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Oxidation of Bauerenol Derivatives with Chromium Trioxide: Confirmation of the Structure of Bauerenol[1]

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The identity of bauerenol and ilexol was established. The position of the double bond in bauerenol was established at 7-position by the chromium trioxide oxidation of bauerene, isobauerene, and bauerenyl acetate. Some observations in the course of the reactions were also described.

Bauerenol is a pentacyclic triterpene alcohol first isolated from *Acronychia baueri* (Rutaceae)[3] and then from *Kopsia longiflora* (Apocynaceae),[4] *Gelonium multiflorum* (Euphorbiaceae),[5] and other plants. Lahey and Leeding[4] proposed a migrated ursane structure (Ia) for the alcohol from the acid-induced migration of the acetate (Ib) to α-amyrenyl acetate and urs-13(18)-enyl acetate and from the comparison of the molecular rotation differences of the derivatives with those of butyrospermol derivatives having the double bond at 7-position.[6] The structure was then supported by rotatory dispersion measurements[7] and by the mass spectrum determinations.[8] However recent development of the chemistry of migrated type triterpenoids revealed that the evidences for the structure (Ia) could not exclude the possibility of the isomeric structure (II) having the double bond at 9(11)-position such as in the case of walsurenol[9] in oleanane series and 9(11)-fernene[10] in hopane series.

On the other hand a triterpene alcohol, named ilexol, was isolated from the barks of several species of the genus *Ilex* (Aquifoliaceae),[11] *Solidago altissima* (Compositae),[12] and *Bladhia japonica* (Myrsinaceae),[13] and the structure (III) was proposed.[11] Enough evidences[11] have been provided to support that ilexol is a migrated ursane but the proposed structure is assumed to be untenable from the present knowledge of triterpene chemistry and the identity of bauerenol and ilexol was suggested,[4] though the sample of the latter might be contaminated with the corresponding 7,9(11)-diene. Although the direct comparisons were carried out by the two groups[4,12] there remained some ambiguity in the identity of the two.

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[1] A part of this work was presented at the 90th Annual Meeting of Pharmaceutical Society of Japan, Sapporo, July 1970, Abstracts of Papers, II, p. 182.

[2] Location: *Kamiyoga-1-chome, Setagaya-ku, Tokyo.*

[3] F.N. Lahey and W.C. Thomas, *Australian J. Sci. Res.*, **2A**, 423 (1949).

[4] F.N. Lahey and M.V. Leeding, *Proc. Chem. Soc.*, **1958**, 342.

[5] P. Sengupta and H.N. Khastgir, *Tetrahedron*, **19**, 123 (1963).

[6] D.S. Irvine, W. Lawrie, A.S. McNab, and F.S. Spring, *J. Chem. Soc.*, **1956**, 2029.

[7] C. Djerassi, "Optical Rotatory Dispersion," McGraw-Hill, New York, 1960, p. 97.

[8] H. Budzikiewicz, J.M. Wilson, and C. Djerassi, *J. Am. Chem. Soc.*, **85**, 3688 (1963).

[9] A. Chatterjee, A.B. Kundu, T. Chakraborty, and S. Chandrasekharan, *Chem. Commun*, **1968**, 418.

[10] H. Ageta, K. Iwata, and S. Natori, *Tetrahedron Letters*, **1963**, 1447. It has now been proved that fern-7-ene, fern-8-ene, and fern-9(11)-ene are not clearly distinguishable by mass spectrum fragmentations (Professor H. Ageta, private communication).

[11] S. Iseda, *Yakugaku Zasshi*, **72**, 1064, 1611 (1952); S. Iseda, K. Yagishita, and N. Toya, *ibid.*, **74**, 422 (1954); K. Yagishita and S. Iseda, *Bull. Agric. Chem. Soc. Japan*, **21**, 274 (1957); K. Yagishita, *ibid.*, **21**, 123, 160 (1957); **22**, 131 (1958); **23**, 217 (1959).

[12] S. Iseda, *Chem. Pharm. Bull.* (Tokyo), **7**, 129 (1959).

[13] M. Aritomi, *Yakugaku Zasshi*, **83**, 659 (1963).

In our course of studies on benzoquinone derivatives from Myrsinaceae plants rather large amount of a triterpene alcohol was isolated from *Ardisia sieboldii*[14a] and *A. colorata*.[14b] The triterpene was proved to be identical with the samples both from *Gelonium sp.*[5] and from *Ilex sp.*[11,15] by every means of identification and the identity of bauerenol and ilexol was finally clarified.

