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Nine new clerodane diterpenoids from rhizomes of *Solidago altissima*

Motoo Tori*, Akiko Katto, Masakazu Sono

Faculty of Pharmaceutical Sciences, Tokushima Bunri University, Yamashiro-cho, Tokushima 770-8514, Japan

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Abstract

Nine new clerodane- and abeoclerodane-type diterpenoids have been isolated from rhizomes of *Solidago altissima* L. and their structures established mainly based on 2D NMR spectral data as well as X-ray analysis. Ten known compounds have also been isolated and some of their ^{13}C NMR data are listed.

Keywords: *Solidago altissima*; Compositae; Clerodane-type diterpenoids; Abeoclerodane; Rhizome

1. Introduction

Solidago altissima L. is native to North America and is now distributed throughout the world. They grow very fast and their roots become quite tough, with a strong smell when cut. Reports on the chemical constituents of this species have been published (Merritt & Ley, 1992) and many diterpenoids reported. We have been engaged in isolation of terpenoids from Compositae (Tori, Kawahara & Sono, 1997, 1998); as a continuation of chemical study on these species, we have investigated the chemistry of the rhizomes of *Solidago altissima*. Because most of these substances are acidic, the crude methanol extract was esterified by diazomethane. The usual method of separation led to isolation of nine new diterpenoids and ten known compounds as well as four artifacts.

2. Results and discussion

A methanol extract of rhizomes of *S. altissima* was partitioned between ethyl acetate and water and then *n*-butanol and water. The ethyl acetate soluble fraction was treated with diazomethane, followed by silica gel column chromatography, Sephadex LH-20 and HPLC.

Compound **1**, $C_{23}H_{34}O_5$, showed a quasi molecular ion peak at m/z 391 (CIMS) and the molecular formula was determined by CIHRMS. The ^1H NMR spectrum (C_6D_6) exhibited the presence of an aldehyde (δ 9.89), a methoxycarbonyl group (δ 3.47), a trisubstituted olefin (δ 5.80), an oxymethine (δ 5.14), an acetyl group (δ 1.67), two tertiary methyl groups (δ 0.84, 0.88), a secondary methyl group (δ 0.69) and two olefinic methyl groups (δ 1.40, 2.18). The ^{13}C NMR spectrum also suggested these functional groups and DEPT experiments indicated the presence of seven methyl, four methylene, five methine and seven quaternary carbons. The HMBC spectrum showed the long-range correlations between Me-16 and C-13, CH_2-12, and CH-14; Me-17 and C-9, CH-8 and CH-7; Me-20 and C-9, CH-10, CH-8 and CH_2-11; Me-19 and C-5, C-4, CH-10 and CH_2-6; Me-18 and C-4, C-2 and C-5. It should be mentioned here that H-18 also showed a long-range correlation (^4J) with C-3 (δ 187.2). The proton at C-14 had correlations with C-12, C-16 and C-15 and the oxymethine proton at δ 5.14 correlated to C-5. The aldehyde proton showed a correlation with C-1 and C-2. Therefore, the partial structures A and B (Fig. 1) were suggested and a

* Corresponding author. Tel.: +81-88-622-9611; fax: +81-88-655-3051.

E-mail address: tori@ph.bunri-u.ac.jp (M. Tori)

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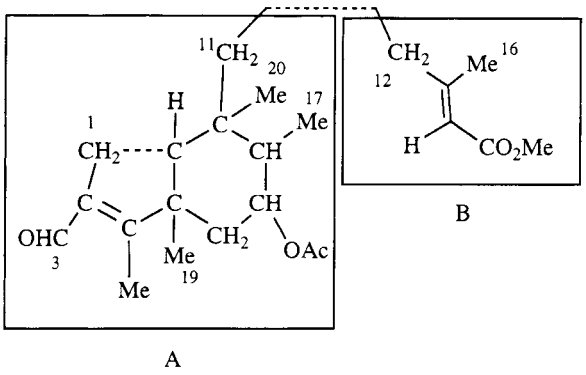


Fig. 1. Two partial structures of compound **1**.

rearranged clerodane skeleton was thus indicated. The detailed analysis of an ^{1}H-^{1}H COSY spectrum established the connection between C-11 and C-12 and between C-1 and C-10. The stereochemistry was revealed by the NOESY spectrum as shown in the formula. The Me-19 had NOE's into H-1α and H-6α, while H-10 exhibited an NOE into H-1β, suggesting *trans*-fused A/B rings. The *cis* arrangement of Me-17 and Me-20 was suggested by the NOE's between Me-20 and H-1α, Me-20 and Me-17, and Me-17 and H-7β. Therefore, compound **1** was established to be the ring contracted clerodane diterpene as depicted in the formula, which is the third example of abeoclerodane reported so far (Bohlmann, Singh, Singh, Joshi & Jakupovic, 1985; Kijjoa, Pinto, Pinto, Tantisewie & Herz, 1990).

