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Two serratane triterpenes from the stem bark of *Picea jezoensis* var. *hondoensis*☆

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Abstract

Two serratane triterpenoids were isolated from the stem bark of *Picea jezoenis* var. *hondoensis*, together with two known compounds, 3β-methoxyserrat-14-en-21-one and 3β-methoxyserrat-14-en-21α-ol. The serratane triterpenoids were characterized as 14β,15β-epoxy-3α-methoxyserratan-21β-ol and 3α-methoxy-21β-hydroxyserrat-14-en-16-one, on the basis of chemical and spectroscopic evidence. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: *Picea jezoensis* var. *hondoensis*; Pinaceae; Stem bark; Triterpenes; 14β,15β-epoxy-3α-methoxyserratan-21β-ol; 3α-methoxy-21β-hydroxyserrat-14-en-16-one

1. Introduction

Previously we reported that the $CHCl_3$ extract of the stem bark of *Picea jezoensis* (Sieb. et Zucc.) Carr. var. *hondoensis* Rhed. (Japanese name: Touhi, Pinaceae), contained eight serratene triterpenoids including 21β-methoxyserrat-14-en-3-one, 21α-methoxyserrat-13-en-3-one and 21β-hydroxyserrat-14-en-3-one (Tanaka, Mun, Usami & Matsunaga, 1994; Tanaka, Tsuboi & Matsunaga, 1994).

Recently, we reported that the stem bark of *P. jezoensis* var. *hondoensis* contained 21α-hydroxy-3β-methoxyserrat-14-en-29-al and 29-*nor*-3α-methoxyserrat-14-en-21-one (Tanaka, Tsujimoto, Muraoka & Matsunaga, 1998).

Further careful examination of the stem bark of this extract has led to the isolation of two new triterpenoids, **1** and **2**, besides two known compounds, 3β-methoxyserrat-14-en-21-one (**3**) (Tanaka, Ohmori, Minoura & Matsunaga, 1996) and 3β-methoxy serrat-14-en-21α-ol (**4**) (Fang, Tsai & Cheng, 1991). This paper deals with the structures of **1** and **2**.

2. Results and discussion

The known compounds were confirmed to be 3β-methoxyserrat-14-en-21-one (**3**) (Tanaka et al., 1996) and 3β-methoxyserrat-14-en-21α-ol (**4**) (Fang et al., 1991), respectively, as physical and spectral data were in good agreement with those already reported in the literature data.

Compound **1** was assigned the molecular formula $C_{31}H_{52}O_3$, by HREIMS. The ^{1}H- and ^{13}C-NMR spectral data (Tables 1 and 2) exhibited the presence of seven tertiary methyl groups, an equatorial methine proton [δ_H 2.78 (1H, *t*, J = 2.5 Hz); δ_C 85.8 (*d*)] geminal to a methoxy group [δ_H 3.31 (3H, *s*, OMe); δ_C 57.1 (*q*)], an equatorial methine proton [δ_H 3.40 (1H, *t*, J = 2.4 Hz); δ_C 75.7 (*d*)] geminal to a hydroxyl group (ν_{max} 3533 cm^{-1}), a trisubstituted epoxy ring [δ_H 2.80 (1H, *br s*); δ_C 59.3(*d*) and 61.4 (*s*)]. Acetylation gave a monoacetate (**1a**). The ^{1}H- and ^{13}C-NMR spectra were similar to those of 14β,15β-epoxy-3β-methoxyserratan-21β-ol (**5**) which was obtained from *Picea jezoensis* var. *jezoensis*

☆ Part 4 in the series 'Serratanes from the stem bark of *Picea jezoensis* var. *hondoensis*'; for Part 3 see Tanaka et al. (1998).

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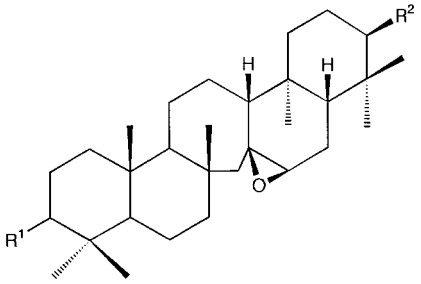
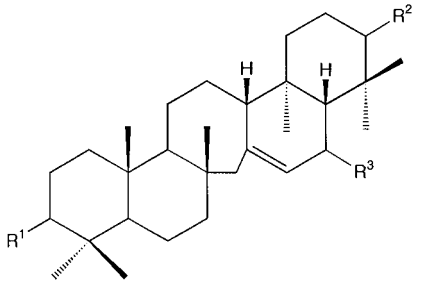