Now the chromium trioxide oxidation of bauerene (Ic), isobauerene (bauer-8-ene) (Xc), and bauerenyl acetate (Ib) was carried out in order to compare the results with those of other triterpenes having the double bond at 7- and 9(11)-positions.[10,16,17]

Bauerene (Ic), prepared by the conventional method,[5] was treated with chromium trioxide at 20°.[16,17] Four enones, $C_{30}H_{48}O$ (V, mp 161—162°, VIa, mp 162—163°, VII, mp 230—232°, and VIII, mp 183—185°), and one enedione, $C_{30}H_{46}O_2$ (IXa, mp 175—176°), were isolated by chromatographic separation of the products. The compound, V, showed no sign of the conjugation of the carbonyl group ($\nu_{\max}^{\text{KBr}}$ 1690 cm^{-1}) with the tri-substituted double bond (δ 5.87, q) in ultraviolet (UV) and infrared (IR). The mass spectrum of V (Fig. 1) showed abundant fragments at *m/e* 300 ($C_{21}H_{32}O$), accompanied by a satellite at *m/e* 285 ($C_{20}H_{29}O$), *m/e* 220 ($C_{15}H_{24}O$), and *m/e* 205 ($C_{15}H_{25}$). The first fragment was assigned as the ion formed by the retro-Diels-Alder fragmentation of 14-ene and the second and the third peaks were assigned as those formed by the cleavages at C_{11}—C_{12} and C_8—C_{14} bonds as was

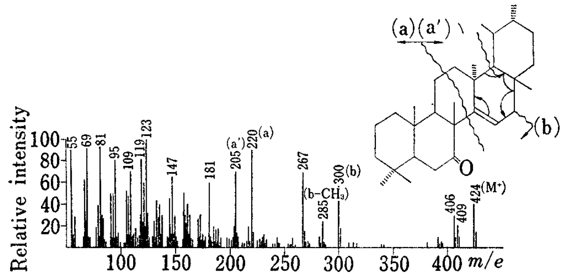

Fig. 1. Mass Spectrum of Isours-14-en-7-one (V)

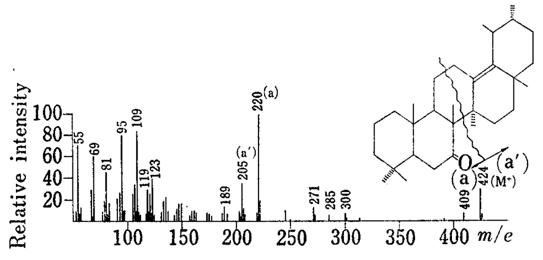

Fig. 2. Mass Spectrum of Urs-13(18)-en-7-one (VIa)

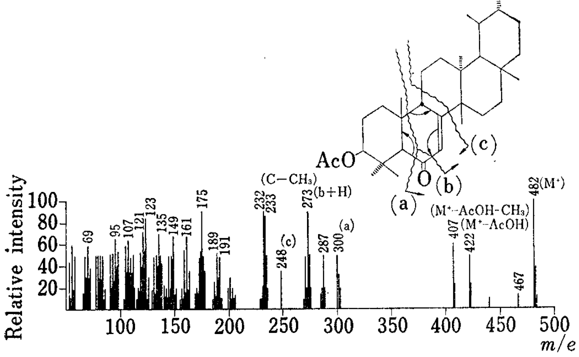

Fig. 3. Mass Spectrum of 3β-Acetoxy-9β-bauer-7-en-6-one (XII)

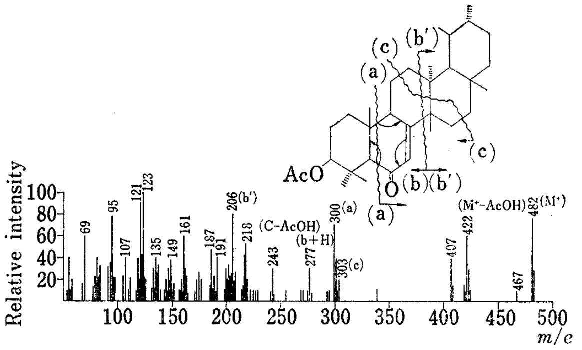

Fig. 4. Mass Spectrum of 3β-Acetoxybauer-7-en-6-one (XIII)

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14) *a*) H. Ogawa and S. Natori, *Chem. Pharm. Bull.* (Tokyo), **16**, 1709 (1968); *b*) P. Kanchanapee, H. Ogawa, and S. Natori, *Shoyakugaku Zasshi*, **21**, 68 (1967).

