X-Ray Crystallographic Studies on the Structure of Alnuserrudiolone Isolated from the Male Flowers of *Alnus serrulatoides*

Toshifumi Hirata, Tadashi Aoki, and Takayuki Suga*

Department of Chemistry, Faculty of Science, Hiroshima University, Higashisenda-machi, Naka-ku, Hiroshima 730

(Received March 23, 1981)

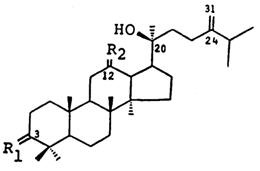
The structure of alnuserrudiolone was corroborated to be (12*R*,20*S*)-12,20-dihydroxy-24-methylenedammaran-3-one by the X-ray crystallography together with the ^{13}C NMR and the high resolution mass spectral measurements.

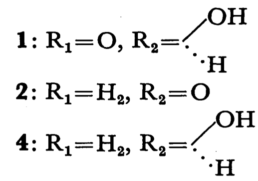
In connection with biochemical and physiological studies of pollination,[1] we investigated chemical constituents of the male flowers of *Alnus serrulatoides* Call. (Japanese name: Kawara-hannoki) and reported the isolation and the structure elucidation of new C_{31} dammarane-type triterpenoids, alnuserol,[2] alnuseric acid,[3] and alnuselide.[3] In advance of these reports, the isolation of a new C_{31} dammarane-type triterpenoid, alnuserrudiolone, had been communicated, and structure (**1**) had been proposed to this triterpenoid on the basis of chemical and spectroscopic studies.[4] The structure has a feature of C_{31} dammarane-type triterpenoid having an acyclic side chain, in contrast to the above-described triterpenoids with the side chain including a tetrahydrofuran ring. It is, however, considered essential to establish the skeletal structure of **1**, because **1** has not been yet related to any compound having the well-defined structure. We, therefore, studied the structure of alnuserrudiolone by the X-ray crystallographic method together with the ^{13}C NMR and the high resolution mass spectral measurements.

Results and Discussion

The male flowers of *Alnus serrulatoides* Call. grown naturally on a river side were collected just before the flowering and immersed in acetone. An ether-soluble fraction of the acetone extract was subjected to chromatography using silica gel to give the sample of alnuserrudiolone (**1**), which showed completely the same physical (mp and optical rotation), spectral (IR, ^{1}H NMR, MS, and ORD) properties, and chemical behaviors as described previously.[4]

The acyclic side chain and functional groups characteristic of the previously-proposed structure (**1**) were first corroborated by measurement of ^{13}C NMR and high resolution mass spectra. Comparison of the ^{13}C NMR chemical shifts of **1** with those of the dammarane-type derivatives[2,5] indicated that **1** possesses a dammarane-type skeleton with a carbonyl group at the 3-position (δ_C 217.8), a secondary hydroxyl group on C-12 (δ_C 70.5), and a tertiary hydroxyl group on C-20 (δ_C 73.6). The last two signals showed that the chirality at C-12 and C-20 is *R* and *S*, respectively.[5] On the other hand, the signals at δ_C 156.5 and 106.2 indicated the presence of an acyclic side chain with a terminal methylene on C-24. This was further supported by the high resolution mass spectrum, which exhibited ions characteristic of such an acyclic side chain at *m*/*z* 141.1280 and 123.1279,[4,6,7] together with an ion derived from the 3-keto dammarane-type skeleton at *m*/*z* 205.1603.[6]

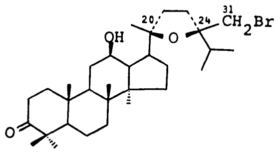




1: R_1=O, R_2=$\overset{\text{OH}}{\underset{\cdot\text{H}}{<}}$

2: R_1=H_2, R_2=O

4: R_1=H_2, R_2=$\overset{\text{OH}}{\underset{\cdot\text{H}}{<}}$



3

Table 1. Final atomic coordinates (× 10^4) of **2**, with standard deviations in parentheses

