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# Studies on the Constituents of *Aster scaber* THUNB. IV.[1] Structures of Four New Echinocystic Acid Glycosides Isolated from the Herb

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**Four new echinocystic acid 3,28-*O*-bisdesmosides, scaberosides Ha, Hb$_1$, Hb$_2$ and Hc$_1$, were isolated as their methyl esters from the ground part of *Aster scaber* THUNB. (Compositae) along with foetidissimoside A and scaberoside A$_2$, and their structures were determined based on spectral and chemical evidence. These glycosides have a common prosapogenin structure, echinocystic acid-3-*O*-glucopyranosiduronic acid, and differ in the structures of the 28-*O*-linked sugar moieties.**

**Scaberoside Ha$_1$ is a 28-[*O*-α-L-rhamnopyranosyl-(1→2)-[*O*-α-L-rhamnopyranosyl-(1→3)]-β-D-xylopyranosyl] ester, Hb$_1$, a 28-[*O*-β-D-xylopyranosyl-(1→4)-*O*-α-L-rhamnopyranosyl-(1→2)-[*O*-α-L-rhamnopyranosyl-(1→3)]-β-D-xylopyranosyl] ester, Hb$_2$, a 28-[*O*-β-D-xylopyranosyl-(1→3)-*O*-β-D-xylopyranosyl-(1→4)-*O*-α-L-rhamnopyranosyl-(1→2)-[*O*-α-L-rhamnopyranosyl-(1→3)]-β-D-xylopyranosyl] ester, and Hc$_1$, a 28-[*O*-β-D-xylopyranosyl-(1→3)-*O*-β-D-xylopyranosyl-(1→3)-[*O*-β-D-xylopyranosyl-(1→4)]-*O*-α-L-rhamnopyranosyl-(1→2)-[*O*-α-L-rhamnopyranosyl-(1→3)]-β-D-xylopyranosyl] ester of the prosapogenin.**

**Keywords** *Aster scaber*; scaberoside; triterpene glycoside; Compositae; echinocystic acid; glucuronide saponin

In the previous papers of this series,[1] we reported the isolation and structure elucidation of several oleanane-type triterpene glycosides obtained from the root of *Aster scaber* THUNB. (Compositae). As a continuation of the chemical investigation of the triterpene glycoside constituents of this plant, the ground part was investigated.

The crude glycoside fraction obtained from the 50% MeOH extract and the H$_2$O extract was subjected to repeated chromatography on silica gel and a reversed phase material (octadecyl silica (ODS)), and to preparative HPLC. After methylation of each fraction with diazomethane, the methyl esters were finally purified by silica gel chromatography and preparative HPLC to give compounds I, II, III, IV, V and VI.

Compound I was obtained as a white powder, and the positive ion FAB-MS showed an $[M+Na]^+$ ion at *m/z* 1109, while the negative ion FAB-MS showed an $[M-H]^-$ ion at *m/z* 1085, indicating the molecular weight to be 1086. The high-resolution (HR) FAB-MS gave the molecular formula $C_{54}H_{86}O_{22}$. On acid hydrolysis, I gave L-rhamnose, D-xylose and D-glucuronic acid as component sugars. The $^1$H-NMR spectrum showed signals of seven tertiary methyl groups ($\delta$ 0.86, 0.95, 0.99, 1.03, 1.13, 1.26, 1.78), a trisubstituted olefin proton [$\delta$ 5.60 (dd, $J=3$, 3 Hz)] and four sugar anomeric protons [$\delta$ 4.97 (d, $J=8$ Hz), 5.67 (d, $J=2$ Hz), 5.76 (d, $J=2$ Hz), 6.48 (d, $J=4$ Hz)]. The $^{13}$C-NMR spectrum showed signals of six C–C bonded quaternary carbons ($\delta$ 30.8, 36.9, 39.5, 40.0, 42.0, 49.4), two ester carbonyl carbons ($\delta$ 170.7, 175.7), a pair of olefinic carbons ($\delta$ 122.7, 144.3) and four anomeric carbons ($\delta$ 94.0, 101.4, 101.9, 107.2). By comparison of these NMR data with those reported for foetidissimoside A methyl ester,[2] I was suggested to be a bisdesmosidic tetraglycoside having an ester-linked sugar moiety and a 3-*O*-(methyl β-D-glucopyranosyluronate)echinocystic acid as a prosapogenin moiety. Compound I showed in the negative ion FAB-MS, a fragment ion peak at *m/z* 661, which was assigned to a $[\text{prosapogenin}-H]^-$ anion. The positive FAB-MS fragment ion at *m/z* 447 ($C_{17}H_{28}NaO_{12}$) undoubtedly originated from the ester-linked sugar moiety.

