Novel Lanostane and Rearranged Lanostane-Type Triterpenoids from *Abies sachalinensis*—II—

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In the previous work we reported five A-*seco*-rearranged lanostane triterpenoids as antibacterial constituents from the ethyl acetate soluble fraction of *Abies sachalinensei* leaves. In further study on the isolation of constituents from the ethyl acetate soluble fraction, two new rearranged lanostane and lanostane-type triterpenoids (3, 4) and three reported compound (1, 2, 5) were isolated. The structures of new compound 3 and 4 were determined to be 3,4-*seco*-4(28),6,8(14),24-mariesatetraen-26,23-olide-23-hydroxy-3-oic acid and 3,4-*seco*-4(28),7,24-lanostatrien-26,23-olide-23-hydroxy-3-oic acid, respectively, by spectral studies on HR-MS, ^{1}H-NMR, ^{13}C-NMR, and 2D-NMR spectra. Compound 1 was identified with pindrolactone and its structure was revised as 7,14,22*Z*,24-mariesatetraen-26,23-olide-3α-ol. Structures of 2 and 5 were determined as 7,14,24-mariesatrien-26,23-olide-3α,23-diol and 3α-hydroxy-7,14,24*E*-mariesatrien-23-oxo-26-oic acid. Of these compounds, 2, 3 and 4 were obtained as lactol tautomer mixtures at γ-lactone structures of side chains.

Key words *Abies sachalinensis*; Pinaceae; lanostane-type; rearranged lanostane-type; tautomerism

In the course of our program on researching biological active constituents from woody plants, we have reported many bioactive constituents, such as anti-bacterial constituents from *Chamaecyparis pisifera*,[1] antitumor-promoting constituents from *Chaenomeles sinensis*,[2] antioxidative constituents from *Alnus japonica*[3] and neurite outgrowth active constituents from *Chamaecyparis obtusa*.[4] In our previous work, we reported the isolation of four new compounds (abiesanolide A, B, C and D) with an A-*seco*-17,14-friedolanostane skeleton along with a mariesane derivative from the ethyl acetate (EtOAc) soluble fraction of methanol (MeOH) extract of *Abies sachalinensis* leaves.[5] Some showed potent antibacterial activity against gram-positive bacteria. Lanostane and rearranged lanostane-type triterpenoids were isolated from *Abies* sp. Plants.[6—9] For the purpose of finding many more new bioactive constituents from the ethyl acetate soluble fraction, further chemical investigation on the fraction led to the isolation of two new rearranged lanostane and lanostane-type triterpenoids (**3**, **4**) and a reported compound (**1**, **2**, **5**). The structural determination of compounds was established by ^{1}H-NMR, ^{13}C-NMR and 2D-NMR spectra, such as HMQC, HMBC, ^{1}H–^{1}H COSY, NOESY, along with HR-MS experiments. The reported structure of **1** was revised by exact ^{1}H-NMR, ^{13}C-NMR and 2D-NMR experiments. The structure of **2** was exactly determined and its NMR data assignments were carried out by 2D-NMR. Compound **5** was determined as 3α-hydroxy-7,14,24*E*-mariesatrien-23-oxo-26-oic acid[7] (Fig. 1) by comparison of the spectral data with the reported data, and it was isolated from *A. sachalinensis* for the first time.

Compound **1** was obtained as white amorphous powder. The molecular formula of **1** was determined to be $C_{30}H_{42}O_3$ based on the molecular ion peak at *m*/*z* 450.3146 $[M]^+$ in the HR-EI-MS. The UV spectrum showed maximum absorption at 290, 258, 239 nm, and the absorption band at 1751 cm^{-1} in the IR spectrum was assigned to a strained lactone carbonyl. The ^{1}H-NMR spectrum of **1** (Table 1) showed the presence of five singlet methyl groups (δ_H 0.80, 0.93, 0.96, 0.98, 1.00), a doublet methyl group (δ_H 1.01, d, J=7.2 Hz), an olefinic methyl group (δ_H 2.00, s) and four olefinic H (δ_H 5.20, br s; δ_H 5.21, br d, J=10.8 Hz; δ_H 5.59, br d, J=6.0 Hz; δ_H 6.98, d, J=1.8 Hz). The ^{1}H- and ^{13}C-NMR spectra of **1**

