in the synthesis of 1,10-epoxy derivative of **15** and opening of this epoxy ring to produce a cation at C_{10} position to induce the migration of C_5-methyl backward to the original C_{10} position. It would form an introduction reaction of a hydroxy group into the A-ring of abietic acid skeleton.

Thus **15** was treated with N-bromosuccinimide in pyridine containing water at room temperature for 12 hr. After the treatment in the usual manner, crude crystal of the epoxide (**23**) was obtained in 65% yield, which was recrystallized from *n*-hexane to give colorless crystals, mp 166.5—178°. The configuration of this epoxide ring is not determined unambiguously yet, but α configuration seems to be more reasonable. If β, therefore *cis* A/B ring juncture, the methyl of the methoxycarbonyl group will be under the aromatic C-ring. It means a diamagnetic shift of the signal of this methyl in its NMR spectrum from the average value of δ 3.6—3.7 to the higher field around δ 3.3 or higher. Nevertheless, this is not the case.

The attempted rearrangement of this epoxide with several acid under anhydrous conditions, such as boron trifluoride ether complex, aluminum chloride, concentrated sulfuric acid, *p*-toluenesulfonic acid, polyphosphoric acid or formic acid was totally unsuccessful and the epoxide was recovered unchanged. When **23** was refluxed with 47% hydrobromic acid in methanol for 80 min, colorless prisms of hydroxy lactone (**25**) were obtained almost quantitatively, which were recrystallized from carbon tetrachloride to give a melting point of 181—184° and IR absorptions at 3590 and 3480 cm^{-1} (OH), at 1783 cm^{-1} (γ-lactone) and at 1688 cm^{-1} (benzylic carbonyl). The configuration of the hydroxy group was determined as α in comparison with the isomeric lactone as will be mentioned in the following section.

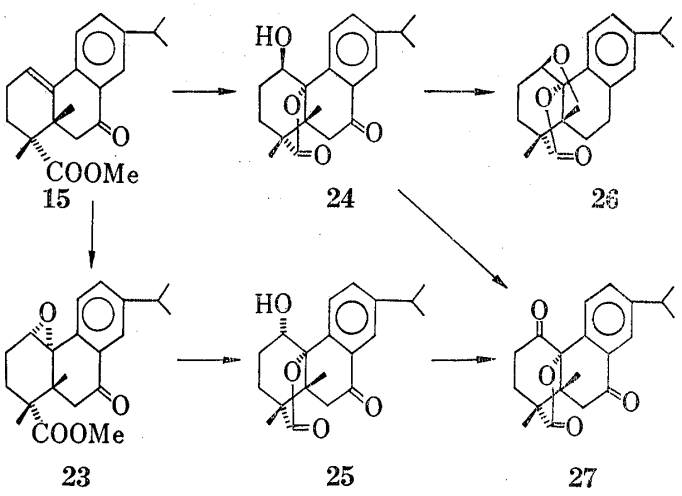


Chart 6

On the other hand, when **15** was treated with 13% peracetic acid in acetic acid at room temperature for 15 hr, colorless crystals of the isomeric hydroxy lactone (**24**) were obtained in 85% yield, which were recrystallized from aqueous methanol to give a melting point of 230—231.5° and the IR absorptions at 3550—3600 cm^{-1} (OH), 1785 cm^{-1} (γ-lactone) and 1695 cm^{-1} (benzylic carbonyl).

These two hydroxy lactones are isomeric each other concerning the configuration of the hydroxy group, as both were oxidized to the same keto lactone (**27**), colorless needles, mp 159—161°, by chromic acid oxidation. The assignment of the configuration of the hydroxy group was done by their NMR spectra. The half-height band width of the signal of C_1–H at the foot of the epoxy ring in the former compound (**25**) and the latter (**24**) are 18 and 8 Hz, respectively. As the A-ring of each compound will assume chair form, the half-height band width of the equatorial proton on the A-ring will be less broad than that of the axial proton.[14]

14) Y. Kawazoe, Y. Sato, T. Okamoto, and K. Tsuda, *Chem. Pharm. Bull.* (Tokyo), **11**, 328 (1963).