Atoms	*x*	*y*	*z*	B_{eq}/Å^2 [a]
O(1)	9963(19)	8721(13)	302(7)	6.6
O(2)	7328(16)	5223(11)	−1072(7)	5.8
C(1)	11293(34)	7677(23)	2902(16)	8.1
C(2)	11604(32)	7676(30)	3835(13)	7.3
C(3)	11780(37)	6285(25)	4512(14)	7.9
C(4)	9458(36)	6056(31)	4116(11)	7.1
C(5)	8521(34)	6498(28)	3317(14)	7.7
C(6)	6933(24)	5656(28)	3046(11)	7.6
C(7)	6066(26)	6145(25)	2316(12)	7.5
C(8)	7443(24)	6188(19)	1678(10)	4.9
C(9)	9070(26)	7057(18)	1921(10)	3.6
C(10)	9949(27)	6657(21)	2649(14)	7.9
C(11)	10433(22)	7208(18)	1293(9)	3.6
C(12)	9499(24)	7719(17)	590(10)	4.0
C(13)	7956(19)	6947(17)	319(9)	3.4
C(14)	6642(22)	6940(22)	964(10)	5.4
C(15)	5065(24)	6315(22)	559(12)	6.2
C(16)	5006(26)	6869(20)	−229(12)	8.3
C(17)	6978(25)	7311(19)	−406(12)	5.8
C(18)	7836(27)	4823(18)	1484(13)	6.4
C(19)	11035(35)	5326(25)	2630(13)	8.3
C(20)	7604(33)	6635(27)	−1116(10)	7.6
C(21)	9619(26)	6803(24)	−1226(11)	6.7
C(22)	6430(31)	7117(23)	−1807(11)	8.2
C(23)	6927(35)	6540(29)	−2528(12)	8.3
C(24)	5522(27)	6852(21)	−3155(12)	6.9
C(25)	3993(39)	5931(31)	−3083(17)	8.7
C(26)	4155(39)	4803(29)	−3749(18)	8.3
C(27)	2362(39)	6397(29)	−3131(26)	9.1
C(28)	8219(37)	6969(35)	4751(13)	7.9
C(29)	9167(43)	4671(20)	4275(13)	8.1
C(30)	6095(31)	8415(16)	1119(11)	8.3
C(31)	5756(41)	7694(28)	−3674(14)	8.5

a) $B_{eq}=8\pi^2(U_1+U_2+U_3)/3$, where U_1, U_2, and U_3 are the principal components of *U* matrix.

Table 2. Interatomic distances (*l*/Å) of **2**, with standard deviations in parentheses

C(1)–C(2)	1.67(3)	C(12)–C(13)	1.48(2)
C(1)–C(10)	1.56(3)	C(12)–O(1)	1.23(2)
C(2)–C(3)	1.60(4)	C(13)–C(14)	1.51(2)
C(3)–C(4)	1.60(4)	C(13)–C(17)	1.53(3)
C(4)–C(5)	1.61(3)	C(14)–C(15)	1.54(2)
C(4)–C(28)	1.60(4)	C(14)–C(30)	1.59(2)
C(4)–C(29)	1.49(3)	C(15)–C(16)	1.64(3)
C(5)–C(6)	1.52(3)	C(16)–C(17)	1.59(2)
C(5)–C(10)	1.61(3)	C(17)–C(20)	1.49(2)
C(6)–C(7)	1.56(3)	C(20)–C(21)	1.54(3)
C(7)–C(8)	1.54(3)	C(20)–C(22)	1.60(3)
C(8)–C(9)	1.55(2)	C(20)–O(2)	1.47(2)
C(8)–C(14)	1.61(2)	C(22)–C(23)	1.44(3)
C(8)–C(18)	1.47(2)	C(23)–C(24)	1.57(3)
C(9)–C(10)	1.57(2)	C(24)–C(25)	1.46(3)
C(9)–C(11)	1.48(2)	C(24)–C(31)	1.21(3)
C(10)–C(19)	1.54(3)	C(25)–C(26)	1.42(4)
C(11)–C(12)	1.52(2)	C(25)–C(27)	1.60(3)