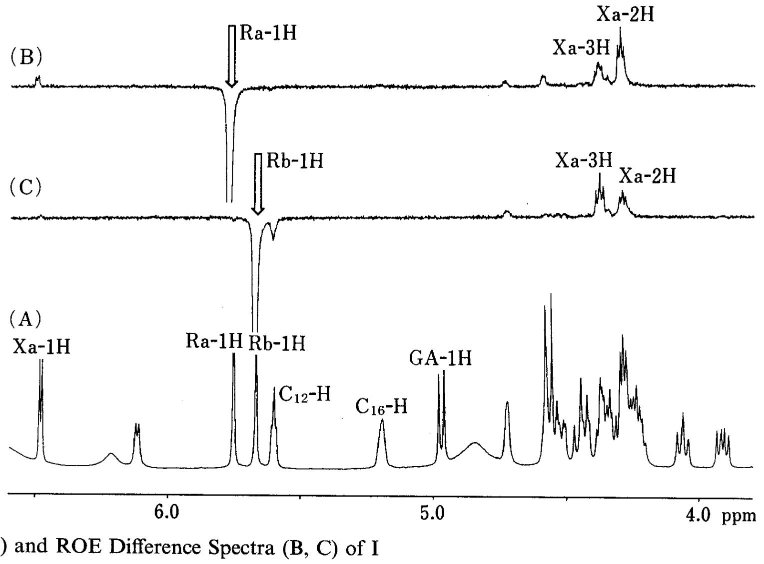

Fig. 1. $^1$H-NMR Spectrum (A) and ROE Difference Spectra (B, C) of I

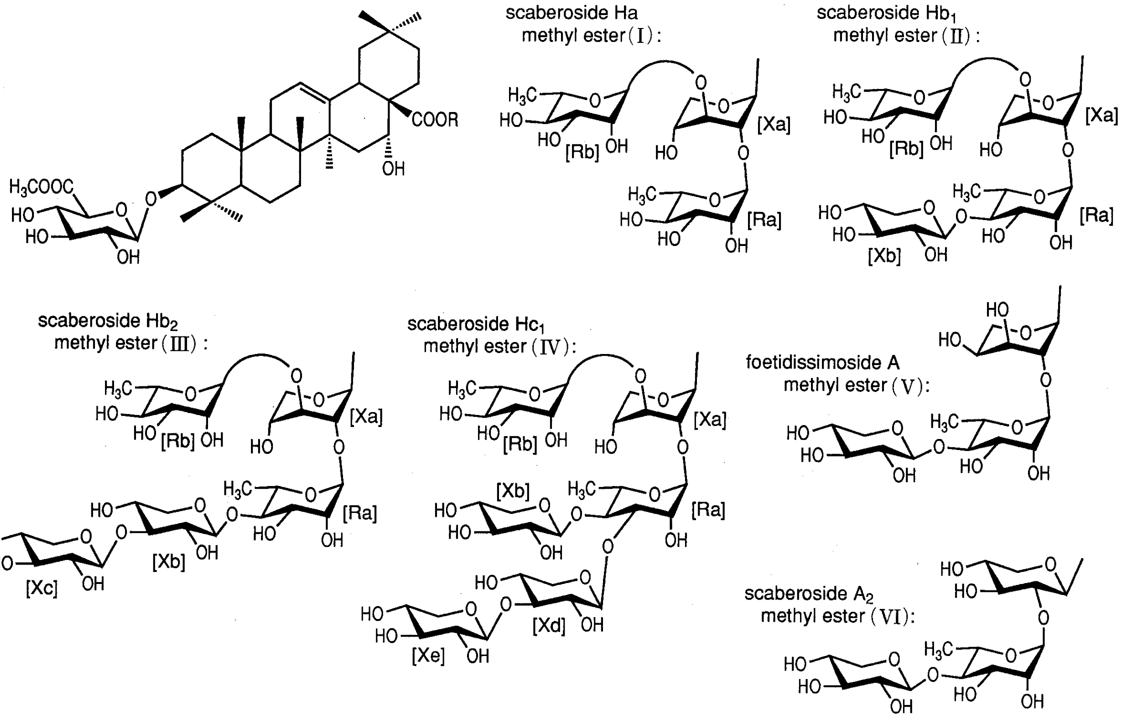

Chart 1

The molecular composition of the ester-linked sugar moiety indicated that it is composed of one mol of D-xylose and two mol of L-rhamnose. The rotating frame nuclear Overhauser effect (ROE) difference spectra were measured by irradiation at the frequencies of the anomeric protons of two rhamnopyranosyl groups (Ra-1H, $\delta$ 5.76 and Rb-1H, $\delta$ 5.67). Nuclear Overhauser effect (NOE) was observed at the signals of assigned Xa-2H ($\delta$ 4.29, dd, $J=4$, 4 Hz) and Xa-3H ($\delta$ 4.38, dd, $J=4$, 4 Hz) of an ester-linked xylopyranosyl group when the signal of Ra-1H was irradiated (Fig. 1B). NOE on the former signal was bigger than that on the latter. When Rb-1H was irradiated, smaller NOE at the signal of Xa-2H and bigger NOE at the signal of Xa-3H were observed (Fig. 1C). These results strongly suggested that one rhamnopyranosyl group (Ra) is linked to $C_2$-OH and the other (Rb) is linked to $C_3$-OH of the ester-linked xylopyranosyl group (Xa). The permethylate of I gave the methyl glycosides of 4-*O*-methylxylopyranose and 2,3,4-tri-*O*-methylrhamnopyranose on methanolysis, as expected. The conformation of the ester-linked $\beta$-D-xylopyranosyl group was determined to be $^1C_4$ from the values of $J_{H_1H_2}$ (4 Hz), $J_{H_2H_3}$ (4 Hz), and $J_{C_1H_1}$ (174 Hz).[3] Therefore, the structure of I was established to be as shown in Chart 1, and it was named scaberoside Ha methyl ester.