Therefore **25** should have an axial, β-C_1–H and **24**, equatorial, α-C_1–H. In other words, **25** has α-hydroxy and **24** has β-hydroxy group.

The same conclusion was drawn from the examination of the chemical shift of C_{11}–H. In **24**, it appeared at δ 7.63 and in **25**, at δ 8.57. This big shift, 0.94 ppm, can be best explained as follows. In the latter, equatorial hydroxy at C_1 position is sterically so close to C_{11}–H and its anisotropic effect causes the diamagnetic shift of 0.94 ppm,[15] while in the former, this situation does not exist.

The assignment of β-hydroxy in **24** is consistent with the following reactivity of it. When **24** in absolute benzene was irradiated by a low pressure mercury lamp with lead tetraacetate and iodine in nitrogen atmosphere at 40° for 8 hr, followed by the usual treatment, an oil was obtained, which was chromatographed on neutral alumina to give colorless prisms of the ether compound (**26**) in 18% in the pet. ether–ether (10: 1) eluate. Repetition of the recrystallization from aqueous methanol gave a melting point of 193—194° and IR absorptions at 1798 cm^{-1} (γ-lactone) and 1699 cm^{-1} (benzylic carbonyl). In the NMR spectrum of it, only one methyl signal was observed at δ 1.11 beside the isopropyl methyls, and another one disappeared. Instead a new signal ascribable to a methylene group was observed at δ 4.16 and 5.60 as an AB type doublet (J=10 Hz). This time, C_1–H appeared at δ 4.54 as multiplet.

Alternatively, this photo-product (**26**) can be synthesized thermally by refluxing with mercuric oxide and iodine in carbon tetrachloride for 19.5 hr, followed by the treatment in the usual manner. The resulting resinous product was submitted to a preparative thin-layer chromatography on a silica gel plate using ethyl acetate and benzene (1: 6) mixture as the developer to give **26** in 55% yield.

The formation of the ether bridge supports the validity of the location of the hydroxy and C_5-methyl group in the 1,3-diaxial relation.

Thus, the attempted rearrangement reaction of the epoxide **15** to the 1-hydroxy derivative, as one approach to a method of the introduction of a functional group into the abietane skeleton, was unsuccessful.[16]

Experimental[17]

13-Isopropyl-5α,10β-podocarp-8,11,13-trien-7-one (12)——A solution of CrO_3 (43 g) in H_2O (34 ml) was added to a solution of dehydroabietane (32.4 g) in AcOH (2.7 liter) and the mixture was diluted with AcOH (1.2 liter) and left standing at room temperature for 15 hr. Work-up in the usual manner gave 26.7 g of **12** in 67% yield after crystallization from MeOH. It was further recrystallized to give colorless needles, mp 91—92°. *Anal.* Calcd. for $C_{20}H_{28}O$: C, 84.44; H, 9.94. Found: C, 84.45; H, 9.92. IR cm^{-1}: 1678. NMR δ: 0.98 and 1.04 (s, 2×4-Me), 1.24 (s, 10-Me), 7.23 (br. s, 11- and 12-H), 7.76 (d, J=1 Hz, 14-H).

13-Isopropyl-10β-podocarp-5,8,11,13-tetraen-7-one (6c)——Compound (**12**) (11 g) was refluxed with SeO_2 (6.6 g) in AcOH (275 ml) for 1 hr. The precipitate was filtered off and the solvent was removed. The resulting residue was extracted with ether and the ethereal solution was washed successively with H_2O, 10% KOH aq. and satd. NaCl aq. Work-up in the usual manner gave 9.3 g of an oil product, which was chromatographed on basic alumina (500 g) to give 7.95 g of **6c** in 73% yield in the *n*-hexane–$CHCl_3$ (5: 1) eluate. Recrystallization from *n*-hexane gave colorless prisms, mp 50—53°. *Anal.* Calcd. for $C_{20}H_{26}O$: C, 85.05; H, 9.28. Found: C, 85.34; H, 9.02. IR cm^{-1}: 1695. NMR δ: 1.27 and 1.34 (s, 2×4-Me), 1.52 (s, 10-Me), 6.45 (s, 6-H), 7.32 (br. s, 11- and 12-H), 7.84 (br. s, 14-H).

