Glycosides of *Atractylodes lancea*

Junichi KITAJIMA,*[,a] Akane KAMOSHITA,[a] Toru ISHIKAWA,[a] Akihito TAKANO,[a] Tatsuo FUKUDA,[b] Susumu ISODA,[c] and Yoshiteru IDA[c]

[a] *Showa Pharmaceutical University; 3 Higashi-Tamagawagakuen, Machida, Tokyo 194–8543, Japan:* [b] *Tokyo Metropolitan Medical Plants Garden; 21–1 Nakajima-machi, Kodaira, Tokyo 187–0033, Japan: and* [c] *School of Pharmaceutical Sciences, Showa University; Hatanodai, Shinagawa-ku, Tokyo 142–8555, Japan.*

Received February 6, 2003; accepted March 20, 2003

Five sesquiterpenoid glycosides (two guaiane-type glycosides and three eudesmane-type glucosides) and a glucoside of an acetylene derivative were newly isolated from the water-soluble portion of the methanolic extract of *Atractylodes lancea* rhizome together with 26 known compounds. Their structures were characterized as atractyloside A 14-*O*-β-D-fructofuranoside, (1*S*,4*S*,5*S*,7*R*,10*S*)-10,11,14-trihydroxyguai-3-one 11-*O*-β-D-glucopyranoside, (5*R*,7*R*,10*S*)-isopterocarpolone β-D-glucopyranoside, *cis*-atractyloside I, (2*R*,3*R*,5*R*,7*R*,10*S*)-atractyloside G 2-*O*-β-D-glucopyranoside, and (2*E*,8*E*)-2,8-decadiene-4,6-diyne-1,10-diol 1-*O*-β-D-glucopyranoside on the basis of chemical and spectroscopic investigation. The presence of six characteristic guaiane-type glucosides in both rhizomes of *A. lancea* and *Atractylodes japonica* suggested a close chemotaxonomic relationship between them.

Key words *Atractylodes lancea*; sesquiterpenoid glycoside; guaiane-type; eudesmane-type; 2,8-decadiene-4,6-diyne-1,10-diol β-D-glucopyranoside

The rhizomes of *Atractylodes* plants (Compositae) have been used as an important crude drug since antiquity. They are listed in the Chinese, Korean, and Japanese pharmacopoeias, and are prescribed in traditional medicine as diuretic and stomachic drugs. They are classified into two groups that contain β-eudesmol and hinesol as the main constituents of the essential oil (*Atractylodes lancea* and *Atractylodes chinensis*; so-jutsu), and atractylon as the main constituent of the essential oil (*Atractylodes japonica* and *Atractylodes ovata*; byaku-jutsu).[1] However, the phylogenetic relationship between *A. lancea* and *A. japonica* is considered to be closer than that of *A. japonica* and *A. ovata*.[2,3] As for the polar constituents of the rhizome of *A. lancea*, nine sesquiterpenoid glycosides (atractyloside A to I), L-tryptophan, and syringin were reported by Yahara *et al.*[4] On the other hand, we reported the isolation and the characterization of eight sesquiterpenoid glycosides, including atractyloside A—E, G, and a compound with a secoguaiane skeleton, a monoterpenoid glucoside, seven aromatic compound glycosides, and L-phenylalanine from the water-soluble portion of *A. japonica*.[5] In the present study, we undertook a reexamination of the water-soluble portion of the rhizome of *A. lancea*.

The dried rhizome of *A. lancea*, which was cultivated in the Tokyo Metropolitan Medical Plants Garden, was extracted with methanol, and the methanolic extract was suspended in water and successively extracted with ether and ethyl acetate. The aqueous layer was chromatographed on Amberlite XAD-II to give water and methanol eluate fractions. The methanol eluate fraction was chromatographed on Sephadex LH-20, and subjected to a combination of silica gel, Lobar RP-8 column chromatography, and HPLC. Then, 16 sesquiterpenoid glycosides (**1**—**16**), four monoterpenoid glucosides (**17**—**20**), two hemiterpenoid glycosides (**21**, **22**), an alkyl glycoside (**23**), five aromatic compound glycosides (**24**—**28**), an acetylene derivative compound glucoside (**29**), two nucleosides (**30**, **31**), and L-tryptophan (**32**) were isolated. Among them, five sesquiterpenoid glycosides (**7**—**9**, **11**, **16**) and an acetylene derivative compound glucoside (**29**) are new, and their structures were characterized as follows. Their molecular formulae were suggested from the accurate mass number of the $[M+H]^+$ or $[M+Na]^+$ ion peaks in the high-resolution positive FAB-MS.

Glycosides **1** to **6** were guaiane-type sesquiterpenoid glucosides that are also found in the rhizome of *A. japonica* and identified as atractyloside A,[4] 10-*epi*-atractyloside A,[5] atractyloside B,[4] (1*S*,4*S*,5*S*,7*R*,10*R*)-10,11,14-trihydroxyguai-3-one 11-*O*-β-D-glucopyranoside,[5] (1*S*,4*S*,5*R*,7*R*,10*R*)-11,14-dihydroxyguai-3-one 11-*O*-β-D-glucopyranoside,[5] and (1*S*,5*R*,7*R*,10*R*)-secoatractylolactone 11-*O*-β-D-glucopyranoside,[5] respectively.

Glycoside **7**, $C_{27}H_{46}O_{15}$, showed $[M+H]^+$, $[M-C_6H_{12}O_6+H]^+$ and $[M-C_{12}H_{24}O_{12}+H]^+$ ion peaks at *m*/*z* 611, 431, and 251, respectively, in the positive FAB-MS. Enzymatic hydrolysis of **7** gave an aglycone, which was identified as the aglycone of **1**, and D-glucose and D-fructose as the sugar components. The NMR data of **7** were similar to those of **1** except for the signals due to a β-D-fructofuranosyl group (Tables 1 and 2). A cross-peak between the H_2-14 and fructosyl C-2 carbon was observed in the heteronuclear multiple bond connectivity (HMBC) spectrum of **7** suggesting that the additional fructosyl group was located at C-14. Therefore **7** was characterized as atractyloside A 14-*O*-β-D-fructofuranoside.

Glycoside **8**, $C_{21}H_{36}O_9$, showed $[M+H]^+$ and $[M-C_6H_{12}O_6+H]^+$ ion peaks at *m*/*z* 433 and 253, respectively, in the positive FAB-MS, and enzymatic hydrolysis of **8** gave an aglycone (**8a**) and D-glucose. It showed similar NMR spectral features to those of **4** (Tables 1, 2), but the signals due to H-1_{ax}, H-2_{ax}, H-8_{ax}, H-9_{ax}, H_2-14, C-1, C-5, and C-9 of **8** appeared significantly lower field than those of **4**. In addition, the observed nuclear Overhauser effect (NOE) interactions between H-1/H-6_{ax}, between H-5/H_3-15, and between H-7/H-14a in the NOE spectroscopy (NOESY) spectrum (Fig. 1) suggested **8** to be an 10-epimer of **4**. This was supported by a positive Cotton effect in the circular dichroism

* To whom correspondence should be addressed. e-mail: Kitajima@ac.shoyaku.ac.jp

Table 1. ^{1}H-NMR Chemical Shifts of **1**, **4**, **7**—**11**, **15**, and **16** (in Pyridine-d_5, 500 MHz)