15) As was well known in the case of tetracyclic triterpenes, the mixed fusion of bauerenol and the corresponding 7,9(11)-diene does not show the depression. The examination by UV absorptions revealed the absence of the diene in our specimens isolated from *Ardisia spp.*

16) W. Laurie, W. Hamilton, F.S. Spring, and H.S. Watson, *J. Chem. Soc.*, **1956**, 3272.

17) H. Ageta, K. Shiojima, and Y. Arai, The 13th Symposium on the Chemistry of Natural Products, Sapporo, September 1969, Abstracts of Papers, p. 161.

reported in the case of Δ^{14}-taraxerene derivatives.[8] The coupling pattern of the vinyl proton (q, J=7.5, 3.5 Hz) is quite similar to that of pteron-14-en-7-one.[17] The acid-treatment of V afforded a mixture of the other enones (VIa and VIII) (*vide infra*). These facts indicated that the compound (V) must be isours-14-ene derivative and the presence of the carbonyl group at 7-position rather than at 11-position was favored from the low chemical shift of the vinyl proton. This was later confirmed from the established position of the double bond in bauerene (Ic). As a matter of convenience, in the following discussion the assignment of the structures of the reaction products will be made from the established position of the double bond at 7-position, though, in some cases, there still remains the possibility of the alternative structures based on the 9(11)-ene structure at the stage of the discussion.

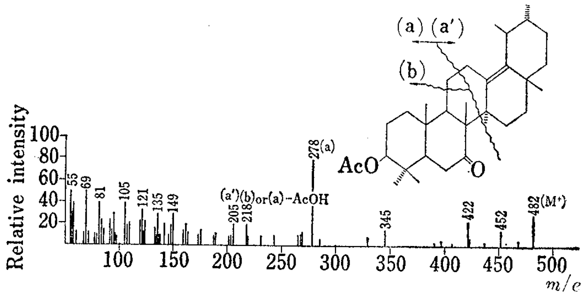
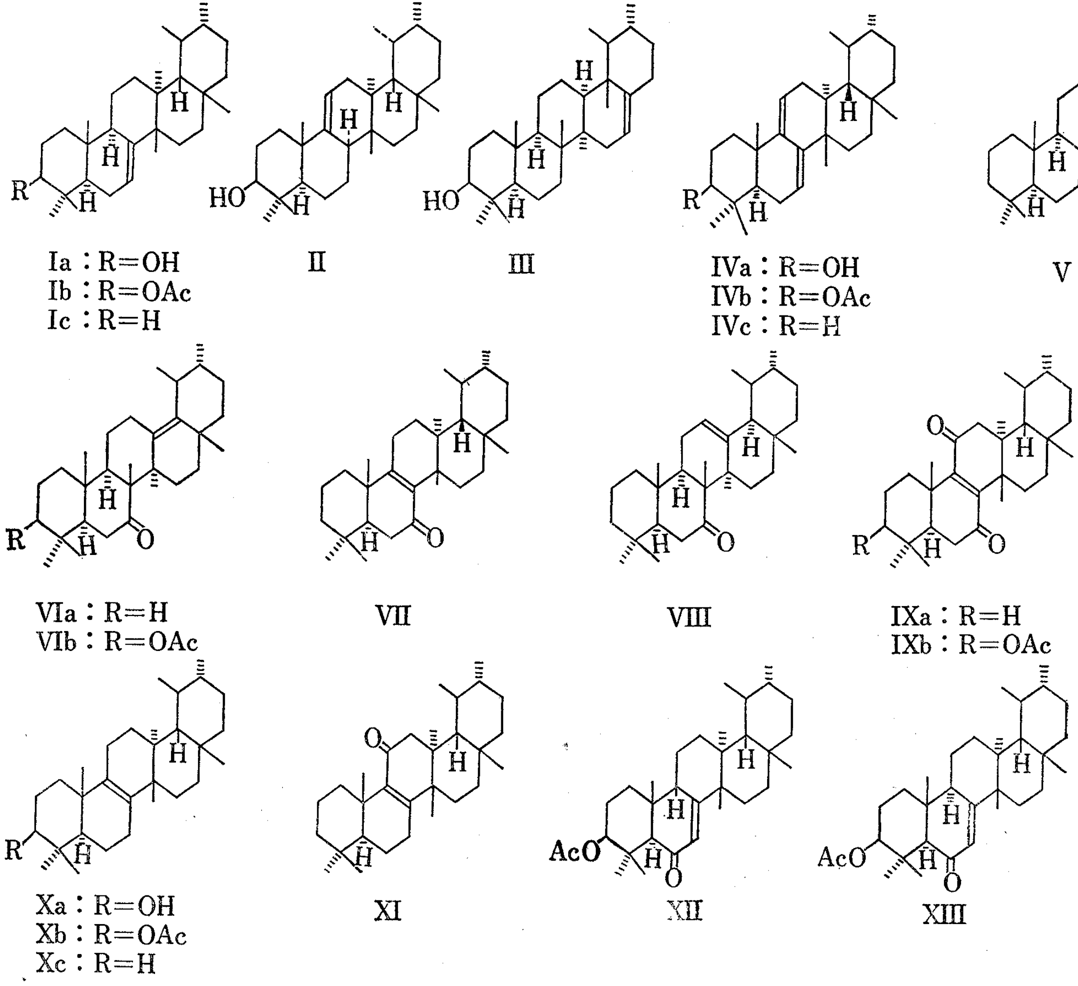