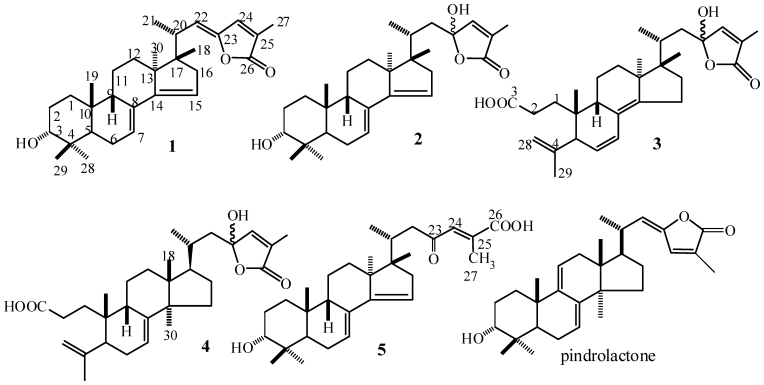

Fig. 1. Structures of Compound **1**—**5** and Pindrolactone

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Table 1. ^{1}H-NMR Spectral Data of **1**—**4** (500 MHz and 600 MHz, in $CDCl_3$)

Position	**1**	**2**	**3**[a)]	**4**
H-1	0.93 (m)	0.94 (overlap)	2.01 (t-like)	1.60 (m)
	2.01 (dd, 13.8, 2.4)	2.00 (dd, 13.8, 3.4)		1.74 (overlap)
2	1.60 (m)	1.61 (m)	1.60 (m)	2.26 (overlap)
	1.95 (overlap)	1.96 (overlap)		
3	3.45 (br s)	3.47 (br s)		
5	1.52 (dd, 11.4, 4.2)	1.54 (dd, 11.7, 4.8)	2.62 (d, 5.4)	2.12 (d, 7.1)
6	1.91 (br d, 12.6)	1.95 (overlap)	5.37 (dd, 10.2, 5.4)	1.99 (overlap)
	1.95 (m)	1.89 (overlap)		2.32 (overlap)
7	5.59 (br d, 6.0)	5.56 (d, 5.1)	6.21 (d, 10.2)	5.34 (br d, 2.9)
9	1.37 (br d, 13.2)	1.40 (overlap)	2.58 (m)	2.58 (m)
11	1.33 (m)	1.44 (overlap)	1.58 (overlap)	2.58 (m)
	1.75 (m)	1.81 (overlap)	1.62 (overlap)	1.66 (overlap)
12	1.22 (dt, 11.3, 4.2)	1.48 (dd, 12.9, 4.8?)	1.64 (overlap)	1.68 (overlap)
	1.69 (m)	1.83 (overlap)	1.67 (overlap)	1.86 (dt, 11.2, 3.4)
15	5.20 (br s)	5.17 (br s)	2.25 (overlap)	1.49 (m)
				1.56 (overlap)
16	1.98 (overlap)	2.17 (d, 15.6)	1.48 (t, 10.8)	1.29 (m)
	2.24 (d, 15.6)	1.90 (dd, 15.6, 3.7)	1.68 (overlap)	1.99 (overlap)
17				1.55 (overlap)
18	1.00 (3H, s)	0.87 (3H, s)	0.67 (3H, s)	0.79 (3H, s)
19	0.96 (3H, s)	0.94 (3H, s)	0.86 (3H, s)	0.87 (3H, s)
20	3.23 (m)	2.02 (m)	1.95 (m)	1.58 (m)
21	1.01 (3H, d, 7.2)	0.94 (3H, d, 6.6)	0.96 (3H, d, 6.6)	1.01 (3H, s)
22	5.21 (br d, 10.8)	1.67 (m)	1.54 (overlap)	1.63 (m)
		2.08 (m)	2.32 (overlap)	2.07 (m)
24	6.98 (d, 1.8)	6.85 (br s)	6.84 (br s)	6.89 (br s)
27	2.00 (3H, s)	1.94 (3H, s)	1.96 (3H, s)	1.92 (3H, br s)
28	0.98 (3H, s)	0.96 (3H, s)	4.83 (br s)	4.83 (br s)
				4.78 (br s)
29	0.93 (3H, s)	0.93 (3H, s)	1.78 (3H, s)	1.80 (3H, s)
30	0.80 (3H, s)	0.88 (3H, s)	1.04 (3H, s)	1.05 (3H, s)

a) Proton signals of **4** was obtained in $CDCl_3$+CD_3OD solvent.

