Studies on the Constituents of *Aster tataricus* L.f. II.[1] Structures of Aster Saponins Isolated from the Root

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Four new oleanane-type triterpene saponins named aster saponins A, B, C and D were isolated from the root of *Aster tataricus* L.f. (Compositae). Their structures were elucidated based on chemical and spectral evidence as follows.

Aster saponin A: a 28-[*O*-β-D-xylopyranosyl-(1→3)-*O*-α-L-arabinopyranosyl-(1→4)-[*O*-β-D-apiofuranosyl-(1→3)]-*O*-α-L-rhamnopyranosyl-(1→2)-β-D-xylopyranosyl]ester of 3-*O*-[*O*-α-L-arabinopyranosyl-(1→6)-β-D-glucopyranosyl]-2β,3β,16α-trihydroxyolean-12-en-28-oic acid (asterogenic acid).

Aster saponin B: an echinocystic acid (3β,16α-dihydroxyolean-12-en-28-oic acid) glycoside corresponding to aster saponin A.

Aster saponin C: a 28-[*O*-β-D-xylopyranosyl-(1→3)-*O*-α-L-arabinopyranosyl-(1→4)-[*O*-β-D-apiofuranosyl-(1→3)]-*O*-α-L-rhamnopyranosyl-(1→2)-[*O*-α-L-rhamnopyranosyl-(1→3)]-β-D-xylopyranosyl]ester of 3-*O*-[*O*-α-L-arabinopyranosyl-(1→6)-β-D-glucopyranosyl]asterogenic acid.

Aster saponin D: an echinocystic acid glycoside corresponding to aster saponin C.

Keywords *Aster tataricus*; Asteris Radix; Compositae; triterpene glycoside; bisdesmoside; aster saponin; asterogenic acid; 2β,3β,16α-trihydroxyolean-12-en-28-oic acid; echinocystic acid; 3β,16α-dihydroxyolean-12-en-28-oic acid

The constituents of the root of *Aster tataricus* L. f. (Compositae) were first investigated by Nakaoki[2] in 1929 and aster saponin, $C_{23}H_{44}O_{10}\cdot 1/2H_2O$, an arabinoside of astersapogenin, was isolated. Following Nakaoki's work, Koyama *et al.*[3] reported the isolation of a hederagenin monoglucoside as a prosapogenin of "aster saponin." However, the structure of "aster saponin" still remained uncharacterized. We have investigated the glycoside constituents of Asteris Radix and obtained a fraction which seems to be Nakaoki's "aster saponin," from which four oleanane-type triterpene saponins named aster saponins A, B, C and D were isolated. This paper deals with the structures of these aster saponins.

Fractionation of the crude saponin mixture on silica gel, purification of the fractions by silica gel column chromatography, octadecyl silica (ODS) column chromatography and final purification by high performance liquid chromatography (HPLC) on reversed-phase material have resulted in the isolation of two less polar saponins, aster saponins A (I) (yield: 0.025% of the dried crude drug) and B(II) (0.002%), and two polar saponins, aster saponins C (III) (0.034%) and D (IV) (0.006%).

Aster saponin C (III), the major polar saponin, was obtained as colorless needles from aqueous MeOH. The fast-atom bombardment mass spectrum (FAB-MS) showed an $[M+Na]^+$ ion at *m/z* 1625 and an $[M-H]^-$ ion at *m/z* 1601, indicating its molecular weight to be 1602. The proton nuclear magnetic resonance (^{1}H-NMR) spectrum showed the signals of seven tertiary methyl groups (δ 1.01, 1.06, 1.19, 1.26, 1.33, 1.43 and 1.75), one trisubstituted olefinic proton (δ 5.57) and eight anomeric protons [δ 4.77 (d, J=7 Hz), 4.83 (d, J=8 Hz), 5.22 (d, J=7 Hz), 5.29 (d, J=8 Hz), 5.61 (br s), 5.69 (br s), 5.95 (d, J=4 Hz) and 6.50 (d, J=4 Hz)]. The carbon-13 NMR (^{13}C-NMR) spectrum revealed the presence of six C–C bonded saturated quaternary carbons (δ 30.8, 37.0, 38.6, 40.1, 42.2, 49.4), one oxygenated quaternary carbon (δ 79.8), a pair of olefinic carbons (δ 123.0 and 144.2), one ester carbon (δ 175.9) and eight anomeric carbons (δ 94.0, 101.0, 101.7, 104.7, 104.8, 105.6, 105.8 and 111.9). These spectral data suggested III to be a glycoside of an oleanane-type triterpene carboxylic acid in which the sugar moiety is linked to the carboxyl group with an ester linkage.

Compound III gave D-glucose, D-apiose and two mol each of L-rhamnose, L-arabinose and D-xylose on acid hydrolysis. Selective cleavage of the ester glycoside linkage of III according to the method reported by Ohtani *et al.*[4] provided an anomeric mixture of methyl oligoglycosides and a prosapogenin, the latter of which was converted into a methyl ester (V) with CH_2N_2. Compound V gave an aglycone methyl ester (VI), D-glucose and L-arabinose on acid hydrolysis. The electron-impact MS (EI-MS) of VI showed a molecular ion at *m/z* 502 and fragment ions at *m/z* 278 and 260. The high-resolution mass analysis of the molecular ion gave the molecular formula $C_{31}H_{50}O_5$ for VI, and the fragment ions indicated that VI is an olean-12-enoic acid methyl ester having one hydroxyl group and a carbomethoxyl group at ring(s) D and/or E, and two hydroxyl groups at ring(s) A and/or B.

The ^{1}H-NMR spectrum (Table I, pyridine-d_5–D_2O) of VI showed signals of an olefinic proton at δ 5.56 (dd, J=3, 3 Hz), carbomethoxyl protons at δ 3.72, and three hydroxymethine protons at δ 4.43 (H_a: ddd, J=4, 3, 3 Hz), δ 3.44 (H_b: d, J=4 Hz) and δ 5.03 (H_c: br dd, J=3, 3 Hz). The ^{1}H–^{1}H correlation spectroscopy (COSY) spectrum indicated that the CH_a–OH group is located between a methylene group [^{1}H-NMR δ: 1.29 (dd, J=14, 3 Hz) and 2.35 (dd, J=14, 3 Hz)] and the second hydroxymethine group (CH_b–OH). The long-range ^{1}H–^{13}C COSY spectrum (J_{CH}=10 Hz) indicated that the methylene group next to the CH_a–OH group is further connected to a quaternary carbon having one methyl group, and the CH_b–OH group is further linked to a quaternary carbon with two methyl groups, thus extending the partial structure to CH_3>C–CH_2–CH_a(OH)–CH_b(OH)–$C(CH_3)_2$–. From these spectral data, the two hydroxyl groups were reasonably allocated to C_2 and C_3. The configuration of the C_2-hydroxyl group was determined to be β from the coupling constants of H_a, while the configuration of the C_3-hydroxyl group was determined to be β from the fact that nuclear Overhauser effect