Table 3. Bond angles (*ϕ*/°) of **2**, with standard deviations in parentheses

C(2)–C(1)–C(10)	111(2)	C(12)–C(13)–C(17)	121(2)
C(1)–C(2)–C(3)	129(2)	C(14)–C(13)–C(17)	100(1)
C(2)–C(3)–C(4)	102(2)	C(13)–C(14)–C(15)	109(1)
C(3)–C(4)–C(5)	131(2)	C(13)–C(14)–C(8)	110(1)
C(3)–C(4)–C(28)	100(2)	C(13)–C(14)–C(30)	108(1)
C(3)–C(4)–C(29)	101(2)	C(14)–C(15)–C(16)	106(2)
C(5)–C(4)–C(28)	103(2)	C(15)–C(16)–C(17)	96(2)
C(5)–C(4)–C(29)	113(2)	C(16)–C(17)–C(13)	111(2)
C(4)–C(5)–C(10)	109(2)	C(16)–C(17)–C(20)	111(1)
C(4)–C(5)–C(6)	116(2)	C(17)–C(20)–C(21)	113(1)
C(5)–C(6)–C(7)	114(2)	C(17)–C(20)–C(22)	109(1)
C(6)–C(7)–C(8)	109(2)	C(17)–C(20)–O(2)	110(1)
C(7)–C(8)–C(9)	111(1)	C(21)–C(20)–O(2)	105(1)
C(7)–C(8)–C(14)	108(1)	C(22)–C(20)–O(2)	104(1)
C(7)–C(8)–C(18)	107(1)	C(21)–C(20)–C(22)	116(1)
C(8)–C(9)–C(10)	116(1)	C(20)–C(22)–C(23)	115(2)
C(8)–C(9)–C(11)	115(2)	C(22)–C(23)–C(24)	112(2)
C(9)–C(10)–C(19)	115(1)	C(23)–C(24)–C(25)	111(2)
C(9)–C(11)–C(12)	112(1)	C(23)–C(24)–C(31)	124(2)
C(11)–C(12)–C(13)	115(1)	C(25)–C(24)–C(31)	125(2)
C(11)–C(12)–O(1)	120(1)	C(24)–C(25)–C(26)	125(2)
C(13)–C(12)–O(1)	125(1)	C(24)–C(25)–C(27)	127(2)
C(12)–C(13)–C(14)	116(2)	C(26)–C(25)–C(27)	108(2)

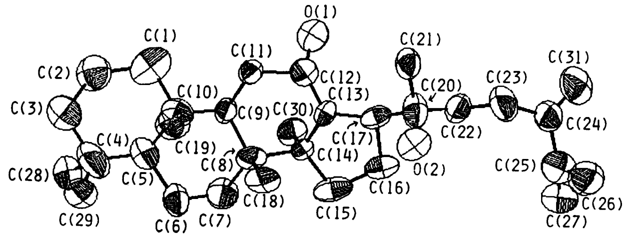


Fig. 1. Perspective view of **2**.

Table 4. Final atomic coordinates (×10^4) of **3**, with standard deviations in parentheses

Atoms	*x*	*y*	*z*	B_{eq}/Å^2 [a]
Br	1029(4)	2164(2)	2091(8)	6.9
O(1)	5727(23)	8986(12)	4576(5)	6.4
O(2)	−1003(18)	4085(11)	3435(4)	4.1
O(3)	−1492(16)	1846(10)	3245(4)	3.1
C(1)	3223(24)	7118(16)	3946(6)	3.6
C(2)	4326(31)	8189(18)	3982(8)	5.5
C(3)	5559(27)	8156(21)	4358(6)	5.1
C(4)	6536(28)	7044(19)	4437(6)	4.5
C(5)	5344(26)	5993(17)	4360(5)	3.4
C(6)	6258(27)	4828(18)	4396(6)	3.9
C(7)	4998(30)	3826(18)	4471(6)	4.4
C(8)	3717(25)	3756(16)	4095(5)	3.1
C(9)	2962(21)	4984(15)	4010(5)	2.2
C(10)	4267(21)	5970(14)	3949(5)	2.2
C(11)	1633(21)	4900(15)	3657(5)	2.2
C(12)	236(23)	4066(14)	3780(6)	2.8
C(13)	1074(23)	2859(15)	3842(5)	2.9
C(14)	2221(22)	2935(17)	4230(5)	2.5
C(15)	2650(27)	1630(18)	4280(7)	4.2
C(16)	994(31)	1091(19)	4274(7)	5.0
C(17)	−164(28)	1818(16)	3955(6)	3.9
C(18)	4734(26)	3270(16)	3702(6)	3.7
C(19)	5287(25)	5906(16)	3529(6)	3.3
C(20)	−778(32)	1095(16)	3572(6)	4.5
C(21)	−2209(31)	271(18)	3712(8)	5.2
C(22)	621(35)	454(16)	3316(7)	5.1
C(23)	−160(38)	372(17)	2867(9)	6.6
C(24)	−1026(31)	1533(15)	2825(7)	4.5
C(25)	−2604(31)	1573(26)	2520(7)	6.1
C(26)	−3485(32)	2718(18)	2488(7)	5.7
C(27)	−3973(42)	712(26)	2704(9)	8.5
C(28)	8064(26)	7055(21)	4140(6)	4.7
C(29)	7112(30)	7067(22)	4916(7)	5.5
C(30)	1406(28)	3308(20)	4643(5)	4.5
C(31)	258(29)	2441(14)	2684(6)	4.1

