Structure and Stereochemistry of Epoxyserratanes from the Cuticle of *Picea jezoensis* var. *jezoensis*

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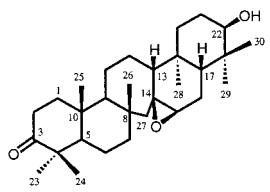
Three new epoxytriterpenes, 14*β*,15*β*-epoxy-21*β*-hydroxyserratan-3-one (**1**), 13α,14α-epoxy-21α-methoxyserratan-3-one (**2**), and 13α,14α-epoxy-3*β*-methoxyserratan-21*β*-ol (**3**), were isolated together with two known triterpenoids, 21α-methoxyserrat-13-en-3-one (**4**) and 21*β*-hydroxyserrat-14-en-3-one (**5**), from the cuticle of *Picea jezoensis* var. *jezoensis*. The structures of these new compounds were established on the basis of spectral data (NMR, MS) and single-crystal X-ray analyses (**1** and **2**) and partial synthesis (**2** and **3**).

The CH_2Cl_2 extract of the cuticle of *Picea jezoensis* (Sieb. et Zucc.) Carr. var. *jezoensis* (Pinaceae) contained 13 triterpenes including 3*β*-methoxyserrat-14-en-21*β*-ol, 21α-hydroxy-3*β*-methoxyserrt-14-en-30-al,[1] 14*β*,15*β*-epoxy-3*β*-methoxyserratan-21-one and the corresponding 21*β*-ol,[2] and 21α-methoxyserrat-13-en-3,15-dione.[3] Investigation of the extract has led to the isolation of novel epoxyserratanes, **1**−**3**, together with two known compounds, 21α-methoxyserrat-13-en-3-one (**4**) and 21*β*-hydroxyserrat-14-en-3-one (**5**), identical in all respects with the corresponding authentic samples already isolated from the stem bark of *P. jezoensis* (Sieb. et Zucc.) Carr. var. *hondoensis* (Mayr.) Rehder.[4,5] This paper deals with the structure elucidation of compounds **1**−**3**.



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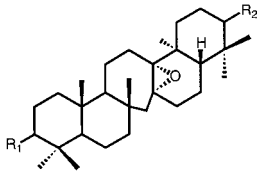
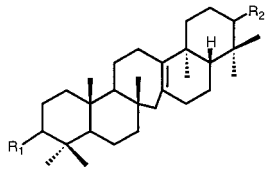
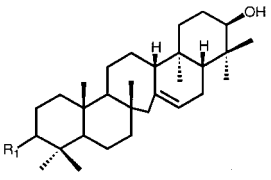


	R^1	R^2
2	=O	α-OMe, β-H
3	β-OMe, α-H	β-OH, α-H
3a	β-OMe, α-H	β-OAc, α-H



	R^1	R^2
4	=O	α-OMe, β-H
6a	β-OMe, α-H	β-OAc, α-H
6b	β-OMe, α-H	β-OH, α-H



5 R_1 = O

6 R_1 = β-OMe, α-H

Results and Discussion

Compound **1** was assigned the molecular formula $C_{30}H_{48}O_3$, by HREIMS. Its IR spectrum showed absorption bands for a hydroxyl group and a cyclohexanone. The ^1H and ^{13}C NMR spectra (Table 1) exhibited signals for seven singlet methyl groups, 10 methylene groups, four methine groups, five quaternary carbons, an axial secondary hydroxyl group, an oxygenated methine, and an oxygenated quaternary carbon attributable to an epoxy ring[2] and a saturated ketone, while no signal was observed for a double bond. Except for the presence of a ketone and the absence of a methoxy group, the ^1H and ^{13}C NMR and EIMS spectra of **1** were closely similar to those of 14*β*,15*β*-epoxy-3*β*-methoxyserratan-21*β*-ol.[2] Along with the chemical shift values and signal pattern of the methine proton geminal to the hydroxyl group, these data indicated that **1** must be 14,15-epoxy-21*β*-hydroxyserratan-3-one. The stereochemistry was determined by single-crystal X-ray analysis and NOESY measurement. The ORTEP diagram (Figure 1) indicated **1** to be 14*β*,15*β*-epoxy-21*β*-hydroxyserratan-3-one, having a flat conformation of the skeletal system due to the presence of a *cis*-fused chairlike/half-chair conformation of the C/D rings, together with a deformed-chair for ring A. The NOESY spectrum exhibited cross correlations among signals of Me-23 with H-6α, Me-24 with H-2*β* and H-6*β*, Me-25 with H-2*β* and H-12*β*, H-15α with H-27*β*, H-27α with H-7α and H-9α, and H-27*β* with H-7α and H-7*β*, indicating **1** to have a three-dimensional structure identical with that obtained from the X-ray analysis. Oxidation of 21*β*-hydroxyserrat-14-en-3-one (**5**) with *m*-chloroperbenzoic acid (MCPBA) in $CHCl_3$ furnished the corresponding epoxide, identical in all respects with **1**, in almost quantitative yield.