	1	**7**	**4**	**8**
H-1$_{ax}$ (β)	2.38 ddd (10.0, 10.0, 10.0)	2.21 ddd (10.0, 11.0, 11.0)	2.26 ddd (10.0, 10.0, 10.0)	2.63 ddd (11.0, 11.0, 11.0)
H-2$_{ax}$ (β)	2.71 dd (10.0, 19.0)	2.76 dd (10.0, 19.0)	2.65 dd (10.0, 19.0)	2.91 dd (11.0, 19.0)
H-2$_{eq}$ (α)	3.14 dd (10.0, 19.0)	3.13 dd (10.0, 19.0)	3.09 dd (10.0, 19.0)	3.05 dd (11.0, 19.0)
H-4$_{ax}$ (β)	—	—	1.89 qd (7.0, 11.0)	1.87 qd (7.0, 10.0)
H-5$_{ax}$ (α)	2.79 br dd (10.0, 11.0)	2.70 br dd (10.0, 11.0)	2.13 br ddd (10.0, 11.0, 11.0)	2.12 dddd (3.0, 10.0, 11.0, 11.0)
H-6$_{ax}$ (β)	1.47 ddd (11.0, 13.0, 13.0)	1.37 ddd (11.0, 13.0, 13.0)	1.24 ddd (11.0, 13.0, 13.0)	1.24 ddd (11.0, 12.0, 12.0)
H-6$_{eq}$ (α)	2.86 br dd (3.0, 13.0)	2.81 br dd (3.0, 13.0)	2.42 br dd (3.0, 13.0)	2.46 ddd (3.0, 3.0, 13.0)
H-7$_{ax}$ (α)	2.29 br ddd (5.0, 11.0, 13.0)	2.19 m	2.04 br ddd (4.0, 11.0, 13.0)	2.01 dddd (3.0, 3.0, 12.0, 12.0)
H-8$_{ax}$ (β)	1.75 br ddd (8.0, 11.0, 14.5)	1.56 br ddd (8.0, 11.0, 14.0)	1.64 br ddd (11.0, 11.0, 14.0)	1.94 dddd (3.0, 11.0, 12.0, 12.0)
H-8$_{eq}$ (α)	2.44 br ddd (4.0, 8.5, 14.5)	2.30 br ddd (5.0, 8.5, 14.0)	2.43 br dd (10.0, 14.0)	2.44 m
H-9$_{ax}$ (β)	2.53 br dd (11.0, 14.0)	2.39 br dd (11.0, 14.0)	1.99 br dd (11.0, 13.0)	2.25 br dd (11.0, 13.0)
H-9$_{eq}$ (α)	2.14 br dd (8.5, 14.0)	2.19 br dd (8.5, 14.0)	2.69 br dd (10.0, 13.0)	2.45 br dd (10.0, 13.0)
H$_3$-12	1.41 s	1.35 s	1.44 s	1.44 s
H$_3$-13	1.49 s	1.43 s	1.45 s	1.47 s
H$_2$-14	3.85 br s (2H)	3.91 d (9.5)	3.79 br s (2H)	3.97 d (10.5)
	—	4.27 d (9.5)	—	4.09 d (10.5)
H$_3$-15	1.36 s	1.28 s	1.15 d (7.0)	1.21 d (7.0)
Glc H-1	5.04 d (8.0)	5.00 d (7.5)	5.05 d (7.5)	5.07 d (8.0)

	9	**10**	**11**
H$_2$-1	2.21 d (16.0, ax)	2.24 d (16.0, ax)	2.24 d (15.5)
	2.33 d (16.0, eq)	2.40 d (16.0, eq)	2.47 d (15.5)
H-3	5.99 br s	—	—
H-5$_{ax}$	2.37 br d (12.5)	2.47 dd (3.0, 12.0)	—
H-5$_{eq}$	—	—	2.26 dd (3.0, 3.0)
H-6$_{ax}$	1.19 ddd (12.5, 12.5, 12.5)	1.18 ddd (12.0, 12.0, 12.0)	1.44 ddd (3.0, 13.0, 13.0)
H-6$_{eq}$	2.47 ddd (3.0, 3.0, 12.5)	2.46 br dd (3.0, 12.0)	2.05 ddd (3.0, 3.0, 13.0)
H-7$_{ax}$	1.78 dddd (3.0, 3.0, 12.5, 12.5)	1.73 dddd (3.0, 3.0, 12.0, 12.0)	1.22 dddd (3.0, 3.0, 13.0, 13.0)
H-8$_{ax}$	1.32 dddd (3.0, 12.5, 12.5, 12.5)	1.29 dddd (3.0, 12.0, 12.0, 12.0)	1.19 dddd (3.0, 13.0, 13.0, 13.0)
H-8$_{eq}$	1.73 br d (12.5)	1.71 br d (12.0)	1.68 dddd (3.0, 3.0, 3.0, 13.0)
H-9$_{ax}$	1.35 ddd (3.0, 12.5, 12.5)	1.24 ddd (3.0, 12.0, 12.0)	1.52 ddd (3.0, 13.0, 13.0)
H-9$_{eq}$	1.42 ddd (3.0, 3.0, 12.5)	1.38 ddd (3.0, 3.0, 12.0)	1.27 ddd (3.0, 3.0, 13.0)
H$_3$-12	1.39 s	1.37 s	1.33 s
H$_3$-13	1.47 s	1.45 s	1.33 s
H$_3$-14	0.82 s	0.90 s	0.91 s
H$_3$-15	1.81 s	2.15 s	2.11 s
Glc H-1	5.05 d (7.5)	5.05 d (8.0)	4.99 d (8.0)
Glc H-1′	—	5.36 d (7.5)	5.51 d (7.5)

	15	**16**
H-1$_{ax}$	1.65 dd (12.0, 12.0)	1.51 dd (12.0, 12.0)
H-1$_{eq}$	2.07 dd (5.0, 12.0)	2.10 dd (5.0, 12.0)
H-2$_{ax}$	4.08 ddd (5.0, 9.0, 12.0)	4.09 ddd (5.0, 12.0, 12.0)
H-3$_{ax}$	4.32 d (9.0)	4.29 d (12.0)
H-5$_{ax}$	1.91 dd (3.0, 12.0)	1.78 dd (3.0, 12.0)
H-6$_{ax}$	1.41 ddd (12.0, 12.0, 12.0)	1.35 ddd (12.0, 12.0, 12.0)
H-6$_{eq}$	2.04 ddd (3.0, 3.0, 12.0)	1.98 ddd (3.0, 3.0, 12.0)
H-7$_{ax}$	1.67 dddd (3.0, 3.0, 12.0, 12.0)	1.60 dddd (3.0, 3.0, 12.0, 12.0)
H-8$_{ax}$	1.39 dddd (3.0, 12.0, 12.0, 12.0)	1.31 dddd (3.0, 12.0, 12.0, 12.0)
H-8$_{eq}$	1.89 dddd (3.0, 3.0, 3.0, 12.0)	1.83 dddd (3.0, 3.0, 3.0, 12.0)
H-9$_{ax}$	1.23 ddd (3.0, 12.0, 12.0)	1.11 ddd (3.0, 12.0, 12.0)
H-9$_{eq}$	1.55 ddd (3.0, 3.0, 12.0)	1.44 m
H$_3$-12	1.44 s	1.42 s
H$_3$-13	1.45 s	1.44 s
H$_3$-14	0.81 s	0.69 s
H$_2$-15a	4.87 br s	4.83 d (1.5)
H$_2$-15b	5.80 br s	5.79 d (1.5)
Glc H-1	5.06 d (8.0)	5.05 d (7.5)
Glc H-1′	—	5.05 d (7.5)

δ in ppm from TMS [coupling constants (J) in Hz are given in parentheses].