Compound **2**, $C_{24}H_{38}O_6$ (HRMS), showed the presence of eight methyl groups including methoxycarbonyl and acetoxyl groups in the ^{1}H and ^{13}C NMR spectra. Since the ^{13}C NMR spectrum exhibited the presence of three carbonyl groups (δ 167.2, 170.5 and 213.1) and a trisubstituted olefin (δ 160.8 and 115.1), this compound must be bicyclic calculated from the six degrees of unsaturation. The ^{1}H NMR data are similar to those of compound **1**, except for the disappearance of the aldehyde group and a tetrasubstituted olefin and the presence of acetyl and hydroxyl groups. The 2D NMR analysis revealed the partial structure around ring A as shown in Fig. 2. The stereochemistry was

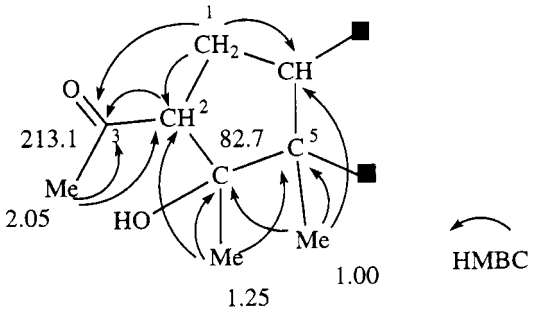


Fig. 2. The partial structure of compound **2**.

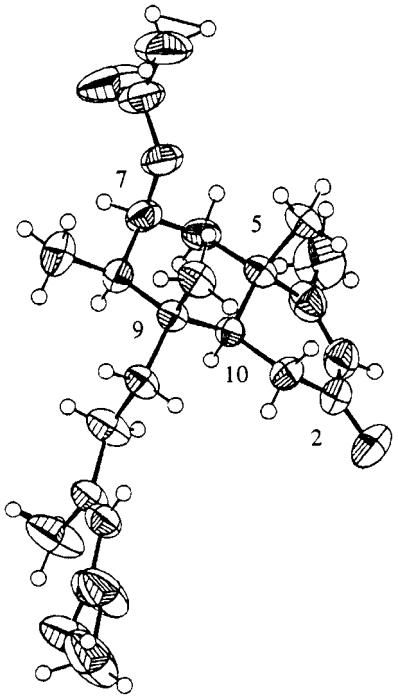
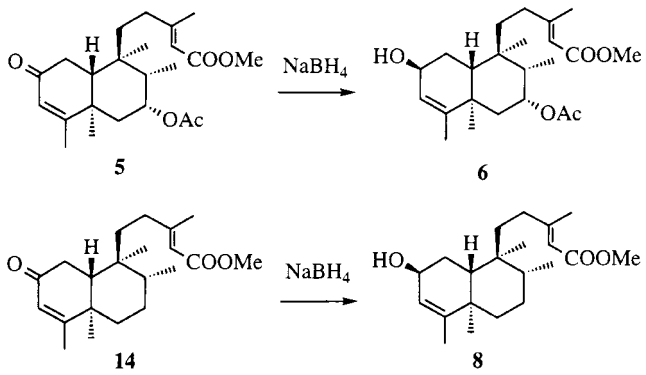


Fig. 3. ORTEP drawing of compound **5**.

similarly established based on the observed NOE's between H-2α and Me-18, between H-2α and Me-19, between H-2α and H-1α, and between H-1β and H-10. This compound is a homoditerpene since one carbon at C-21 is attached to C-3 of abeoclerodane. However, because the crude extract was treated with diazomethane, this could be an artifact as the reaction product. This seems to imply the presence of compound **2a** in the mixture.