Compounds **2** and **3** were assigned the molecular formulas $C_{31}H_{50}O_3$ and $C_{31}H_{52}O_3$, respectively, by HREIMS. The IR and ^1H and ^{13}C NMR spectra of **2** (Table 1) revealed signals due to seven singlet methyl groups, 11 methylene groups, three methine groups, five sp^3 quaternary carbons, an equatorial secondary methoxy group, and two sp^3 quaternary carbons combined with one oxygen atom. The ^1H and ^{13}C NMR spectra of **3** (Table 1) were similar to those of **2**, except for the absence of a ketone and the presence of a secondary hydroxyl group, and exhibited signals for an equatrial methoxy group, a secondary hydroxyl group, and two sp^3 quaternary carbons geminal to an ether oxygen.

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Table 1. ^{1}H and ^{13}C NMR Data of Compounds **1**, **2**, and **3** in $CDCl_3$[a]

	1		**2**		**3**	
	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C
1α	1.48, m	39.6, t	1.45, m	39.6, t	0.84, m	38.5, t
1*β*	2.28, m		1.98, m		1.83, m	
2α	2.46, dd (9.2, 3.1)	34.0, t	2.43, m	33.9, t	1.81, m	22.2, t
2*β*	2.48, dd (9.2, 5.6)		2.49, m		1.42, m	
3		218.1, s		218.1, s	2.62, dd (12.2, 4.4)	88.3, d
4		47.3, s		47.1, s		38.8, s
5α	1.40, m	55.0, d	1.45, dd (13.1, 2.0)	54.3, d	0.70, dd (13.1, 1.4)	55.8, d
6α	1.43, m	19.7, t	1.46, m	19.7, t	1.46, m	18.2, t
6*β*	1.55, m		1.55, m		1.46, m	
7α	1.43, m	43.3, t	1.22, m	43.7, t	1.43, m	44.8, t
7*β*	1.20, td (13.0, 3.6)		1.49, m		1.18, m	
8		37.0, s		37.0, s		37.1, s
9α	0.85, dd (11.1, 1.2)	62.6, d	0.88, dd (10.7, 1.4)	64.8, d	0.74, dd (12.5, 1.5)	65.7, d
10		39.0, s		38.0, s		38.4, s
11α	1.93, m	25.9, t	1.64, m	22.3, t	1.68, m	21.5, t
11*β*	1.37, m		1.36, m		1.36, m	
12α	1.93, m	27.1, t	2.52, dd (15.6, 8.9)	34.0, t	2.52, dd (15.8, 8.9)	33.8, t
12*β*	1.07, m		1.02, m		0.98, m	
13*β*	1.48, dd (12.8, 4.1)	56.6, d		72.5, s		72.9, s
14		61.1, s		65.5, s		65.7, s
15α	2.82, brs	59.3, d	1.96, dt (14.1, 3.0)	36.8, t	1.93, dt (14.4, 3.3)	36.5, t
15*β*			1.78, ddd (14.1, 12.1, 6.0)		1.83, m	
16α	1.70, ddd (14.6, 13.1, 2.1)	22.7, t	1.23, m	16.9, t	1.20, m	16.8, t
16*β*	1.96, m		1.29, m		1.20, m	
17*β*	1.47, m	37.9, d	0.87, dd (11.1, 1.6)	53.2, d	1.35, m	46.2, d
18		35.2, s		37.7, s		37.9, s
19α	1.52, m	31.7, t	1.83, dt (13.1, 3.6)	34.3, t	2.02, m	29.3, t
19*β*	1.43, m		1.58, m		1.70, m	
20α	1.78, ddd (14.8, 4.5, 2.7)	25.1, t	1.55, m	23.2, t	1.50, m	26.4, t
20*β*	1.56, m		1.96, m		2.05, m	
21α	3.41, t (2.7)	75.6, d		88.0, d		75.3, d
21*β*			2.71, dd (11.8, 4.4)		3.35, t (2.6)	
22		37.7, s		39.1, s		38.1, s
23	1.08, s	26.9, q	1.08, s	27.3, q	0.94, s	28.0, q
24	1.03, s	20.8, q	1.03, s	20.8, q	0.74, s	16.2, q
25	0.91, s	16.3, q	0.89, s	16.7, q	0.82, s	16.4, q
26	1.12, s	19.9, q	1.09, s	20.4, q	1.08, s	21.0, q
27α	0.80, d (14.2)	55.2, t	1.58, d (14.9)	53.7, t	1.54, d (14.5)	54.0, q
27*β*	1.93, d (14.2)		1.58, d (14.9)		1.54, d (14.5)	
28	0.75, s	14.8, q	1.01, s	16.5, q	1.00, s	16.3, q
29	0.90, s	22.8, q	0.71, s	16.5, q	0.80, s	22.2, q
30	0.94, s	27.7, q	0.95, s	28.0, q	0.92, s	27.9, q
OMe			3.35, s	57.6, q	3.35, s	57.5, q