TABLE I. ^{1}H-NMR Chemical Shifts of VI

No.	Pyridine-d_5	Pyridine-d_5–D_2O	No.	Pyridine-d_5	Pyridine-d_5–D_2O
1	*ca.* 1.25	1.29 dd (14, 3)	19	*ca.* 1.40	*ca.* 1.30
	2.35 dd (14, 3)	2.35 dd (14, 3)		2.77 dd (14, 14)	2.75 dd (14, 14)
2	4.41 br s	4.43 ddd (4, 3, 3)	21	*ca.* 1.30 m	—
3	3.45 dd (6, 4)	3.44 d (4)		2.42 ddd (14, 14, 5)	2.41 ddd (14, 14, 5)
5	*ca.* 1.05	—	22	1.98 ddd (14, 14, 5)	1.95 ddd (14, 14, 5)
6	*ca.* 1.65 (2H)	—		2.22 ddd (14, 5, 3)	2.22 ddd (14, 5, 3)
7	*ca.* 1.65	—	23	1.25 s	1.24 s
	1.41 dd (9, 3)	—	24	1.37 s	1.35 s
9	*ca.* 1.30, 1.80	—	25	1.58 s	1.55 s
11	*ca.* 2.10 m (2H)	—	26	0.97 s	0.94 s
12	5.58 dd (3, 3)	5.56 dd (3, 3)	27	1.79 s	1.76 s
15	*ca.* 1.65	1.70 dd (14, 3)	29	1.02 s	1.01 s
	2.06 br d (14)	2.05 dd (14, 3)	30	1.10 s	1.09 s
16	5.03 br ddd (5, 3, 3)	5.03 br dd (3, 3)	OCH_3	3.69 s	3.72 s
18	3.41 dd (14, 4)	3.39 dd (14, 4)			

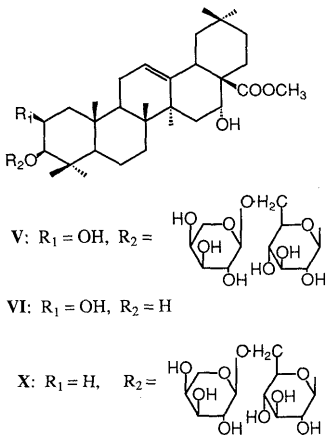
Numbers in parentheses are coupling constants in Hz.

TABLE II. ^{13}C-NMR Chemical Shifts of the Aglycone Moieties of Aster Saponins and Related Compounds

C	I	III	II	IV	V	X	VI
1	44.0	43.9	38.9	38.9	43.9	38.8	45.0
2	69.5	69.5	26.7	26.7	69.6	26.7	71.4
3	90.0	90.0	89.1	89.1	89.9	89.0	78.3
4	38.6	38.6	39.5	39.4	38.6	39.5	38.8
5	55.9	55.9	56.0	55.9	55.9	55.8	56.0
6	18.5	18.5	18.6	18.5	18.5	18.5	18.6
7	33.5	33.5	33.5	33.5	33.4	33.3	33.5
8	40.2	40.1	40.1	40.0	40.0	39.8	40.0
9	47.5	47.4	47.1	47.1	47.4	47.0	47.6
10	37.0	37.0	37.0	37.0	37.0	37.0	37.4
11	23.9	23.9	23.8	23.8	23.9	23.7	23.9
12	122.8	123.0	122.7	122.9	122.9	122.7	122.8
13	144.3	144.2	144.3	144.2	144.4	144.4	144.4
14	42.3	42.2	42.1	42.0	42.1	41.9	42.1
15	36.0	35.9	36.1	36.0	35.9	35.9	35.9
16	74.1	74.1	74.1	74.0	74.4	74.3	74.4
17	49.5	49.4	49.5	49.4	49.1	49.0	49.1
18	41.6	41.5	41.5	41.5	41.3	41.2	41.3
19	47.4	47.1	47.4	47.1	47.0	47.0	47.0
20	30.8	30.8	30.8	30.8	30.8	30.8	30.8
21	36.0	35.9	36.0	35.9	35.9	35.8	35.9
22	31.9	32.1	31.9	32.1	32.4	32.5	32.5
23	29.8	29.8	28.2	28.2	29.8	28.2	30.2
24	18.8	18.8	17.1	17.0	18.8	17.0	18.1
25	16.7	16.6	15.7	15.6	16.6	15.6	16.7
26	17.5	17.6	17.6	17.6	17.2	17.2	17.3
27	27.1	27.1	27.1	27.1	27.2	27.1	27.2
28	176.0	175.9	176.0	175.8	177.7	177.7	177.7
29	33.1	33.2	33.2	33.2	33.2	33.2	33.1
30	24.7	24.8	24.7	24.8	24.6	24.6	24.6
OMe					51.7	51.7	51.7

(NOE) was observed between H_b (C_3-H) and the protons (δ 1.24) on C_{23} (the α-methyl group on C_4), and not observed between H_b and the protons (δ 1.35) on C_{24} (the β-methyl group on C_4), which showed NOE with the protons (δ 1.55) on C_{25}.

Further examination of the spectra (^{1}H–^{1}H COSY, long-range ^{1}H–^{13}C COSY) revealed that the third hydroxymethine group (CH_c–OH) is between a quaternary carbon and a methylene group, which is further linked to a quaternary carbon with one methyl group. Therefore the third hydroxyl group is unambiguously allocated to C_{16}.



The configuration of the hydroxyl group was determined to be α from the coupling constants of H_c.

The ^{13}C-NMR signals of VI were assigned as shown in Table II. Assignments of the carbons of ring A and methyl carbons (C_{23}, C_{24} and C_{25}) were performed with the aid of the ^{1}H–^{13}C COSY spectrum after assignment of the ^{1}H-NMR signals, and other carbon signals were assigned by comparison with the data of known compounds. The ^{13}C-NMR chemical shifts assignable to the carbons of rings C, D and E were almost the same as those of 3-*O*-glycosylquillaic acid methyl ester.[5]

From these spectral data, VI was determined as 2β,3β,16α-trihydroxyolean-12-en-28-oic acid methyl ester, and the name "asterogenic acid" was given to the free acid.