15) Y. Kawazoe, Y. Sato, M. Natsume, H. Hasegawa, T. Okamoto, and K. Tsuda, *Chem. Pharm. Bull.* (Tokyo), **10**, 338 (1962); T. Okamoto and Y. Kawazoe, *ibid.*, **11**, 643 (1963).

16) A. Tahara and H. Mizuno, *Tetrahedron Letters*, **1974**, 523.

17) All melting points were measured on a Kofler type block and were not corrected. NMR spectra were measured at 60 MHz in CCl_4 *vs.* Me_4Si as an internal standard unless stated otherwise and coupling patterns, singlet, broad singlet, doublet, triplet and quartet were abbreviated as "s", "br. s", "d", "t" and "q", respectively. The symbol "Δw 1/2" is used for half-height band width. The signals described were limited to those which were significant in each discussion. IR spectra were measured usually in CCl_4. GLC was carried out under the condition: 1.5% OV-17 on Shimalite-W, 80—100 mesh, ϕ 4 mm×2 m at various temperature.

15-Acetoxy-13-isopropyl-5α,10β-podocarp-8,11,13-trien-7-one (13)——A solution of CrO_3 (68.4 g) in H_2O (60 ml) was added to a solution of **11** (38 g) in AcOH (3.04 liter) and after dilution with AcOH (1.33 liter), the mixture was left standing at room temperature for 15 hr. The residue obtained from the work-up in the usual manner was extracted with ether. From the ethereal extract, 3.2 g of an oil was obtained, which was chromatographed on silica gel (500 g) to give 26 g of **13** in 65% yield. *Anal.* Calcd. for $C_{22}H_{30}O_3$: C, 77.15; H, 8.83. Found: C, 77.43; H, 8.94. IR cm^{-1}: 1740, 1681, 1220. NMR δ: 1.04 (s, 4-Me), 1.26 (s, 10-Me), 1.98 (s, 15-OAc), 3.75 (s, 4-CH_2O-), 7.24 (br. s, 11- and 12-H), 7.76 (br. s, 14-H).

15-Acetoxy-13-isopropyl-10β-podocarp-5,8,11,13-tetraen-7-one (6d)——Compound **(13)** (1.0 g) was refluxed with SeO_2 (1.0 g) in AcOH (60 ml) for 1 hr. Work-up in the usual manner gave 550 mg of an oil, which was chromatographed on silica gel (30 g) to give 456 mg of **6d** as an oil in 46% yield. *Anal.* Calcd. for $C_{22}H_{28}O_3$: C, 77.61; H, 8.29. Found: C, 77.13; H, 8.22. IR cm^{-1}; 1740, 1648, 1220. NMR δ: 1.34 (s, 4-Me), 1.53 (s, 10-Me), 2.01 (s, 15-OAc), 4.04 and 4.11 (s, each, inner two of AB-d.d., CH_2-OAc), 6.28 (s, 6-H), 7.24 (br. s, 11- and 12-H), 7.87 (br. s, 14-H).

Rearrangement of Methyl 13-Isopropyl-7-oxo-10β-podocarp-5,8,11,13-tetraen-15-oate (6a) to the Enol Acetate (14) and the Oxo Ester (15)——i) Reaction with Ac_2O/H_2SO_4: To a solution of **6a** (250 mg) in Ac_2O (30 ml), 0.5% H_2SO_4/Ac_2O (2 ml) was added and the mixture was left standing at room temperature for 4 hr. After the reaction mixture was poured into ice water containing $NaHCO_3$, it was extracted with ether. Work-up in the usual manner gave an oil (320 mg), which was chromatographed on silica gel (15 g) to give 250 mg of **14** as an oil in 64% yield in the benzene-$CHCl_3$ (7: 3) eluate. *Anal.* Calcd. for $C_{23}H_{30}O_4$: C, 74.97; H, 7.66. Found: C, 74.54; H, 7.52. IR cm^{-1}: 1766, 1721, 1188. NMR δ: 2.25 (s, 7-OAc), 3.55 (s, 4-COOMe), 5.68 (s, 6-H), 5.99 (q, J=4 and 4 Hz, 1-H), 6.76 (d, J=2 Hz, 14-H), 6.95 (q, J=2 and 7 Hz, 12-H), 7.32 (d, J=7 Hz, 11-H).