Table 2. ^{13}C-NMR Chemical Shifts of **1**, **4**, **7**—**11**, **15**, **16**, **8a**, **9a**, and **16a** (in Pyridine-d_5, 125 MHz)

	1	**7**	**4**	**8**	**8a**	**9**	**9a**
C-1	43.58	44.32	46.80	51.01	51.20	54.87	54.86
C-2	36.13	36.15	39.38	40.24	40.24	198.39	198.26
C-3	220.47	220.26	219.73	219.38	219.31	126.74	126.99
C-4	80.96	80.94	52.27	52.59	52.59	163.93	163.31
C-5	46.58	46.54	44.17	46.06	46.29	47.91	47.85
C-6	29.83	29.80	36.71	37.58	37.79	24.18	24.44
C-7	48.85	49.01	50.80	50.93	53.15	48.73	50.24
C-8	23.25	23.23	23.45	23.27	23.62	22.39	22.37
C-9	36.05	35.89	37.13	39.80	39.73	40.34	40.35
C-10	74.35	73.74	74.60	75.43	75.43	37.53	37.53
C-11	81.02	80.87	80.42	80.43	72.27	79.55	71.29
C-12	24.45	24.27	23.98	24.13	27.43	23.51	27.13
C-13	24.45	24.49	24.48	24.26	27.62	25.52	28.42
C-14	70.07	69.53	69.74	68.12	68.14	16.88	16.76
C-15	19.11	19.08	12.95	13.29	13.24	21.79	21.63
Glc-1	98.65	98.63	98.63	98.70		98.75	
Glc-2	75.43	75.42	75.39	75.40		75.43	
Glc-3	78.84	78.82	78.92	78.99		78.94	
Glc-4	71.67	71.64	71.97	72.01		71.94	
Glc-5	78.16	78.14	78.10	78.15		78.13	
Glc-6	62.70	62.66	62.05	63.06		63.13	
Fru-1		63.53					
Fru-2		105.50					
Fru-3		79.04					
Fru-4		76.32					
Fru-5		83.58					
Fru-6		62.99					

	10	**11**	**15**	**16**	**16a**
C-1	54.55	52.85	49.30	46.60 (−2.7)	49.26
C-2	194.89	195.19	73.41	83.74 (+10.3)	73.42
C-3	146.77	146.59	79.62	76.91 (−2.7)	79.61
C-4	151.07	148.82	152.33	150.24	152.48
C-5	47.51	46.42	48.53	48.05	48.43
C-6	24.77	25.25	25.43	25.23	25.51
C-7	48.53	44.49	48.57 (−1.2)	48.56 (−1.2)	49.73
C-8	22.15	22.69	22.38	22.15	22.48
C-9	40.04	32.32	41.10	40.82	41.11
C-10	37.08	35.64	35.46	35.16	35.37
C-11	79.51	78.90	79.50 (+8.1)	79.41 (+8.0)	71.39
C-12	23.53	23.29	24.13 (−3.5)	24.09 (−3.5)	27.61
C-13	25.46	24.10	24.79 (−3.2)	24.79 (−3.2)	27.96
C-14	16.97	26.27	17.82	17.41	17.69
C-15	15.21	15.97	104.83	106.02	104.73
Glc-1	98.74	98.53	98.71	98.72	
Glc-2	75.43	75.53	75.41	75.43	
Glc-3	78.97	78.98	78.94	78.97	
Glc-4	71.96	71.94	71.99	72.03	
Glc-5	78.16	78.16	78.03	78.06	
Glc-6	63.14	63.03	63.14	63.16	
Glc-1′	105.50	103.94		104.12	
Glc-2′	76.22	76.00		74.94	
Glc-3′	78.81	78.90		78.65	
Glc-4′	71.43	71.57		71.63	
Glc-5′	78.48	78.56		78.47	
Glc-6′	62.75	62.86		62.55	

δ in ppm from TMS. $\Delta\delta$ (δ glucoside − δ aglycone) are given in parentheses.

(CD) of **8** [**4**, 295 nm ($\Delta\varepsilon$+3.10); **8**, 296 nm ($\Delta\varepsilon$+2.47)], and the absolute structure of the aglycone moiety of **8** was determined to be 1*S*,4*S*,5*S*,7*R*,10*S*. Therefore **8** was characterized as (1*S*,4*S*,5*S*,7*R*,10*S*)-10,11,14-trihydroxyguai-3-one 11-*O*-β-D-glucopyranoside.

Glycosides **9** to **16** were eudesmane-type sesquiterpenoid glucosides, and **10** and **12** to **15** were identified as atractyloside I,[4] C,[4] D,[4] E[4] and G,[4] respectively.

Glycoside **9**, $C_{21}H_{34}O_7$, showed $[M+H]^+$ and $[M-C_6H_{12}O_6+H]^+$ ion peaks at *m*/*z* 399 and 219, respectively, in the positive FAB-MS, and the NMR spectral data (Tables 1, 2) showed the presence of four *tert*-methyls, four methylenes,

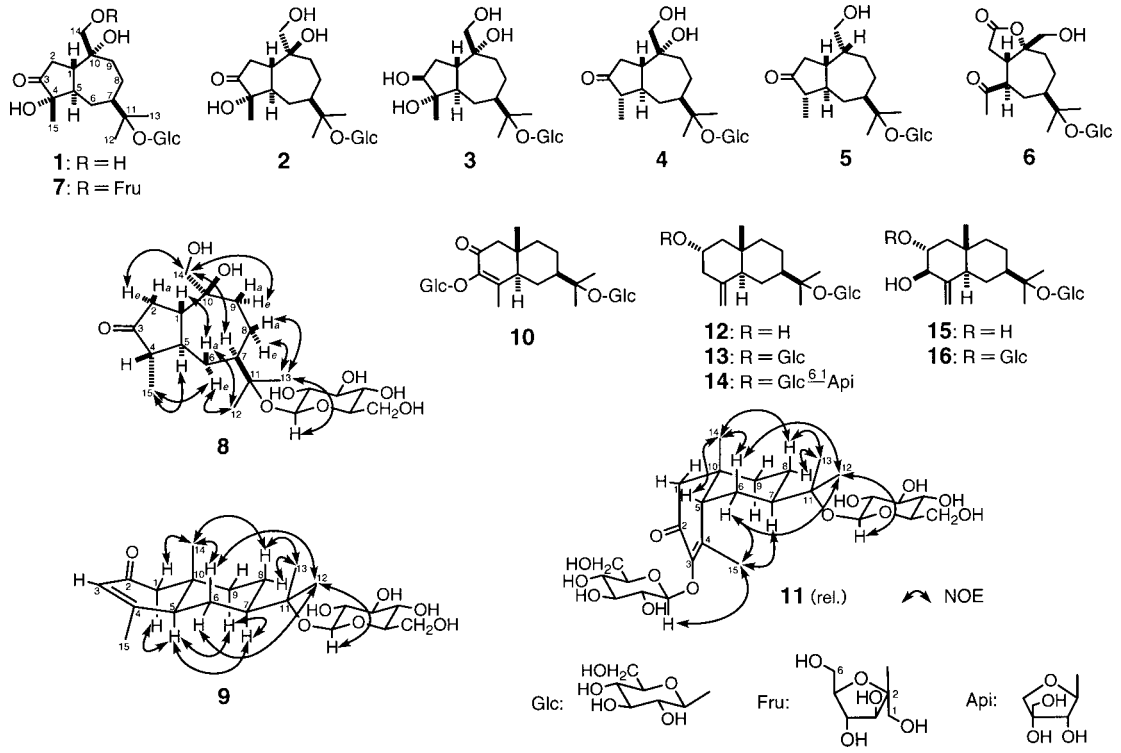
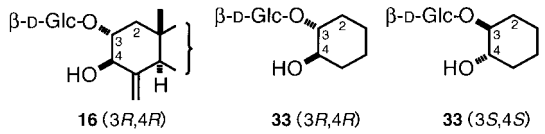