The prosapogenin methyl ester (V) showed an $[M+Na]^+$ ion at *m/z* 819 in its FAB-MS. The ^{1}H-NMR spectrum showed two anomeric proton signals at δ 4.78 (d, J=7 Hz) and 4.87 (d, J=8 Hz), and the corresponding anomeric carbon signals were observed at δ 105.8 and 104.8. The ^{13}C-NMR signal of C_6 of the glucopyranosyl group appeared at δ 69.7. These spectral data indicated that the sugar moiety is *O*-α-L-arabinopyranosyl-(1→6)-β-D-glucopyranose. The position of the sugar linkage was determined to be the C_3-hydroxyl group from the fact that glycosylation shifts were observed at C_3 (+11.6 ppm), C_2 (−1.8 ppm) and C_4 (−0.2 ppm) of the aglycone. Therefore V is 3-*O*-[*O*-α-L-arabinopyranosyl-(1→6)-β-D-glucopyranosyl]asterogenic

acid methyl ester.

The methyl oligoglycoside fraction obtained by the selective cleavage of the ester glycoside linkage of III was a mixture of two anomers (VIIa and VIIb), which were separated preparatively by HPLC on a reversed-phase material (RP-18). The major one (VIIb) showed an $[M+Na]^+$ ion at *m/z* 875 in its FAB-MS and it gave L-arabinose, D-apiose and two mol each of L-rhamnose and D-xylose on acid hydrolysis. The permethylate of VIIb gave methyl glycosides of 2,3,4-tri-*O*-methyl-L-rhamnopyranose, 2,3,4-tri-*O*-methyl-D-xylopyranose, 2,3,4-tri-*O*-methyl-D-apiofuranose, 2,4-di-*O*-methyl-L-arabinopyranose, 2-*O*-methyl-L-rhamnopyranose and 4-*O*-methyl-D-xylopyranose on methanolysis. These results showed that VIIb is a methyl hexaglycoside doubly branched at a rhamnosyl group and a xylosyl group and having L-rhamnopyranose, D-xylopyranose and D-apiofuranose at three terminals.

When VIIb was treated with HCl at mild conditions, a desapiofuranosyl methyl glycoside (VIIIb) was obtained. Mild acid hydrolysis of VIIa gave the corresponding desapiofuranosyl methyl glycoside (VIIIa). Permethylation of VIIIb and methanolysis of the product gave methyl glycosides of 2,3,4-tri-*O*-methyl-L-rhamnopyranose, 2,3,4-tri-*O*-methyl-D-xylopyranose, 2,4-di-*O*-methyl-L-arabinopyranose, 2,3-di-*O*-methyl-L-rhamnopyranose and 4-*O*-methyl-D-xylopyranose.

Comparison of the methanolysis products of permethylates of VIIb and VIIIb revealed that the apiofuranosyl group is linked to the C_3-hydroxyl group of one of the two rhamnopyranosyl groups.

The enzymatic hydrolysis of the mixture of VIIIa and VIIIb with cellulase furnished an anomeric mixture of methyl triglycosides (IX) composed of D-xylose and two mol of L-rhamnose. The permethylate of IX gave methyl glycosides of 2,3,4-tri-*O*-methyl-L-rhamnopyranose and 4-*O*-methyl-D-xylopyranose on methanolysis. Therefore, IX was concluded to be methyl 2,3-bis-*O*-α-L-rhamnopyranosyl-D-xylopyranoside. The configurations of the sugar linkages of the rhamnopyranosyl groups were determined from the $J_{C_1H_1}$ values (168 Hz), supposing that both rhamnopyranosyl groups take the $^1C_4$ conformation. Compound VIIIb is, therefore, a methyl pentaglycoside in which a D-xylopyranosyl-(1→3)-L-arabinopyranosyl group is linked to the C_4-hydroxyl group of either one of two α-L-rhamnopyranosyl groups of IX.

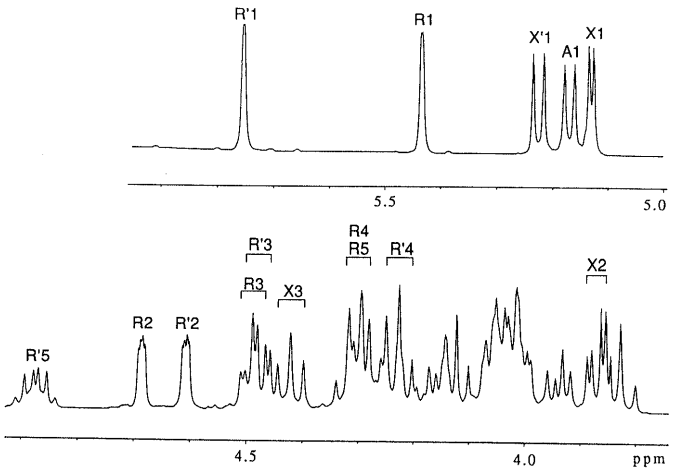


Fig. 1. ^{1}H-NMR Spectrum of VIIIb

The ^{1}H-NMR spectrum of VIIIb showed five anomeric proton signals, among which two broad singlets at δ 5.43 and 5.75 were assigned to the anomeric protons of the rhamnopyranosyl groups. A doublet (J=3 Hz) at δ 5.13 should be an anomeric proton of the methyl α-D-xylopyranoside unit and two doublets at δ 5.17 (J=7 Hz) and 5.23 (J=8 Hz) were reasonably assigned to the anomeric protons of the α-L-arabinopyranosyl group and the β-D-xylopyranosyl group. The C_2-H (X2) and C_3-H (X3) of the methyl α-D-xylopyranoside unit were assigned at δ 3.87 (dd, J=9, 3 Hz) and δ 4.42 (dd, J=9, 9 Hz), respectively, with the aid of the ^{1}H–^{1}H COSY spectrum.

In order to differentiate the rhamnopyranosyl groups which are linked to the C_2 and C_3-hydroxyl groups of the methyl xylopyranoside unit, the NOE difference spectra were measured with irradiation at the frequencies of the two rhamnosyl anomeric protons. When the signal at δ 5.75 (R′1) was irradiated, NOE was observed on the signal at δ 4.42 (X3), and irradiation at δ 5.43 (R1) yielded NOE on the signal at δ 3.87 (X2), thus indicating that one rhamnosyl group (**R′**) is linked to C_3-OH and the other rhamnosyl group (**R**) is linked to the C_2-OH of the methyl xylopyranoside unit. Other oxymethine protons of each rhamnosyl group were assigned as shown in the figure on the basis of the ^{1}H–^{1}H COSY spectrum. The signal [δ 4.22 (dd, J=9, 9 Hz)] of the C_4-H (R′4) of the **R′** group is isolated from other signals, but the C_4-H (R4) (*ca.* δ 4.30) of the **R** group overlapped with the C_5-H (R5) of the **R** group. The corresponding carbon signals appeared at δ 73.9 (R′-C_4), 83.4 and 68.1. One (δ 68.1) of the latter two signals should be that of the R-C_5, and accordingly, the other (δ 83.4) is the signal of the R-C_4. The downfield shift (Δ 9.5 ppm) of the R-C_4 compared with the R′-C_4 indicated that the β-D-xylopyranosyl-(1→3)-α-L-arabinopyranosyl group is linked to the C_4-hydroxyl group of the α-L-rhamnopyranosyl (**R**) group which is further linked to the C_2-hydroxyl group of the methyl xylopyranoside unit. Irradiation of the signal at δ 5.17 (the anomeric proton of the arabinosyl group) caused NOE on the signal at δ 4.30 (R4), supporting the above conclusion.