Fig. 5. Mass Spectrum of 3β-Acetoxyurs-13 (18)-en-7-one (VIb)

VIa is again a non-conjugated enone ($\nu_{\max}^{\mathrm{KBr}}$ 1705 cm^{-1}), the double bond in which occupies a tetra-substituted position (from IR and nuclear magnetic resonance (NMR)). The mass spectrum (Fig. 2) showed the base peak at *m/e* 220 ($C_{15}H_{24}O$) and a peak at *m/e* 205



Ia : R=OH
Ib : R=OAc
Ic : R=H

II

III

IVa : R=OH
IVb : R=OAc
IVc : R=H

V

VIa : R=H
VIb : R=OAc

VII

VIII

IXa : R=H
IXb : R=OAc

Xa : R=OH
Xb : R=OAc
Xc : R=H

XI

XII

XIII

Chart 1

($C_{15}H_{25}$), as in the case of V.[8] Since VIa was formed from V by the acid-treatment, the 13(18)-en-7-one structure[16] (VIa) was assigned for the compound.

The third enone (VII) showed the presence of a conjugated ketone system ($\nu_{\max}^{\text{KBr}}$ 1660, 1590 cm^{-1}, $\lambda_{\max}^{\text{hexane}}$ 249 mμ (ε 8900)), in which the double bond is tetra-substituted (from IR and NMR). Since the Wolff–Kischner reduction of the enone afforded bauerene (Ic), the compound was assigned as 8-en-7-one (VII).

In the fourth enone (VIII) the carbonyl group ($\nu_{\max}^{\text{KBr}}$ 1706 cm^{-1}) and the tri-substituted double bond (δ 5.2 (1H, m)) are not conjugated. The compound (VIII) was also obtained from V by the acid-treatment. The presence of VIa and VIII in equilibrium[18] was confirmed by the acid-treatment of the both compounds and the formation of the same mixture of VIa and VIII (*ca.* 7: 3) was checked by gas chromatography. Thus the enone was formulated as 12-en-7-one (VIII).

The structure of the enedione (IXa) was established by IR ($\nu_{\max}^{\text{KBr}}$ 1670 cm^{-1}), UV ($\lambda_{\max}^{\text{hexane}}$ 270 mμ (ε 8100)), and NMR (no vinyl proton) as 8-ene-7,11-dione (IXa).

The oxidation of isobauerene (bauer-8-ene) (Xc), formed by the acid-induced migration of the double bond in bauerenol, under the same condition afforded the corresponding 7,9(11)-diene (IVc), the conjugated enone (VII), the enedione (IXa) and a new enone (XI), $C_{30}H_{48}O$, mp 214—216°, and a mixture of non-conjugated enones, which formed VII and XI by the acid-treatment. The enone (XI) showed the presence of α,β-unsaturated carbonyl group in its IR and UV ($\nu_{\max}^{\text{KBr}}$ 1645, 1585 cm^{-1}, $\lambda_{\max}^{\text{hexane}}$ 250.5 mμ (ε 11000)) and, since no vinyl proton was observed, the structure as 8-en-11-one (XI) was assigned for the compound.