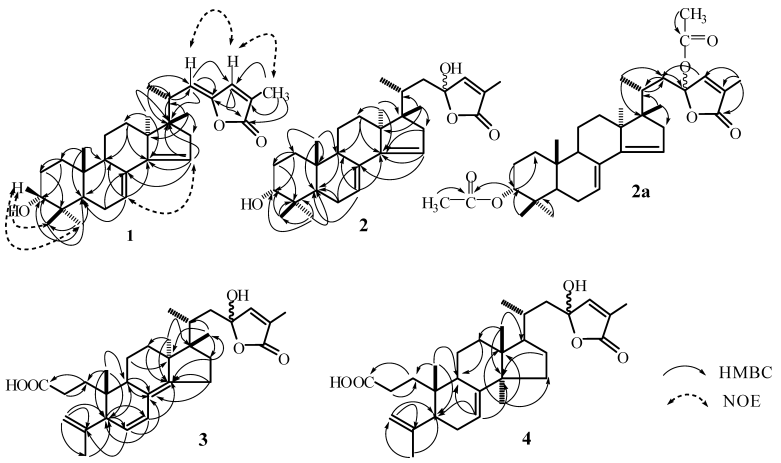

Fig. 2. Key Correlations in HMBC Spectra of **1**—**4** and **2a**, and NOE of **1**

exhibited a similar signal pattern to that of **5** except for the side chain. The ^{13}C-NMR spectrum of **1** showed almost the same chemical shifts in C-1—C-19 and C-28—C-30 carbons with those of **5** (Table 2). This indicated that the A—D ring part of **1** should be same as that of **5**. This was confirmed from the HMBC correlations of **1**, as shown for the correlations of Me-28 and 29 (δ_H 0.98, s. 0.93, s) to C-3 and 5 (δ_C 76.6, 37.9); Me-19 (δ_H 0.96, s) to C-1, 5 and 9 (δ_C 28.7, 37.9, 53.0); Me-18 (δ_H 1.00, s) to C-13, 16 and 20 (δ_C 51.8, 44.6, 36.4); Me-30 (δ_H 0.80, s) to C-12, 14 and 17 (δ_C 32.0, 153.0, 50.5); H-7 (δ_H 5.59, br d, J=6.0 Hz) to C-5, 9, 14 (δ_C 37.9, 53.0, 153.0); H-15 (δ_H 5.20, br s) to C-8, 14 and 20 (δ_C 136.4, 153.0, 36.4) (see Fig. 2). The α-configuration of the hydroxyl group at C-3 was confirmed from the ^{1}H-NMR signal of H-3 (δ_H 3.45, br s) and the NOE correlation of H-3 to Me-28 and Me-29 (Fig. 2). The side chain part of **1** showed similar ^{1}H- and ^{13}C-NMR spectral patterns to those in the reported data of abiesanolides, which were isolated from the same source.[5)] The HMBC correlations of H-22 (δ_H 5.21, br d, J=10.8 Hz) to C-17, 21, 23 and 24 (δ_C 50.5, 17.4, 146.8, 138.0); Me-27 (δ_H 2.00, s) to C-24, 25 and 26 (δ_C 138.0, 128.8, 171.3) confirmed the side chain structure (Fig.