	R^1	R^2
1	α-OMe	OH
1a	α-OMe	OAc
5	β-OMe	OH
5a	β-OMe	OAc



	R^1	R^2	R^3
2	α-OMe	β-OH	: O
2a	α-OMe	β-OAc	: O
3	β-OMe	: O	H_2
4	β-OMe	α-OH	H_2
4a	β-OMe	α-OAc	H_2
6	α-OMe	β-OH	H_2
6a	α-OMe	β-OAc	H_2
7	β-OMe	β-OH	H_2
7a	β-OMe	β-OAc	H_2

(Ezomatsu) (Tanaka et al., 1996), except for C-3 configuration. The C-3 chemical shift values of **5** were extremely different from those of **1** which appeared at [δ_H 2.62 (1H, *dd*, J = 12.2, 4.4 Hz) and δ_C 88.5 (*d*)]. Hence, compound **1** was suggested to be the C-3α epimer of **5**. The conclusive evidence for this structure including an epoxy configuration was confirmed by the NOESY experiment, in which H-3β correlated with Me-23 and Me-24, and H-15 correlated with H-27β and Me-28. The EIMS spectra of **1** and **1a** (see Section 3) exhibited the same fragment ion peaks (ions **a**, **d**, **e**, **f**, **g**, **h**, **j**, **k**, **l** and **m**) as **5** and 14β,15β-epoxy-3β-methoxyserratan-21β-yl acetate (**5a**) (Tanaka et al., 1996). These data suggested that **1** should be 14β,15β-epoxy-3α-methoxyserratan-21β-ol, and this assumption was proved by synthesis. Oxidation of 3α-methoxyserrat-14-en-21β-ol (**6**), the most abundant triterpene constituent of this plant, with *m*-chloroperbenzoic acid (*m*-CPBA) furnished an epoxy compound identical in all respects with compound **1**.

Compound **2** was determined the molecular formula as $C_{31}H_{50}O_3$, from HREIMS. The UV and IR spectra indicated absorption bands for a hydroxyl group (ν_{max} 3396 cm^{-1}) and an α,β-unsaturated six membered ring ketone [λ_{max} 272 nm (ε 8000); ν_{max} 1661 cm^{-1}]. The ^{1}H- and ^{13}C-NMR spectra (Tables 1 and 2) exhibited signals for seven tertiary methyl groups, an equatorial methine proton [δ_H 2.78 (1H, *t*, J = 2.5 Hz); δ_C 85.7 (*d*)] geminal to a methoxy group [δ_H 3.31 (3H, *s*, OMe); δ_C 57.1 (*q*)], an equatorial methine proton [δ_H 3.34 (1H, *t*, J = 2.7 Hz); δ_C 76.8 (*d*)] geminal to a hydroxyl group, a trisubstituted double bond [δ_H 5.70 (1H, *br s*); δ_C 128.6 (*d*) and 163.7 (*s*)] and a conjugated ketone group [δ_C 201.2 (*s*)]. The DEPT spectrum of **2** revealed seven methyls, nine methylenes, four methines, a methoxy group, two oxymethines, a trisubstituted double bond, five quaternary carbons and a ketone group. Acetylation of compound **2** gave a monoacetate (**2a**), whose C-21 carbinolic methine proton resonance was shifted to δ 4.58 (1H, *t*, J = 2.7 Hz). The ^{13}C-NMR chemical shifts of **2** related to C-14, C-15, C-16, C-17 and C-18 were considerably different from those of **6**, although the other signals of both compounds had very close chemical shifts. The ^{1}H-NMR signals of Me-28, Me-29 and Me-30 showed paramagnetic shift ($\Delta\delta_C$ 0.11, 0.24 and 0.33) when compared to those of **6**. These data indicated that **2** must be a serrat-14-en-16-one derivative bearing an axial methoxyl group at C-3 and an axial hydroxyl group at C-21. This assumption was supported by analyzing HMQC, HMBC, ^{1}H/^{1}H COSY and NOESY spectra. In the HMBC spectrum, C-16 was correlated with H-15 and H-17β protons. Accordingly, **2** was proved as 3α-methoxy-21β-hydroxyserrat-14-en-16-one; this structure was confirmed by synthesis (Tanaka & Matsunaga, 1991). Treatment of 3α-methoxyserrat-14-en-21β-yl acetate (**6a**) with tertiary-butyl chromate in carbon tetrachloride furnished 3α-methoxy-21β-acetoxyserrat-14-en-16-one which was identical in all respects with **2a**.