a) $B_{eq}=8\pi^2(U_1+U_2+U_3)/3$, where U_1, U_2, and U_3 are the principal components by U matrix.

The structure (**1**) for alnuserrudiolone was finally established by X-ray crystallography of a 3-deoxo-12-keto derivative (**2**) and a 31-bromo derivative (**3**) derived from **1**, because a good single crystal of **1** is not available. Huang-Minlon reduction of **1** gave a 3-deoxo compound (**4**), which could be converted to the 3-deoxo-12-keto derivative (**2**) by the Jones oxidation. The structure of **2** was determined by the direct method using MULTAN[8] and refined by full-matrix least-squares techniques to R=0.105 for 1876 reflections. Final atomic coordinates, bond lengths, and bond angles are given in Tables 1—3. A perspective view of the molecule of **2** is shown in Fig. 1. Since the ORD and the CD curves of **2** exhibited a negative Cotton effect similar to that of 3*β*-acetoxy-20-hydroxydammaran-12-one,[9,10] the absolute configuration is as given in **2**.

Bromination of **1** was carried out with pyridinium tribromide[11] with a view to preparing the bromo derivative of **1** for an X-ray crystallographic study. However, when **1** was treated with the above reagent,

Table 5. Interatomic distances (l/Å) of **3**, with standard deviations in parentheses

C(1)-C(2)	1.53(3)	C(12)-O(2)	1.49(2)
C(1)-C(10)	1.57(3)	C(13)-C(14)	1.55(2)
C(2)-C(3)	1.56(3)	C(13)-C(17)	1.60(3)
C(3)-C(4)	1.53(3)	C(14)-C(15)	1.56(3)
C(3)-O(1)	1.20(3)	C(14)-C(30)	1.54(3)
C(4)-C(5)	1.57(3)	C(15)-C(16)	1.46(3)
C(4)-C(28)	1.55(3)	C(16)-C(17)	1.62(3)
C(4)-C(29)	1.61(3)	C(17)-C(20)	1.57(3)
C(5)-C(6)	1.54(3)	C(20)-C(21)	1.56(3)
C(5)-C(10)	1.58(2)	C(20)-C(22)	1.58(3)
C(6)-C(7)	1.56(3)	C(20)-O(3)	1.48(2)
C(7)-C(8)	1.59(3)	C(22)-C(23)	1.58(3)
C(8)-C(9)	1.57(3)	C(23)-C(24)	1.52(3)
C(8)-C(14)	1.59(3)	C(24)-C(25)	1.60(3)
C(8)-C(18)	1.61(3)	C(24)-O(3)	1.45(2)
C(9)-C(10)	1.56(2)	C(24)-C(31)	1.54(3)
C(9)-C(11)	1.56(2)	C(25)-C(26)	1.51(4)
C(10)-C(19)	1.58(3)	C(25)-C(27)	1.60(4)
C(11)-C(12)	1.53(2)	C(31)-Br	2.03(2)
C(12)-C(13)	1.57(2)		