Compounds **3** and **4** showed similar spectral data except for the chemical shift and coupling pattern of the oxymethine proton at C-3. The one for compound **3** appeared at δ 4.34 (m), while that for compound **4** was at δ 4.66 (dd, J = 12 and 5.4 Hz). The data for both compounds **3** and **4** are similar to those of compounds **1** and **2** except for those around ring A. Therefore, the structure was deduced as methyl 7-acetoxy-3-hydroxycleroda-4(18),13-dien-15-oate. The *trans* fused nature of A/B rings was indicated by the NOE between Me-19 and Me-20, between Me-19 and H-6α, and between H-10 and H-1β for both cases. The stereochemistry of the hydroxyl group at C-3 of compound **3** should be α-axial and the H-3β must be equatorial (Ekong & Okogn, 1969), because it appeared as a multiplet, which couples with both H-2α (equatorial) and H-2β (axial). Moreover, H-3β had NOE's into both H-2α and H-2β, which means that the H-3 is equatorial. By contrast, the H-3 of compound **4** appeared as dd with J = 12 and 5.4 Hz, suggesting the axial nature of this proton. This was further supported by the NOE between Me-19 and H-3α. The ^{1}H NMR



5 6 14 8

Fig. 4. Reduction of compounds **5** and **14**.

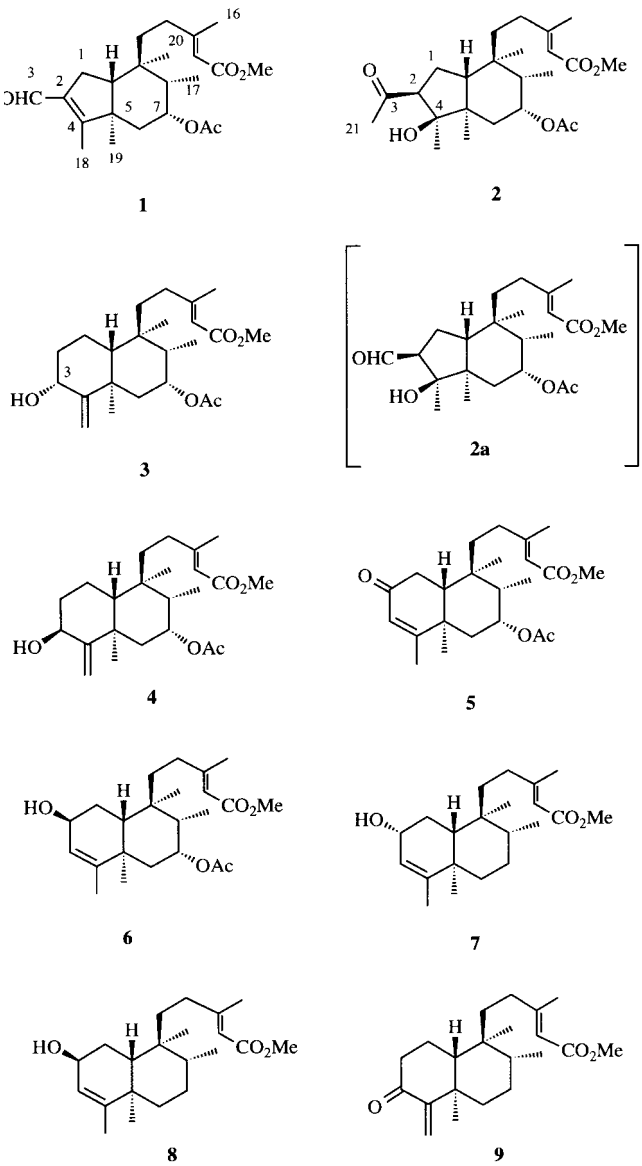
spectrum of the known compound **11**, which lacks the acetoxyl group at C-7, was very similar to that of **4**, especially the chemical shift and the coupling pattern of H-3. Thus, structures of both compounds **3** and **4** were fully established as depicted in the formulae.

Compound **5** gave colourless crystals, m.p. 195–198, from EtOAc, $C_{23}H_{34}O_5$ (HRMS). The spectral data indicated the presence of an α, β-unsaturated ketone (δ_H 5.71; δ_C 199.4, 125.3, 171.8), an α, β-unsaturated ester (δ_H 5.65 and 3.15; δ_C 167.1, 115.5, 159.7) and an acetoxyl group (δ_H 2.10; δ_C 74.3) as well as an oxymethine proton (δ_H 5.20). Although it was easy to imagine the clerodane skeleton from these data, the X-ray analysis of the crystal was carried out. The ORTEP drawing of compound **5** was shown in Fig. 3. The *trans* fused A/B rings and *cis* dimethyl groups of Me-20 and Me-17 were clearly shown.