This is the first report for the isolation of **2** in the literature, although 16-oxoserratenediol (3β,21α-dihydroxyserrat-14-en-16-one) and its 3α,21β- and 3β,21β-dihydroxyl analogues (Tsuda, Fujimoto & Kimpara, 1975), 16-oxoclavanol (3α,24,30-trihydroxyserrat-14-en-16-one), 16-oxolycoclavanol (3α,21β,24-trihydroxyserrat-14-en-16-one) and 16-oxoserratriol (3β,21α,24-trihydroxyserrat-14-en-16-one) (Tsuda, Fujimoto &

Table 1
500 MHz ^{1}H-NMR spectral data of **1**, **2**, and **2a**[a]

H	1	2	2a
1α	1.18 *m*	1.22 *m*	1.24 *m*
1β	1.50 *m*	1.46 *dt* (13.6, 3.9)	1.46 *m*
2α	1.72 *m*	1.72 *m*	1.73 *m*
2β	1.72 *m*	1.72 *m*	1.73 *m*
3β	2.78 *t* (2.5)	2.78 *t* (2.5)	2.78 *t* (2.5)
5α	1.23 *dd* (13.1, 2.3)	1.28 *dd* (10.5, 4.6)	1.28 *m*
6α	1.43 *m*	1.43 *m*	1.38 *m*
6β	1.37 *m*	1.43 *m*	1.44 *m*
7α	1.21 *m*	1.33 *m*	1.34 *m*
7β	1.34 *dt* (12.8, 3.1)	1.41 *m*	1.45 *m*
9α	0.89 *dd* (12.2, 2.1)	1.07 *dd* (12.2, 2.2)	1.10 *dd* (12.2, 2.2)
11α	1.98 *m*	2.10 *ddd* (12.2, 7.3, 3.4)	2.13 *ddd* (12.2, 7.2, 3.4)
11β	1.28 *m*	1.24 *m*	1.28 *m*
12α	1.04 *m*	1.20 *m*	1.20 *m*
12β	1.88 *m*	1.86 *dd* (11.6, 7.3)	1.84 *dd* (11.6, 7.2)
13β	1.47 *dd* (15.1, 2.1)	2.33 *dd* (11.6, 2.0)	2.33 *dd* (11.6, 2.0)
15	2.80 *br s*	5.70 *br s*	5.72 *br s*
16α	1.69 *ddd* (14.6, 13.1, 2.0)	–	–
16β	1.94 *ddd* (14.6, 4.3, 2.0)	–	–
17β	1.46 *dd* (13.1, 4.3)	2.53 *s*	2.44 *s*
19α	1.52 *m*	1.54 *dt* (13.3, 3.5)	1.59 *dt* (13.5, 3.5)
19β	1.38 *m*	1.79 *ddd* (15.0, 13.3, 3.5)	1.59 *ddd* (15.0, 13.3, 3.5)
20α	1.77 *ddd* (14.8, 4.5, 2.3)	1.90 *m*	1.88 *m*
20β	1.55 *m*	1.65 *ddd* (13.8, 6.5, 2.7)	1.72 *m*
21α	3.40 *t* (2.4)	3.34 *t* (2.7)	4.58 *t* (2.7)
23	0.91 *s*	0.93 *s*	0.93 *s*
24	0.82 *s*	0.832 *s*	0.84 *s*
25	0.83 *s*	0.825 *s*	0.85 *s*
26	1.07 *s*	0.86 *s*	0.90 *s*
27α	1.91 *d* (14.4)	2.44 *d* (14.7)	2.45 *d* (15.1)
27β	0.72 *d* (14.4)	1.90 *d* (14.7)	1.92 *d* (15.1)
28	0.73 *s*	0.79 *s*	0.81 *s*
29	0.89 *s*	1.12 *s*	1.18 *s*
30	0.93 *s*	1.26 *s*	1.16 *s*
OMe	3.31 *s*	3.31 *s*	3.31 *s*
OAc	–	–	2.10 *s*

[a] Measured in $CDCl_3$. Assignments were made by HMQC, HMBC, ^{1}H–^{1}H COSY and NOESY experiments.

Kimpara, 1975), lycoclavanin (3α,20β,21β,24-tetrahydroxyserrat-14-en-16-one) (Tsuda, Fujimoto, Morimoto & Sano, 1975), and 16-oxolyclanitin (3α,20β,21β,24,29-pentahydroxyserrat-14-en-16-one) (Tsuda, Fujimoto, Isobe, Sano & Kobayashi, 1974) had been isolated from *Lycopodium clavatum* and *Lycopodium serratum*.