Fig. 1. Structures of **1**—**16**, and NOE Correlations of **8**, **9**, and **11**

two methines, one tri-substituted double bond, two quaternary carbons, and one carbonyl carbon, in addition to the β-D-glucopyranosyl moiety. Enzymatic hydrolysis of **9** gave an aglycone (**9a**) and D-glucose. The results of an HMBC experiment (see Experimental) indicated that the aglycone of **9** was 11-hydroxyeudesm-3-en-2-one, and the glucosyl group was located at C-11. The NOE interactions between H-5/H-7_{ax}, H-9_{ax}, and between H_3-14/H-6_{ax}, H-8_{ax} in the NOESY spectrum suggested that the A/B ring juncture was trans, the configuration of H-5 and C-10 methyl was axial, and the configuration of C-7 hydroxyisopropyl was equatorial (Fig. 1). Then **9a** was deduced to be isopterocarpolone first isolated from *Pterocarpus santalinus*.[6] The absolute structure of the aglycone was concluded to be 5*R*,7*R*,10*S*, since the optical rotation of **9a** {$[\alpha]_D^{21}$ +68° ($CHCl_3$)} was positive as isopterocarpolone {$[\alpha]_D$ +47° ($CHCl_3$)} which was obtained as a biotransformation product of (−)-α-eudesmol {(5*R*,7*R*,10*S*)-eudesm-3-en-11-ol.[7,8] Therefore **9** was characterized as (5*R*,7*R*,10*S*)-isopterocarpolone β-D-glucopyranoside [(5*R*,7*R*,10*S*)-11-hydroxyeudesm-3-en-2-one 11-*O*-β-D-glucopyranoside].

Glycoside **11**, $C_{27}H_{44}O_{13}$, showed $[M+Na]^+$, $[M+H]^+$, $[M-C_6H_{10}O_5+H]^+$, and $[M+C_{12}H_{22}O_{11}+H]^+$ ion peaks at *m/z* 599, 577, 415, and 235, respectively, in the positive FAB-MS. As the NMR spectra showed similar features to those of **10** (Tables 1, 2), **11** was indicated to be a sesquiterpenoid diglucoside with the same planar structure as **10**. But since the proton signals due to the H-5 and H-6_{ax} at δ 2.26 (dd, J=3.0, 3.0 Hz) and δ 1.44 (ddd, J=3.0, 13.0, 13.0 Hz) were apparently distinct from those of **10** at δ 2.47 (dd, J=3.0, 12.0 Hz) and δ 1.18 (ddd, J=12.0, 12.0, 12.0 Hz), the configuration of H-5 should be equatorial. This was supported by NOE interactions between H_3-14/H-5, H-6_{ax}, H-8_{ax}, and between H_3-15/H-6_{eq}, H-7 (Fig. 1). Then, the A/B ring juncture was suggested to be *cis*, and **11** was concluded to be *cis*-atractyloside I as described in Fig. 1.



	16 (3*R*,4*R*)	**33** (3*R*,4*R*)	**33** (3*S*,4*S*)
C-2	− 2.7	− 2.7	− 1.2
C-3	+10.3	+ 8.9	+11.2
C-4	− 2.7	− 2.4	− 0.8
Glc C-1	δ 104.12	δ 104.1	δ 106.9

Fig. 2. Glycosylation Shift Values and Glc C-1 Chemical Shifts of **16**, **33** (3*R*,4*R*), and **33** (3*S*,4*S*) in Pyridine-d_5

Glycoside **16**, $C_{27}H_{46}O_{13}$, exhibited $[M+H]^+$, $[M-C_6H_{12}O_5+H]^+$ and $[M-C_{12}H_{24}O_{12}+H]^+$ ion peaks at *m/z* 579, 399, and 219, respectively, in the positive FAB-MS. Enzymatic hydrolysis of **16** gave an aglycone (**16a**) identical to 3β-hydroxypterocarpol[4] and D-glucose. It showed similar NMR spectral features to those of **15** except for the signals due to another β-D-glucopyranosyl group (Tables 1, 2), and from the cross-peak between the Glc H-1′ and C-2 carbon in the HMBC spectrum, the location of the additional glucosyl group was indicated to be C-2. The values of the ^{13}C glycosylation shift [$\Delta\delta$(δ glycoside − δ aglycone)] of the α- and β-carbon, and the chemical shift of the glucosyl anomeric carbon were known to be affected by the absolute configuration of 1,2-cyclohexanediol 1-*O*-β-D-glucopyranoside (**33**).[9,10] In the case of **16**, the absolute configuration at C-2 was considered to be *R*, as explained in Fig. 2. Thus **16** was characterized as atractyloside G 2-*O*-β-D-glucopyranoside [(2*R*,3*R*,5*R*,7*R*,10*S*)-eudesm-4(15)-ene-2,3,11-triol 2,11-di-*O*-β-D-glucopyranoside] with the 2*R*,3*R* configuration of the aglycone.

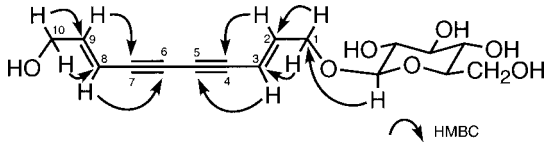


Fig. 3. Structure and HMBC Correlations of **29**

Monoterpenoid glucosides **17** to **20**, hemiterpenoid glycosides **21** and **22**, alkyl glycoside **23**, aromatic compound glycosides **24** to **28**, and nucleosides **30** and **31** were identified as (1*R*,2*R*,4*S*)-2-hydroxy-1,8-cineole *β*-D-glucopyranoside,[11] (1*S*,2*S*,4*R*)-2-hydroxy-1,8-cineole *β*-D-glucopyranoside,[11] (4*S*)-*p*-menth-1-ene-7,8-diol 8-*O*-*β*-D-glucopyranoside,[12] (1*S*,2*R*,4*S*)-*p*-menthane-1,2,8-triol 8-*O*-*β*-D-glucopyranoside,[13] 3-methyl-3-butenyl *β*-D-apiofuranosyl-(1-6)-*β*-D-glucopyranoside,[14] 3-methyl-2-butenyl *β*-D-apiofuranosyl-(1→6)-*β*-D-glucopyranoside,[15] isopropyl β-D-apiofuranosyl-(1→6)-*β*-D-glucopyranoside,[16] 4-hydroxy-3-methoxyphenyl *β*-D-glucopyranoside,[17] 4-hydroxy-3-methoxyphenyl *β*-D-apiofuranosyl-(1→6)-*β*-D-glucopyranoside,[18] 4-hydroxy-3-methoxyphenyl *β*-D-xylopyranosyl-(1→6)-*β*-D-glucopyranoside,[5] icariside F_2,[19] syringin,[19] uridine, and adenosine, respectively.