And in the later part of the same eluate 85 mg of **15** was obtained as colorless prisms, mp 86—87° (MeOH) in 24% yield. *Anal.* Calcd. for $C_{21}H_{26}O_3$: C, 77.27; H, 8.03. Found: C, 77.21; H, 8.14. IR cm^{-1}: 1725, 1681. NMR δ: 3.68 (s, 4-COOMe), 6.26 (q, J=4 and 4 Hz, 1-H), 7.30 (q, J=2 and 7 Hz, 12-H), 7.43 (d, J=7 Hz, 11-H), 7.70 (d, J=2 Hz, 14-H).

ii) Reaction with Ac_2O/H_3PO_4: A solution of **6a** (40 mg) in Ac_2O (3 ml)-85% H_3PO_4 aq. (0.04 ml) was left standing at room temperature for 6 hr and treated as in i). The resulting oil was hydrolyzed with 12% KOH-EtOH (3 ml) at room temperature for 30 min. Work-up in the usual manner gave 25 mg of crystals in 60% yield, which was recrystallized from MeOH to give colorless prisms, mp 85—87°, and it was identified with the authentic sample of **15**.

iii) Reaction with Ac_2O/p-TsOH: A solution of **6a** (40 mg) in Ac_2O (3 ml)-p-TsOH (50 mg) was left standing at room temperature for 20 hr and by work-up in the same manner as in ii) 25 mg of crystals were obtained in 60% yield, which was recrystallized from MeOH to give colorless prisms, mp 85—87°, and it was identified with the authentic sample of **15**.

Hydrolysis of 14 to 15——A solution of **14** (200 mg) in 12% KOH-EtOH (50 ml) or in conc. HCl (0.2 ml)-EtOH (5 ml)-H_2O (0.5 ml) was left standing at room temperature for 30 min or 2 hr, respectively. After the reaction mixture was treated in the usual manner, 155 mg of crystals in 88% yield and 130 mg in 70% yield were obtained, respectively. The colorless prisms from both origins, mp 86—87° from MeOH aq., were identified with the authentic sample of **15**.

Rearrangement of Methyl 7-Oxo-10α-podocarp-5,8,11,13-tetraen-15-oate (6b) to the Enol Acetate (16) with Ac_2O-conc. H_2SO_4——A solution of **6b** (220 mg) in Ac_2O (30 ml) containing conc. H_2SO_4 (0.07 ml) was heated at 100° for 5 hr. Work-up as in the case of **6a** gave 210 mg of an oil, which was chromatographed on silica gel (10 g) to give 90 mg of **16** as colorless needles, mp 111—112° from MeOH aq., in 36% yield in the benzene-n-hexane (7: 3) eluate. *Anal.* Calcd. for $C_{20}H_{22}O_4$: C, 73.60; H, 6.97. Found: C, 73.44; H, 6.92. IR cm^{-1}: 1768, 1188. NMR δ: 2.25 (s, 7-OAc), 3.71 (s, 4-COOMe), 5.94 (q, J=3 and 4 Hz, 1-H), 6.08 (s, 6-H), 6.90—7.50 (m, 11-, 12- and 14-H).