3. Experimental

3.1. General

Mps.: uncorr. Optical rotations: $CHCl_3$ at 23°; UV: EtOH; IR: KBr discs; ^{1}H-NMR (500 MHz) and ^{13}C-NMR (125 MHz): $CDCl_3$ with TMS as internal standard; EIMS: 70 eV (probe). CC: silica gel 60 and alumina 90 (each 70–230 mesh, Merck); TLC: silica gel HF_{254} and PF_{254} (Merck).

3.2. Isolation of compounds

Extraction, isolation of 21α-hydroxy-3β-methoxyserrat-14-en-29-al and 29-*nor*-3α-methoxyserrat-14-en-21-one by residues A and B from the silica gel CC of the $CHCl_3$ extract of the stem bark of *P. jezoensis* var. *hondoensis* has been reported (Tanaka et al., 1998).

Repeated silica gel CC (1 kg) of the frs 41–56 (residue C, 35.73 g) of the $CHCl_3$ extract of *P. jezoensis* var. *hondoensis* gave a crystalline mass (207 mg) from the frs 16–19. Rechromatography with Al_2O_3 eluting with *n*-hexane:C_6H_6 5:1 gave 3β-methoxyserrat-14-en-21-one (**3**), 111 mg, mp 268–270° (MeOH–$CHCl_3$), $[\alpha]_D$ −29 (*c* 0.57) (lit. (Tanaka et al., 1996) mp 268.5–270°, $[\alpha]_D$ −29), identical in all respects with an authentic sample. Subsequent CC of residue C with the same solvent afforded 3α-methoxyserrat-14-en-21β-ol (**6**) (21.76 g) from frs 21–37, 3β-methoxyserrat-14-en-21β-ol (**7**) (2.38 g) from frs 55–72, and a poorly-separ-

able mixt. (1.66 g) from frs 73–81. Acetylation of 1 g of the mixt. with Ac_2O–pyridine (1:1, 10 ml) at room temp. for 24 h and subsequent usual workup gave a residual solid (1.01 g), which was subjected to a 10% $AgNO_3$ impregnated silica gel (150 g) CC using *n*-hexane–C_6H_6 (5:1) to afford the acetate **7a** (813 mg) from frs 22–78 and 3β-methoxyserrat-14-en-21α-yl acetate (**4a**) (79 mg) from frs 94–102. Hydrolysis of compound **4a** (50 mg) with N/30 KOH/EtOH gave 3β-methoxyserrat-14-en-21α-ol (**4**), (48 mg), mp 318–321.5° (MeOH–$CHCl_3$), $[\alpha]_D$ −5 (*c* 0.44), which was identified by literature data (Fang et al., 1991).

Repeated silica gel CC (1 kg) of frs 104–122 (residue D, 14.30 g) of the extract yielded a crystalline solid (38 mg), from frs 23–38. Purification of the solid by prep. TLC [plate: 0.5 mm thick, 20 × 20 cm, solvent: $CHCl_3$–MeOH, 50:1] afforded compound **2** (22 mg). Subsequent CC with the same solvent yielded a crystalline solid (44 mg), from frs 44–49, which was purified by prep. TLC [plate: 0.5 mm thick, 20 × 20 cm, solvent: $CHCl_3$–MeOH, 50:1] to give compound **1** (39 mg).

3.3. 14β,15β-epoxy-3α-methoxyserratan-21β-ol (*1*)

Prisms, mp 279-281° (MeOH–$CHCl_3$), $[\alpha]_D$ −36 (*c* 0.12, $CHCl_3$), HREIMS *m/z* 472.3913 $[M]^+$ ($C_{31}H_{52}O_3$ requires 472.3913), IR ν_{max} cm^{-1}: 3533 (OH), 2968, 2892, 1457, 1388 and 1360 (gem-dimethyl), 1106, 1067 and 1000; ^1H- and ^{13}C-NMR: see Tables 1 and 2; EIMS *m/z* (rel. int) (Tanaka et al., 1996): 472 $[M]^+$ (21), 457 $[M–Me]^+$ (9), 454.3798 $[M–H_2O]^+$ (11), 440.3654 [ion **a**, calc for 440.3652] (36), 425 [**a**–Me] (12), 422 [**a**–H_2O] (7), 287 [ion **b**] (12), 257 [ion **d**] (18), 248 [ion **e**] (33), 237.1864 [ion **f**, calc for 237.1853] (16), 224.1766 [ion **g**, calc for 224.1775] (56), 221 [ion **h**] (29), 209.1521 [ion **j**, calc for 209.1540] (52), 203 (ion **k**) (25), 201 [ion **l**] (35), 191 [ion **m**] (23), 189 [ion **n**] (61) and 136 (100).