Table 2. ^{13}C-NMR Spectral Data of **1**—**5** and Anhydrosibiric Acid (125 MHz and 150 MHz, in $CDCl_3$)

No.	**1**	Pindrolactone[10]	**2**[a]	**3**[a]	Anhydrosibiric acid[5]	**4**[a,b]	**5**
1	28.7	28.7	28.7	28.4	28.4	29.5	28.7
2	25.1	25.1	25.2	29.4	29.5	29.6	25.2
3	76.6	76.6	76.6	178.7	180.1	177.9	76.3
4	37.1	37.1	37.1	145.8	145.8	150.3	37.1
5	37.9	37.9	38.0	50.6	50.8	45.8	38.0
6	23.1	23.1	23.1	126.7	126.8	30.1	23.1
7	121.0	121.0	120.7	125.0	125.1	118.5	120.8
8	136.4	146.8	136.7	125.2	125.2	147.0	136.6
9	53.0	153.0	52.9	39.4	39.9	39.3	52.9
10	34.7	34.7	34.7	37.1	37.2	36.7	34.7
11	25.0	114.5	25.3	19.7	19.6	19.0	25.3
12	32.0	44.6	33.6	32.0	30.5	34.5	33.9
13	51.8	50.5	51.5	47.4	47.5	44.1	51.7
14	153.0	51.8	153.1	146.6	146.2	52.2	152.8
15	114.5	32.0	114.0	23.7	23.8	34.4	115.1
16	44.6	25.0	45.0	35.9	35.8	29.0	45.0
17	50.5	53.0	51.6	49.5	49.0	54.0	50.5
18	17.1	17.1	16.8	15.7	16.2	21.9	17.1
19	22.3	22.3	22.3	21.8	21.9	24.3	22.3
20	36.4	36.4	33.3	33.0	36.5	33.1	33.6
21	17.4	17.3	17.4	17.9	17.2	20.8	16.6
22	118.4	118.4	41.3	40.9	118.3	44.5	48.7
23	146.8	136.4	106.3	106.4	146.5	105.1	202.0
24	138.0	138.1	147.7	147.5	137.9	149.0	134.2
25	128.8	128.8	131.6	131.9	129.0	131.4	139.4
26	171.3	171.3	171.6	171.8	171.1	173.5	171.7
27	10.6	10.5	10.4	10.5	10.5	10.4	14.1
28	28.2	19.2	28.2	115.5	115.5	112.1	28.2
29	23.0	23.0	23.0	24.8	24.7	26.1	23.0
30	19.2	28.2	19.1	21.7	21.7	27.6	19.3

a) C-20—27 carbon signals appeared broad weak peaks in the ^{13}C-NMR spectra of **2**, **3** and **4**. *b*) Carbon signals of **4** was obtained in $CDCl_3+CD_3OD$ solvent.

2). The NOESY spectrum of **1** showed the correlations of H-24 (δ_H 6.98, 1H, d, J=1.8 Hz) to H-22 (δ_H 5.21, 1H, br d, J=10.8 Hz) and Me-27 (δ_H 2.00, 3H, s) (Fig. 2). This indicated that the geometrical isomerism of the C-22,23-double bond resulted to be *Z*. Thus, the structure of **1** was exactly determined as 7,14,22*Z*,24-mariesatetraen-26,23-olide-α-3-ol. The ^{13}C-NMR chemical shifts of **1** were completely identical with those of reported data (Table 2) of pindrolactone isolated from *Abies pindrow*.[10] But its structure having lanostane skeleton was different with that of **1** having mariesane (rearranged lanostane) skeleton. Thus, the structure of pindrolactone must be revised as 7,14,22*Z*,24-mariesatetraen-26,23-olide-α-3-ol and its ^{13}C-NMR assignment as shown in Table 2.