Compound II was obtained as a white powder, and the positive ion FAB-MS showed an $[M+Na]^+$ ion at *m*/*z* 1241 and a fragment ion of the ester-linked sugar moiety at *m*/*z* 579, while the negative ion FAB-MS showed an $[M-H]^-$ ion at *m*/*z* 1217 and a fragment ion derived from the prosapogenin moiety at *m*/*z* 661. The HR-FAB-MS gave the molecular formula $C_{59}H_{94}O_{26}$. On acid hydrolysis, II gave L-rhamnose, D-xylose and D-glucuronic acid as component sugars. The FAB-MS and NMR spectra suggested that II is also a 3,28-*O*-bisdesmosidic pentaglycoside having the same prosapogenin as that of I. On selective cleavage of the ester-linked sugar moiety[4] followed by treatment with $CH_2N_2$, II provided a prosapogenin methyl ester (VII) and an anomeric mixture

Table I. $^{13}$C-NMR Chemical Shifts of Aglycone Moieties of I[a], V and VII

| | I | V | VII |
|---|---|---|---|
| 1 | 38.8 | 38.8 | 38.7 |
| 2 | 26.6 | 26.6 | 26.6 |
| 3 | 89.1 | 89.1 | 89.1 |
| 4 | 39.5 | 39.5 | 39.5 |
| 5 | 55.9 | 55.9 | 55.8 |
| 6 | 18.4 | 18.5 | 18.4 |
| 7 | 33.5 | 33.4 | 33.3 |
| 8 | 40.0 | 40.0 | 39.8 |
| 9 | 47.1 | 47.1 | 47.0 |
| 10 | 36.9 | 37.0 | 37.0 |
| 11 | 23.8 | 23.8 | 23.7 |
| 12 | 122.7 | 122.7 | 122.6 |
| 13 | 144.3 | 144.4 | 144.4 |
| 14 | 42.0 | 42.0 | 41.9 |
| 15 | 36.1 | 36.1 | 35.9 |
| 16 | 73.9 | 74.0 | 74.3 |
| 17 | 49.4 | 49.5 | 49.0 |
| 18 | 41.4 | 41.3 | 41.2 |
| 19 | 47.1 | 47.1 | 46.9 |
| 20 | 30.8 | 30.8 | 30.8 |
| 21 | 35.9 | 36.0 | 35.8 |
| 22 | 32.1 | 32.0 | 32.4 |
| 23 | 28.1 | 28.1 | 28.1 |
| 24 | 16.9 | 16.9 | 16.9 |
| 25 | 15.6 | 15.6 | 15.5 |
| 26 | 17.4 | 17.5 | 17.2 |
| 27 | 27.0 | 27.1 | 27.1 |
| 28 | 175.7 | 175.8 | 177.7 |
| 29 | 33.1 | 33.2 | 33.1 |
| 30 | 24.6 | 24.7 | 24.6 |
| COOMe | — | — | 51.7 |

*a*) Signals of the aglycone moieties of II, III, IV and VI have almost the same chemical shifts as those of I.

TABLE II. $^{13}$C-NMR Chemical Shifts of Sugar Moieties of Scaberosides and Related Compounds