3.4. Acetylation of *1*

Compound **1** (13 mg) was dissolved in a mixt. of Ac_2O and C_5H_5N (1:1, 1 ml) and the mixt. was kept at room temp. overnight. Usual workup yielded a crude solid (13 mg), which was purified by prep. TLC to afford the corresponding acetate **1a**, 12 mg, mp 238–240° (MeOH–$CHCl_3$), $[\alpha]_D$ −47 (*c* 0.67, $CHCl_3$), IR ν_{max} cm^{-1}: 1738 and 1245 (OAc), 2935, 2872, 1457, 1387 and 1363 (gem-dimethyl), 1165, and 1099; ^1H-NMR (C_5D_5N) δ: 0.73 (3H, *s*, Me-28), 0.81 (3H, *s*, Me-24), 0.83 (3H, *s*, Me-25), 0.84 (3H, *s*, Me-30), 0.88 (3H, *s*, Me-29), 1.03 (3H, *s*, Me-23),1.21 (3H, *s*, Me-26), 2.06 (3H, *s*, OAc) 2.76 (1H, *t*, *J* = 2.5 Hz, H-3β), 2.78 (1H, *br s*, H-15), 3.32 (3H, *s*, OMe), 4.82 (1H, *t*, *J* = 2.7 Hz, H-21α); ^{13}C-NMR: see Table 2; EIMS *m/z* (rel. int) (Tanaka et al., 1996): 514.4020 [M^+, calc for 514.4020] (35), 499 $[M–Me]^+$ (9), 482 [ion **a**] (8), 467 [**a**–Me] (4), 454 $[M–HOAc]^+$ (10), 439 $[M–HOAc–Me]^+$ (12), 287 [ion **b**] (7), 266.1862 [ion **g**, calc for 266.1881] (80), 257 [ion **d**] (20), 251.1626 [ion **j**, calc for 251.1646] (67), 248.2137 [ion **e**, calc for 248.2139] (44), 221 [ion **h**] (27), 203 (ion **k**) (25), 201.1643 [ion **l**, calc for 201.1643] (37), 191 [ion **m**] (30), 189 [ion **n**] (50) and 136 (100).

Table 2
125 MHz ^{13}C-NMR spectral data of compounds **1**, **1a**, **2**, and **2a**[a]

C	1	1a	2	2a
1	33.6 *t*	33.7 *t*	33.4 *t*	33.5 *t*
2	20.2 *t*	20.3 *t*	20.2 *t*	20.2 *t*
3	85.8 *d*	85.5 *d*	85.7 *d*	85.6 *d*
4	38.0 *s*	38.2 *s*	38.0 *s*[b]	38.0 *s*[b]
5	50.0 *d*	50.0 *d*	50.0 *d*	50.0 *d*
6	18.3 *t*	18.6 *t*	18.6 *t*	18.6 *t*
7	44.4 *t*	44.9 *t*	44.7 *t*	44.7 *t*
8	39.3 *s*	39.4 *s*	38.2 *s*[b]	38.2 *s*[b]
9	62.8 *d*	62.9 *d*	62.2 *d*	62.2 *d*
10	38.0 *s*	38.3 *s*	38.0 *s*[b]	38.1 *s*[b]
11	25.2 *t*	25.4 *t*	26.5 *t*	26.5 *d*
12	27.1 *t*	27.2 *t*	25.0 *t*	25.0 *t*
13	56.8 *d*	57.3 *d*	58.7 *d*[c]	58.8 *d*
14	61.4 *s*	60.8 *s*	163.7 *s*	163.6 *s*
15	59.3 *d*	59.0 *d*	128.6 *d*	128.6 *d*
16	22.8 *t*	23.0 *t*	201.2 *s*	200.4 *s*
17	38.0 *d*	39.6 *d*	58.8 *d*[c]	59.7 *d*
18	35.2 *s*	35.5 *s*	44.3 *s*	44.3 *s*
19	31.8 *t*	32.8 *t*	31.4 *t*	32.2 *t*
20	25.1 *t*	23.1 *t*	24.5 *t*	22.3 *t*
21	75.7 *d*	77.7 *d*	76.8 *d*	78.8 *d*
22	37.1 *s*	36.4 *s*	36.7 *s*	35.9 *s*
23	28.4 *q*	28.8 *q*	28.4 *q*	28.4 *q*
24	22.4 *q*	22.4 *q*	22.5 *q*	22.5 *q*
25	16.3 *q*	16.5 *q*	15.8 *q*	15.8 *q*
26	20.5 *q*	20.8 *q*	20.0 *q*	20.2 *q*
27	55.4 *t*	55.7 *t*	55.8 *t*	55.9 *t*
28	14.7 *q*	14.8 *q*	14.8 *q*	14.7 *q*
29	22.9 *q*	22.5 *q*	21.5 *q*	21.3 *q*
30	27.8 *q*	27.6 *q*	27.8 *q*	27.6 *q*
OMe	57.1 *q*	56.7 *q*	57.1 *q*	57.1 *q*
OCOMe	–	21.0 *q*	–	21.3 *q*
OCOMe	–	170.8 *s*	–	170.5 *s*