Compound **2** was obtained as white amorphous powder. The molecular formula of **2** was determined to be $C_{30}H_{44}O_4$ based on the pseudo-molecular ion peak at *m/z* 469.3297 $[M+H]^+$ in the HR-ESI-MS. The successive dehydration peaks at *m/z* 451.3179 $[M+H-H_2O]^+$ and 433.3115 $[M+H-H_2O-H_2O]^+$ suggested the presence of two hydroxyl groups at least in the structure. The UV spectrum of **2** showed maximum absorption at 238 nm. The IR spectrum of **2** showed absorption bands at 3469 cm^{-1} (hydroxyl group) and 1763 cm^{-1} (strained lactone carbonyl). The ^{1}H-NMR spectrum of **2** showed a similar signal pattern to that of **1** (Table 1). One of seven methyl group appeared as a broad singlet, which was assigned to be Me-27. The ^{13}C-NMR spectrum of **2** showed a similar signal pattern to those of **1** (Table 2), but some signals appeared as broad weak peaks, which were supposed to be belonged to the side chain. These spectral data suggested that **2** had the same A—D ring structure as that of **1**. This was confirmed from the HMBC experiment of **2**, as shown in Fig. 2. The signal broadening phenomenon was supposed to be based on a tautomerism of γ-lactone ring having a lactol structure, as shown in Fig. 3. Compound **2** was acetylated with Ac_2O-pyridine to give product **2a**. The EI-MS of **2a** showed the molecular ion peak at *m/z* 552 $[M]^+$ for $C_{34}H_{48}O_6$ along with elimination of two acetic acid fragments, *m/z* 492 $[M-CH_3COOH]^+$ and *m/z* 432 $[492-CH_3COOH]^+$. This indicated that **2a** was diacetate of **2**, while, ^{13}C-NMR signals (see Experimental) showed duplicated pair signal peaks of more than 50. This indicated that **2a** was an approximately 1 : 1 ratio mixture of two acetate epimers at C-23 obtained from two tautomers of **2** (as shown in Fig. 3). The HMBC spectrum of **2a** showed correlations of H-22 to C-23, and correlations of H-24 to C-22, 23, 25, 27 (Fig. 2). The mixture of **2a** could not be separated each other not only by TLC but also by HPLC under the usual conditions for **2a**, however, under the condition with reverse phase columns (Mighty sil RP-18, Kanto Chemical Co., Ltd.), these was on very polar solvent of CH_3CN–H_2O (v/v 60 : 40) and flow rate (2 ml/min) for **2a** analysis, which take a long time to obtain the peaks, but **2a** gave two peaks (t_R=223, 224 min). This indicated that **2a** was obtained as an approximately 1 : 1 mixture of epimers at C-23 obtained from the tautomer mixture of **2**. Thus, the structure of **2** was determined to be 7,14,24-mariesatrien-26,23-olide-3α,23-diol. This structure was reported as the constituent from *Abies sibirica*.[11] However, its exact NMR data could not be obtained. Thus the ^{1}H- and ^{13}C-NMR data were de-

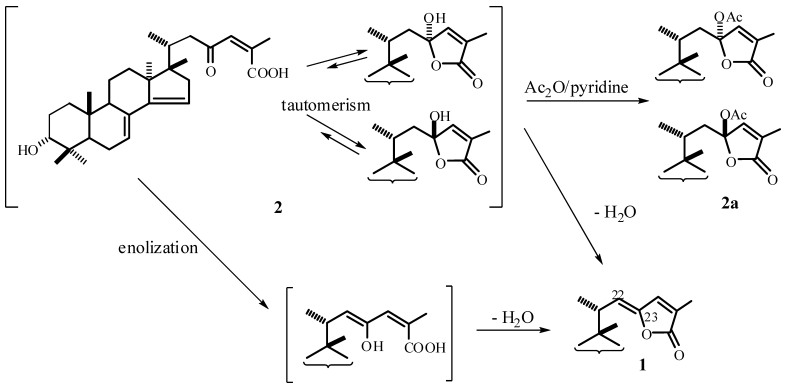

Fig. 3. Hypothetical Mechanism for Tautomers of **2**—**4**, and Formation of the Acetate **2a** and **1**

scribed in Tables 1 and 2.