Glucoside **29**, $C_{16}H_{20}O_7$, showed $[M+Na]^+$ and $[M-C_6H_{12}O_6+H]^+$ ion peaks at *m/z* 347 and 145, respectively, in the positive FAB-MS. The NMR spectrum showed the presence of two di-substituted double bonds, two triple bonds, and two hydroxymethyls, in addition to the *β*-D-glucopyranosyl group. From the result of an HMBC experiment (Fig. 3), the aglycone of **29** was indicated to be decadiene-4,6-diyne-1,10-diol, and the glucosyl group was located at C-1. Furthermore, the coupling constant values of H-3 and H-8 (J=16.0 Hz) suggested the stereochemistry of the double bond should be *E*.[20] Therefore **29** was concluded to be (2*E*,8*E*)-decadiene-4,6-diyne-1,10-diol 1-*O*-*β*-D-glucopyranoside.

While no common constituent of nucleoside, amino acid, and eudesmane-type sesquiterpenoid glycoside could found between the water-soluble portion of *A. lancea* and *A. japonica*, we were able to isolate six characteristic guaiane-type sesquiterpenoid glucosides (**1** to **6**) from both rhizomes in relatively high yield. Thus the chemotaxonomic relationship between *A. lancea* and *A. japonica* can be considered to be close, as is the phylogenetic relationship.

Experimental

HPLC separation was carried out on Symmetryprep C_{18} 7 μm (Waters; column size, 7.8×300 mm; ODS), carbohydrate analysis (Waters; column size, 3.9×300 mm; CHA), and Wakobeads T-100s (Wako; column size, 6.0×150 mm; WBT) columns. The other instruments used and the experimental conditions for obtaining spectral data and for chromatography were the same as reported in a previous paper.[5]

Extraction and Separation The dried rhizome of *A. lancea* (1.5 kg), which was cultivated in the Tokyo Metropolitan Medical Plant Garden (Kodaira City, Tokyo, Japan), was extracted with methanol (3 l×3) for 2 weeks, and the extract (286.4 g) was partitioned into ether–water and ethyl acetate–water, respectively. The aqueous portion (217.7 g) was chromatographed over Amberlite XAD-II (H_2O→MeOH) to give water eluate (198.8 g) and methanol eluate (18.9 g) fractions.

The methanol fraction was subjected to Sephadex LH-20 (MeOH) to give seven fractions (frs. A—G). Fraction C (7.73 g) was chromatographed on silica gel [$CHCl_3$–MeOH–H_2O (4 : 1 : 0.1→6 : 4 : 0.5)→MeOH] to give 12 fractions (frs. C_1—C_{12}). Fraction C_2 (0.43 g) was chromatographed on a Lobar RP-8 column [MeCN–H_2O (3 : 17—3 : 7)] to give 12 fractions (frs. $C_{2\text{-}1}$—$C_{2\text{-}12}$), and fr. $C_{2\text{-}4}$ was subjected to HPLC [CHA, MeCN–H_2O (97 : 3)] to give **17** (6 mg) and **18** (2 mg). Fraction $C_{2\text{-}10}$ was chromatographed on silica gel [$CHCl_3$–MeOH–H_2O (4 : 1 : 0.1)] to give four fractions (frs. $C_{2\text{-}10a}$—$C_{2\text{-}10d}$), and fr. $C_{2\text{-}10b}$ and fr. $C_{2\text{-}10d}$ were subjected to HPLC [ODS, MeCN–H_2O (1 : 3)] to give **9** (55 mg) and **12** (13 mg), respectively. Fraction C_3 (0.44 g) was chromatographed on a Lobar RP-8 column [MeCN–H_2O (3 : 17)] to give 14 fractions (frs. $C_{3\text{-}1}$—$C_{3\text{-}14}$), and fr. $C_{3\text{-}2}$ was subjected to Sephadex LH-20 (MeOH) to give **28** (16 mg). Fraction $C_{3\text{-}5}$ was subjected to HPLC [ODS, MeCN–H_2O (3 : 17)] to give **19** (8 mg), and fr. $C_{3\text{-}9}$ was subjected to HPLC [ODS, MeCN–H_2O (3 : 17)] to give **5** (20 mg), respectively. Fraction C_4 (0.54 g) was chromatographed on a Lobar RP-8 column [MeCN–H_2O (3 : 17)] to give 16 fractions (frs. $C_{4\text{-}1}$—$C_{4\text{-}16}$). Fraction $C_{4\text{-}2}$ was subjected to HPLC [ODS, MeCN–H_2O (1 : 9)] to give **6** (20 mg), and fr. $C_{4\text{-}11}$ was subjected to HPLC [ODS, MeCN–H_2O (3 : 17)] to give **15** (30 mg). Fraction C_5 (0.86 g) was chromatographed on a Lobar RP-8 column [MeCN–H_2O (3 : 17)] to give 12 fractions (frs. $C_{5\text{-}1}$—$C_{5\text{-}12}$), and fr. $C_{5\text{-}5}$ was subjected to HPLC [ODS, MeCN–H_2O (1 : 9)] to give fr. $C_{5\text{-}5a}$ and **8** (10 mg). Fraction $C_{5\text{-}5a}$ was subjected to HPLC [WTS, MeCN–H_2O (9 : 1)] to give **21** (3 mg) and **22** (6 mg). Fraction $C_{5\text{-}6}$ and fr. $C_{5\text{-}7}$ were subjected to HPLC [ODS, MeCN–H_2O (1 : 7)] to give **4** (90 mg) and **27** (10 mg), respectively. Fraction C_7 (0.10 g) was chromatographed on a Lobar RP-8 column [MeCN–H_2O (3 : 17→3 : 7)] to give 12 fractions (frs. $C_{7\text{-}1}$—$C_{7\text{-}12}$), and fr. $C_{7\text{-}1}$ was subjected to HPLC [ODS, MeCN–H_2O (1 : 9)] to give **23** (5 mg) and **20** (3 mg). Fraction $C_{7\text{-}3}$ was subjected to HPLC [ODS, MeCN–H_2O (3 : 37)] to give **2** (25 mg) and **1** (350 mg), and fr. $C_{7\text{-}7}$ was subjected to repeated HPLC [ODS, MeCN–H_2O (3 : 17) and CHA, MeCN–H_2O (37 : 3)] to give **10** (65 mg) and **11** (6 mg). Fraction $C_{7\text{-}10}$ was subjected to HPLC [ODS, MeCN–H_2O (7 : 33) and CHA, MeCN–H_2O (37 : 3)] to give **13** (13 mg). Fraction C_8 (0.65 g) was chromatographed on a Lobar RP-8 column [MeCN–H_2O (3 : 17)] to give eight fractions (frs. $C_{8\text{-}1}$—$C_{8\text{-}8}$), and fr. $C_{8\text{-}6}$ was subjected to HPLC [ODS, MeCN–H_2O (3 : 17)] to give **16** (30 mg). Fraction C_{10} (0.59 g) was chromatographed on a Lobar RP-8 column [MeCN–H_2O (3 : 17→3 : 7)] to give nine fractions (frs. $C_{10\text{-}1}$—$C_{10\text{-}9}$), and fr. $C_{10\text{-}2}$ was subjected to HPLC [ODS, MeCN–H_2O (3 : 47) and CHA, MeCN–H_2O (17 : 3)] to give **3** (12 mg) and **7** (33 mg). Fraction $C_{10\text{-}5}$ was subjected to HPLC [ODS, MeCN–H_2O (3 : 17)] to give **14** (6 mg). Fraction E (0.88 g) was chromatographed over silica gel [$CHCl_3$–MeOH–H_2O (4 : 1 : 0.1→6 : 4 : 0.5)→MeOH] to give eight fractions (frs. E_1—E_8). Fraction E_2 (0.16 g) was chromatographed on a Lobar RP-8 column [MeCN–H_2O (3 : 17)] to give nine fractions (frs. $E_{2\text{-}1}$—$E_{2\text{-}9}$), and fr. $E_{2\text{-}8}$ was subjected to HPLC [ODS, MeCN–H_2O (3 : 17)] to give **29** (5 mg). Fraction E_3 (0.12 g) was chromatographed on a Lobar RP-8 column [MeCN–H_2O (3 : 17)] to give nine fractions (frs. $E_{3\text{-}1}$—$E_{3\text{-}9}$), and fr. $E_{3\text{-}3}$ was subjected to HPLC [ODS, MeCN–H_2O (1 : 39)] to give **24** (8 mg). Fraction E_5 was chromatographed on a Lobar RP-8 column [MeCN–H_2O (3 : 17)] to give seven fractions (frs. $E_{5\text{-}1}$—$E_{5\text{-}7}$). Fraction $E_{5\text{-}3}$ was subjected to HPLC [CHA, MeCN–H_2O (14 : 1)] to give **25** (10 mg) and **26** (2 mg), and fr. $E_{5\text{-}5}$ was subjected to HPLC [ODS, MeCN–H_2O (1 : 39)] to give **32** (66 mg). Fraction F (0.35 g) was chromatographed on a Lobar RP-8 column [MeCN–H_2O (3 : 17)] to give six fractions (frs. F_1—F_6), and fr. F_3 was subjected to Sephadex LH-20 (MeOH) to give **30** (25 mg). Fraction G (0.06 g) was chromatographed on a Lobar RP-8 column [MeCN–H_2O (3 : 17)] to give four fractions (frs. G_1—G_4), and fr. G_2 was subjected to Sephadex LH-20 (MeOH) to give **31** (12 mg).