In the case of the oxidation of bauerenyl acetate (Ib) the reaction was carried out in boiling acetic acid[10,19] to afford four products; three enones, $C_{32}H_{50}O_3$ (XII, mp 267—269°; XIII, mp 262—263°; and VIb, mp 278—279°), and one enedione (IXb), which has already been reported and assigned as 8-ene-7,11-dione.[4,5] XII, the major product, and XIII showed similar UV (XII, $\lambda_{\max}^{\text{hexane}}$ 243.5 mμ (ε 13000), XIII, $\lambda_{\max}^{\text{hexane}}$ 240 mμ (ε 13500)), IR (XII, 1663 cm^{-1}, XIII, 1670 cm^{-1}), and NMR (XII, δ 5.57 (s), XIII, δ 5.72 (d, $J=3$ Hz)). Contrary to the positive Cotton effects observed in fern-9(11)-en-12-one system,[10,18] the both compounds showed negative Cotton effects. Since the mass spectra of XII and XIII showed the peak at *m/e* 300 formed by the retro-Diels-Alder fragmentation of 7-ene derivatives (Fig. 3, 4) and the coupling patterns of the vinyl protons in XII and XIII were similar to those of 8β-fern-9(11)-en-12-one[17] (δ 5.51 (s))[20] and 8α-fern-9(11)-en-12-one[17] (δ 5.65 (d, $J=2.8$ Hz)),[20] XII and XIII are respectively assigned as 9β- and 9α-bauer-7-en-6-one. In the other enone (VIb) the carbonyl group ($\nu_{\max}^{\text{KBr}}$ 1705 cm^{-1}) is not conjugated with the tetra-substituted double bond (from IR and NMR) and the abundant peak at *m/e* 278 ($C_{17}H_{26}O_3$) in the mass spectrum (Fig. 5) suggests that the double bond at the same position as VIa. Thus the 13(18)-en-7-one structure (VIb) was assigned for the compound.

These observations, especially the formation of V from Ic by chromium trioxide oxidation at 20°, are similar to those in the oxidation of fern-7-ene[17] and butyrospermol[16] having the double bond at 7-position in the triterpenoids bearing 13α and 14β methyls. In the other hand the oxidation of Ib in boiling acetic acid afforded two 7-en-6-ones and 13(18)-en-7-one, while 9(11)-ene derivatives had been proved to form 9(11)-en-12-ones as the main reaction products.[10,19] These results could be harmoneously explained by the structure (Ia) of bauerenol having the double bond at 7-position and the oxidation products were assigned as shown in above. Thus our results provided the conclusive evidence for the position of the double bond and excluded the alternative structure (II).

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18) J.M. Beaton, F.S. Spring, R. Stevenson, and W.S. Strachan, *J. Chem. Soc.*, **1955**, 2610.
19) K. Nishimoto, M. Ito, S. Natori, and T. Ohmoto, *Tetrahedron*, **24**, 735 (1968).
20) H. Ageta, K. Shiojima, and Y. Arai, the 88th Annual Meeting of Pharmaceutical Society of Japan, Tokyo, April 1968, Abstracts of Papers, p. 252.

Experimental[21]

Bauerenyl Acetate (Ib)——The sample of bauerenol isolated from *Ardisia sieboldii*[14a] was further purified and derived to the acetate (Ib), mp 280—282° (from $CHCl_3$–acetone), $[\alpha]_D^{20}$ ±0° (c=1.0, $CHCl_3$) (lit.[4] mp 293—294°, $[\alpha]_D$ −3.7°, lit.[5] mp 280—282°, $[\alpha]_D$ ±0° ($CHCl_3$), lit.[11] mp 290—291°, $[\alpha]_D$ −30° ($CHCl_3$)). *Anal.* Calcd. for $C_{32}H_{52}O_2$: C, 81.99; H, 11.18. Found: C, 81.51; H, 11.10. The identity with the samples from *Ilex sp.*[11] and from *Gelonium sp.*[5] was confirmed by mixed fusions, IR, TLC, and GLC.

Bauerenol (Ia)——Prepared from Ib, mp 207—208° (from acetone), $[\alpha]_D^{19}$ −20.7° (c=0.7, $CHCl_3$) (lit.[4] mp 207—208°, $[\alpha]_D$ −30°, lit.[5] mp 206—207°, $[\alpha]_D$ −25° ($CHCl_3$), lit.[11] mp 205—206°, $[\alpha]_D$ −29.1° ($CHCl_3$)). *Anal.* Calcd. for $C_{30}H_{50}O$: C, 84.44; H, 11.81. Found: C, 84.62; H, 11.85.

Bauer-7-ene (Ic) from Ia——The alcohol (Ia) was oxidized with CrO_3 in pyridine to the ketone,[4,11] mp 240—241.5° (from $CHCl_3$–EtOH), $[\alpha]_D^{18}$ −52.7° (c=1.9, $CHCl_3$)(lit.[11] mp 239.5—240.5°, $[\alpha]_D$ −68.7° ($CHCl_3$)). *Anal.* Calcd. for $C_{30}H_{48}O$: C, 84.84; H, 11.39. Found: C, 84.64; H, 11.16. The Wolff–Kischner reduction was applied for the ketone and the product was recrystallized from $CHCl_3$–MeOH to give Ic, mp 247°, $[\alpha]_D^{19}$ −19.5° (c=1.3, $CHCl_3$) (lit.[11] mp 241—242°). *Anal.* Calcd. for $C_{30}H_{50}$: C, 87.73; H, 12.27. Found: C, 87.89; H, 12.27.