Table 6. Bond angles (ϕ/°) of **3**, with standard deviations in parentheses

C(10)-C(1)-C(2)	113(2)	C(13)-C(12)-O(2)	113(1)
C(1)-C(2)-C(3)	114(2)	C(12)-C(13)-C(14)	108(1)
C(2)-C(3)-C(4)	118(2)	C(8)-C(14)-C(13)	105(1)
C(2)-C(3)-O(1)	120(2)	C(8)-C(14)-C(30)	113(2)
C(4)-C(3)-O(1)	121(2)	C(13)-C(14)-C(15)	99(1)
C(3)-C(4)-C(5)	109(2)	C(14)-C(15)-C(16)	102(2)
C(3)-C(4)-C(28)	107(2)	C(15)-C(16)-C(17)	108(2)
C(5)-C(4)-C(29)	107(2)	C(13)-C(17)-C(16)	101(2)
C(4)-C(5)-C(6)	113(2)	C(13)-C(17)-C(20)	115(2)
C(4)-C(5)-C(10)	119(2)	C(16)-C(17)-C(20)	114(2)
C(6)-C(5)-C(10)	108(2)	C(17)-C(20)-C(21)	109(2)
C(5)-C(6)-C(7)	111(2)	C(17)-C(20)-C(22)	116(2)
C(6)-C(7)-C(8)	110(2)	C(21)-C(20)-C(22)	113(2)
C(7)-C(8)-C(9)	110(2)	C(22)-C(20)-O(3)	100(2)
C(7)-C(8)-C(18)	107(2)	C(20)-O(3)-C(24)	115(1)
C(7)-C(8)-C(14)	108(2)	C(20)-C(22)-C(23)	103(2)
C(8)-C(9)-C(10)	116(1)	C(22)-C(23)-C(24)	102(2)
C(8)-C(9)-C(11)	109(1)	C(23)-C(24)-O(3)	105(2)
C(9)-C(10)-C(1)	106(1)	C(23)-C(24)-C(31)	109(2)
C(9)-C(10)-C(19)	115(1)	C(25)-C(24)-O(3)	111(2)
C(5)-C(10)-C(1)	106(1)	C(24)-C(25)-C(26)	116(2)
C(5)-C(10)-C(9)	106(1)	C(24)-C(25)-C(27)	107(2)
C(9)-C(11)-C(12)	110(1)	C(26)-C(25)-C(27)	105(2)
C(11)-C(12)-C(13)	107(1)	C(24)-C(31)-Br	112(1)
C(11)-C(12)-O(2)	106(1)		

the bromination took place with the cyclization of the acyclic side chain of **1**. The presence of the brominated side chain including a tetrahydrofuran ring was evidenced by the high resolution mass spectrum, which exhibited ions at m/z 491.2332, 489.2344, and 139.1104. The ^{13}C NMR signals at δ_C 88.2, 87.5, and 32.9 also demonstrated the presence of the tetrahydrofuran ring[2,3] with a bromomethyl group on C-24. On the other hand, comparison of the high resolution mass and the ^{13}C NMR spectra of the bromo derivative (**3**) with those of **1** suggested that **3** possesses the same tetracyclic skeleton as **1**. Further, the bromo derivative (**3**) was confirmed to be convertible into **1** in a quantitative yield by treatment with zinc dust in acetic acid. The structural elucidation of **3** was carried out by X-ray crystallography using the heavy atom method. Refinement by least-squares calculation gave a final R value of 0.075 for 1707 reflections. Final atomic coordinates, bond lengths, and bond angles are shown in Tables 4—6. A perspective view of the molecule of **3** is shown in Fig. 2. The ORD and CD curves of **3** exhibited a positive Cotton effect, which indicated the absolute configuration to be as shown in **3**.

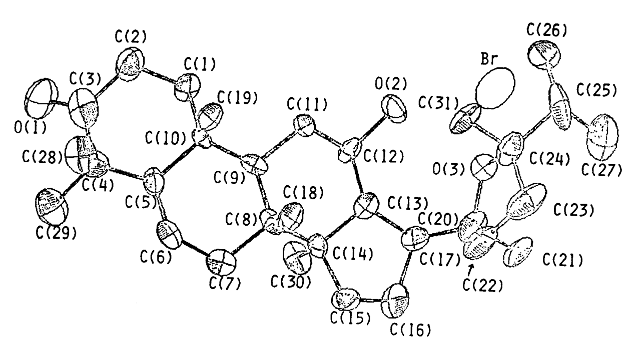


Fig. 2. Perspective view of **3**.

From the spectroscopic evidence of **1** and the X-ray crystallographic results of **2** and **3** derived from **1**, it has now been established that alnuserrudiolone is (12R,20S)-12,20-dihydroxy-24-methylenedammaran-3-one (**1**).