Compound **3** was obtained as white amorphous powder. The molecular formula of **3** was determined to be $C_{30}H_{42}O_5$ based on the pseudo-molecular ion peak at *m/z* 505.2903 $[M+Na]^+$ in HR-ESI-MS. The UV spectrum of **3** showed the maximum absorption at 242 nm. The IR spectrum of **3** showed the absorption bands at 1746 cm^{-1} (strained lactone carbonyl) and 1712 cm^{-1} (carboxyl group). The ^{1}H- and ^{13}C-NMR spectra (Tables 1, 2) showed the presence of an isopropenyl group (δ_C 145.8, 115.5, 24.8), a carboxyethyl group (δ_C 28.4, 29.4, 178.7) and two olefine group (δ_C 125.0, 125.2, 126.7, 146.6) in the ring part. The ^{13}C-NMR spectrum of **3** showed similar signal patterns to those of 3,4-*seco*-4(28),6,8(14),22*Z*,24-mariesapenten-26,23-olide-3-oic acid (anhydrosibiric acid).[5,9] The ^{13}C-NMR signals of the A—D ring part, and Me-28, 29 and 30 of **3** showed identical chemical shifts to those of anhydrosibiric acid (Table 2).[5] The 3,4-*seco*-4(28),6,8(14)-triene ring structure was further confirmed by the HMBC experiment as shown the correlations of Me-29 (δ_C 1.78, s) to C-5 and 28 (δ_C 50.6, 115.5); Me-19 (δ_H 0.86, s) to C-1, 5 and 9 (δ_C 28.4, 50.6, 39.4); Me-30 (δ_H 1.04, s) to C-12, 14, 17 (δ_C 32.0, 146.6, 49.5); Me-18 (δ_H 0.67, s) to C-13, 16 and 20 (δ_C 47.4, 35.9, 33.0); H-6 (δ_H 5.37, dd, J=10.2, 5.4 Hz) to C-4, 8 and 10 (δ_C 145.8, 125.2, 37.1); H-7 (δ_H 6.21, d, J=10.2 Hz) to C-5, 9 and 14 (δ_C 50.6, 39.4, 146.6) (see Fig. 2). The side chain part ^{13}C-NMR signal of **3** showed broad weak signals as in **2**, and had an approximately similar signal pattern to that of **2**, which is the tautomer mixture at the γ-lactone part. Thus, the structure of **3** was determined to be 3,4-*seco*-4(28),6,8(14),24-mariesatetraen-26,23-olide-23-hydroxy-3-oic acid and named abiesanolide E.

Compound **4** was obtained as white amorphous powder. The molecular formula of **4** was determined to be $C_{30}H_{44}O_5$ based on the pseudo-molecular ion peak at *m/z* 485.3289 $[M+H]^+$ in the HR-ESI-MS. The UV spectrum of **4** showed the maximum absorption at 216 nm. The IR spectrum of **4** showed absorption bands at 3376 cm^{-1} (hydroxyl group), 1747 cm^{-1} (strained lactone carbonyl group), 1709 (carboxyl group). The ^{1}H-NMR spectrum of **4** showed similar signal pattern to that of **3**, which has a 3,4-*seco*-A ring. The ^{13}C-NMR spectrum of **4** showed the presence of an isopentenyl group (δ_C 150.3112.1, 26.1), a carboxyethyl group (δ_C 177.9, 29.6, 29.5), and a trisubstituted olefine group (δ_C 147.0, 118.5) in the ring part. The structure of the ring part was determined by HMBC experiment. The correlations of Me-19 (δ_H 0.87, s) to C-1, 5 and 9 (δ_C 29.5, 45.8, 39.3); Me-18 (δ_H 0.79, s) to C-12, 14 and 17 (δ_C 34.5, 52.2, 54.0); Me-30 (δ_H 1.05, s) to C-8, 13 and 15 (δ_C 147.0, 44.1, 34.4); Me-29 (δ_H 1.80, s) to C-4, 5 and 28 (δ_C 150.3, 45.8, 112.1); H-1 (δ_H 1.60, m) to C-3 (δ_C 177.9); H-7 (δ_H 5.34, br s) to C-5, 9 and 14 (δ_C 45.8, 39.3, 52.2) were observed in the HMBC experiment of **4** (Fig. 2). These data showed that **4** was a 3,4-*seco*-9β-4(28),7,24-lanostatrien derivative. The side chain part ^{13}C-NMR signal of **4** showed broad weak signals as in **2** and **3**, and had an approximately similar signal pattern (Table 2) to that of **2** and **3**, which are tautomer mixtures at the γ-lactone part. Thus, the structure of **4** was determined to be 3,4-*seco*-4(28),7,24-lanostatrien-26,23-olide-23-hydroxy-3-oic acid and named abiesanolide F.