[a] Assignments based on DEPT, COSY, HMQC, HMBC, and NOESY experiments.

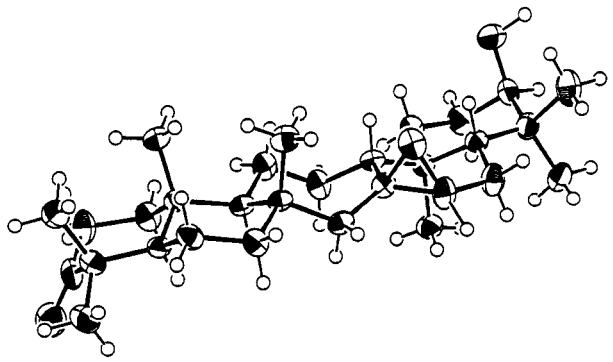

Figure 1. ORTEP drawing of compound **1**.

The HMBC spectra of **2** and **3** revealed the gross structures, suggesting the ketone, the secondary methoxy group, and the epoxy ring to be placed at C-3 and C-21α and between the C-13 and C-14 positions for **2**, and the secondary methoxy group, the secondary hydroxyl group, and the epoxy ring to be placed at C-3*β* and C-21*β* and between the C-13 and C-14 positions for **3**, respectively. Acetylation of **3** furnished a monoacetate (**3a**), in which the hydroxymethine proton signal was shifted to *δ* 4.65 (1H, t, *J* = 2.6 Hz). The EIMS of **2** and **3** showed fragment peaks corresponding to ions characteristic of the fragmentation of C-13,14-epoxyserratanes.

Oxidation of 21α-methoxyserrat-13-en-3-one (**4**) with *m*-chloroperbenzoic acid (MCPBA) in $CHCl_3$ furnished the corresponding epoxide, identical in all respects with **2**, in almost quantitative yield. Treatment of 3*β*-methoxyserrat-14-en-21*β*-ol (**6**) with concentrated H_2SO_4 in glacial acetic acid, followed by alkaline hydrolysis of the resulting acetate (**6a**), yielded 3*β*-methoxyserrat-13-en-21*β*-ol (**6b**).[6,7] Oxidation of **6b** with MCPBA afforded the corresponding epoxy derivative identical in all respects with those of compound **3** in almost quantitative yield.