Experimental

The ^{1}H NMR spectra were taken on a Varian T-60 spectrometer using TMS as an internal standard. The ^{13}C NMR spectra were obtained on a JEOL JNM FX-60 (15.1 MHz) and a Hitachi R-42 FT NMR (22.6 MHz) spectrometers (δ_{TMS}=0). The ORD and the CD curves were taken on a JASCO ORD/UV-5 spectropolarimeter, equipped with a circular dichroism attachment, at 25 °C. The X-ray intensity data were collected on a syntex R3 and a Rigaku AFC-5 diffractometers using graphite-monochromated radiation.

Extraction and Isolation. The male flowers (10.3 kg) of *Alnus serrulatoides* Call. Grown naturally on a river side in the suburbs of Hiroshima city were collected just before the flowering in December, 1975. The flowers, after minced mechanically, were immersed in acetone (54 l) at room temp for 2 months. Removal of the solvent from the acetone solution gave a viscous sirup, which was extracted with ether (500 ml × 5) to give a viscous oil (66.0 g). A part (7.0 g) of the viscous oil was subjected to centrifugal chromatography using silica gel (160 g) and a hexane–EtOAc mixture with EtOAc increasing 0 to 100% as a solvent, and then to preparative TLC (silica gel GF$_{254}$; 0.75 mm thick) with hexane–EtOAc (7 : 3 v/v) to give alnuserrudiolone (**1**) (1.27 g; R_f 0.20).

Alnuserrudiolone (1). Mp 174—175 °C; $[\alpha]_D^{25}$ +50.7° (c 0.61, CHCl$_3$); IR (0.005 M,† CCl$_4$) ν_{max} 3613 (free OH), 3432 (intramolecularly hydrogen-bonded OH), 1708 (C=O), 3082 and 1638 cm^{-1} ($\rangle$C=CH$_2$); ^{1}H NMR (CDCl$_3$) δ=0.90—

---

† 1 M=1 mol dm^{-3}.

1.19 (Me×8), 3.60 (1H, br, >C$\underline{\mathrm{H}}$-OH), 4.71 and 4.73 (2H, br, >C=CH_2); ^{13}C NMR ($CDCl_3$) δ_c=217.8 (s, C-3), 156.5 (s, C-24), 106.2 (t, C-31), 73.6 (s, C-20), 70.5 (d, C-12), 26.7 (q, Me), 26.4 (q, Me), 21.9 (q, Me×2), 21.0 (q, Me), 16.8 (q, Me), 15.9 (q, Me), and 15.3 (q, Me); MS (70 eV) *m/z* 454.3869 (Calcd for $C_{31}H_{50}O_2$ ($M-H_2O$): 454.3808), 436.3731 ($C_{31}H_{48}O$ ($M-2H_2O$): 436.3705), 375.2911 ($C_{24}H_{39}O_3$: 375.2900), 205.1603 ($C_{14}H_{21}O$: 205.1592), 141.1280 ($C_9H_{17}O$: 141.1279), 123.1183 (C_9H_{15}: 123.1174); ORD (*c* 0.38, dioxane) $[\phi]_{600}$ +216°, $[\phi]_{589}$ +216°, $[\phi]_{315}$ +2095°, $[\phi]_{309}$ +2033°, $[\phi]_{305}$ +2077°, $[\phi]_{279}$ +73.9°; CD (*c* 0.56, dioxane) $[\theta]_{320}$ 0, $[\theta]_{293}$ +1170, $[\theta]_{243}$ 0.

Found: C, 79.00; H, 11.04%. Calcd for $C_{31}H_{52}O_3$: C, 78.76; H, 11.09%.

*Huang-Minlon Reduction of **1**.* A mixture of **1** (200 mg), hydrazine hydrate (3 ml), and diethylene glycol (30 ml) was refluxed for 2 h to give a 3-deoxo compound (**4**) (157 mg): mp 167—168 °C; $[\alpha]_D^{25}$ +10.7° (*c* 0.56, $CHCl_3$); IR (0.0004 M, CCl_4) ν_{max} 3649, 3431 (OH), and 3081 cm^{-1} (>C=CH_2); ^{1}H NMR ($CDCl_3$) δ=3.64 (1H, br, >C$\underline{\mathrm{H}}$-OH), 4.73 (2H,br, >C=CH_2).