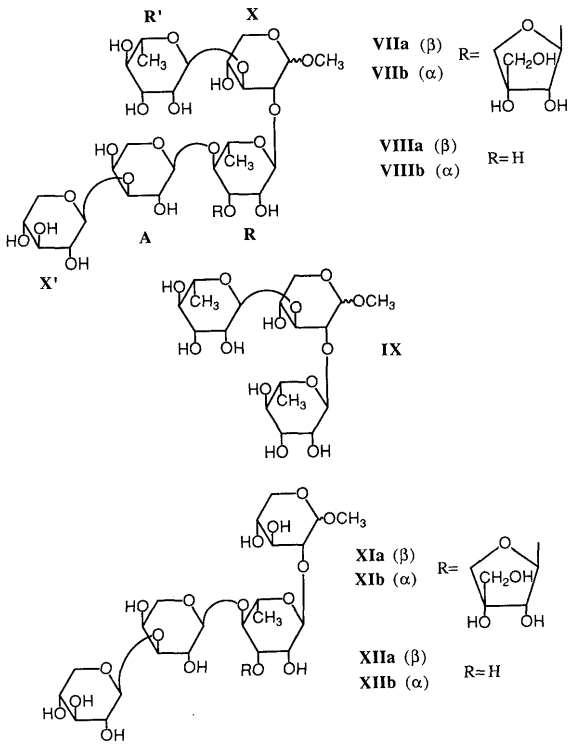
Compound VIIIb is, therefore, methyl *O*-β-D-xylopyranosyl-(1→3)-*O*-α-L-arabinopyranosyl-(1→4)-*O*-α-L-rhamnopyranosyl-(1→2)-[*O*-α-L-rhamnopyranosyl-(1→3)]-α-D-xylopyranoside and VIIIa is its β-anomer. The configuration of the apiofuranosyl group in the original methyl oligoglycosides, VIIb and VIIa, was determined to be β from the difference ($\Delta[M]_D-181°$) between the molecular rotations of VIIb ($[M]_D-395°$) and VIIIb ($[M]_D-214°$).[6] Consequently, VIIb is methyl *O*-β-D-xylopyranosyl-(1→3)-*O*-α-L-arabinopyranosyl-(1→4)-[*O*-β-D-apiofuranosyl-(1→3)]-*O*-α-L-rhamnopyranosyl-(1→2)-[*O*-α-L-rhamnopyranosyl-(1→3)]-α-D-xylopyranoside, and VIIa is its β anomer.

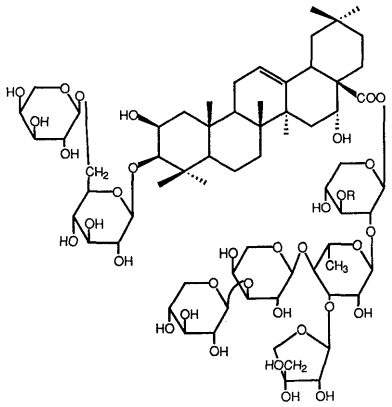
The last problem to be solved on the structure of III is the configuration of the ester-linked xylopyranosyl group. The $J_{H_1H_2}$ value (4 Hz) and $J_{C_1H_1}$ value (170 Hz) of the ester-linked D-xylopyranosyl group suggested at first that the xylopyranosyl group in the $^4C_1$ conformation was linked in α-configuration,[7] however, these J values can be explained by the β-linkage of the $^1C_4$ conformer. The spectroscopic specification of the two possible configurations and confor-

mations of the D-xylopyranosyl group can be achieved only by the examination of the splitting patterns of the other protons of the xylopyranosyl group. The chemical shifts and coupling constants of the protons of the ester-linked xylopyranosyl group in III could hardly be determined in the ordinary ^{1}H-NMR spectrum owing to the overlapping of other sugar signals. Therefore the ^{1}H 1D-HOHAHA (homonuclear Hartmann–Hahn spectroscopy) technique was employed, and the chemical shifts and the coupling constants of the C_2-H (δ 4.22, br dd, J=4, 2 Hz), C_3-H (δ 4.40, br dd, J=5, 2 Hz) and C_4-H (δ 4.32, br ddd, J=5, 5, 4 Hz) could be distinguished. These J values are in favor of the β-D-xylopyranose in the $^1C_4$ conformation, somewhat distorted because of the steric crowdedness. The difference ($\Delta[M]_D$ −1058°) between the molecular rotation ($[M]_D$ −980°) of III and that ($[M]_D$ +78°) of its prosapogenin methyl ester (V) is closer to the molecular rotation ($[M]_D$ −775°) of VIIa (β-anomer) than that ($[M]_D$ −395°) of VIIb (α-anomer). This value supports the β-configuration. The favored conformation of the ordinary β-D-xylopyranosyl group is the $^4C_1$ conformation, and the $^1C_4$ conformation in this case seems to be very unusual; however, the predominance of the $^1C_4$ conformer of the ester-linked β-D-xylopyranosyl group of this type would be probable if it is taken into consideration that several cases have been reported of the occurrence of predominant $^1C_4$ conformation for glycosylated α-L-arabinopyranosyl groups which are linked to the sterically hindered carboxylic acid groups of the triterpene carboxylic acids.[8]

From the above-mentioned chemical and spectral evidence, the structure of III was built up as shown.