Compounds **2** and **3** provide two possible pairs of conformers, by changing the epoxy ring from an α- to a *β*-orientation. The stereochemistry was examined by single-crystal X-ray analysis of **2** and NOESY spectra of **2** (Figure 2) and **3** (Figure 3). The ORTEP diagram (Figure 4) showed **2** to have the structure 13α,14α-epoxy-21α-methoxyserratan-3-one with a "bent-up" conformation, viz., the *trans*-fused half-chair/chair form of the D/E rings was lifted upward ca. 85° from the plane of the A/B/C rings due to the presence of an α-oriented epoxy ring in the joint of the *cis*-fused chair-like/half-chair form of the C/D rings. Furthermore, ring A, which contains a 4,4-dimethyl-3-one

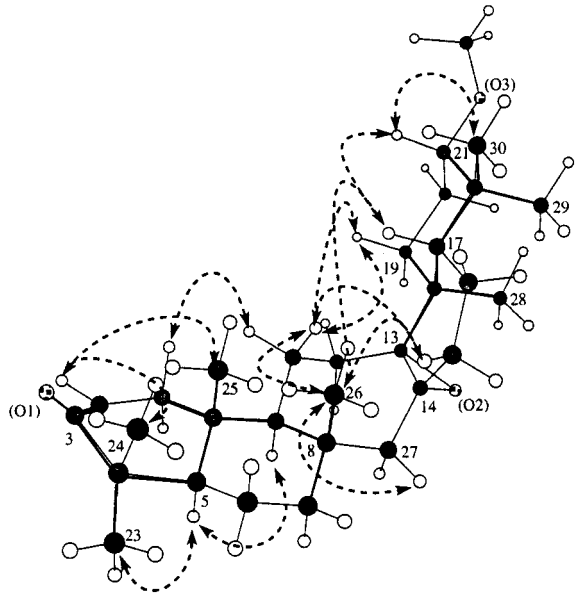

Figure 2. NOESY correlations (dashed arrow) of **2**.

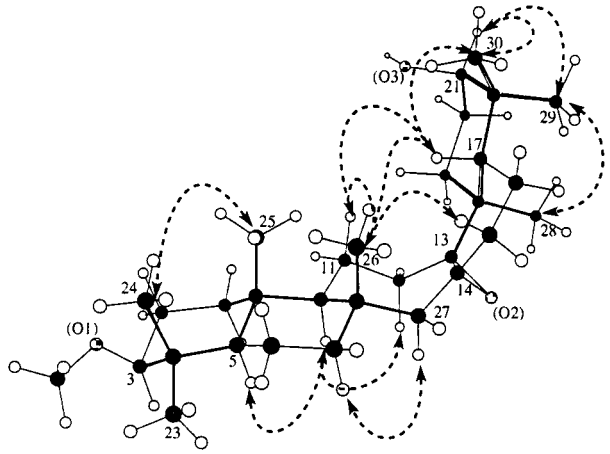

Figure 3. NOESY correlations (dashed arrow) of **3**.

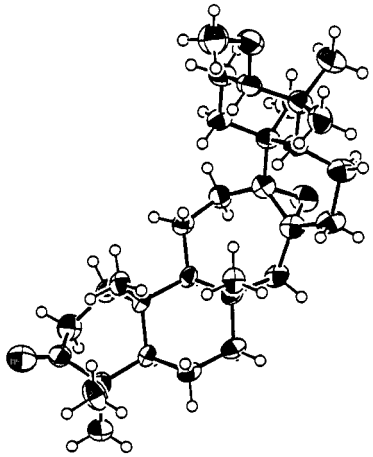

Figure 4. ORTEP drawing of compound **2**.

grouping, adopts a deformed-boat conformation. Thus, **3** was determined to be 13α,14α-epoxy-3*β*-methoxyserratan-21*β*-ol.

Experimental Section

General Experimental Procedures. Melting points were determined on a Yanagimoto micro-melting point apparatus and are uncorrected. Optical rotations were measured using a Jasco DIP-1000 digital polarimeter. IR spectra were recorded using a Perkin-Elmer 1720X FT-IR spectrophotometer. ^{1}H and ^{13}C NMR spectra were obtained using a JEOL GX-500 spectrometer with standard pulse sequences, operating at 500 and 125 MHz, respectively. $CDCl_3$ was used as the solvent and TMS as the internal standard. EIMS were recorded on a Hitachi 4000H double-focusing mass spectrometer (70 eV). Column chromatography was carried out over silica gel (70−230 mesh). Fractions obtained from column chromatography were monitored by TLC (silica gel 60 HF_{254}). Preparative TLC was carried out on Merck silica gel PF_{254} plates (20 × 20 cm, 0.5 mm thick).