The further elaborate purification of AcOEt soluble fraction of *A. sachalinensis* leaves gave novel lanostane and rearranged lanostane-type triterpenoids, some of which have a γ-lactone structure in the side chain and were obtained as an epimer mixture arising from tautomerism at C-23 of the γ-lactone part. The tautomerism was confirmed by derivatization of **2** to mixture of diacetate-epimers. The same tautomerism example of lanostane-type triterpene having a γ-lactone side chain was reported in the constituents of *A. sibirica*.[11,12] This type of compound should be considered an intermediate of 22-en-26,23-olide-type compound such as **1** (Fig. 3). The tautomerism gives signal broadening in ^{13}C-NMR of **2**—**4**. Compound **1** was identified with pindrolactone, but its structure was revised as 7,14,22*Z*,24-mariesatetraen-26,23-olide-3α-ol.

Experimental

Melting points were recorded on Yanaco MP-3 micro-melting point apparatus and the temperatures were not corrected. Optical rotations were recorded with a JASCO P-1010 polarimeter at 25 °C. UV spectrum was recorded by U-2001 Spectrophotometer (Hitachi). IR spectrum was recorded by FT-IR Spectroscopy (Perkin Elmer) as KBr tablets. NMR spectra were recorded on a Bruker-DRX (^{1}H-NMR; 600 MHz, ^{13}C-NMR; 150 MHz) and a JEOL α-500 (^{1}H-NMR; 500 MHz, ^{13}C-NMR; 125 MHz) the spectrometer using $CDCl_3$ or CD_3OD as solvents and TMS as an internal standard. 2D-NMR was done in common conditions. HR-MS and EI-MS spectrum were recorded by JEOL-HX110 mass spectrometer. Preparative and analytical HPLC were performed on the reverse phase columns (mightysil RP-18 and RP-8, Kanto Chemical Co., Inc.) with the CH_3CN–H_2O and MeOH–H_2O solvent system. Silica gel 60N (Kanto Chemical Co., Inc.) was used for column chromatography. The analytical and preparative thin layer chromatography (PLC) were carried out on precoated Kieselgel 60 F_{254} (0.25 mm thick for analysis and 0.5 mm thick for preparation, Merck) and spots were visual-

ized by spraying the plates with 50% H_2SO_4 solution, followed by heating.

Plant Material The needles of *A. sachalinensis* were collected in Assabu, Hokkaido, Japan in September 1997, and the vouch specimen was deposited in the herbarium of The Faculty of Life and Environmental Sciences, Prefectural University of Hiroshima.

Extraction and Isolation The process for the extraction was reported in our previous report.[1] Air dried needles of *A. sachalinensis* (1.5 kg) were extracted with MeOH and the filtrate was evaporated under reduced pressure to give the MeOH extracts. Then the extract was suspended in water and partitioned successively with EtOAc and *n*-BuOH to afford EtOAc soluble fraction (150 g), *n*-BuOH soluble fraction (60 g) and aqueous residues. The EtOAc layer showed the most potent antibacterial activity against gram positive bacteria *Straphylococcus aureus* and *Bacillus subtilis*. The EtOAc extract was chromatographyed on a silica gel column with the gradient solvent system $CHCl_3$–MeOH to afford ten fractions (Fr. 1—10). Some of these fraction were purified and to give five the rearranged lanostane triterpenes. Their structures and anti-bacterial activity was reported in the previous report.[5] The residual Fr. 3 (16.0 g) was further purified by silica gel column chromatography and preparative HPLC with reverse phase columns and preparative layer chromatography (PLC) to afford compound **1** (3.6 mg), **2** (30.1 mg), **3** (18.9 mg), **4** (9.7 mg), and **5** (9.8 mg) were isolated.