Compound **6** was an alcohol (3450 cm^{-1}) and the molecular formula, $C_{23}H_{36}O_5$ was indicated by HRMS, which corresponded to the dihydro derivative of compound **5**. The 2D NMR data were carefully analyzed and the gross structure of methyl 7-acetoxy-2-hydroxycleroda-3,13-dien-15-oate was suggested. The stereochemistry except for at C-2 was deduced by the NOESY spectrum as shown in the formula. Because it was not easy to predict the configuration at C-2, compound **5** was reduced with $NaBH_4$ (Fig. 4) to afford the β-alcohol as a main product, which was identical with compound **6** in every respect.

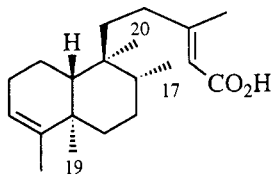
Compounds **7** and **8** had the same molecular formula, $C_{21}H_{34}O_3$, and the detailed analyses of 2D NMR data indicated the gross structures as methyl 2-hydroxycleroda-3,13-dien-15-oate. However, the proton at C-2 of **7** was observed at δ 4.17 (br s), which was different from that of **8** (δ 4.23, br t). The NOESY spectrum did not indicate unambiguous differentiation. Known compound **14** was reduced with $NaBH_4$ (Fig. 4) to afford the β-alcohol **8** as a main product. Therefore, the structures of compounds **7** and **8** were determined as depicted in the formulae.

The last compound **9**, $C_{21}H_{32}O_3$, showed the presence of an exomethylene (δ_H 5.58, 5.04), a ketone (δ_C 203.6) and an α,β-unsaturated ester (δ_H 5.67; δ_C 167.1, 115.2, 160.7). Because both exomethylene protons correlated to the ketone at C-3 and C-5 in the HMBC spectrum, the enone system should be at C-3 and C-4 (C-18). Other spectral features are very similar to those discussed above. Therefore, the structure of compound **9** was established as depicted in the formula. The ^{13}C NMR data for some compounds are listed in Table 1.



1 2 3 2a 4 5 6 7 8 9

The other compounds **10**–**23** were identified by comparing the spectral data or by independent 2D NMR analyses. Compounds **17**–**20** were artefacts



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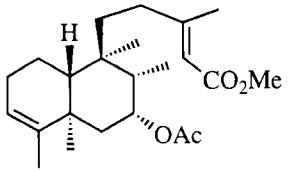

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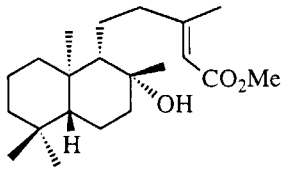

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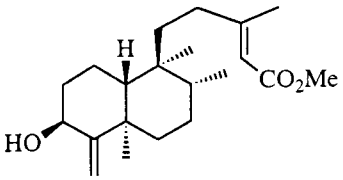

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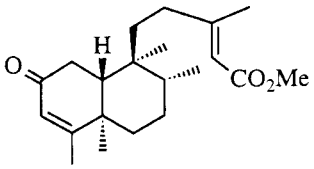

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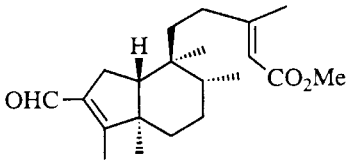

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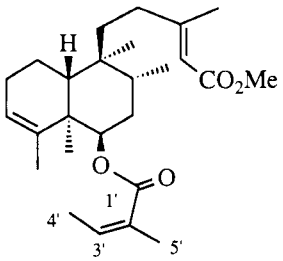

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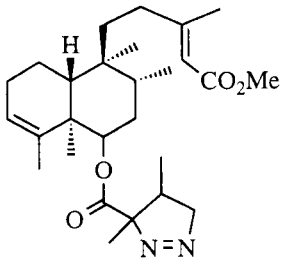
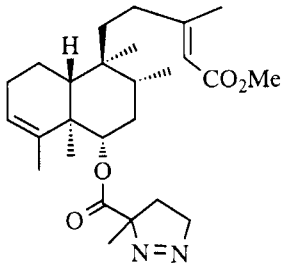
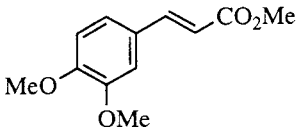


17,18



19,20



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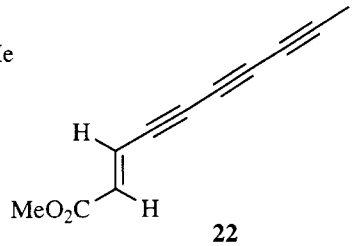

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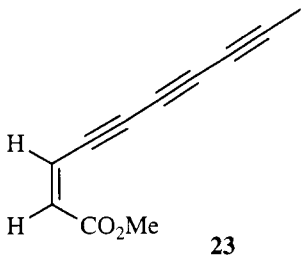

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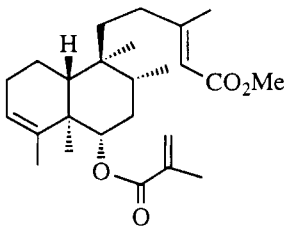

19a

produced by diazomethane treatment, implying the presence of compound **19a** in the mixture, although this has not been isolated in this work. The ^{13}C NMR data for some compounds have been listed in Table 2 for the purpose of identification hereafter.