Plant Material. Cuticles of *P. jezoensis* (sieb. et Zucc.) Carr. var. *jezoensis* were collected at ca. 1000 m in the mountains of Okujyozankei district under the management of National Hokkaido Forestry Bureau, Sapporo City, Japan, in August 1997. A voucher specimen (PJJ-97−01) is deposited at the Herbarium of the Laboratory of Medicinal Chemistry, Osaka University of Pharmaceutical Sciences.

Extraction and Isolation. In previous papers, we reported the isolation of several triterpene constituents from the CH_2Cl_2 extract of the cuticle of *P. jezoensis* (sieb. et Zucc.) Carr. var. *jezoensis*.[1−3] We have now enlarged the scale of the extraction and reexamined the constituents. The air-dried and chopped cuticle of *P. jezoensis* (8.5 kg) was extracted with CH_2Cl_2 (10 L) employing an automatic glass percolator for 24 h at 40 °C. The CH_2Cl_2 solution was then evaporated under reduced pressure, and the resulting dark green residue (530.7 g) was subjected to silica gel (10 kg) column chromatography. Elution of the column with $CHCl_3$ afforded residues A (61.8 g), B (15.5 g), C (32.4 g), and D (40.3 g) from fractions 7−17, 23−27, 28−40, and 41−50 (each 2 L). Elution was continued with $CHCl_3$−EtOAc (10:1) to give residue E (45.3 g) from fractions 51−80. Repeated CC of residue A on silica gel (1.8 kg) afforded a crystalline solid (fractions 15−33, 2.23 g), which was crystallized from MeOH−$CHCl_3$ to give compound **4**, 1.82 g, mp 223−225 °C, $[\alpha]_D$ +110 (*c* 1.35, $CHCl_3$).[4] Rechromatography of residue D on silica gel (900 g) afforded compound **5** (186 mg), mp 261.5−264 °C, $[\alpha]_D$ +19 (*c* 0.33, $CHCl_3$),[5] and compound **1** (125 mg), from fractions 56−58 and 92−98. Repeated column chromatography of residue E on silica gel (2 kg) furnished residue C_1 (1.45 g) from fractions 17−30, which was rechromatographed on silica gel (100 g) to furnish compounds **2** (226 mg) and **3** (123 mg).

14*β*,15*β*-Epoxy-21*β*-hydroxyserratan-3-one (1): needles; mp 310−312 °C (MeOH−$CHCl_3$); $[\alpha]_D$ −14.5 (*c* 0.52); IR ν_{max} cm^{-1} 3470, 2934, 2872, 1702 (six-membered ring C=O), 1457, 1387, and 1365 (*gem* dimethyl), 1082, 1067, 1035 and 996; ^{1}H and ^{13}C NMR, see Table 1; EIMS *m*/*z* (rel int) 456 (57) $[M]^+$, 441 (19) $[M - Me]^+$, 438.3488 (9) $[M - H_2O]^+$, 425 (6) $[M - CH_2OH]^+$, 423 (11) $[M - Me - H_2O]^+$, 420 (7) $[M - 2H_2O]^+$, 409 (26) $[M - H_2O - CO]^+$, 405 (26) $[M - Me - 2H_2O]^+$, 303 (4), 289 (8), 273 (13), 257 (10), 237 (31), 232 (17), 224 (89), 219 (9), 209 (100), 205 (18), 191 (16), 154 (35), 136 (64) 121 (54); HREIMS *m*/*z* 456.3608 $[M]^+$ ($C_{30}H_{48}O_3$ requires 456.3603).

13α,14α-Epoxy-21α-methoxyserratan-3-one (2): prisms; mp 219−222 °C (MeOH−$CHCl_3$); $[\alpha]_D$ −98 (*c* 0.83); IR ν_{max} cm^{-1} 2954, 2872, 1709 (six-membered ring C=O), 1464, 1386 and 1363 (*gem* dimethyl), 1181, 1103, 1000, 987, 943; ^{1}H and ^{13}C NMR, see Table 1; EIMS *m*/*z* (rel int) 470 (6) $[M]^+$, 452.3652 (8) $[M - H_2O]^+$, 438.3499 (2) $[M - MeOH]^+$, 420 (5) $[M - MeOH - H_2O]^+$, 405 (13) $[420 - Me]^+$, 351 (13), 303 (6), 285 (2), 205 (8), 201 (11), 168 (22), 136 (100), 121 (42); HREIMS *m*/*z* 470.3758 $[M]^+$ ($C_{31}H_{50}O_3$ requires 470.3756).