| | I | II | III | IV$^{a)}$ | VII | VIIIa | VIIIb | IXa | IXb | IXb$^{b)}$ | Xa | Xb | Xb$^{b)}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| GA-1 | 107.2 | 107.2 | 107.2 | 107.1 | 107.2 | | | | | | | | |
| 2 | 75.3 | 75.3 | 75.3 | 75.3 | 75.4 | | | | | | | | |
| 3 | 77.8 | 77.9 | 77.8 | 77.8 | 77.9 | | | | | | | | |
| 4 | 73.1 | 73.1 | 73.1 | 73.0 | 73.1 | | | | | | | | |
| 5 | 77.1 | 77.1 | 77.1 | 77.1 | 77.1 | | | | | | | | |
| 6 | 170.7 | 170.7 | 170.7 | 170.7 | 170.7 | | | | | | | | |
| COOMe | 51.9 | 51.9 | 51.9 | 51.9 | 51.9 | | | | | | | | |
| OMe | | | | | | 56.1 | 54.8 | 56.1 | 54.8 | 56.2 | 56.1 | 54.8 | 56.2 |
| Xa-1 | 94.0 | 94.0 | 93.8 | 94.0 | | 103.8 | 100.0 | 103.8 | 100.1 | 101.4 | 103.7 | 100.0 | 101.3 |
| 2 | 74.8 | 74.5 | 74.6 | 75.2 | | 79.1 | 82.5 | 79.1 | 82.5 | 83.8 | 79.5 | 83.3 | 84.0 |
| 3 | 79.5 | 79.5 | 78.5 | | | 86.0 | 79.9 | 86.0 | 79.8 | 81.2 | 85.8 | 79.1 | 81.1 |
| 4 | 68.3 | 68.3 | 68.1 | | | 69.8 | 69.8 | 69.8 | 69.7 | 70.4$^{c)}$ | 69.8 | 69.6 | 70.5$^{c)}$ |
| 5 | 65.2 | 65.2 | 65.0 | | | 66.5 | 62.7 | 66.4 | 62.6 | 63.4 | 66.5 | 62.7 | 63.4 |
| Ra-1 | 101.4 | 100.9 | 100.9 | 100.8 | | 102.8 | 104.0 | 102.8 | 104.4 | 105.2 | 102.6 | 104.2 | 105.0 |
| 2 | 72.1 | 72.5 | 72.5 | 71.2 | | 71.9 | 72.0 | 71.9 | 72.0 | 72.9 | 71.6 | 71.4 | 72.9 |
| 3 | 72.4 | 71.6 | 71.6 | 82.1 | | 72.7 | 72.5 | 72.7 | 72.4 | 73.2 | 82.1 | 82.2 | 82.8 |
| 4 | 73.6 | 83.8 | 83.5 | | | 84.4 | 83.9 | 83.9 | 83.3 | 84.1 | 78.5 | 78.2 | 79.4 |
| 5 | 70.7 | 68.8 | 68.7 | | | 68.1 | 68.2 | 68.0 | 68.1 | 69.5 | 68.3 | 68.5 | 69.8 |
| 6 | 18.6 | 18.4 | 18.4 | | | 18.1 | 18.4 | 18.0 | 18.4 | 19.1 | 18.3 | 18.7 | 19.2 |
| Rb-1 | 101.9 | 102.0 | 101.8 | 101.8 | | 103.4 | 102.8 | 103.3 | 102.8 | 103.7 | 103.2 | 102.7 | 103.7 |
| 2 | 72.3 | 72.3 | 72.2 | 72.3 | | 72.5 | 72.4 | 72.4 | 72.4 | 73.2 | 72.5 | 72.6 | 73.4 |
| 3 | 72.5 | 72.5 | 72.5 | 72.5 | | 72.5 | 72.7 | 72.4 | 72.6 | 73.2 | 72.4 | 72.6 | 73.3 |
| 4 | 73.7 | 73.7 | 73.7 | | | 73.6 | 73.9 | 73.5 | 73.9 | 74.8 | 73.5 | 73.8 | 74.8 |
| 5 | 70.5 | 70.6 | 70.5 | | | 70.4 | 69.9 | 70.4 | 69.8 | 70.8 | 70.4 | 69.7 | 70.8 |
| 6 | 18.3 | 18.3 | 18.3 | | | 18.3 | 18.4 | 18.3 | 18.4 | 18.6 | 18.3 | 18.4 | 18.6 |
| Xb-1 | | 106.9 | 106.2 | 105.1 | | 107.1 | 107.0 | 106.3 | 106.2 | 106.9 | 105.1 | 105.2 | 105.7 |
| 2 | | 75.8 | 74.7 | 75.5 | | 76.1 | 76.5 | 74.8 | 74.8 | 75.8 | 75.7$^{c)}$ | 75.6$^{c)}$ | 76.5 |
| 3 | | 78.5 | 86.9 | | | 78.6 | 78.5 | 86.9 | 87.0 | 88.3 | 78.9 | 78.6 | 79.2 |
| 4 | | 70.9 | 68.9 | | | 71.0 | 70.9 | 69.0 | 69.0 | 71.0$^{c)}$ | 71.2 | 71.1 | 72.2 |
| 5 | | 67.4 | 66.7 | | | 67.5 | 67.4 | 66.7 | 66.7 | 67.5 | 67.1$^{d)}$ | 67.1$^{d)}$ | 67.9 |
| Xc-1 | | | 105.9 | | | | | 105.8 | 105.9 | 106.5 | | | |
| 2 | | | 75.2 | | | | | 75.2 | 75.3 | 76.0 | | | |
| 3 | | | 78.0 | | | | | 78.0 | 78.0 | 78.4 | | | |
| 4 | | | 70.8 | | | | | 70.8 | 70.9 | 71.7 | | | |
| 5 | | | 67.2 | | | | | 67.3 | 67.2 | 67.9 | | | |
| Xd-1 | | | | 105.1 | | | | | | | 105.1 | 105.1 | 106.2 |
| 2 | | | | 73.8 | | | | | | | 73.9 | 73.9 | 75.0 |
| 3 | | | | 86.4 | | | | | | | 86.5 | 86.6 | 87.7 |
| 4 | | | | | | | | | | | 69.1 | 69.1 | 71.0$^{c)}$ |
| 5 | | | | | | | | | | | 66.2 | 66.1 | 67.1 |
| Xe-1 | | | | 105.8 | | | | | | | 105.8 | 105.8 | 106.5 |
| 2 | | | | | | | | | | | 75.3$^{c)}$ | 75.3$^{c)}$ | 76.1 |
| 3 | | | | | | | | | | | 77.7 | 77.7 | 78.5 |
| 4 | | | | | | | | | | | 70.7 | 70.7 | 71.8 |
| 5 | | | | | | | | | | | 67.0$^{d)}$ | 67.0$^{d)}$ | 67.9 |

Abbreviations: GA, 6-*O*-methyl-*β*-D-glucuronopyranosyl; X, D-xylopyranosyl; R, α-L-rhamnopyranosyl. *a*) Blank spaces indicate that signals were not assigned. *b*) Data measured in $CD_3OD$. *c*, *d*) Assignments may be interchanged in each column.