3. Experimental

3.1. General

The IR spectra were measured with a JASCO FT/IR-5300 spectrophotometer. The ^{1}H-, ^{13}C- and 2D

Table 1
^{13}C NMR spectral data of compounds **1–9**

C	**1**[a]	**2**[b]	**3**[b]	**4**[b]	**5**[b]	**6**[b]	**7**[b]	**8**[b]	**9**[b]
1	26.7	25.1	20.3	20.0	34.7	28.6	27.9	29.1	20.2
2	137.0	56.2	37.4	32.2	199.4	69.3	65.2	69.5	40.6
3	187.2	213.1	68.9	82.4	125.3	124.1	122.1	124.4	203.6
4	168.7	82.7	161.2	156.5	171.8	147.8	149.9	147.8	158.9
5	49.7	47.8	39.5[c]	39.7	39.0	38.0	38.7[c]	38.6	40.8
6	38.2	33.7	40.4	39.9	38.3	39.5	36.2[d]	36.4	37.4
7	75.0	76.1	74.9	74.8	74.3	74.8	36.2[d]	27.2	27.1
8	40.2	39.4	38.1	38.1	37.8	37.8	27.4	36.0	36.6
9	37.7	38.0	39.0[c]	39.0	38.5	37.9	38.4[c]	38.4	39.5
10	54.0	46.7	48.2	48.3	45.5	45.1	40.9	45.2	45.4
11	38.8	38.9	37.2	37.2	36.4	37.1	36.1[d]	36.2	36.2
12	34.8	34.9	34.6	34.5	34.2	34.6	34.0	34.5	34.6
13	160.2	160.8	160.5	160.4	159.7	160.4	162.0	161.1	160.7
14	115.8	115.1	115.2	115.2	115.5	115.3	114.8	115.0	115.2
15	166.8	167.5	167.1	167.1	167.1	167.1	167.3	167.2	167.1
16	19.0	18.9	19.1	19.1	19.1[c]	19.2	19.2	19.2	19.2
17	10.9	11.0	13.0	12.0	11.9	12.1	15.8	15.9	15.8
18	9.0	22.3	100.1	101.1	19.1[c]	21.5	18.0	17.8	114.2
19	19.0	18.2	22.1	21.8	19.0[c]	17.8	18.4	19.9	22.1
20	18.1	19.2	19.5	19.4	19.9	19.7	18.3	18.4	18.1
21	–	31.5	–	–	–	–	–	–	–
–OMe	50.5	50.8	50.9	50.9	50.8	50.9	50.7	50.8	50.9
–OAc	169.4	170.5	170.6	170.6	170.5	170.7	–	–	–
	20.8	21.4	21.4	21.4	21.4	21.5	–	–	–

[a] In C_6D_6.
[b] In $CDCl_3$.
[c] Assignments may be interchanged in each vertical column.
[d] Assignments may be interchanged in each vertical column.

Table 2
^{13}C NMR spectral data of compounds **10–16** (in $CDCl_3$)

C	**10**[a]	**11**[a,b]	**12**[c]	**13**[d]	**14**[e]	**15**[f]	**16**[a]
1	18.2	17.8	39.0	20.3	34.9	34.0	21.6
2	26.8	26.6	18.1	32.4	199.9	137.1	26.5
3	120.4	120.0	42.0	83.1	125.5	188.6	124.5
4	144.3	144.3	33.4	157.5	172.4	172.0	138.0
5	38.7[g]	37.2	55.9	40.4	39.8	50.8	42.9
6	36.8[h]	39.8	18.2	36.9	35.5	28.3	74.0
7	27.4	75.1	42.3	27.1	26.8	26.2	31.6
8	36.3	38.1	73.1	36.6	36.0	37.3	31.9
9	38.1[g]	38.3	58.8	39.3	38.7	38.0	38.4
10	46.4	46.2	39.2	48.5	45.7	54.0	44.3
11	36.3[h]	37.2	23.6	36.2	35.5	37.9	34.2
12	34.9	34.6	44.6	34.4	34.0	34.8	35.3
13	164.5	160.9	160.7	161.2	160.4	161.0	161.4
14	114.9	115.0	114.9	114.9	115.2	115.0	114.9
15	172.6	167.1	167.3	167.2	167.1	167.2	167.2
16	19.4	19.1	19.0	19.1	19.2	19.2	19.2
17	15.9	12.0	30.5	15.7	15.7	15.1	15.5
18	18.0	18.0	21.6	100.3	19.0	9.7	18.3
19	19.9	21.3	33.3	20.9	18.4	18.0	24.7
20	18.2	19.5	15.1	18.0	17.8	17.1	28.5
OMe	–	50.7	50.8	50.8	50.8	50.8	50.8
–OAc	–	170.6	–	–	–	–	161.4(1′)
	–	21.4	–	–	–	–	128.3(2′)
							137.5(3′)
							15.3(4′)
							20.7(5′)