Preparation of 2 from 4. A solution of MCPBA (52 mg) in dry $CHCl_3$ (5 mL) was gradually added to a solution of **4** (83 mg) in dry $CHCl_3$ (15 mL) under stirring at room temperature. After standing for 24 h, the reaction mixture was washed with 5% $NaHSO_3$, 5% Na_2CO_3, and H_2O and the organic layer dried over Na_2SO_4. Evaporation of the solvent under reduced pressure yielded a residue, which was purified by PTLC ($CHCl_3$−MeOH, 30:1) to give a crystalline solid. Recrystallization from MeOH−$CHCl_3$ afforded **4a** (70 mg) as prisms, mp 219−222 °C; $[\alpha]_D$ −97 (*c* 0.45). It was identified as

2 by direct comparison (co-TLC, mp, $[\alpha]_D$, IR, ^{1}H NMR, ^{13}C NMR, and EIMS) with an authentic sample of **2** isolated from the cuticle.

13α,14α-Epoxy-3β-methoxyserratan-21β-ol (3): prisms; mp 242−244 °C (MeOH−$CHCl_3$); $[\alpha]_D$ +31 (*c* 0.38); IR ν_{max} (KBr) cm^{-1} 3340 (OH), 2928, 2871, 1466, 1388, and 1363 (*gem* dimethyl), 1261, 1183, 1095, 1074, 991, and 975; ^{1}H and ^{13}C NMR, see Table 1; EIMS *m*/*z* (rel int) 472 (2) $[M]^+$, 456 (8) $[M - 16]^+$, 454.3816 (8) $[M - H_2O]^+$, 440 (5) $[M - MeOH]^+$, 421 (19) $[M - 2H_2O - Me]^+$, 407 (1) $[M - H_2O - MeOH - Me]^+$, 367 (6), 319 (4), 287 (9), 269 (14), 221 (19), 203 (9), 201 (7), 189 (20), 154 (28), 136 (100), 121 (46); HREIMS *m*/*z* 472.3922 $[M]^+$ ($C_{31}H_{52}O_3$ requires 472.3916).

Acetylation of 3. Compound **3** (15 mg) was acetylated as usual (Ac_2O−pyridine, 1:1, 2 mL) to yield a crystalline mass. Purification by PTLC ($CHCl_3$−MeOH, 30:1) afforded 13α,14α-epoxy-3β-methoxyserratan-21β-yl acetate (**3a**), mp 228−231 °C (MeOH−$CHCl_3$), 16 mg, as prisms: IR ν_{max} (KBr) cm^{-1} 1734 (OAc), 1466, 1373, 1365, 1248 (OAc), 1185, 1102, 1043, 1015, 993, 985 and 946; ^{1}H NMR δ 0.70 (1H, m, H-5α), 0.74 (3H, s, Me-24), 0.77 (1H, m, H-9α), 0.84 (9H, s, Me-25, Me-29, and Me-30), 0.95 (3H, s, Me-23), 1.02 (3H, s, Me-28), 1.10 (3H, s, Me-26), 1.36 (1H, m, H-17β), 1.56 (2H, d, *J* = 4.5 Hz, H-27), 1.80 (1H, m, H-15β), 1.94 (1H, m, H-15α), 2.07 (3H, s, OAc), 2.50 (1H, dd, *J* = 15.8 and 8.3 Hz, H-12α), 2.62 (1H, dd, *J* = 12.2 and 4.4 Hz, H-3α), 3.35 (3H, s, OMe) and 4.65 (1H, t, *J* = 2.6 Hz, H-21α); ^{13}C NMR δ 16.1 (q, C-24), 16.4 (q, C-25 and C-28), 16.6 (t, C-16), 18.3 (t, C-6), 20.6 (q, C-26), 21.2 (q, OAc), 21.6 (t, C-11), 21.7 (q, C-29), 22.2 (t, C-2), 23.9 (t, C-20), 27.5 (q, C-30), 28.0 (q, C-23), 30.0 (t, C-19), 33.8 (t, C-12), 36.5 (t, C-15), 37.1 (s, C-8), 37.3 (s, C-22), 37.6 (s, C-18), 38.4 (s, C-10), 38.5 (t, C-1), 38.9 (s, C-4), 44.8 (t, C-7), 47.4 (d, C-17), 53.8 (t, C-27), 55.8 (d, C-5), 57.5 (q, OMe), 65.6 (s, C-14), 65.6 (d, C-9), 72.8 (s, C-13), 76.6 (t, C-21), 88.5 (d, C-3), 170.5 (s, OAc); EIMS *m*/*z* (rel int) 514 (1) $[M]^+$, 496 (2) $[M - H_2O]^+$, 472 (4) $[M - CH_2O]^+$, 454 (6) $[M - HOAc]^+$, 436 (5) $[M - HOAc - H_2O]^+$, 421 (16) $[436 - Me]^+$, 407 (2) $[M - HOAc - 2H_2O - Me]^+$, 367 (5), 319 (6), 287 (7), 269 (10), 221 (7), 203 (5), 201 (5), 196 (22), 189 (13), 187 (5), 136 (100), 121 (50).