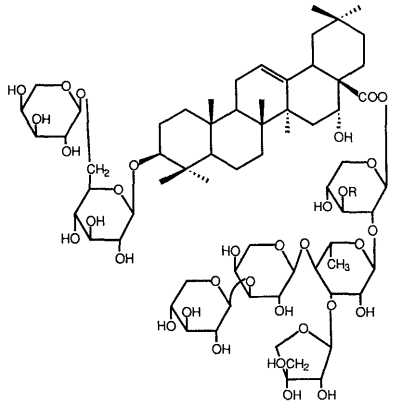
Aster saponin D (IV), the minor polar saponin, was obtained as a white powder and the FAB-MS showed an $[M+Na]^+$ ion at m/z 1609 and an $[M-H]^-$ ion at m/z 1585, 16 mass units less than those of III. Its NMR spectra were similar to those of III, and in particular the signals of the sugar moiety were almost superimposable on those of III, suggesting that IV is a deoxy-aster saponin C having the same sugar moiety. Selective cleavage of the ester glycoside linkage of IV followed by methylation with CH_2N_2 gave a prosapogenin methyl ester (X) and an anomeric mixture of methyl oligoglycosides. The two anomers were identical with VIIa and VIIb which were obtained from III. Compound X showed in the FAB-MS an $[M+Na]^+$ ion at m/z 803, 16 mass units less than V, and the ^{1}H- and ^{13}C-NMR spectra showed signals of the sugar moiety almost superimposable on those of V. The ^{13}C-NMR spectrum showed a pattern slightly different from that of V in the carbon signals of ring A, suggesting that the aglycone of X is a methyl ester of echinocystic acid (3β,16α-dihydroxyolean-12-en-28-oic acid). The ^{13}C-NMR signals of the aglycone moiety of X were compared with those of echinocystic acid-3-*O*-glycoside, a prosapogenin of entada saponin-III isolated from the bark of *Entada phaseoloides* (L.) MERRILL.[9] The chemical shifts of carbon signals of the aglycone moiety were in good agreement. The differences of the chemical shifts were within 0.5 ppm, although the chemical shift of the C_{28} was different because the reference





I (aster saponin A) : R = H

III (aster saponin C) : R =



II (aster saponin B) : R = H

IV (aster saponin D): R =

compound is a free acid.

Compound X was concluded to be 3-*O*-[*O*-α-L-arabinopyranosyl-(1→6)-β-D-glucopyranosyl]echinocystic acid methyl ester, and the structure of IV was therefore elucidated as shown.

Aster saponin A (I), the major less polar saponin, was obtained as colorless needles, and the FAB-MS showed an $[M+Na]^+$ ion at *m/z* 1479 and an $[M-H]^-$ ion at *m/z* 1455 indicating the molecular weight to be 1456. The ^{1}H- and ^{13}C-NMR spectra of the aglycone moiety were almost superimposable on those of III, although the signal patterns of the sugar moiety were different. The selective cleavage of the ester glycoside linkage of I gave an anomeric mixture of methyl oligoglycosides and a prosapogenin. The methyl ester of the latter was identical with V. The methyl oligoglycosides were separated preparatively by HPLC to give XIa and XIb. The minor anomer (XIa) showed an $[M+Na]^+$ ion at *m/z* 729 in its FAB-MS and it gave D-apiose, L-arabinose, L-rhamnose and two mol of D-xylose on acid hydrolysis. The ^{1}H-NMR spectrum showed five anomeric proton signals indicating that XIa is a methyl pentaglycoside.

The mild acid hydrolysis of XIa caused a selective cleavage of the apiose linkage and afforded a methyl tetraglycoside (XIIa). The same treatment of XIb gave a corresponding desapiosyl methyl glycoside (XIIb). Permethylation of XIIa and methanolysis of the product gave methyl glycosides of 2,3,4-tri-*O*-methyl-D-xylopyranose, 2,4-di-*O*-methyl-L-arabinopyranose, 3,4-di-*O*-methyl-D-xylopyranose and 2,3-di-*O*-methyl-L-rhamnopyranose. These methanolysis products indicated that XIIa is a linear methyl tetraglycoside having a xylopyranosyl group at the terminal.

The negative FAB-MS of XIIa showed an $[M-H]^-$ ion at *m/z* 573 and fragment ions at *m/z* 441 (573 − pentosyl group), 309 (441 − pentosyl group) and 163 (309 − rhamnosyl group). The above chemical and spectral data indicated that the sugar sequence of XIIa is XIIa (a) or XIIb (b).

XIIa (a) Me–*O*–Xyl^2–^{1}Rha^4–^{1}Ara^3–^{1}Xyl
XIIa (b) Me–*O*–Ara^3–^{1}Rha^4–^{1}Xyl^2–^{1}Xyl

The enzymatic hydrolysis of the mixture of XIIa and XIIb gave methyl α- and β-D-xylopyranosides, rhamnose, arabinose and xylose, and methyl arabinopyranosides were not obtained. Therefore the sugar sequence of XIIa was determined to be XIIa (a).

The permethylate of XIa gave methyl glycosides of 2,3,4-tri-*O*-methyl-D-xylopyranose, 2,3,4-tri-*O*-methyl-D-apiofuranose, 2,4-di-*O*-methyl-L-arabinopyranose, 3,4,-di-*O*-methyl-D-xylopyranose and 2-*O*-methyl-L-rhamnopyranose on methanolysis. Comparison of the methanolysis products of the permethylates of XIIa and XIa apparently indicated that the apiofuranosyl group is attached to the C_3-hydroxyl group of the L-rhamnopyranosyl group. Thus, the structure of XIa was concluded to be methyl *O*-β-D-xylopyranosyl-(1→3)-*O*-α-L-arabinopyranosyl-(1→4)-[*O*-β-D-apiofuranosyl-(1→3)]-*O*-α-L-rhamnopyranosyl-(1→2)-β-D-xylopyranoside. The configurations of the sugar linkages of the D-xylopyranosyl groups and the L-arabinopyranosyl group were determined from the coupling constants of the anomeric protons, that of the L-rhamnopyranosyl group, from the $J_{C_1H_1}$ value (170 Hz), and that of the apiofuranosyl group, from the $\Delta[M]_D$ (−219°) between the $[M]_D$ (−671°) of XIa and the $[M]_D$ (−452°) of XIIa.[6] Compound XIb is the α-anomer of XIa.

Combining the structures of the prosapogenin and the methyl oligoglycoside obtained from the ester-linked sugar moiety, the structure of I was elucidated to be as shown. The β-configuration and the predominance of the $^1C_4$ conformer of the ester-linked xylopyranosyl group were suggested from the ^{1}H-NMR signal patterns of the C_1-H (d, *J*=5 Hz) and C_2-H (br d, *J*=5 Hz), the $J_{C_1H_1}$ (170 Hz) and from the fact that the difference ($\Delta[M]_D$ −725°) between the molecular rotation ($[M]_D$ −647°) of I and that ($[M]_D$ +78°) of V is closer to the $[M]_D$ (−671°) of XIa (β-anomer) than the $[M]_D$ (−259°) of XIb (α-anomer).