Found: C, 81.35; H, 12.16%. Calcd for $C_{31}H_{54}O_2$: C, 81.16; H, 11.87%.

*Jones Oxidation of **4**.* The Jones reagent[12] (2 ml) was added to a solution of **4** (150 mg) in acetone (30 ml), followed by stirring for 1 h at 5 °C, to yield a 3-deoxo-12-keto derivative (**2**) (114 mg): mp 195—197 °C; $[\alpha]_D^{25}$ +44.3° (*c* 0.70, $CHCl_3$); IR (0.0002 M, CCl_4) ν_{max} 3652, 3452 (OH), 1702, 1689 (C=O), and 3083 cm^{-1} (>C=CH_2); ^{1}H NMR ($CDCl_3$) δ=4.73 (2H, br, >C=CH_2); MS (70 eV) *m/z* (rel. int.) 456 (M^+, 16), 438 ($M-H_2O$, 55), 359 (88), 315 (49), 191 (85), 141 (44), 124 (100), 123 (73); ORD (*c* 0.23, dioxane) $[\phi]_{600}$ +97°, $[\phi]_{589}$ +97°, $[\phi]_{309}$ −1069°, $[\phi]_{295}$ 0°, $[\phi]_{260}$ +3645°; CD (*c* 0.22, dioxane) $[\theta]_{318}$ 0, $[\theta]_{287}$ −1980, $[\theta]_{244}$ 0.

Found: C, 81.48; H, 11.30%. Calcd for $C_{31}H_{52}O_2$: C, 81.52; H, 11.48%.

*Conversion of **1** to a Bromo Derivative (**3**).* Pyridinium tribromide (264 mg)[11] was added to a warmed solution (55 °C) of **1** (300 mg) in EtOH (7.7 ml) and then the mixture was stirred for 1 min. After removal of the solvent, the reaction mixture was subjected to preparative TLC [silica gel GF_{254}; EtOAc-hexane (3 : 7 v/v); developed continuously for 3 h] to give a bromo derivative (**3**) (146 mg): mp 174—176 °C; $[\alpha]_D^{25}$ +33.5° (*c* 0.82, $CHCl_3$); IR (Nujol) ν_{max} 3329 (OH) and 1731 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=3.53 (2H, d, *J*=2.5 Hz, $-CH_2Br$); ^{13}C NMR ($CDCl_3$) δ_c=217.8 (d, C-3), 88.2 (s, C-24), 87.5 (s, C-20), 70.6 (s, C-12), 32.9 (t, C-31), 28.6 (q, Me), 26.7 (q, Me), 21.0 (q, Me), 18.0 (q, Me×2), 17.3 (q, Me), 16.2 (q, Me), 15.4 (q, Me); MS (70 eV) *m/z* 491.2332 (Calcd for $C_{28}H_{42}O_2Br$: 491.2347), 489.2344 ($C_{28}H_{42}O_2Br$: 489.2367), 205.1571 ($C_{14}H_{21}O$: 205.1591), 139.1104 ($C_9H_{15}O$: 139.1122), 43.0539 (C_3H_7: 43.0547); ORD (*c* 0.38, dioxane) $[\phi]_{600}$ +204°, $[\phi]_{589}$ +204°, $[\phi]_{317}$ +1750°, $[\phi]_{312}$ +1640°, $[\phi]_{308}$ +1714°, $[\phi]_{292}$ 0°, $[\phi]_{276}$ −985°, $[\phi]_{246}$ −79°; CD (*c* 0.38, dioxane) $[\theta]_{320}$ 0, $[\theta]_{292}$ +1224, $[\theta]_{264}$ 0.

Found: C, 67.24; H, 9.46%. Calcd for $C_{31}H_{51}O_3Br$: C, 67.60; H, 9.43%.

*Conversion of **3** to **1**.* A suspension of **3** (8 mg) and Zn powder (5 mg) in ether (3 ml) and acetic acid (0.5 ml) was refluxed for 3 h at room temp. The reaction mixture was diluted with water and extracted with ether to give a crude product (6 mg), which was then purified by preparative TLC [silica gel GF_{254}; EtOAc–hexane (3 : 7 v/v)] to afford alnuserrudiolone (**1**) (mp 171—173 °C; direct comparison with mixed mp, ^{1}H NMR, and MS).