(VIII) of a methyl tetraglycoside which is composed of L-rhamnose and D-xylose. Compound VII was determined to be echinocystic acid 3-*O*-*β*-D-glucopyranosiduronic acid dimethyl ester by examination of the NMR spectra. The negative ion FAB-MS of VIII showed an $[M-H]^-$ ion at *m/z* 587 and fragment ions at *m/z* 455, 441, 309 and 163, clearly indicating that the ester-linked sugar is a branched tetraglycoside having a rhamnopyranosyl group and a xylopyranosyl-rhamnopyranosyl group attached to the xylopyranosyl group. The permethylate of VIII gave methyl glycosides of 4-*O*-methylxylose, 2,3-di-*O*-methylrhamnose, 2,3,4-tri-*O*-methylxylose and 2,3,4-tri-*O*-methylrhamnose. The anomers of VIII were separated to a *β*-anomer (VIIIa) and an α-anomer (VIIIb) by HPLC, and their NMR spectra were carefully examined. The signal assignments are summarized in Tables II and III. The ROE difference spectra of VIIIb measured by irradiation at the frequencies of the anomeric protons of the two rhamnopyranosyl groups (Ra-1H, δ5.45 and Rb-1H, δ5.77) and the terminal xylopyranosyl group (Xb-1H, δ5.12) showed NOE at the signals of Xa-2H (δ3.88), Xa-3H (δ4.43) and Ra-4H (δ4.32), respectively. Thus, the structure of VIIIb was identified as methyl *O*-*β*-D-xylopyranosyl-(1→4)-*O*-α-L-rhamnopyranosyl-(1→2)-[*O*-α-L-rhamnopyranosyl-(1→3)]-α-D-xylopyranoside, and VIIIa is its *β* anomer. The structure of II was determined to be as shown in Chart 1, and II was named scaberoside $Hb_1$ methyl ester.

Compound III, $C_{64}H_{102}O_{30}$, was obtained as colorless needles. On acid hydrolysis, III gave L-rhamnose, D-xylose and D-glucuronic acid. The FAB-MS and NMR spectra suggested that III is also an echinocystic acid glucuronide saponin having an ester-linked pentaglycoside which is composed of 2 mol of L-rhamnose and 3 mol of D-xylose.

TABLE III. $^1$H-NMR Chemical Shifts of Sugar Moieties of Scaberosides and Related Compounds