Conversion of 3β-Methoxyserrat-13-en-21β-ol (6b) to 3β-Methoxyserrat-14-en-21β-ol (6) via 3β-Methoxyserrat-13-en-21β-yl Acetate (6a). A mixture of glacial HOAc (3 mL) and *c*-H_2SO_4 (2.3 mL) was gradually added into a solution of compound **6** (200 mg) in HOAc (30 mL) under ice cooling, and the mixture was kept at room temperature for 24 h. Then, the mixture was poured into ice water, and the resulting precipitate was extracted with $CHCl_3$ (30 mL × 3). The $CHCl_3$ extract was neutralized with 5% NaOH solution, washed with H_2O, and dried over Na_2SO_4. Evaporation of $CHCl_3$ yielded a crystalline mass (191 mg), which was subjected to CC on 10% $AgNO_3$−SiO_2 (20 g) to afford 3β-methoxyserrat-13-en-21β-yl acetate (**6a**): 131 mg, as prisms, mp 204−206 °C (MeOH−$CHCl_3$), from the fraction eluted with *n*-hexane−C_6H_6 (17:1), IR ν_{max} (KBr) cm^{-1} 2963, 2934, 2895, 1735 (OAc), 1457, 1389,-1376, 1248 (OAc), 1184, 1105, 1094, 1042, and 934; ^{1}H NMR δ 0.74, 0.78, 0.85, and 0.87 (each 3H, s), 0.90 (6H, s), 0.96 (3H, s), 2.08 (3H, s, OAc), 2.16 (1H, d, *J* = 14.0 Hz), 2.25 (1H, dd, *J* = 14.4 and 7.5 Hz), 2.64 (1H, dd, *J* = 12.2 and 4.0 Hz, H-3α), 3.36 (3H, s, OMe), and 4.69 (1H, t, *J* = 2.7 Hz, H-21α); ^{13}C NMR δ 16.1 (q), 16.3 (q), 18.8 (t), 19.0 (t), 19.2 (q × 2), 21.4 (t), 21.5 (q), 21.8 (q), 22.3 (t), 23.4 (t), 27.6 (q), 28.0 (q), 28.2 (t), 30.1 (t), 35.7 (s), 36.0 (t), 36.8 (s), 38.2 (t), 38.4 (s), 38.9 (s), 44.9 (t), 46.4 (d), 52.8 (t), 56.2 (d), 64.8 (d), 77.8 (d, CHOAc), 88.5 (d, CHOMe), 129.7 (s), 142.9 (s) and 170.9 (s, OAc); EIMS (rel int) *m*/*z* 498 (48) $[M]^+$, 483 (11) $[M - HOAc - Me - MeOH]^+$, 438 (37) $[M - HOAc]^+$, 423 (76) $[M - HOAc - Me]^+$, 391 (13) $[M - HOAc - MeOH - Me]^+$, 285 (7), 269 (6), 255 (21), 221 (54), 203 (100), 189 (83), 135 (62), 95 (48).