[a] Measured in $CDCl_3$: **1**, **2**, **2a**, and C_5D_5N: **1a**.
[b,c] May be interchanged within the same column.

3.5. Synthesis of *1* from *6*

A solution of *m*-CPBA (30 mg) in $CHCl_3$ (3 ml) was gradually added to a solution of compound **6** (30 mg) in $CHCl_3$ (2 ml) with stirring at room temperature for 4 h, when the reaction mixture was washed with 5% aqueous Na_2CO_3 and H_2O. Evaporation of the solvent under reduced pressure afforded a residue which was purified by prep. TLC [plate: 0.5 mm thick, 20 × 20 cm, solvent: $CHCl_3$–MeOH, 50:1] to give

14β,15β-epoxy-3α-methoxyserratan-21β-ol, 26 mg, mp 280–281° (MeOH–$CHCl_3$), $[\alpha]_D$ −36 (*c* 0.25, $CHCl_3$). The resulting product was identified by direct comparison with data for compound **1**.

3.6. 3α-methoxy-21β-hydroxyserrat-14-en-16-one (2)

Needles, mp 320–322° (MeOH–$CHCl_3$), $[\alpha]_D$ −83 (*c* 0.13, $CHCl_3$), HREIMS: *m/z* 470.3757 ($C_{31}H_{50}O_3$ requires 470.3756); UV λ_{max} (ε) nm: 230 sh, 272 (3500, 8000); IR ν_{max} cm^{-1}: 3396 (OH), 2933, 2861, 1661 (C═C-C═O), 1458, 1387 and 1361 (gem-dimethyl), 1245, 1184, 1132, 1107, 1090, 1103, 986, 935, 876 and 793 (HC═C<); ^{1}H- and ^{13}C-NMR: see Tables 1 and 2; EIMS *m/z* (rel. int.): 470 $[M]^+$ (100), 452 $[M–H_2O]^+$ (6), 438 $[M–MeOH]^+$ (21), 405 (18), 371 (4), 330 (6), 261 (24), 221 (46), 203 (26), 189 (65).

3.7. Acetylation of 2

Treatment of compound **2** (10 mg) as described for **1** yielded a crude solid (10 mg), which was purified by prep. TLC to afford the corresponding acetate (**2a**), 10 mg, amorphous solid, EIMS: *m/z* 512 $[M]^+$; ^{1}H- and ^{13}C-NMR: see Tables 1 and 2.

3.8. Synthesis of 2a from 6a

A soln of freshly prepd. $CrO_2(O\text{-}t\text{-}Bu)_2$ (1 ml) in CCl_4 (7.5 ml) was dropwise added to a soln of 3α-methoxyserrat-14-en-21β-yl acetate (**6a**) (102 mg) in CCl_4 (20 ml) and the mixt. was heated at 80° for 12 h. After cooling, 10 ml of 5% aqueous $NaHSO_3$ was added to the mixt. to destroy any excess oxidant. The organic layer was washed with H_2O and dried over Na_2SO_4; removal of the solvent under reduced pressure yielded a residual solid (99 mg), which was purified by prep. TLC (plate: 0.5 mm thick, 20 × 20 cm, solvent: $CHCl_3$–MeOH, 50:1) to give 3α-methoxy-21β-acetoxyserrat-14-en-16-one, $[M]^+$ *m/z*: 512. It was identified by direct comparison with the data for compound **2a**.

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