Aster saponin B (II), the minor less polar saponin, showed in the FAB-MS an $[M+Na]^+$ ion at *m/z* 1463 and an $[M-H]^-$ ion at *m/z* 1439, 16 mass units less than those of I, suggesting that II is an echinocystic acid bisdesmoside having the same sugar moiety as those of I.

On the selective cleavage of the ester glycoside linkage, II gave a prosapogenin and an anomeric mixture of methyl oligoglycosides. The methyl ester of the former was identical with X and the latter was identified as a mixture of XIa and XIb. Therefore the structure of II was concluded to be as shown.

Hederagenin glycosides were not detected in spite of detailed examination of the glycoside fraction.

Experimental[10]

Isolation of Aster Saponins Preparation of the saponin fraction (Fr. I-Cb) from the root (4.5 kg) of *Aster tataricus* L. f. was reported in the previous paper.[1] Fraction I-Cb (17 g) showed three spots on silica gel thin layer chromatography (TLC) [solvent: AcOEt–MeOH–H_2O (6:2:1)], and this fraction was repeatedly chromatographed on silica gel using AcOEt–MeOH–H_2O (7:2:1) as an eluant to yield into three fractions (monitored by silica gel TLC). Fraction 1, which showed the upper spot, was proved to be a complex mixture when it was examined by HPLC. Fractions 2 and 3 showed middle and lower spots, respectively, but each spot was separated into two spots on RP-18 TLC. Fraction 2 was chromatographed on Sephadex LH-20 (MeOH) and RP-18 (55% MeOH), and purified by HPLC (Capcell pak C_{18}, 250 mm × 10 mm i.d. column, Shiseido Company, Ltd.; eluant, 65% MeOH) to give aster saponins A (I) (1.14 g) and B (II) (70 mg). Fraction 3 was treated in the same manner as fraction 2 to give aster saponins C (III) (1.55 g) and D (IV) (290 mg).

I (Aster Saponin A): Colorless needles from MeOH–H_2O, mp 223—224 °C (dec.). $[\alpha]_D^{23}$ −44.4° (*c*=1.1, MeOH). *Anal.* Calcd for $C_{67}H_{108}O_{34}\cdot 3.5H_2O$: C, 53.41; H, 7.69. Found: C, 53.06; H, 7.74. FAB-MS *m/z*: 1479 ($[M+Na]^+$), 1455 ($[M-H]^-$). ^{1}H-NMR δ: aglycone moiety; >CH_3; 1.01 (C_{29}-H), 1.11 (C_{26}-H), 1.13 (C_{30}-H), 1.28 (C_{23}-H), 1.36 (C_{24}-H), 1.45 (C_{25}-H), 1.80 (C_{27}-H). >C=CH–; 5.59 (br dd). sugar moiety; anomeric H; 4.77 (d, *J*=7 Hz), 4.85 (d, *J*=8 Hz), 5.17 (d, *J*=7 Hz), 5.34 (d, *J*=8 Hz), 5.95 (d, *J*=4 Hz), 6.00 (br s), 6.25 (d, *J*=5 Hz). >CH–C<u>H</u>$_3$; 1.72 (d, *J*=6 Hz). ^{13}C-NMR δ: aglycone moiety; shown in the Table I. sugar moiety; anomeric C (in the order of corresponding anomeric protons) 104.8, 105.6, 105.8, 104.7, 111.8, 101.6. 95.2. C_6 of the rhamnopyranosyl group; 18.9. C_3 of the apiofuranosyl group; 79.7.

II (Aster Saponin B): White amorphous powder. $[\alpha]_D^{27}$ −63.7° (*c*=0.8, MeOH). *Anal.* Calcd for $C_{67}H_{108}O_{33}\cdot 4H_2O$: C, 53.17; H, 7.73. Found: C, 53.32; H, 7.74. FAB-MS *m/z*: 1463 ($[M+Na]^+$), 1439 ($[M-H]^-$). ^{1}H-NMR δ: aglycone moiety; >CH_3; 0.88 (C_{25}-H), 1.02 (C_{24}-H, C_{29}-H), 1.08 (C_{26}-H), 1.12 (C_{30}-H), 1.25 (C_{23}-H), 1.80 (C_{27}-H). >C=CH–; 5.60 (br dd). sugar moiety; anomeric H; 4.84 (d, *J*=7 Hz), 4.95 (d, *J*=7 Hz), 5.16 (d, *J*=7 Hz), 5.34 (d, *J*=8 Hz), 5.95 (d, *J*=4 Hz), 6.00 (br s), 6.25 (d, *J*=5 Hz). >CH–C<u>H</u>$_3$; 1.72 (d, *J*=6 Hz). ^{13}C-NMR δ: aglycone moiety; shown in the Table I. sugar moiety; anomeric C; 106.8, 105.2, 105.9, 104.7, 111.7, 101.6, 95.2. C_6 of the rhamnopyranosyl group; 18.9. C_3 of the apiofuranosyl group; 79.7.

III (Aster Saponin C): Colorless needles from MeOH–H_2O, mp

234—235 °C (dec.). $[\alpha]_D^{24}$ −61.2° (c=1.0, MeOH). *Anal.* Calcd for $C_{73}H_{118}O_{38}\cdot 6H_2O$: C, 51.22; H, 7.66. Found: C, 51.37; H, 7.95. FAB-MS m/z: 1625 ($[M+Na]^+$), 1601 ($[M-H]^-$). ^{1}H-NMR δ: aglycone moiety; ≻CH_3; 1.01 (C_{29}-H), 1.06 (C_{26}-H), 1.19 (C_{30}-H), 1.26 (C_{23}-H), 1.33 (C_{24}-H), 1.43 (C_{25}-H), 1.75 (C_{27}-H). >C=CH–; 5.57 (br dd). sugar moiety; anomeric H; 4.77 (d, J=7 Hz), 4.83 (d, J=8 Hz), 5.22 (d, J=7 Hz), 5.29 (d, J=8 Hz), 5.61 (br s), 5.69 (br s), 5.95 (d, J=4 Hz), 6.50 (d, J=4 Hz). >CH–C$\underline{H}_3$; 1.60 (d, J=6 Hz), 1.64 (d, J=6 Hz). ^{13}C-NMR δ: aglycone moiety; shown in the Table I. sugar moiety; anomeric C; 104.8, 105.6, 105.8, 104.7, 101.7, 101.0, 111.9, 94.0. C_6 of the rhamnopyranosyl groups; 18.4 (×2). C_3 of the apiofuranosyl group; 79.8.