The following compounds were identified by comparison with authentic compounds or published physical and spectral data: atractyloside A (**1**; the ^{1}H- and ^{13}C-NMR spectral data are described in Tables 1 and 2), 10-*epi*-atractyloside A (**2**), atractyloside B (**3**), (1*S*,4*S*,5*S*,7*R*,10*R*)-10,11,14-trihydroxyguai-3-one 11-*O*-*β*-D-glucopyranoside (**4**; the ^{1}H- and ^{13}C-NMR spectral data are described in Tables 1 and 2), (1*S*,4*S*,5*R*,7*R*,10*R*)-11,14-dihydroxyguai-3-one 11-*O*-*β*-D-glucopyranoside (**5**), (1*S*,5*R*,7*R*,10*R*)-secoatractylolactone 11-*O*-*β*-D-glucopyranoside (**6**), atractyloside I (**10**; the ^{1}H- and ^{13}C-NMR spectral data are described in Tables 1 and 2), atractyloside C (**12**), atractyloside D (**13**), atractyloside E (**14**), atractyloside G (**15**; the ^{1}H- and ^{13}C-NMR spectral data are described in Tables 1 and 2), (1*R*,2*R*,4*S*)-2-hydroxy-1,8-cineole *β*-D-glucopyranoside (**17**), (1*S*,2*S*,4*R*)-2-hydroxy-1,8-cineole *β*-D-glucopyranoside (**18**), (4*S*)-*p*-menth-1-ene-7,8-diol 8-*O*-*β*-D-glucopyranoside (**19**), (1*S*,2*R*,4*S*)-*p*-menthane-1,2,8-triol 8-*O*-*β*-D-glucopyranoside (**20**), 3-methyl-3-butenyl *β*-D-apiofuranosyl-(1→6)-*β*-D-glucopyranoside (**21**), 3-methyl-2-butenyl *β*-D-apiofuranosyl-(1→6)-*β*-D-glucopyranoside (**22**), isopropyl *β*-D-apiofuranosyl-(1→6)-*β*-D-glucopyranoside (**23**), 4-hydroxy-3-methoxyphenyl *β*-D-glucopyranoside (**24**), 4-hydroxy-3-methoxyphenyl *β*-D-apiofuranosyl-(1→6)-*β*-D-glucopyranoside (**25**), 4-hydroxy-3-methoxyphenyl *β*-D-xylopyranosyl-(1→6)-*β*-D-glucopyranoside

(**26**), icariside F_2 (**27**), syringin (**28**), uridine (**30**), adenosine (**31**), and L-tryptophan (**32**).

Atractyloside A 14-*O*-β-D-Fructofuranoside (7) An amorphous powder, $[\alpha]_D^{22}$ +2° (c=1.3, MeOH). Positive FAB-MS m/z: 633 $[M+Na]^+$, 611.2905 $[M+H]^+$ (Calcd for $C_{27}H_{47}O_{15}$, 611.2895), 431 $[M-C_6H_{12}O_6+H]^+$, 251 $[M-C_{12}H_{24}O_{12}+H]^+$ (base). ^{1}H-NMR: Table 1. ^{13}C-NMR: Table 2. HMBC correlations: H-1_{ax}/C-2, C-4, C-5, C-6, C-9, C-10, C-14; H_2-2/C-1, C-3, C-4, C-5, C-10; H-5_{ax}/C-1, C-4, C-6, C-7, C-10, C-15; H-6_{ax}/C-1, C-4, C-5, C-7, C-8, C-11; H-6_{eq}/C-1, C-4, C-7, C-8, C-11; H-7_{ax}/C-5, C-6, C-8, C-9, C-11, C-12, C-13; H_2-8/C-6, C-7, C-9, C-10, C-11; H_2-9/C-1, C-7, C-8, C-10, C-14; H_3-12/C-7, C-11, C-13; H_3-13/C-7, C-11, C-12; H_2-14/C-1, C-9, C-10, Fru C-2; H_3-15/C-3, C-4, C-5; Glc H-1/C-11.

Enzymatic Hydrolysis of 7 A mixture of **7** (16 mg) and β-glucosidase (5 mg; Toyobo Co. Ltd., lot 93240) in water (5 ml) was shaken in a water bath at 37 °C for 30 d. The mixture was concentrated *in vacuo* to dryness and the residue was chromatographed over silica gel [$CHCl_3$–MeOH (4 : 1 to 1 : 1)] to afford (1*S*,4*S*,5*R*,7*R*,10*R*)-4,10,11,14-tetrahydroxyguai-3-one (**1a**; 3 mg) and a sugar fraction. The sugar fraction was passed through Sephadex LH-20 (MeOH) to give a syrup, and HPLC [carbohydrate analysis (Waters), detector; JASCO RI-930 detector and JASCO OR-990 chiral detector, solvent; MeCN–H_2O (9 : 1), 2 ml/min; t_R 5.50 min (same location as that of D-glucose) and t_R 6.80 min (same location as that of D-fructose)] showed the presence of D-glucose and D-fructose.