[a] Lu, Minelaou, Vargas, Fronczek and Fischer (1993).
[b] Kusumoto, Okazaki, Ohsuka and Kotake (1969).
[c] Hugel, Oehlschlager and Ourisson (1966), Caputo, Mangoni, Monaco, Pelosi and Previtera (1976), and Zdero, Bohlmann and Niemeyer (1990).
[d] Wijerathne, Silva, Tezuka and Kikuchi (1995).
[e] Lajide, Escoubas and Mizutani (1995), Avila and Medina (1992), Castillo, Jakupovic, Bohlmann, Castro and King (1989), and Hasan, Healey and Waterman (1982).
[f] Singh and Singh (1986).
[g] Assignments may be interchanged in each vertical column.
[h] Assignments may be interchanged in each vertical column.

NMR spectra were taken with a Varian Unity 600 (600 MHz), a JEOL GX400 (400 MHz) or a Varian Unity 200 (200 MHz) spectrometer. The mass spectra including high resolution mass spectra were taken with a JEOL JMS AX-500 spectrometer. The specific rotation and the CD spectra were taken on a JASCO DIP-140 polarimeter and a JASCO J-500 spectrometer, respectively. Chemcopak Nucleosil 50-5 was used for HPLC (JASCO pump system). Silica gel 60 (70–230 mesh, Merck) was used for column chromatography and silica gel 60 F_{254} plates (Merck) were used for TLC.

3.2. Plant material

Rhizomes of *Solidago altissima* L. were collected in Tokushima city in October, 1995. A voucher specimen is deposited to the Herbarium of Tokushima Bunri University and was identified by Dr Takayuki Kawahara, The Hokkaido Center, Forestry and Forest Products Research Institute, Sapporo, Japan.

3.3. Extraction and isolation

The methanol extract (138 g) of rhizomes (5.8 kg) was subjected to silica gel CC and was eluted by hexane–EtOAc, in gradient, followed by $CHCl_3$–MeOH, in gradient. Each fr was treated with diazomethane in ether overnight and the residue was purified by silica gel CC, Sephadex LH-20 ($CHCl_3$–MeOH, 1:1), and by HPLC (Nucleosil 50-5, hexane–EtOAc) to afford nine new compounds and 14 known compounds and artefacts.

Compound **1**: $[\alpha]_D^{23}$ +12.0° (*c* 0.69, $CHCl_3$). IR: 1740, 1720, 1680 cm^{-1}. ^{1}H NMR (600 MHz, C_6D_6): δ 0.69 (3H, d, J = 7.2Hz), 0.84 (3H, s), 0.88 (3H, s), 1.07 (1H, dd, J = 13.5, 3.5 Hz), 1.12 (1H, m), 1.16 (1H, m), 1.22 (2H, m), 1.40 (3H, s), 1.62 (2H, m), 1.67 (3H, s), 1.80 (1H, dd, J = 13.5, 1.5 Hz), 2.10 (1H, ddd, J = 13.5, 12, 1.5 Hz), 2.18 (3H, s), 2.40 (1H, dd, J = 13.8, 5.4 Hz), 3.47 (3H, s), 5.14 (1H, q-like, J = ca. 2.5 Hz), 5.80 (1H, s), 9.89 (1H, s). MS (CI) *m*/*z*: 391 $(M+H)^+$, 359, 330, 315, 299, 203, 173, 122, 83,

55, 43 (base). CI-HRMS obs.: 391.2484 $(M+H)^+$, calcd for $C_{23}H_{35}O_5$: 391.2485.