Treatment of acetate **6a** (108 mg) in boiling 0.2 N KOH/MeOH (32.5 mL) for 8 h and subsequent workup as usual furnished **6b**: 91 mg, as needles, mp 268−270° (MeOH−$CHCl_3$), IR ν_{max} (KBr) cm^{-1} 3537 (OH), 2961, 2937, 2871, 1459, 1385, 1374, 1182, 1126, 1098, 991, 964; ^{1}H NMR δ 0.73, 0.76, 0.83,0.85, 0.89, 0.95, and 0.97 (each 3H, s), 2.16 (1H, d, *J* = 14.0 Hz), 2.26 (1H, dd, *J* = 14.4 and 7.5 Hz), 2.63 (1H, dd, *J* = 12.2 and 4.0 Hz, H-3α), 3.36 (1H, brs, H-21α); ^{13}C NMR δ 16.1 (q), 16.3 (q), 18.8 (t), 19.2 (q and t), 19.4 (q), 21.5 (t), 22.2 (q), 22.3 (t), 25.8 (t), 28.03 (q), 28.08 (q), 28.18 (t), 35.8 (s), 36.1 (t), 37.7 (s), 38.18 (s), 38.24 (t), 38.40 (s), 38.9 (t), 44.9 (t), 45.2 (d), 52.8 (t and s), 56.2 (d), 57.5 (q, OMe), 65.0 (d), 75.8 (d, CHOMe), 88.5 (d, H−C−OH), 129.6 (s), 143.1 (s); EIMS *m*/*z* (rel int) 456 (45) $[M]^+$, 441 (40) $[M - Me]^+$, 438 (29) $[M - H_2O]^+$, 424 (40) $[M - MeOH]^+$, 409 (15) $[M - Me - MeOH]^+$, 391 (14) $[M - Me - MeOH - H_2O]^+$, 285 (10), 269 (9), 255 (25), 221 (85), 203 (78), 189 (100), 135 (82), 95 (60).

Preparation of 3 from 6b. A solution of MCPBA (31 mg) in dry $CHCl_3$ (5 mL) was gradually added over a solution of **6b** (87 mg) in dry $CHCl_3$ (12 mL) under stirring at room temparature and allowed to stand 21 h. Workup as described above yielded a residue, which was purified by PTLC ($CHCl_3$−MeOH, 20:1) to furnish the corrresponding 13,14-epoxyalcohol: 62 mg, mp 242−244 °C (MeOH−$CHCl_3$), $[\alpha]_D$ +32 (*c* 0.51); EIMS *m*/*z* 472 $[M]^+$, which was identified as **3** by direct comparison with an authentic sample of **3**.

Crystal Data for Compounds 1 and 2. (i) Compound **1**: $C_{30}H_{48}O_3$, $M = 456.71$, space group *P212121*, $a = 13.123(2)$ Å, $b = 31.213(3)$ Å, $c = 6.129(2)$ Å, $V = 2510.7(8)$ Å^3, $D_x = 1.208$ g·cm^{-3}, $Z = 4$. (ii) Compound **2**: $C_{31}H_{50}O_3$, $M = 470.74$, orthorhombic, space group *P212121*, $a = 17.421(3)$ Å, $b = 20.811(5)$ Å, $c = 7.553(1)$ Å, $V = 2738.3(9)$ Å^3, $D_x = 1.142$ g·cm^{-3}, $Z = 4$. A total of 2065 independent reflection intensities up to $2\theta = 130°$ were measured for compound **1** on a Rigaku automatic four-circle diffractometer with graphite-monochromated Cu Kα radiation, as well as a total of 2552 independent reflection intensities up to $2\theta = 130°$ for compound **2**. The structures were solved by direct methods using the SIR 92 program.[8] The non-hydrogen atoms were refined by a full-matrix least-squares method with anisotropic thermal parameters using the SHELXL-97 programs.[9] Hydrogen atoms were calculated assuming idealized geometries but not refined. Final cycles of least-squares refinement yielded $R = 0.061$ and $R_w = 0.082$ for 2065 for **1** and $R = 0.056$ and $R_w = 0.080$ for 2552 for **2** observed reflections of $F > 3\sigma(F)$. All calculations were performed using the teXan[10] crystallographic software package of Molecular Structure Corporation. Lists of atomic coordinates, thermal parameters, bond lengths and angles, torsion angles and the calculated and observed structure factors have been deposited at the Cambridge Crystallographic Data Centre, U.K.

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