Hydrolysis of 16 to 17——A solution of **16** (80 mg) in 12% KOH-EtOH (8 ml) was left standing at room temperature for 30 min. Work-up in the usual manner gave an oil, which was chromatographed on silica gel (5 g) to give **17** in almost quantitative yield in the benzene-n-hexane (7: 3) eluate. *Anal.* Calcd. for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09. Found: C, 75.91; H, 7.11. IR cm^{-1}: 1730, 1691. NMR δ: 3.58 (s, 4-COOMe), 6.34 (q, J=4 and 4 Hz, 1-H), 6.99—7.56 (m, 11-, 12- and 13-H), 7.77 (q, J=2 and 7 Hz, 14-H).

Rearrangement of 13-Isopropyl-10β-podocarp-5,8,11,13-tetraen-7-one (6c)——To a solution of 6c (400 mg) in Ac_2O (80 ml), 5.4 ml of 0.5% (v/v) sulfuric acid in Ac_2O was added and left standing at 0° for 2 hr. Work-up in the same manner as the preceding rearrangement reactions gave 545 mg of an oil, which was chromatographed on silica gel (27 g) to give 440 mg of **18** as an oil in 82% yield in the n-hexane-ether (10: 1) eluate. Mass spectrum (M^+), Calcd. for $C_{24}H_{32}O_4$: 384.230. Found: 384.232. IR cm^{-1}: 1770, 1725, 1240, 1195. UV (EtOH), nm (log ε): 285 (3.78), 314 (3.24), 322 (3.03), 329 (3.32). NMR δ: 1.37 and 1.27 (s, each, 2×4-Me), 1.87 (s, 4-OAc), 2.37 (s, 7-OAc), 2.45 (s, 5-Me), 7.01 (s, 6-H), 7.39 (q, J=2 and 9 Hz, 12-H), 7.57 (d, J=2 Hz, 14-H), 7.92 (d, J=9 Hz, 11-H).

Hydrolysis-Methylation Reaction of 18——The compound **18** (150 mg) was refluxed with Me_2SO_4 (2 ml) and K_2CO_3 (500 mg) in methyl ethyl ketone (30 ml) for 3 hr. After dilution with ice water, the excess Me_2SO_4 was decomposed by NH_3 and the mixture was extracted with ether. Work-up in the usual manner gave

120 mg of an oil, which was chromatographed on silica gel (6 g) to give **19** as an oil in 28% yield in the *n*-hexane–$CHCl_3$ (5: 1) eluate. Mass spectrum (M^+), Calcd. for $C_{21}H_{28}O$: 296.214. Found: 296.214. IR cm^{-1}: 1240, 1110. NMR δ: 1.59 and 1.71 (s, each, 2×4–Me), 2.45 (s, 5–Me), 3.97 (s, 7–OMe), 5.28 (m, Δw 1/2= 18 Hz, 3–H), 6.50 (s, 6–H), 7.30 (q, J=2 and 9 Hz, 12–H), 7.81 (d, J=9 Hz, 11–H), 7.95 (d, J=2 Hz, 14–H).

Rearrangement of 15-Acetoxy-13-isopropyl-10β-podocarp-5,8,11,13-tetraen-7-one (6d)——Compound (**6d**) (2 g) was treated with conc. H_2SO_4 (0.96 ml) in Ac_2O (600 ml) at room temperature for 2 hr. Work-up in the same manner as the preceding rearrangement reactions gave an oil, which was chromatographed on silica gel (100 g) to give 265 mg of **20** as an oil in 10% yield in the *n*-hexane–ether (5: 1) eluate. *Anal.* Calcd. for $C_{26}H_{34}O_6$: C, 70.56; H, 7.74. Found: C, 70.65; H, 7.76. Mass spectrum (M^+), Calcd. for $C_{26}H_{34}O_6$: 442.251. Found: 442.255. IR cm^{-1}: 1765, 1740, 1735, 1220, 1195. NMR δ: 1.38 (s, 4–Me), 1.91 and 1.95 (s, each, 4– and 15–OAc), 2.37 (s, 7–OAc), 2.44 (s, 5–Me), 4.18 (br. s, 4–CH_2O–), 6.98 (s, 6–H), 7.35 (q, J=2 and 9 Hz, 12–H), 7.54 (d, J=2 Hz, 14–H), 7.86 (d, J=9 Hz, 11–H).