Chromium Trioxide Oxidation of Bauerene (Ic)——To a solution of Ic (300 mg) in CH_2Cl_2 (12 ml), benzene (68 ml), and AcOH (80 ml) was added CrO_3 (130 mg) in 90% AcOH (21 ml) and the mixture was allowed to stand at 20° for 20 hr. The reaction mixture was diluted with water and extracted with benzene. The benzene layer was washed with 5% $NaHCO_3$ and water, dried and evaporated. The residue was applied on preparative layer chromatography (Kieselgel HF_{254}) using benzene as the developer and six homogeneous fractions were obtained. Fraction 1 (151 mg) was crystallized from CH_2Cl_2–EtOH to recover the starting material. Fraction 2 (39 mg) was recrystallized from CH_2Cl_2–EtOH to give VIa, mp 162—163°, ORD (cyclohexane) negative Cotton, $[\alpha]$ (mμ): −25° (589), −286° (325) (trough), −250° (315) (shoulder), +273° (280) (peak). IR ν_{max} cm^{-1}: 1705. Mass Spectrum m/e: 424.3686 (calcd. for $C_{30}H_{48}O$, 424.3705). Fraction 3 (17 mg) was crystallized from CH_2Cl_2–EtOH to give VIII,[22] mp 183—184°, ORD (cyclohexane) negative Cotton, $[\alpha]$ (mμ): +22° (589), −967° (322) (trough), −879° (312), −549° (300) (shoulder), +1664° (225) (peak). IR ν_{max} cm^{-1}: 1706. NMR δ: 5.2 (1H, m). Mass Spectrum m/e: 424.369 (M^+) (calcd. for $C_{30}H_{48}O$, 424.371). Fraction 4 (3 mg) was crystallized from CH_2Cl_2–EtOH to give VII, mp 230—232°, and identified with the compound obtained from Xc by a mixed fusion, TLC, and GLC. Fraction 5 (33 mg) was crystallized from CH_2Cl_2–EtOH to give V, mp 161—162°, $[\alpha]_D^{18}$ +6.6° (c=0.75, $CHCl_3$). ORD (cyclohexane) negative Cotton, $[\alpha]_D$ (mμ): −167° (325) (trough), +500° (280) (peak). IR ν_{max} cm^{-1}: 1690. NMR δ: 5.87 (1H, q, J=7.5, 3.5 Hz). Mass Spectrum, m/e 424.371 (M^+) (calcd. for $C_{30}H_{48}O$, 324.371). Fraction 6 (49 mg) was crystallized from CH_2Cl_2–EtOH to give IXa, mp 175—176°, $[\alpha]_D^{18}$ −11.3° (c=1.0, $CHCl_3$), UV λ_{max} mμ (ε): 270 (8100). IR ν_{max} cm^{-1}: 1670. Mass Spectrum m/e: 438.3512 (M^+) (calcd. for $C_{30}H_{46}O_2$, 438.3497).

Isobauerene (bauer-8-ene) (Xc) from Ib——The acetate (Ib) was derived to isobauerenyl acetate (Xb) by HCl in $CHCl_3$, mp 231—233° (from $CHCl_3$–MeOH), $[\alpha]_D^{18}$ +52.1° (c=0.96, $CHCl_3$) (lit.[4] mp 229—231°, $[\alpha]_D$ +46°, lit.[5] mp 223—225°, $[\alpha]_D$ +42° ($CHCl_3$), lit.[11] mp 226—227°, $[\alpha]_D$ +49° ($CHCl_3$)). *Anal.* Calcd. for $C_{32}H_{52}O_2$: C, 81.99; H, 11.18. Found: C, 81.95; H, 11.21. The identity with the authentic sample[5] was confirmed by a mixed fusion, IR, GLC, and TLC. Xb was hydrolysed to the alcohol (Xa),[4,11] mp 177—178° (from $CHCl_3$–MeOH), $[\alpha]_D^{19}$ +50.7° (c=1.1, $CHCl_3$) (lit.[11] mp 177—178°, $[\alpha]_D$ +41.7°). *Anal.* Calcd. for $C_{30}H_{50}O$: C, 84.44; H, 11.81. Found: C, 84.69; H, 11.71. Xa was oxidized with CrO_3–pyridine to isobauerenone, mp 194—195°, $[\alpha]_D^{19}$ +85.2° (c=1.0, $CHCl_3$) (lit.[11] mp 194—195°, $[\alpha]_D$ +75.9°). *Anal.* Calcd. for $C_{30}H_{48}O$: C, 84.84; H, 11.39. Found: C, 84.75; H, 11.35. The Wolff–Kischner reduction of the ketone afforded bauer-8-ene (Xc), mp 175—176°, $[\alpha]_D^{19}$ +53.8° (c=1.0, $CHCl_3$) (lit.[11] mp 183—185°, $[\alpha]_D$ +48° ($CHCl_3$)). *Anal.* Calcd. for $C_{30}H_{50}$: C, 87.73; H, 12.27. Found: C, 87.38; H, 12.26.