(1*S*,4*S*,5*S*,7*R*,10*S*)-10,11,14-Trihydroxyguai-3-one 11-*O*-β-D-Glucopyranoside (8) An amorphous powder, $[\alpha]_D^{22}$ +1° (c=0.7, MeOH). Positive FAB-MS m/z: 455 $[M+Na]^+$, 433.2439 $[M+H]^+$ (Calcd for $C_{21}H_{37}O_9$, 433.2437), 415 $[M-H_2O+H]^+$, 397 $[M-2H_2O+H]^+$, 253 $[M-C_6H_{12}O_6+H]^+$ (base). ^{1}H-NMR: Table 1. ^{13}C-NMR: Table 2. CD: (c=0.0085 M, MeOH) $\Delta\varepsilon$ (nm): +2.47 (296). HMBC correlations: H-1_{ax}/C-2, C-4, C-5, C-6, C-9, C-10, C-14; H-2_{ax}/C-1, C-3, C-4, C-5; H-2_{eq}/C-1, C-3, C-4, C-5, C-10; H-4_{ax}/C-3, C-5, C-6, C-15; H-5_{ax}/C-1, C-4, C-6, C-7, C-10, C-15; H-6_{eq}/C-1, C-4, C-5, C-7, C-11; H-7_{ax}/C-6, C-8, C-11, C-12, C-13; H-8_{ax}/C-6, C-7, C-9, C-10, C-11; H-8_{eq}/C-6, C-7, C-9, C-10; H_2-9/C-1, C-7, C-8, C-10, C-14; H_3-12/C-7, C-11, C-13; H_3-13/C-7, C-11, C-12; H_2-14/C-1, C-2, C-9, C-10; H_3-15/C-3, C-4, C-5; Glc H-1/C-11.

Enzymatic Hydrolysis of 8 A mixture of **8** (7 mg) and β-glucosidase in water (5 ml) was shaken in a water bath at 37 °C for 15 d. The mixture was treated in the same way as described for **7** to afford an aglycone **8a** (6 mg) and a sugar fraction. From the sugar fraction, D-glucose was detected as described for **7**.

(1*S*,4*S*,5*S*,7*R*,10*S*)-10,11,14-Trihydroxyguai-3-one (8a) An amorphous powder, $[\alpha]_D^{22}$ +20° (c=0.2, MeOH). ^{1}H-NMR (pyridine-d_5, 500 MHz) δ: 4.10 (1H, d, J=10.5 Hz, H-14b), 3.98 (1H, d, J=10.5 Hz, H-14a), 3.07 (1H, dd, J=11.0, 19.0 Hz, H-2_{eq}), 2.94 (1H, br dd, J=10.0, 19.0 Hz, H-2_{ax}), 2.68 (1H, ddd, J=10.0, 11.0, 11.0 Hz, H-1_{ax}), 2.55 (1H, ddd, J=3.0, 3.0, 13.0 Hz, H-6_{eq}), 2.45 (1H, br dd, J=10.0, 12.0 Hz, H-9_{eq}), 2.33 (1H, m, H-8_{eq}), 2.28 (1H, br dd, J=10.0, 13.0 Hz, H-9_{ax}), 2.11 (1H, br ddd, J=11.0, 11.0, 11.0 Hz, H-5_{ax}), 2.03 (1H, dddd, J=3.0, 12.0, 12.0, 12.0 Hz, H-8_{ax}), 1.93 (1H, dd, J=7.0, 11.0 Hz, H-4_{ax}), 1.87 (1H, dddd, J=3.0, 3.0, 12.0, 12.0 Hz, H-7_{ax}), 1.42 (6H, s, H_3-12, -13), 1.35 (1H, ddd, J=11.0, 12.0, 12.0 Hz, H-6_{ax}), 1.18 (3H, d, J=7.0, H_3-15).

(5*R*,7*R*,10*S*)-Isopterocarpolone β-D-Glucopyranoside (9) An amorphous powder, $[\alpha]_D^{24}$ +43° (c=1.6, MeOH). Positive FAB-MS m/z: 421 $[M+Na]^+$, 399.2364 $[M+H]^+$ (Calcd for $C_{21}H_{35}O_7$, 399.2383), 219 $[M-C_6H_{12}O_6+H]^+$ (base). ^{1}H-NMR: Table 1. ^{13}C-NMR: Table 2. HMBC correlations: H_2-1/C-2, C-3, C-5, C-9, C-10, C-14; H-3/C-1, C-5, C-15; H-5_{ax}/C-3, C-4, C-6, C-10, C-14; H-6_{ax}/C-4, C-5, C-7, C-8, C-10, C-11; H-6_{eq}/C-4, C-5, C-8, C-10; H-7_{ax}/C-8, C-9, C-11; H-8_{ax}/C-6, C-9; H-8_{eq}/C-6, C-10; H_2-9/C-8, C-10, C-14; H_3-12/C-7, C-11, C-13; H_3-13/C-7, C-11, C-12; H_3-14/C-1, C-9, C-10; H_3-15/C-3, C-4, C-5; Glc H-1/C-11.

Enzymatic Hydrolysis of 9 A mixture of **9** (11 mg) and β-glucosidase (5 mg) in water (5 ml) was shaken in a water bath at 37 °C for 20 d. The mixture was treated in the same way as described for **7** to afford isopterocarpolone [**9a**; $[\alpha]_D^{21}$ +68° (c=0.4, $CHCl_3$), 5 mg] and a sugar fraction. From the sugar fraction, D-glucose was detected as described for **7**.

***cis*-Atractyloside I (11)** An amorphous powder, $[\alpha]_D^{22}$ −23° (c=0.4, MeOH). Positive FAB-MS m/z: 615 $[M+K]^+$, 599.2673 $[M+Na]^+$ (Calcd for $C_{27}H_{44}NaO_{13}$, 599.2679), 577 $[M+H]^+$, 415 $[M-C_6H_{10}O_5+H]^+$, 253 $[M-C_{12}H_{20}O_{10}+H]^+$, 235 $[M-C_{12}H_{22}O_{11}+H]^+$ (base). ^{1}H-NMR: Table 1. ^{13}C-NMR: Table 2. HMBC correlations: H-1a/C-2, C-3, C-5, C-9, C-10, C-14; H-1b/C-2, C-5, C-9, C-10, C-14; H-5_{eq}/C-3, C-4, C-9, C-10, C-14; H-6_{ax}/C-7, C-11; H-6_{eq}/C-10; H-7_{ax}/C-6, C-8, C-11, C-12, C-13; H-8_{ax}/C-7; H-9_{ax}/C-8, C-10, C-14; H-9_{eq}/C-5, C-7, C-8, C-10, C-14; H_3-12/C-7, C-11, C-13; H_3-13/C-7, C-11, C-12; H_3-14/C-1, C-5, C-9, C-10; H_3-15/C-3, C-4, C-5; Glc H-1/C-11; Glc H-1′/C-3.