Further elution with *n*-hexane–ether (5: 1) gave 600 mg of **21** as an oil in 27% yield. *Anal.* Calcd. for $C_{24}H_{30}O_4$: C, 75.36; H, 7.91. Found: C, 74.68; H, 7.88. Mass spectrum (M^+) Calcd. for $C_{24}H_{30}O_4$: 382.214. Found: 382.217. IR cm^{-1}: 1765, 1735, 1220, 1195. NMR δ: 1.53 (s, 4–Me), 1.97 (s, 15–OAc), 2.35 (s, 7–OAc), 2.43 (s, 5–Me), 4.35 (br. s, 4–CH_2O–), 5.53 (q, J=6 and 9 Hz, 3–H), 6.96 (s, 6–H), 7.30 (q, J=2 and 9 Hz, 12–H), 7.53 (d, J=2 Hz, 14–H), 7.87 (d, J=9 Hz, 11–H).

Reversed Rearrangement of the Enol Acetate (14) and the Oxo Ester (15) to the Phenacylidene Compound (6a) with conc. H_2SO_4——A solution of **14** or **15** (60 mg each) in conc. H_2SO_4 (6 ml) was left standing at room temperature for 6 or 2 hr, respectively. An oil obtained quantitatively by the usual work-up was identified with the authentic sample of **6a** by GLC and IR spectrum. Furthermore, 2,4-dinitrophenylhydrazone of it was synthesized in the usual manner, followed by the recrystallization from EtOH aq. to give yellow needles, mp 155—156°, which was identified with the corresponding 2,4-dinitrophenylhydrazone of the authentic **6a** by mixed melting point. *Anal.* Calcd. for $C_{27}H_{30}O_6N_4$: C, 64.02; H, 5.97; N, 11.06. Found: C, 64.04; H, 6.01; N, 11.22.

Reversed Rearrangement of the Enol Acetate (16) and the Oxo Ester (17) to the Phenacylidene Compound (6b) with conc. H_2SO_4——A solution of **16** or **17** (40 mg each) in conc. H_2SO_4 (4 ml) was left standing at room temperature for 2 hr. Work-up gave 30 mg of crystals in 75% yield, which was recrystallized from MeOH aq. to give colorless prisms, mp 148—149°. It was identified with the authentic sample of **6b** by GLC, IR spectrum and mixed melting point.

Reversed Rearrangement of the Enol Acetate (14) or the Oxo Ester (15) to the Phenacylidene Compound (6a) with BF_3·Ether——a) A solution of **14** (100 mg) in BF_3·ether (10 ml) was left standing at room temperature for a day and diluted with H_2O. The extraction with ether, followed by the work-up in the usual manner gave 82 mg of residue, which was identified with the authentic **15** by IR spectrum and GLC.

b) A solution of **14** (50 mg) in MeOH (5 ml) containing BF_3·ether (0.5 ml) was left at roomtemperature for 4 hr. Work-up gave 42 mg of an oil, which was identified with **14** by GLC and IR spectrum.

c) A solution of the recovered **14** (42 mg) in b) in a mixture of BF_3·ether (5 ml) and MeOH (0.5 ml) was left at room temperature for a day. Work-up gave 27 mg of an oil, which was shown to be composed of **15** and **6a** in a ratio of 6.3: 1 by GLC and IR spectrum.

d) A solution of **15** (20 mg) in BF_3·ether (3 ml) containing LiCl (50 mg) was left standing at room temperature for a day. Work-up gave an oil, which was composed of **15** and **6a** in a ratio of 3: 1 (GLC).

Reversed Rearrangement of the Oxo Ester (15) to the Phenacylidene Compound (6a) with BF_3·AcOH——a) To a solution of **15** (100 mg) in AcOH (10 ml), BF_3·AcOH (10 ml) was added and left standing at room temperature for a day. After dilution with H_2O, the mixture was extracted with ether, followed by work-up in the usual manner, giving 86 mg of a product. The IR spectrum and GLC examination revealed that it consisted of **15** and **6a** in a ratio of 1: 2.

b) A solution of **15** (100 mg) in BF_3·AcOH (10 ml) was left standing at room temperature for a day. Work-up gave 93 mg of an oil. The IR spectrum and GLC showed quantitative conversion of **15** to **6a**.