IV (Aster Saponin D): White amorphous powder. $[\alpha]_D^{27}$ −70.2° (c=1.4, MeOH). *Anal.* Calcd for $C_{73}H_{118}O_{37}\cdot 5H_2O$: C, 52.26; H, 7.69. Found: C, 52.02; H, 7.95. FAB-MS m/z: 1609 ($[M+Na]^+$), 1585 ($[M-H]^-$). ^{1}H-NMR δ: aglycone moiety; ≻CH_3; 0.86 (C_{25}-H), 0.98 (C_{24}-H), 1.02 (C_{26}-H, C_{29}-H), 1.17 (C_{30}-H), 1.24 (C_{23}-H), 1.74 (C_{27}-H). >C=CH–; 5.59 (br dd). sugar moiety; anomeric H; 4.84 (d, J=8 Hz), 4.94 (d, J=7 Hz), 5.21 (d, J=8 Hz), 5.29 (d, J=8 Hz), 5.61 (br s), 5.65 (br s), 5.94 (d, J=4 Hz), 6.50 (d, J=4 Hz), >CH–C$\underline{H}_3$; 1.59 (d, J=6 Hz), 1.64 (d, J=6 Hz). ^{13}C-NMR δ: aglycone moiety; shown in the Table I. sugar moiety; anomeric C; 106.8, 105.2, 105.8, 104.8, 101.7, 101.0, 111.8, 93.9. C_6 of the rhamnopyranosyl groups; 18.5 (×2). C_3 of the apiofuranosyl group; 79.8.

Selective Cleavage of the Ester-Glycoside Linkages of Aster Saponins Compound III (1 g) was dissolved in 2,6-lutidine (8 ml) containing anhydrous MeOH (5 ml) and LiI (1 g). After heating the reaction mixture at 160 °C for 16 h, the reaction mixture was diluted with 50% MeOH (10 ml) and passed through a column of Amberlite MB-3 (100 ml). The eluate was concentrated *in vacuo* and treated with CH_2N_2. The product was chromatographed on Diaion HP-20 using 50% MeOH and MeOH as eluants. The 50% MeOH eluate contained an anomeric mixture of methyl oligoglycosides (390 mg) and MeOH eluted a prosapogenin methyl ester (V, 400 mg). The methyl oligoglycosides were separated preparatively by HPLC to give an α-anomer (VIIb, 165 mg) and a β-anomer (VIIa, 137 mg).

V: White amorphous powder. $[\alpha]_D^{24}$ +9.8° (c=2.7, MeOH): FAB-MS m/z: 819 ($[M+Na]^+$). ^{1}H-NMR δ: aglycone moiety; ≻CH_3; 0.92 (C_{26}-H), 1.04 (C_{29}-H), 1.21 (C_{30}-H), 1.29 (C_{23}-H), 1.37 (C_{24}-H), 1.49 (C_{25}-H), 1.77 (C_{27}-H). >C=CH–; 5.51 (br dd). COOC$\underline{H}_3$; 3.68. sugar moiety; anomeric H; 4.87 (d, J=8 Hz, Glc), 4.78 (d, J=7 Hz, Ara). ^{13}C-NMR δ: aglycone moiety; shown in the Table I, sugar moiety; glucopyranosyl group; 105.8 (1), 75.2 (2), 78.6 (3), 72.1 (4), 76.5 (5), 69.7 (6). arabinopyranosyl group; 104.8 (1), 72.4 (2), 74.1 (3), 68.9 (4), 66.3 (5).

VIIa: White amorphous powder. $[\alpha]_D^{24}$ −90.9° (c=2.1, MeOH). FAB-MS m/z: 875 ($[M+Na]^+$). ^{1}H-NMR δ: anomeric H; 4.42 (d, J=7 Hz), 5.20 (d, J=7 Hz), 5.38 (d, J=8 Hz), 5.57 (br s), 5.65 (br s), 6.10 (d, J=4 Hz). >CH–C$\underline{H}_3$; 1.62 (d, J=6 Hz), 1.65 (d, J=6 Hz). OC$\underline{H}_3$; 3.49. ^{13}C-NMR δ: anomeric C; 103.8, 105.7, 104.6, 103.4, 102.5, 111.7. C_3 of the apiofuranosyl group; 79.8. C_6 of the rhamnopyranosyl groups; 18.3 (×2). O$\underline{C}H_3$; 56.1.

VIIb: White amorphous powder. $[\alpha]_D^{24}$ −46.4° (c=2.7, MeOH). FAB-MS m/z: 875 ($[M+Na]^+$). ^{1}H-NMR δ: anomeric H; 5.15 (d, J=3 Hz), 5.23 (d, J=8 Hz), 5.30 (d, J=8 Hz), 5.37 (br s), 5.60 (br s), 5.92 (d, J=4 Hz). >CH–C$\underline{H}_3$; 1.60 (d, J=6 Hz), 1.63 (d, J=6 Hz). OC$\underline{H}_3$; 3.35. ^{13}C-NMR δ: anomeric C; 100.0, 105.8, 104.7, 104.0, 103.2, 111.9. C_3 of the apiofuranosyl group; 79.8. C_6 of the rhamnopyranosyl groups; 18.5, 18.7. O$\underline{C}H_3$; 54.9.

Compounds I, II and IV were treated in the same manner. Compound I gave a prosapogenin methyl ester (V) and methyl oligoglycosides (XIa and XIb).

XIa: White amorphous powder. $[\alpha]_D^{21}$ −95.1° (c=0.8, MeOH). FAB-MS m/z: 729 ($[M+Na]^+$). ^{1}H-NMR δ: anomeric H; 4.52 (d, J=7 Hz), 5.20 (d, J=7 Hz), 5.41 (d, J=7 Hz), 6.05 (d, J=4 Hz), 6.10 (br s). >CH–C$\underline{H}_3$; 1.69 (d, J=6 Hz). OC$\underline{H}_3$; 3.54. ^{13}C-NMR δ: anomeric C; 104.1, 105.7, 104.7, 111.9, 102.4. C_3 of the apiofuranosyl group; 79.8. C_6 of the rhamnopyranosyl group; 18.4. O$\underline{C}H_3$; 56.0.

XIb: White amorphous powder. $[\alpha]_D^{22}$ −36.7° (c=1.0, MeOH). FAB-MS m/z: 729 ($[M+Na]^+$). ^{1}H-NMR δ: anomeric H; 5.21 (d, J=3 Hz), 5.23 (d, J=7 Hz), 5.35 (d, J=7 Hz), 5.63 (br s), 5.81 (d, J=4 Hz). >CH–C$\underline{H}_3$; 1.64 (d, J=6 Hz). OC$\underline{H}_3$; 3.39. ^{13}C-NMR δ: anomeric C; 100.6, 105.8, 104.7, 104.5, 111.8. C_3 of the apiofuranosyl group; 79.6. C_6 of the rhamnopyranosyl group; 18.7. O$\underline{C}H_3$; 54.8.