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21) Melting points were measured in a Yanagimoto mp apparatus and are uncorrected. Optical rotations were determined witha A pplied Electric Lab. Automatic Polarimeter Model MP-1T, UV spectra in hexane solution by a Hitachi EPS-3T Spectrophotometer, and IR spectra in KBr discs by Nihon Bunko DS-301 or IR-S. NMR spectra were measured on a JEOL Model C60HL and a Varian HR-100 in $CDCl_3$ with Me_4Si as an internal standard and chemical shifts are given in δ values (ppm). The mass spectra were determined on a Hitachi Model RMU-7L and a JEOL 01SG-2 High Resolution Mass Spectrometer with direct inlet system. The optical rotatory dispersion (ORD) and circular dichroism (CD) curves were measured on a Nihon Bunko ORD-UV5.

At each stage of the separation and purification, thin-layer (TLC) and gas chromatography (GLC) were adopted for monitorring the purity of the specimen. For thin-layer plates Kieselgel HF_{254} or Kieselgel H impregnated with $AgNO_3$ were used. Gas chromatography was carried out on 1.5% SE-30, 1.8% QF-1, or 1.5% OV-17 at 255° in a Hitachi F6D or O63 gas chromatograph.

22) Before the recrystallization the fraction showed two peaks in GLC.

Chromium Trioxide Oxidation of Isobauerene (Bauer-8-ene) (Xc)——Xc (201 mg) in benzene (12 ml), AcOH (16 ml), and CH_2Cl_2 (3 ml) was treated with CrO_3 (82 mg) in 90% HOAc (10 ml) as in the case of Ic. After the treatment as before six fractions were obtained. Fraction 1 (108 mg) was crystallized from CH_2Cl_2–EtOH to recover the starting material (Xc). Fraction 2 (9 mg) was recrystallized from CH_2Cl_2–EtOH to give the diene (IVc), mp 195—197°, $[\alpha]_D^{18}$ $-136°$ ($c=1.0$, $CHCl_3$). UV λ_{max} mμ (ε): 232 (10400), 239.5 (13000), 247 (7300). IR ν_{max} cm^{-1}: 815, 798. NMR δ: 5.22 (1H), 5.42 (1H). Mass Spectrum *m/e*: 408.3728 (M$^+$) (calcd. for $C_{30}H_{48}$, 408.3755). The hydrocarbon was also obtained as the major product from Ic by the treatment with dibromodimethylhydantoin.[23] Fraction 3 (5 mg) was crystallized from EtOH to give a mixture of ketones, which formed VII and XI by the acid-treatment and identified by TLC and GLC. Fraction 4 (6 mg) was crystallized from CH_2Cl_2–EtOH to give XI, mp 214—216°, $[\alpha]_D^{20}$ $+33.4°$ ($c=0.3$, $CHCl_3$). UV λ_{max} mμ (ε): 250.5 (11000). IR ν_{max} cm^{-1}: 1645, 1585. Mass Spectrum *m/e*: 424.3694 (M$^+$) (calcd. for $C_{30}H_{48}O$, 424.3705). Fraction 5 (13 mg) was crystallized from CH_2Cl_2–EtOH to give VII, mp 230—232°, $[\alpha]_D^{20}$ $+57.1°$ ($c=0.7$, $CHCl_3$). UV λ_{max} mμ (ε): 249 (8900). IR ν_{max} cm^{-1}: 1660, 1590. Mass Spectrum *m/e*: 424.3676 (M$^+$) (calcd. for $C_{30}H_{48}O$, 424.3705). Fraction 6 (56 mg) was recrystallized from CH_2Cl_2–EtOH to afford IXa and identified with the compound obtained from Ic.

Wolff-Kischner Reduction of VII——VII (6 mg) in diethylene glycol (1 ml) was refluxed with hydrazine hydrate (0.6 ml) for 1 hr and, after the addition of KOH (6 mg), the mixture was further refluxed for 1 hr. The condensor was removed and the mixture was heated to 190° for 4 hr. The reaction mixture was cooled under N_2, diluted with water, and extracted with $CHCl_3$. The product was examined by GLC and TLC (solvent: hexane) and identified with Ic.