Methyl 1α,10α-Epoxy-13-isopropyl-5β-methyl-7-oxo-10-norpodocarp-8,11,13-trien-15-oate (23)——A solution of **15** (700 mg) in pyridine (70 ml) containing H_2O (5 ml) was stirred with N-bromosuccinimide (1.5 g) at room temperature for 12 hr. After the solvent was removed at 50° under reduced pressure, the residue was treated in the usual manner to give 479 mg of crystals of **23** in 65% yield, which was recrystallized from *n*-hexane to give colorless prisms, mp 166.5—178°. *Anal.* Calcd. for $C_{21}H_{26}O_4$: C, 73.66; H, 7.66. Found: C, 73.50; H, 7.57. IR cm^{-1}: 1734, 1698. NMR (CCl_4, 100 MHz): 1.09 (s, 4–Me), 1.17 (d, J=1 Hz, 5–Me), 2.68 (d, J=16 Hz, 6β–H), 3.63 (s, 4–COOMe), 3.82 (m, Δw 1/2=6 Hz, 1–H), 4.05 (q, J=1 and 16 Hz, 6α–H), 6.92 (d, J=8 Hz, 11–H), 7.31 (q, J=2 and 8 Hz, 12–H), 7.81 (d, J=2 Hz, 14–H).

Attempted Epoxide Rearrangement of 23 with Acids under Anhydrous Conditions——Epoxide rearrangement of **23** was tried under the following conditions at room temperature to recover the starting material unchanged. i) **23** (10 mg)/BF_3·ether (0.1 ml)/ether (2 ml), 24 hr. ii) **23** (10 mg)/BF_3·ether (0.1 ml)/benzene (2 ml), 24 hr. iii) **23** (10 mg)/BF_3·ether (2 ml), 3 hr. iv) **23** (16 mg)/$AlCl_3$ (65 mg)/$CHCl_3$ (1.5 ml), 17 hr. v) **23** (10 mg)/conc. H_2SO_4 (2 ml), 3 hr. vi) **23** (9 mg)/*p*-TsOH (10 mg)/benzene (1 ml), 40 hr. vii) **23** (9 mg)/PPA (20 mg)/benzene (1 ml), 40 hr. viii) **23** (14 mg)/70% $HClO_4$ (2 ml), 41 hr. ix) **23** (8 mg)/HCOOH (2 ml), 68 hr.

1α,10α-Dihydroxy-13-isopropyl-5β-methyl-7-oxo-norpodocarp-8,11,13-trien-15-oic Acid 15→10α-Lactone (25)——A solution of **23** (194 mg) in 47% HBr aq. (0.3 ml)–MeOH (30 ml)–H_2O (6 ml) was refluxed for 80 min. Work-up gave **25** quantitatively, which was recrystallized from CCl_4 to give colorless prisms, mp 181—184°. *Anal.* Calcd. for $C_{20}H_{24}O_4$: C, 73.14; H, 7.37. Found: C, 72.63; H, 7.29. IR ($CHCl_3$) cm^{-1}: 3590, 3480, 1783, 1688. NMR δ: 1.10 and 1.12 (s each, 4- and 5-Me), 5.82 (m, Δw 1/2=18 Hz, 1-H), 7.46 (q, J=2 and 8 Hz, 12-H), 7.87 (d, J=2 Hz, 14-H), 8.57 (d, J=8 Hz, 11-H).