Compound II gave a prosapogenin methyl ester (X) and methyl oligoglycosides, XIa and XIb, and IV gave X, VIIa and VIIb.

X: White amorphous powder. $[\alpha]_D^{27}$ −12.2° (c=1.5, MeOH). FAB-MS m/z: 803 ($[M+Na]^+$). ^{1}H-NMR δ: aglycone moiety; ≻CH_3; 0.88 (C_{26}-H), 0.92 (C_{25}-H), 1.01 (C_{24}-H), 1.05 (C_{29}-H), 1.11 (C_{30}-H), 1.26 (C_{23}-H), 1.76 (C_{27}-H). >C=CH–; 5.52 (br dd). COOC$\underline{H}_3$; 3.68. sugar moiety; anomeric H; 4.87 (d, J=8 Hz, Glc), 4.95 (d, J=7 Hz, Ara). ^{13}C-NMR δ: aglycone moiety; shown in the Table I. sugar moiety; glucopyranosyl group; 106.9 (1), 75.6 (2), 78.6 (3), 72.0 (4), 76.6 (5), 69.9 (6). arabinopyranosyl group; 105.2 (1), 72.2 (2), 74.2 (3), 68.9 (4), 66.2 (5).

Acid Hydrolysis of V, Preparation of VI Compound V (300 mg) was dissolved in 50% ethanolic 1 N H_2SO_4 and heated at 105 °C for 1 h. After EtOH was evaporated off, the aqueous solution was extracted with $CHCl_3$. The $CHCl_3$ extract (86 mg) was purified by silica gel column chromatography and crystallization from MeOH–H_2O to give VI: colorless needles from MeOH–H_2O, mp 259—260 °C. $[\alpha]_D^{21}$ +45.5° (c=1.5, MeOH). EI-MS m/z: 502.364 (M^+). $C_{31}H_{50}O_5$ requires m/z 502.365. ^{1}H-NMR: chemical shifts obtained in the pyridine-d_5 and pyridine-d_5–D_2O solutions are shown in Table II. ^{13}C-NMR: Table I.

Partial Methanolysis of VIIa, VIIb, XIa and XIb Compound VIIa (100 mg) was dissolved in 0.1 N HCl–MeOH and stirred for 24 h at room temperature. After neutralization with Ag_2CO_3, the reaction product was chromatographed on silica gel to give VIIIa (60 mg). Partial methanolysis of VIIb, XIa and XIb in the same manner gave VIIIb, XIIa and XIIb, respectively.

VIIIa: White amorphous powder. $[\alpha]_D^{21}$ −81.6° (c=0.9, MeOH). FAB-MS m/z: 743 ($[M+Na]^+$). ^{1}H-NMR δ: anomeric H; 4.41 (d, J=7 Hz), 5.18 (d, J=7 Hz), 5.22 (d, J=7 Hz), 5.62 (br s), 5.66 (br s). >CH–C$\underline{H}_3$; 1.63 (d, J=6 Hz), 1.68 (d, J=6 Hz). OC$\underline{H}_3$; 3.46. ^{13}C-NMR δ: anomeric C; 103.8, 106.3, 105.8, 103.4, 102.7. C_6 of the rhamnopyranosyl groups; 18.1, 18.3. O$\underline{C}H_3$; 56.1.

VIIIb: White amorphous powder. $[\alpha]_D^{22}$ −29.7° (c=0.8, MeOH). FAB-MS m/z: 743 ($[M+Na]^+$). ^{1}H-NMR δ: anomeric H; 5.13 (d, J=3 Hz), 5.17 (d, J=7 Hz), 5.23 (d, J=8 Hz), 5.43 (br s), 5.75 (br s). >CH–C$\underline{H}_3$; 1.61 (d, J=6 Hz), 1.63 (d, J=5 Hz). OC$\underline{H}_3$; 3.31. ^{13}C-NMR δ: anomeric C; 100.1, 106.2, 105.9, 104.4, 102.8. C_6 of the rhamnopyranosyl groups; 18.4 (×2). O$\underline{C}H_3$; 54.8.

XIIa: White amorphous powder. $[\alpha]_D^{24}$ −78.8° (c=1.1, MeOH). FAB-MS m/z: 597 ($[M+Na]^+$). ^{1}H-NMR δ: anomeric H; 4.52 (d, J=7 Hz), 5.18 (d, J=7 Hz), 5.22 (d, J=8 Hz), 6.12 (br s). >CH–C$\underline{H}_3$; 1.72 (d, J=6 Hz). OC$\underline{H}_3$; 3.53. ^{13}C-NMR δ: anomeric C; 104.3, 106.4, 105.8, 102.2. C_6 of the rhamnopyranosyl group; 18.2. O$\underline{C}H_3$; 56.2

XIIb: White amorphous powder. $[\alpha]_D^{22}$ −7.1° (c=1.5, MeOH). FAB-MS m/z: 597 ($[M+Na]^+$). ^{1}H-NMR δ: anomeric H; 5.16 (d, J=7 Hz), 5.20 (d, J=4 Hz), 5.21 (d, J=7 Hz), 5.70 (br s). >CH–C$\underline{H}_3$; 1.68 (d, J=5 Hz). OC$\underline{H}_3$; 3.40. ^{13}C-NMR δ: anomeric C; 106.3, 100.5, 105.9, 104.2. C_6 of the rhamnopyranosyl group; 18.5. O$\underline{C}H_3$; 54.9.

Enzymatic Hydrolysis of VIII and XII A mixture (50 mg) of VIIIa and VIIIb was dissolved in H_2O (4 ml) and cellulase (60 mg) was added to the solution. The mixture was stirred at 38 °C for 40 h. After evaporation of the solvent, the residue was chromatographed on silica gel to give IX (23 mg).

IX: White amorphous powder. FAB-MS m/z: 479 ($[M+Na]^+$), 455 ($[M-H]^-$), 309 ($[455-Rha]^-$), 163 ($[309-Rha]^-$).

The mixture (20 mg) of XIIa and XIIb was treated with cellulase in the same way, and the product was chromatographed on silica gel. The eluates were checked by GLC after trimethylsilylation. Methyl α- and β-D-xylopyranosides, rhamnose, arabinose and xylose were identified by comparison with the authentic samples. Methyl arabinopyranosides could not be detected.

Identification of the Component Monosaccharides and Partially Methylated Monosaccharides Identification of the monosaccharides and partially methylated sugars were performed in the same manner as described in an earlier paper[1] from this laboratory, and the results are shown in the text.

Acknowledgements The authors wish to express their gratitude to Ms Y. Iwase and Miss J. Honda for measurements of NMR spectra, MS and elemental analyses.

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