*X-Ray Crystallographic Analyses. (i) 3-Deoxo-12-keto Derivative (**2**).* The crystal used was about 0.7 mm×0.5 mm×0.05 mm in size. Cell dimensions were obtained by least-squares calculations from 2θ values of 15 well-centered, resolved Cu $K\alpha$ diffraction peaks. Crystal data: monoclinic, space group $P2_1$, two molecules per unit cell with dimensions a=7.629(5), b=10.438(5), c=17.714(6) Å, β=90.84(4)°; U=1410.4 Å^3; D_c=1.08 g cm^{-3}; D_m=1.12 g cm^{-3}; μ(Cu $K\alpha$)=4.30 cm^{-1}. A total of 2506 reflections were collected on an automatic four-circle diffractometer by the 2θ-ω scan method (θ_{max}=70°); 1876 reflections with intensities greater than 2.0 times the standard deviations were used in the structure determination. The phases of 456 strong reflections with $|E|>1.30$ were determined by the direct method, by the use of the program MULTAN.[8] The E map for the best solution yielded positions for all non-hydrogen atoms. The structure was refined by full-matrix least-squares methods. Anisotropic refinement for carbon and oxygen atoms reduced the R index to 0.105.

*(ii) 31-Bromo Derivative (**3**).* The crystal used was about 0.2 mm×0.3 mm×0.6 mm in size. Cell dimensions were obtained by least-squares calculations from 2θ values of 14 well-centered, resolved Mo $K\alpha$ diffraction peaks. Crystal data: orthorhombic, space group $P2_12_12_1$, four molecules per unit cell with dimensions a=7.991(3), b=11.610(9), c=31.214(21) Å; U=2898.2 Å^3; D_c=1.26 g cm^{-3}; D_m=1.21 g cm^{-3}; μ(Mo $K\alpha$)=15.3 cm^{-1}. A total of 2702 reflections were collected by using the ω-scan technique (θ_{max}=60°); 1707 reflections with intensities greater than 1.96 times the standard deviations were used in the structure determination. The bromine atom position was obtained from a Patterson function, and then the positions of oxygen and carbon atoms were determined by difference-Fourier syntheses. A least-squares refinement using anisotropic temperature factors for bromine, carbon, and oxygen atoms and isotropic ones for hydrogen atoms reduced the R index to 0.075.

The complete F_o-F_c data and the tables of anisotropic thermal parameters for **2** and **3** are deposited as Document No. 8151, respectively, at the Office of the Editor of the Bulletin of the Chemical Society of Japan.

The authors thank Mr. Akio Wada of JASCO Instruments Co. Ltd. for useful advice for the X-ray crystallographic analyses and JEOL Co. Ltd. for obtaining the ^{13}C NMR spectra. The present work was partially supported by a Grant-in-Aid for Scientific Research No. 354189 (1978, to T.A.) from the Ministry of Education, Science and Culture and Matsunaga Science Foundation in 1977 (to T.H.).

References

1) J. Heslop-Harrison, "Pollen: Development and Physiology," London Butterworths Co. Ltd., London (1971).

2) T. Hirata and T. Suga, *J. Chem. Soc., Perkin Trans. 2*, **1978**, 347.

3) T. Suga and T. Hirata, *Bull. Chem. Soc. Jpn.*, **52**, 1153 (1979).

4) T. Suga, T. Hirata, and N. Iwata, *Chem. Lett.*, **1974**, 971.

5) P. M. Baker, E. J. L. Barreiro, and B. Gilbert, *Phytochemistry*, **15**, 785 (1976).

6) M. Tori, T. Tsuyuki, and T. Takahashi, *Bull. Chem. Soc. Jpn.*, **50**, 3349 (1977).

7) J. Asakawa, R. Kasai, K. Yamasaki, and O. Tanaka, *Tetrahedron*, **33**, 1935 (1977).

8) G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. A*, **27**, 368 (1971).

9) O. Tanaka, M. Nagai, and S. Shibata, *Chem. Pharm. Bull.*, **14**, 1150 (1966).

10) Y. Nagai, O. Tanaka, and S. Shibata, *Tetrahedron*, **27**, 881 (1971).

11) C. Djerassi and C. R. Scholy, *J. Am. Chem. Soc.*, **70**, 417 (1948).

12) K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, **1946**, 36.