1β,10α-Dihydroxy-13-isopropyl-5β-methyl-7-oxo-10-norpodocarp-8,11,13-trien-15-oic Acid 15→10-Lactone (24)——A solution of **15** (100 mg) in 13% AcO_2H–AcOH (9 ml) was left standing at room temperature for 15 hr. Work-up gave 85 mg of crystals in 85% yield, which was recrystallized from MeOH aq. to give colorless needles of **24**, mp 230.5—231.5°. *Anal.* Calcd. for $C_{20}H_{24}O_4$: C, 73.14; H, 7.37. Found: C, 72.89; H, 7.36. IR cm^{-1}: 3400—3550, 1785, 1695. NMR ($CDCl_3$) δ: 1.11 (s, 4-Me), 1.35 (s, 5-Me), 1.79 (br. s, 1-OH), 4.90 (m, Δw 1/2=8 Hz, 1-H), 7.63 (br. s, 11- and 12-H), 7.99 (br. s, 14-H).

10α-Hydroxy-13-isopropyl-5β-methyl-1,7-dioxo-10-norpodocarp-8,11,13-trien-15-oic Acid 15→10-Lactone (27)——i) A solution of **24** (200 mg) in acetone (10 ml) was left standing with Jones reagent (0.5 ml) at room temperature for 30 min. Work-up in the usual manner gave crystals of **27** quantitatively, which, on recrystallization from EtOH aq., gave colorless needles, mp 159—161°. *Anal.* Calcd. for $C_{20}H_{22}O_4$: C, 73.60; H, 6.79. Found: C, 73.52; H, 6.52. IR cm^{-1}: 1760, 1734, 1696. NMR δ: 1.09 and 1.17 (s, each, 4- and 5-Me), 7.16 (d, J=8 Hz, 11-H), 7.48 (q, J=2 and 8 Hz, 12-H), 7.76 (d, J=2 Hz, 14-H).

ii) A solution of **25** (70 mg) in AcOH (5 ml) was left standing with CrO_3 (70 mg)–AcOH (1 ml) at room temperature for 2 hr. Work-up gave crystals, which were recrystallized from MeOH aq. to give colorless needles, mp 157—159.5°. These crystals were identified with **27** in i).

1β,5β-Epoxymethano-10α-hydroxy-13-isopropyl-7-oxo-10-norpodocarp-8,11,13-trien-15-oic Acid 15→10-Lactone (26)——i) Reaction with $Pb(OAc)_4$: In N_2-stream, a solution of **24** (230 mg) in ab. benzene (100 ml) was stirred with $Pb(OAc)_4$ (330 mg) and I_2 (230 mg) under the irradiation by a low-pressure mercury lamp for 8 hr at 40°. The mixture was washed with 10% $Na_2S_2O_3$ aq., satd. Na_2CO_3 aq. and satd. NaCl aq. successively, and the solvent was removed to give 240 mg of an oil. It was chromatographed on neutral alumina (12 g) to afford 41 mg of crystals in 18% yield in the pet. ether–ether (10: 1) eluate, which was recrystallized from MeOH aq. to give colorless prisms of **26**, mp 193—194°. *Anal.* Calcd. for $C_{20}H_{22}O_4$: C, 73.60; H, 6.79. Found: C, 73.53; H, 7.01. IR cm^{-1}: 1798, 1699, 1002. NMR δ: 1.11 (s, 4-Me), 2.30 and 2.60 (d each, J=16 Hz, 6-H), 4.06 and 5.60 (d each, J=10 Hz, 1-CH_2O-), 4.54 (m, Δw 1/2=7 Hz, 1-H), 7.51 (br. s, 11- and 12-H), 7.83 (br. s, 14-H).

ii) A solution of **24** (98 mg) in CCl_4 (20 ml) was refluxed with HgO (195 mg) and I_2 (229 mg) for 19.5 hr. Work-up in the same manner as in i) gave 93 mg of a resinous product, which was submitted to the preparative thin-layer chromatography on silica gel plate upon development with EtOAc–benzene (1: 6) mixture to give 54 mg of crystals in 57% yield. Colorless prisms, mp 141—142°, from the recrystallization from MeOH aq. was identified with **26** in i).

Acknowledgement Financial support from the Ministry of Education (Grant-in-Aid for Scientific Research, No. 67031 (1972)) is acknowledged. The authors are grateful to Miss Yoshiko Yamanaka of this laboratory for her assistance.