Compound **2**: $[\alpha]_D^{24}$ −28.0° (*c* 0.25, $CHCl_3$). IR: 3500, 1720, 1650 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): δ 0.90 (3H, d J = 7.1 Hz), 1.00 (3H, s), 1.03 (3H, s), 1.25 (3H, s), 1.34 (1H, td, J = 12.3, 4.8 Hz), 1.42 (1H, td, J = 12.3, 4.2 Hz), 1.62 (2H, m), 1.72 (1H, ddd, J = 12.6, 7.8, 4.8 Hz), 1.89 (1H, dt, J = 12.6, 11.7 Hz), 1.95 (1H, dd, J = 14.4, 2.5 Hz), 2.02 (2H, m), 2.05 (3H, s), 2.17 (3H, s), 2.23 (3H, s), 2.26 (1H, dd, J = 11.7, 4.8 Hz), 3.01 (1H, dd, J = 11.7, 4.8 Hz), 3.58 (1H, s), 3.68 (3H, s), 5.20 (1H, q, J = 2.5 Hz), 5.68 (1H, s). MS (EI) *m*/*z*: 422 (M^+), 390, 362, 330, 295, 262, 217, 173, 149, 135 (base), 95, 43. EI-HRMS obs. 422.2648, calcd for $C_{24}H_{38}O_6$: 422.2668.

Compound **3**: $[\alpha]_D^{24}$ −1.7° (*c* 0.24, $CHCl_3$). IR: 3500, 1730, 1650 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): δ 0.92 (3H, d, J = 7.2 Hz), 0.99 (3H, s), 1.17 (2H, m), 1.23 (3H, s), 1.42 (1H, m), 1.46 (1H, m), 1.65 (3H, m), 1.78 (1H, dd, J = 15, 3 Hz), 1.86 (1H, dd, J = 12, 4 Hz), 1.89 (1H, dd, J = 12, 4 Hz), 2.06 (3H, s), 2.10 (1H, dd, J = 15, 2.4 Hz), 2.15 (3H, s), 2.26 (1H, m), 3.68 (3H, s), 4.34 (1H, m), 4.71 (1H, d, J = 1.2 Hz), 4.95 (1H, d, J = 1.8 Hz), 5.21 (1H, q-like, J = 3.0 Hz), 5.64 (1H, s). MS (EI) *m*/*z*: 392 (M^+), 374, 360, 332, 314, 300, 248, 205, 187 (base), 171, 159, 119, 55. EI-HRMS obs. 392.2574, calcd for $C_{23}H_{36}O_5$: 392.2563.

Compound **4** was relatively labile and the specimen decomposed before measuring the specific rotation and the exact mass: IR: 3375, 1700, 1620 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): δ 0.92 (3H, d, J = 7.2 Hz), 0.99 (3H, s), 1.18 (1H, dd, J = 12.0, 3.0 Hz), 1.25 (3H, s), 1.26 (1H, m), 1.42 (1H, m), 1.44 (1H, m), 1.64 (1H, m), 1.71 (2H, m), 1.79 (1H, dd, J = 15.0, 3.6 Hz), 1.87 (1H, m), 1.89 (1H, m), 2.06 (3H, s), 2.08 (1H, dd, J = 15, 3.0 Hz), 2.15 (3H, s), 2.35 (1H, m), 3.68 (3H, s), 4.66 (1H, dd, J = 12.0, 5.4 Hz), 4.74 (1H, s), 4.89 (1H, d, J = 1.8 Hz), 5.22 (1H, q-like, J = 3.0 Hz). MS (CI) *m*/*z*: 391 (M^+), 375, 359, 331, 315, 299 (base), 283, 261, 255, 203, 187, 159, 95, 61.

Compound **5**: m.p. 195–198°C (EtOAc). $[\alpha]_D^{22}$ −80.9° (*c* 1.02, $CHCl_3$). CD[θ]335 nm −5343 ($CHCl_3$). $\Delta\varepsilon = -1.62$. IR: 1735, 1715, 1670 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 0.95 (3H, d, J = 7.0 Hz), 1.08 (3H, s), 1.31 (3H, s), 1.90 (3H, s), 2.10 (3H, s), 2.15 (3H, s), 3.60 (3H, s), 5.20 (1H, q-like, J = 2.5 Hz), 5.65 (1H, s), 5.71 (1H, s). MS (EI) *m*/*z*: 390 (M^+), 375, 358, 343, 330, 317, 283, 264, 241, 221, 203, 161, 135, 109, 95 (base), 83, 43. EI-HRMS obs. 390.2404, calcd for $C_{23}H_{34}O_5$: 390.2407.