| | I | II | III | IV[a] | VII | VIIIa | VIIIb | IXa | IXb | IXb[b] | Xa | Xb | Xb[b] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| GA-1 | 4.97 (d, 8) | 4.96 (d, 8) | 4.97 (d, 8) | 4.97 (d, 8) | 4.98 (d, 8) | | | | | | | | |
| 2 | 4.06 (dd, 8, 9) | 4.05 (dd, 8, 9) | 4.05 (dd, 8, 9) | 4.06 (dd, 8, 9) | 4.07 (dd, 8, 9) | | | | | | | | |
| 3 | 4.24 (dd, 9, 9) | 4.24 (dd, 9, 9) | 4.24 (dd, 9, 9) | 4.24 (dd, 9, 9) | 4.24 (dd, 9, 9) | | | | | | | | |
| 4 | 4.45 (dd, 9, 9) | 4.45 (dd, 9, 9) | 4.45 (dd, 9, 9) | 4.45 (dd, 9, 9) | 4.45 (dd, 9, 9) | | | | | | | | |
| 5 | 4.57 (d, 9) | 4.57 (d, 9) | 4.57 (d, 9) | 4.57 (d, 9) | 4.57 (d, 9) | | | | | | | | |
| COOMe | 3.73 | 3.73 | 3.73 | 3.73 | 3.74 | | | | | | | | |
| OMe | | | | | | 3.45 | 3.30 | 3.46 | 3.31 | 3.37 | 3.48 | 3.34 | 3.36 |
| Xa-1 | 6.48 (d, 4) | 6.44 (d, 4) | 6.48 (d, 4) | 6.48 (d, 4) | | 4.41 (d, 7) | 5.13 (d, 3) | 4.41 (d, 7) | 5.13 (d, 3) | 4.73 (d, 3) | 4.43 (d, 7) | 5.17 (d, 3) | 4.73 (d, 3) |
| 2 | 4.29 (dd, 4, 4) | 4.25 (dd, 4, 4) | 4.24 (dd, 4, 4) | 4.28 (dd, 4, 4) | | 3.88 (dd, 7, 9) | 3.88 (dd, 3, 9) | 3.87 (dd, 7, 9) | 3.87 (dd, 3, 9) | 3.46 (dd, 3, 9) | 3.88 (dd, 7, 9) | 3.86 (dd, 3, 9) | 3.46 (dd, 3, 9) |
| 3 | 4.38 (dd, 4, 4) | 4.36 (dd, 4, 4) | 4.38 (dd, 4, 4) | | | 3.97 (dd, 9, 9) | 4.43 (dd, 9, 9) | 3.95 (dd, 9, 9) | 4.42 (dd, 9, 9) | 3.73 (dd, 9, 9) | *ca.* 3.90 | 4.47 (dd, 9, 9) | 3.74 (dd, 9, 9) |
| 4 | *ca.* 4.27 | *ca.* 4.25 | *ca.* 4.30 | | | *ca.* 3.90 | *ca.* 4.03 | *ca.* 3.90 | *ca.* 4.00 | *ca.* 3.60 | *ca.* 3.86 | *ca.* 4.00 | *ca.* 3.55 |
| 5 | 3.91 (dd, 6, 12) | 3.91 (dd, 6, 12) | 3.94 (dd, 6, 12) | | | 3.50 (dd, 9, 12) | 3.83 (dd, 11, 11) | *ca.* 3.50 | 3.83 (dd, 11, 11) | *ca.* 3.50 | *ca.* 3.49 | *ca.* 3.85 | 3.44 (dd, 5, 12) |
| | *ca.* 4.36 | *ca.* 4.35 | 4.36 (dd, 5, 12) | | | 4.19 (dd, 5, 12) | 3.94 (dd, 6, 11) | 4.19 (dd, 5, 12) | 3.94 (dd, 6, 11) | *ca.* 3.60 | *ca.* 4.20 | *ca.* 4.02 | *ca.* 3.55 |
| Ra-1 | 5.76 (d, 2) | 5.73 (d, 2) | 5.69 (d, 2) | 5.70 (d, 2) | | 5.66 (d, 2) | 5.45 (d, 2) | 5.65 (d, 2) | 5.42 (d, 2) | 4.79 (d, 2) | 5.64 (d, 2) | 5.39 (d, 2) | 4.79 (d, 2) |
| 2 | 4.58 (br s) | 4.56 (br s) | 4.54 (br s) | 4.72 (br s) | | 4.69 (dd, 2, 3) | 4.71 (dd, 2, 3) | *ca.* 4.65 | 4.68 (br s) | *ca.* 3.89 | 4.84 (br s) | 4.81 (br s) | *ca.* 4.05 |
| 3 | 4.43 (dd, 3, 9) | 4.51 (dd, 3, 9) | 4.48 (dd, 3, 9) | 4.54 (dd, 3, 9) | | 4.53 (dd, 3, 9) | 4.52 (dd, 3, 9) | 4.49 (dd, 3, 9) | 4.49 (dd, 3, 9) | *ca.* 3.88 | 4.62 (dd, 3, 9) | 4.53 (dd, 3, 9) | 3.97 (dd, 3, 9) |
| 4 | 4.22 (dd, 9, 9) | 4.32 (dd, 9, 9) | 4.32 (dd, 9, 9) | | | 4.34 (dd, 9, 9) | *ca.* 4.32 | 4.33 (dd, 9, 9) | 4.32 (dd, 9, 9) | 3.58 (dd, 9, 9) | 4.52 (dd, 9, 9) | 4.46 (dd, 9, 9) | 3.71 (dd, 9, 9) |
| 5 | *ca.* 4.33 | *ca.* 4.25 | *ca.* 4.20 | | | *ca.* 4.47 | *ca.* 4.32 | *ca.* 4.43 | *ca.* 4.25 | 3.78 (dq, 9, 6) | *ca.* 4.48 | 4.37 (dq, 9, 6) | *ca.* 3.83 |
| 6 | 1.66 (d, 6) | 1.72 (d, 6) | 1.68 (d, 6) | | | 1.72 (d, 6) | 1.67 (d, 6) | 1.68 (d, 6) | 1.63 (d, 6) | 1.29 (d, 6) | 1.72 (d, 6) | 1.66 (d, 6) | 1.28 (d, 6) |
| Rb-1 | 5.67 (d, 2) | 5.64 (d, 2) | 5.64 (d, 2) | 5.65 (d, 2) | | 5.64 (d, 2) | 5.77 (d, 2) | 5.62 (d, 2) | 5.75 (d, 2) | 4.94 (d, 2) | 5.61 (d, 2) | 5.74 (d, 2) | 4.95 (d, 2) |
| 2 | 4.73 (br s) | 4.72 (br s) | 4.70 (dd, 2, 3) | 4.67 (br s) | | 4.73 (dd, 2, 3) | 4.62 (dd, 2, 3) | 4.71 (dd, 2, 3) | 4.60 (br s) | 3.84 (dd, 2, 3) | 4.68 (br s) | 4.55 (br s) | 3.82 (dd, 2, 3) |