(2*R*,3*R*,5*R*,7*R*,10*S*)-Atractyloside G 2-*O*-β-D-Glucopyranoside (16) An amorphous powder, $[\alpha]_D^{22}$ −20° (c=1.5, MeOH). Positive FAB-MS m/z: 601 $[M+Na]^+$, 579.3015 $[M+H]^+$ (Calcd for $C_{27}H_{47}O_{12}$, 579.3017), 417 $[M-C_6H_{10}O_5+H]^+$, 399 $[M-C_6H_{12}O_6+H]^+$, 219 $[M-C_{12}H_{24}O_{12}+H]^+$ (base). ^{1}H-NMR: Table 1. ^{13}C-NMR: Table 2. HMBC correlations: H_2-1/C-2, C-3, C-5, C-9, C-10, C-14; H-2_{ax}/C-1, C-3, Glc C-1; H-3_{ax}/C-2, C-4, C-15; H-5_{ax}/C-3, C-4, C-15; H-6_{ax}/C-4, C-5, C-7, C-8, C-10, C-11; H-6_{eq}/C-7, C-8, C-10; H-7_{ax}/C-9, C-11, C-12, C-13; H-8_{ax}/C-5, C-6, C-7, C-9, C-10; H-8_{eq}/C-6, C-10; H-9_{ax}/C-1, C-10, C-14; H-9_{eq}/C-10; H_3-12/C-7, C-11, C-13; H_3-13/C-7, C-11, C-12; H_3-14/C-1, C-5, C-9, C-10; H-15a/C-3, C-5; H-15b/C-3, C-4, C-5; Glc H-1/C-11; Glc H-1′/C-2.

Enzymatic Hydrolysis of 16 A mixture of **16** (11 mg) and β-glucosidase (5 mg) in water (5 ml) was shaken in a water bath at 37 °C for 20 d. The mixture was treated in the same way as described for **7** to afford (2*R*,3*R*,5*R*,7*R*,10*S*)-eudesm-4(15)-ene-2,3,11-triol [**16a**; $[\alpha]_D^{22}$ +17° (c=0.4, MeOH), 4 mg] and a sugar fraction. From the sugar fraction, D-glucose was detected as described for **7**.

(2*E*,8*E*)-2,8-Decadiene-4,6-diyne-1,10-diol 1-*O*-β-D-Glucopyranoside (29) An amorphous powder, $[\alpha]_D^{21}$ −77° (c=0.2, MeOH). Positive FAB-MS m/z: 347.1090 $[M+Na]^+$ (Calcd for $C_{16}H_{20}NaO_7$, 347.1106), 145 $[M-C_6H_{12}O_6+H]^+$ (base). ^{1}H-NMR (pyridine-d_5, 500 MHz) δ: 6.69 (1H, td, J=4.0, 16.0 Hz, H-9), 6.47 (1H, td, J=4.0, 16.0 Hz, H-2), 6.32 (1H, d, J=16.0 Hz, H-8), 6.24 (1H, d, J=16.0 Hz, H-3), 4,59, 4.37 (each 1H, ddd, J=1.5, 4.0, 16.0 Hz, H_2-1), 4.42 (2H, dd, J=2.0, 4.0 Hz, H_2-10), 4.86 (1H, d, J=7.5 Hz, Glc H-1). ^{13}C-NMR (pyridine-d_5, 125 MHz) δ: 68.42 (C-1), 144.27 (C-2), 109.71 (C-3), 80.41 (C-4), 75.26 (C-5), 74.73 (C-6), 81.32 (C-7), 107.20 (C-8), 149.58 (C-9), 61.92 (C-10), 104.11 (Glc C-1), 75.17 (Glc C-2), 78.55, 78.67 (Glc C-3, C-5), 71.57 (Glc C-4), 62.72 (Glc C-6). HMBC correlations: H_2-1/C-2, C-3, Glc C-1; H-$_2$/C-1, C-4; H-3/C-1, C-2, C-5; H-8/C-6, C-9, C-10; H-9/C-7, C-8, C-10; H_2-10/C-8, C-9; Glc H-1/C-1.

Acknowledgments The authors thank Mr. Y. Takase and Dr. H. Suzuki of the Analytical Center of this university for MS and NMR measurements.

References

1) "Japanese Pharmacopoeia," 14th edition, Hirokawa Publishing Co., Tokyo, 2001, pp. 2708—2709, 2869—2871.
2) Mizukami H., Shimizu R., Kohda H., Kohjyouma M., Kawanishi F., Hiraoka N., *Biol. Pharm. Bull.*, **19**, 577—580 (1996).
3) Kohjyouma M., Kohda H., *Biol. Pharm. Bull.*, **20**, 502—506 (1997).
4) Yahara S., Higashi T., Iwaki K., Nohara T., Marubayashi N., Ueda I., Kohoda H., Goto K., Izumi H., Nuno M., Katsuki S., Isoda S., Satake M., *Chem. Pharm. Bull.*, **37**, 2995—3000 (1989).
5) Kitajima J., Kamoshita A., Ishikawa T., Takano A., Fukuda T., Isoda S., Ida Y., *Chem. Pharm. Bull.*, **51**, 152—157 (2003).
6) Kumar N., Ravindranath B., Seshadri T. R., *Phytochemistry*, **13**, 633—636 (1974).
7) Toyota M., Yonehara Y., Horibe I., Minagawa K., Asakawa Y., *Phytochemistry*, **52**, 689—694 (1999).
8) Toyota M., *Yakugaku Zasshi*, **120**, 1359—1372 (2000).
9) Itano K., Yamasaki K., Kihara C., Tanaka O., *Carbohydr. Res.*, **87**, 27—34 (1980).
10) Tanaka O., *Yakugaku Zasshi*, **105**, 323—351 (1985).
11) Ishikawa T., Kitajima J., Tanaka Y., Ono M., Ito Y., Nohara T., *Chem. Pharm. Bull.*, **46**, 1587—1590 (1998).
12) Kitajima J., Aoki Y., Ishikawa T., Tanaka Y., *Chem. Pharm. Bull.*, **47**, 639—642 (1999).
13) Matsumura T., Ishikawa T., Kitajima J., *Tetrahedron*, **57**, 8067—8074 (2001).
14) Baltenweek-Guyot R., Trendel J.-M., Albrecht P., *J. Nat. Prod.*, **60**, 1326—1327 (1997).
15) Ono M., Yoshida A., Ito Y., Nohara T., *Phytochemistry*, **51**, 819—823 (1999).
16) Ishikawa T., Sega Y., Kitajima J., *Chem. Pharm. Bull.*, **49**, 584—588 (2001).
17) Inoshiri S., Sasaki M., Kohoda H., Otsuka H., Yamasaki K., *Phytochemistry*, **26**, 2811—2814 (1987).
18) Shibuya H., Takeda Y., Zhang R., Tanitame A., Tsai Y.-L., Kitagawa I., *Chem. Pharm. Bull.*, **40**, 2639—2646 (1992).
19) Kitajima J., Ishikawa T., Tanaka Y., Ono M., Ito Y., Nohara T., *Chem. Pharm. Bull.*, **46**, 1587—1590 (1998).
20) Takahashi A., Endo T., Nozoe S., *Chem. Pharm. Bull.*, **40**, 3181—3184 (1992).