Compound **1**: White amorphous powder. mp 181—183 °C (MeOH), $[\alpha]_D$ −73.9° (c=0.036, MeOH), UV λ_{max} nm (ε) (MeOH): 239 (4381), 258 (4348), 290 (3884). HR-EI-MS: *m*/*z* 450.3146 $[M]^+$ (Calcd for $C_{30}H_{42}O_3$; 450.3134), IR ν_{max} cm^{-1} (KBr): 2924, 1751, 1622, 1465, 1062. ^{1}H-NMR data, see Table 1 and ^{13}C-NMR data, see Table 2.

Compound **2**: White amorphous powder. mp 106—108 °C (MeOH), $[\alpha]_D$ +52.0° (c=0.249, $CHCl_3$), UV λ_{max} nm (ε) (MeOH): 238 (5854). IR ν_{max} cm^{-1} (KBr): 3469, 2966, 1764, 1621, 1451, 1385, 1103. HR-ESI-MS: *m*/*z* 469.3297 $[M+H]^+$ (Calcd for $C_{30}H_{45}O_4$; 469.3318). ^{1}H-NMR data, see Table 1 and ^{13}C-NMR data, see Table 2.

Compound **3** (Abiesanolide E): White amorphous powder. mp 173—175 °C (MeOH), $[\alpha]_D$ −437.8° (c=0.207, CH_3OH), UV λ_{max} nm (ε) (MeOH): 242 (8135), 266sh (7095). IR ν_{max} cm^{-1} (KBr): 2967, 1746, 1712, 1639, 1451, 1373, 1106. HR-ESI-MS: *m*/*z* 505.2903 $[M+Na]^+$ (Calcd for $C_{30}H_{42}O_5Na$; 505.2930). ^{1}H-NMR data, see Table 1 and ^{13}C-NMR data , see Table 2.

Compound **4** (Abiesanolide F): White amorphous solid. mp 158—160 °C (MeOH), $[\alpha]_D$ −755.9° (c=0.053, $CHCl_3$), UV λ_{max} nm (ε) (MeOH): 216 (5136), 241sh (1547). IR ν_{max} cm^{-1} (KBr): 3376, 2957, 1747, 1709, 1639, 1444, 1377. HR-ESI-MS: *m*/*z* 485.3289 $[M+H]^+$ (Calcd for $C_{30}H_{45}O_5$; 485.3267). ^{1}H-NMR data, see Table 1 and ^{13}C-NMR data , see Table 2.

Acetylation of Compound 2 A solution of compound **1** (10 mg) in pyridine (2 ml) and Ac_2O (2 ml) was heated on water bath (80 °C) for 3 h. After cooling the reaction mixture was poured into cool water and extracted with EtOAc to give an amorphous solids (**2a**, 8.9 mg).

Compound **2a**: White amorphous powder. EI-MS: *m*/*z* 552 $[M]^+$ $C_{34}H_{48}O_6$, *m*/*z* 492 $[M-CH_3COOH]^+$, *m*/*z* 432 $[492-CH_3COOH]^+$. ^{13}C-NMR ($CDCl_3$): δ_C 29.46 (C-1), 22.60, 22.62 (C-2), 78.74, 78.77 (C-3), 36.30 (C-4), 38.83, 38.87 (C-5), 22.90 (C-6), 120.72, 120.78 (C-7), 136.56 (C-8), 52.70 (C-9), 34.65 (C-10), 25.18, 25.26 (C-11), 33.29, 33.36 (C-12), 51.42, 51.49 (C-13), 153.03, 152.97 (C-14), 114.76, 114.92 (C-15), 44.97 (C-16), 51.52, 51.66 (C-17), 16.74, 16.77 (Me-18), 22.27, 22.30 (Me-19), 33.41, 32.93 (C-20), 17.10, 17.50 (Me-21), 39.25, 38.32 (C-22), 107.95, 108.44 (C-23), 145.96, 145.54 (C-24), 132.01, 132.14 (C-25), 170.79, 170.85 (C-26), 10.51, 10.56 (Me-27), 27.89 (Me-28), 22.27, 22.30 (Me-29), 19.08 (Me-30), 170.78, 21.30, 170.76, 21.36 (C_3-OAc), 168.84, 21.69, 169.14, 21.72 (C_{23}-OAc).

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