| 3 | 4.52 (dd, 3, 9) | 4.54 (dd, 3, 9) | 4.51 (dd, 3, 9) | 4.51 (dd, 3, 9) | | 4.45 (dd, 3, 9) | 4.48 (dd, 3, 9) | *ca.* 4.43 | 4.47 (dd, 3, 9) | 3.68 (dd, 3, 9) | 4.42 (dd, 3, 9) | *ca.* 4.45 | 3.67 (dd, 3, 9) |
| 4 | 4.30 (dd, 9, 9) | 4.27 (dd, 9, 9) | 4.27 (dd, 9, 9) | | | 4.25 (dd, 9, 9) | 4.23 (dd, 9, 9) | 4.25 (dd, 9, 9) | 4.23 (dd, 9, 9) | 3.39 (dd, 9, 9) | 4.23 (dd, 9, 9) | 4.18 (dd, 9, 9) | 3.39 (dd, 9, 9) |
| 5 | *ca.* 4.58 | *ca.* 4.50 | *ca.* 4.50 | | | 4.65 (dq, 9, 6) | 4.88 (dq, 9, 6) | *ca.* 4.65 | 4.88 (dq, 9, 6) | 4.02 (dq, 9, 6) | *ca.* 4.65 | 4.91 (dq, 9, 6) | *ca.* 4.05 |
| 6 | 1.59 (d, 6) | 1.59 (d, 6) | 1.58 (d, 6) | | | 1.63 (d, 6) | 1.62 (d, 6) | 1.63 (d, 6) | 1.62 (d, 6) | 1.24 (d, 6) | 1.62 (d, 6) | 1.61 (d, 6) | 1.25 (d, 6) |
| Xb-1 | | 5.10 (d, 7) | 5.12 (d, 7) | 5.31 (d, 8) | | 5.14 (d, 7) | 5.12 (d, 8) | 5.18 (d, 7) | 5.17 (d, 7) | 4.60 (d, 8) | 5.38 (d, 8) | 5.30 (d, 8) | 4.70 (d, 8) |
| 2 | | 3.99 (dd, 7, 9) | 4.00 (dd, 7, 9) | 3.91 (dd, 8, 9) | | 4.03 (dd, 7, 9) | 4.01 (dd, 8, 9) | *ca.* 4.05 | *ca.* 4.00 | 3.41 (dd, 8, 9) | *ca.* 3.95 | *ca.* 3.95 | 3.12 (dd, 8, 9) |
| 3 | | 4.06 (dd, 9, 9) | *ca.* 4.02 | | | 4.09 (dd, 9, 9) | 4.07 (dd, 9, 9) | *ca.* 4.05 | *ca.* 4.05 | 3.49 (dd, 9, 9) | 4.07 (dd, 9, 9) | 4.05 (dd, 9, 9) | 3.27 (dd, 9, 9) |
| 4 | | 4.12 (m) | *ca.* 4.00 | | | 4.15 (m) | 4.15 (m) | *ca.* 4.05 | *ca.* 4.05 | *ca.* 3.60 | *ca.* 4.15 | *ca.* 4.15 | *ca.* 3.45 |
| 5 | | 3.49 (dd, 10, 11) | *ca.* 3.45 | | | 3.55 (dd, 10, 11) | 3.53 (dd, 10, 11) | *ca.* 3.50 | 3.49 (dd-like) | 3.23 (dd, 10, 11) | 3.45 (dd, 10, 11) | 3.46 (dd, 10, 11) | 3.16 (dd, 10, 11) |
| | | 4.20 (dd, 5, 11) | 4.16 (dd, 5, 10) | | | 4.26 (dd, 5, 11) | 4.26 (dd, 5, 11) | *ca.* 4.25 | *ca.* 4.25 | 3.91 (dd, 5, 11) | *ca.* 4.20 | *ca.* 4.20 | *ca.* 3.83 |
| Xc-1 | | | 5.20 (d, 8) | | | | | 5.21 (d, 8) | 5.22 (d, 8) | 4.51 (d, 7) | | | |
| 2 | | | 4.00 (dd, 8, 9) | | | | | 4.00 (dd, 8, 9) | *ca.* 4.00 | 3.29 (dd, 7, 9) | | | |
| 3 | | | 4.11 (dd, 9, 9) | | | | | 4.11 (dd, 9, 9) | 4.12 (dd, 9, 9) | 3.36 (dd, 9, 9) | | | |
| 4 | | | *ca.* 4.15 | | | | | *ca.* 4.15 | *ca.* 4.15 | *ca.* 3.55 | | | |
| 5 | | | 3.66 (dd, 10, 11) | | | | | 3.67 (dd, 10, 11) | 3.68 (dd, 10, 11) | 3.25 (dd, 10, 11) | | | |
| | | | *ca.* 4.30 | | | | | 4.29 (dd, 5, 11) | *ca.* 4.30 | 3.92 (dd, 5, 11) | | | |
| Xd-1 | | | | 5.17 (d, 7) | | | | | | | 5.31 (d, 7) | 5.06 (d-like) | 4.65 (d-like) |
| 2 | | | | 3.97 (dd, 7, 9) | | | | | | | 3.99 (dd, 7, 9) | *ca.* 3.95 | *ca.* 3.50 |
| 3 | | | | *ca.* 4.00 | | | | | | | *ca.* 4.04 | *ca.* 3.95 | *ca.* 3.50 |
| 4 | | | | | | | | | | | *ca.* 3.90 | *ca.* 3.90 | *ca.* 3.55 |
| 5 | | | | | | | | | | | 3.59 (dd, 10, 11) | 3.65 (dd, 10, 11) | 3.32 (dd, 10, 11) |
| | | | | | | | | | | | *ca.* 4.20 | 4.33 (dd, 5, 11) | *ca.* 4.05 |
| Xe-1 | | | | 5.08 (d, 7) | | | | | | | 5.08 (d, 7) | 5.00 (d, 7) | 4.52 (d, 7) |
| 2 | | | | | | | | | | | *ca.* 3.95 | *ca.* 3.95 | 3.29 (dd, 7, 9) |
| 3 | | | | | | | | | | | *ca.* 4.04 | 4.03 (dd, 9, 9) | 3.36 (dd, 9, 9) |
| 4 | | | | | | | | | | | *ca.* 4.10 | *ca.* 4.10 | *ca.* 3.50 |
| 5 | | | | | | | | | | | 3.54 (dd, 10, 11) | 3.53 (dd, 10, 11) | 3.24 (dd, 10, 11) |
| | | | | | | | | | | | *ca.* 4.20 | 4.22 (dd, 5, 11) | 3.92 (dd, 5, 11) |