The X-ray data have been deposited at the Cambridge Crystallographic Data Centre.

Compound **6**: $[\alpha]_D^{22}$ −31.7° (*c* 0.59, $CHCl_3$). IR: 3450, 2900, 1720 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): δ 0.91 (3H, d, J = 7.2 Hz), 1.00 (3H, s), 1.24 (3H, s), 1.37 (1H, dd, J = 3.6, 15 Hz), 1.43 (2H, m), 1.51 (2H, m), 1.63 (3H, s), 1.66 (1H, m), 1.91 (2H, m), 2.01 (1H, dd, J = 12.2, 6.8 Hz), 2.06 (3H, s), 2.11 (1H, m), 2.17 (3H, s), 3.69 (3 H, s), 4.25 (1H, m), 5.12 (1H, q-like, J= 3.6 Hz), 5.19 (1H, s), 5.67 (1H, s). MS (FAB) *m*/*z*: 415 $(M+Na)^+$, 391 $(M+H)^+$, 359, 329, 307, 289, 176, 154 (base), 136, 107, 77. FAB-HRMS obs. 415.2435 $(M+Na)^+$, calcd for $C_{23}H_{36}O_5Na$: 415.2461.

Compound **7**: $[\alpha]_D^{24}$ −78.3° (*c* 0.41, $CHCl_3$). IR: 3450, 1730, 1660 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$):δ 0.74 (3H, s), 0.82 (3H, d, J = 6 Hz), 0.94 (3H, s), 1.21 (1H, m), 1.40 (2H, m), 1.43 (1H, m), 1.49 (2H, m), 1.57 (1H, m), 1.63 (3H, s), 1.68 (2H, m), 1.71 (1H, m), 1.97 (1H, td, J = 12.9, 4.2 Hz), 2.17 (3H, s), 2.25 (1H, td, J = 13.2, 4.2 Hz), 3.67 (3H, s), 4.17 (1H, br s), 5.35 (1H, dt, J = 4.2, 1.8 Hz), 5.70 (1H, s). MS (EI) *m*/*z*: 334 (M^+), 316, 302, 285, 269, 242, 227, 187 (base), 159, 132, 119, 105, 91, 55, 41, 32. EI-HRMS obs. 334.2509, calcd for $C_{21}H_{34}O_3$: 334.2336.

Compound **8**: $[\alpha]_D^{24}$ −5.9° (*c* 0.8, $CHCl_3$). IR: 3400, 1730, 1660 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$):δ 0.75 (3H, s), 0.81 (3H, d, J = 6 Hz), 1.05 (3H, s), 1.15 (1H, m), 1.34 (1H, t, J = 12.6 Hz), 1.39 (1H, m), 1.40 (1H, m), 1.43 (3H, m), 1.52 (1H, ddd, J = 14.3, 12.4, 4.9 Hz), 1.62 (3H, t, J = 1.3 Hz), 1.72 (1H, dt, J = 12.9, 1 Hz), 1.90 (1H, td, J = 12.6, 4.1 Hz), 1.96 (1H, dd, J = 12, 6.9 Hz), 2.00 (1H, td, J = 12.6, 4.1 Hz), 2.16 (1H, s) 3.69 (3H, s), 4.23 (1H, m), 5.22 (1H, s), 5.66 (1H, s). MS (EI) *m*/*z*: 334 (M^+), 319, 302, 287, 250, 205, 189, 123 (base), 95. EI-HRMS obs. 334.2493, calcd for $C_{21}H_{34}O_3$: 334.2508.

Compound **9** decomposed before measuring the specific rotation: IR: 1720, 1700, 1640 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$):δ 0.81 (3H, s), 0.87 (3H, d, J = 6 Hz), 1.04 (3H, s), 1.45 (4H, m), 1.55 (3H, m), 1.78 (1H, m), 1.85 (2H, m), 1.93 (1H, td, J = 12.6, 4.8 Hz), 2.06 (1H, td, J = 12.6, 4.2 Hz), 2.17 (3H, s), 2.31 (1H, m), 2.67 (1H, ddd, J = 16.5, 4.9, 4.6 Hz), 3.69 (3H, s), 5.03 (1H, s), 5.58 (1H, s), 5.67 (1H, s). MS (CI) *m*/*z*: 333 $(M+H)^+$, 301 (base), 287, 259, 205, 163, 95. CI-HRMS obs. 333.2447 $(M+H)^+$, calcd for $C_{21}H_{33}O_3$: 333.2430.

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