Isomerization of V by Acid——To a solution of V (10.1 mg) in benzene (0.2 ml) and AcOH (1.0 ml) was added conc. H_2SO_4 (0.03 ml) and the mixture was allowed to stand at room temperature for 3 hr. The reaction mixture was diluted with water and extracted with benzene. The benzene layer was washed with 5% $NaHCO_3$ and water, dried, and evaporated. The GLC of the residue showed two peaks (approximately 7:3 in ratio), which were identical with those of VIa and VIII. The residue was crystallized from CH_2Cl_2–EtOH to give VIa, showing identity with the sample obtained from Ic by a mixed fusion, TLC, and GLC.

Isomerization of VIII by Acid——VIII was treated as in the case of V. The product showed two peaks in GLC just the same as in the former case. The recrystallization gave VIa and identified.

Chromium Trioxide Oxidation of Bauerenyl Acetate (Ib)——To a solution of Ib (380 mg) in boiling AcOH (150 ml) was added CrO_3 (382 mg) in AcOH (147 ml) and H_2O(3 ml) in a period of 30 min and the mixture was then refluxed for 2 hr. The reaction mixture was diluted with water and extracted with $CHCl_3$. The extract was washed with 5% $NaHCO_3$ and water, dried, and evaporated. The residue was recrystallized from $CHCl_3$–MeOH to give XII (80 mg), mp 267—269°, $[\alpha]_D^{18}$ $+91.3°$ ($c=0.58$, $CHCl_3$). CD (cyclohexane) (θ) (mμ): +115 (386), −488 (374), −144 (367), −1205 (357), −402 (349), 1122 (342), −380 (335), −574 (330), 230 (275). UV λ_{max} mμ (ε): 243.5 (13000). IR ν_{max} cm^{-1}: 1735, 1663, 1620, 1240. NMR δ: 5.57 (1H, s), 4.5 (1H, m), 2.8 (1H, m), 2.34 (1H, s), 2.03 (3H, s). Mass Spectrum *m/e*: 482.3770 (M$^+$) (calcd. for $C_{32}H_{50}O_3$, 482.3759).

The mother liquor was separated into four fractions by preparative layer chromatography using a mixture of benzene and AcOEt (4:1) as the developer. Fraction 1 (32 mg) was crystallized from $CHCl_3$–MeOH to give XIII, mp 262—263°, $[\alpha]_D^{20}$ $-45.4°$ ($c=1.0$, $CHCl_3$), CD (cyclohexane) (θ) (mμ): −821 (374), 0 (365), −970 (356), +373 (348), −380 (340), +149 (333), −149 (326), −1597 (277). UV λ_{max} mμ (ε): 240 (13500). IR ν_{max} cm^{-1}: 1740, 1670, 1618, 1237. NMR δ: 5.72 (1H, d, $J=3$ Hz), 4.4 (1H, m), 2.6 (1H, m), 2.14 (1H, s), 2.00 (3H, s). Mass Spectrum *m/e*: 482.3756 (M$^+$) (calcd. for $C_{32}H_{50}O_3$, 482.3760). Fraction 2(70 mg) was crystallized from $CHCl_3$–MeOH to give IXb, mp 267—268°, $[\alpha]_D^{21}$ $-12.6°$ ($c=0.9$, $CHCl_3$) (lit.[5] mp 256—258°, $[\alpha]_D$ $-27°$ ($CHCl_3$)). UV λ_{max} mμ (ε): 269 (8500). IR ν_{max} cm^{-1}: 1737, 1685 (inf.), 1670, 1243. Mass Spectrum *m/e*: 496.3561 (M$^+$) (calcd. for $C_{32}H_{48}O_4$, 496.3552.) Fraction 3 (50 mg) was crystallized from $CHCl_3$–MeOH to give VIb, mp 278—279°, $[\alpha]_D^{18}$ $-37.0°$ ($c=0.8$, $CHCl_3$). ORD (cyclohexane) negative Cotton, $[\alpha]$ (mμ): $-302°$ (322) (trough), $-233°$ (302) (shoulder), $+547°$ (270) (peak). IR ν_{max} cm^{-1}: 1735, 1705, 1240. Mass Spectrum *m/e*: 482.3763 (M$^+$) (calcd. for $C_{32}H_{50}O_3$ 482.3759). Fraction 4 (132 mg) afforded further amount of XII after recrystallization from $CHCl_3$–MeOH.

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