Values in parentheses are coupling constants in hertz (Hz). *a*) Blank spaces indicate that signals were not assigned. *b*) Data measured in $CD_3OD$.

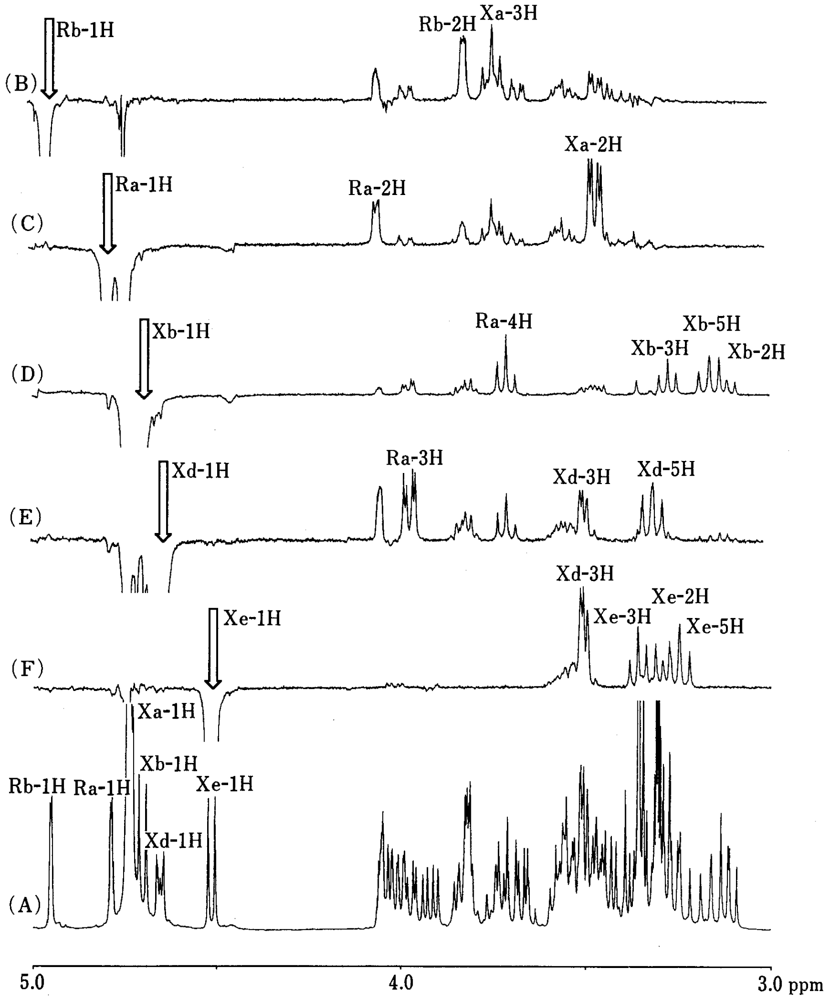

Fig. 2. $^1$H-NMR Spectrum (A) and ROE Difference Spectra (B, C, D, E, F) of IV in $CD_3OD$

On selective cleavage of the ester-linked sugar moiety followed by treatment with $CH_2N_2$, III gave VII and an anomeric mixture (IX) of a pentaglycoside. The permethylate of IX gave the methyl glycosides of 4-*O*-methylxylose, 2,4-di-*O*-methylxylose, 2,3-di-*O*-methylrhamnose, 2,3,4-tri-*O*-methylxylose and 2,3,4-tri-*O*-methylrhamnose on methanolysis. The anomers of IX were separated to a *β*-anomer (IXa) and an *α*-anomer (IXb). $^1$H-NMR and $^{13}$C-NMR signals were assigned as shown in Tables II and III. In the ROE difference spectra of IXb measured in $CD_3OD$,[5] irradiation at the signals of Ra-1H (*δ* 4.79), Rb-1H (*δ* 4.94), Xb-1H (*δ* 4.60) and Xc-1H (*δ* 4.51) resulted in NOE enhancement at the signals of Xa-2H (*δ* 3.46), Xa-3H (*δ* 3.73), Ra-4H (*δ* 3.58) and Xb-3H (*δ* 3.49), respectively. Thus, the structure of IXb was established as a methyl *O*-*β*-D-xylopyranosyl-(1→3)-*O*-*β*-D-xylopyranosyl-(1→4)-*O*-*α*-L-rhamnopyranosyl-(1→2)-[*O*-*α*-L-rhamnopyranosyl-(1→3)]-*α*-D-xylopyranoside, and IXa, its *β* anomer. The structure of III was determined to be as shown in the Chart 1. Compound III was named scaberoside Hb$_2$ methyl ester.

Compound IV, $C_{69}H_{110}O_{34}$, was obtained as colorless needles, and it gave L-rhamnose, D-xylose and D-glucuronic acid on acid hydrolysis. The FAB-MS and NMR spectra suggested that IV is also a 3,28-*O*-bisdesmosidic heptaglycoside of echinocystic acid, having the same prosapogenin as that of I and an ester-linked hexaglycosyl group. Compound IV gave a prosapogenin methyl ester (VII) and an anomeric mixture (X) of a methyl hexaoside on selective cleavage of the ester-linked sugar moiety followed by treatment with $CH_2N_2$. The permethylate of X gave methyl glycosides of 4-*O*-methylxylose, 2-*O*-methylrhamnose, 2,4-di-*O*-methylxylose, 2,3,4-tri-*O*-methylrhamnose and 2,3,4-tri-*O*-methylxylose on methanolysis. These data indicated that X is a methyl hexaglycoside doubly branched at a xylopyranosyl unit and a rhamnopyranosyl unit having two terminal sugars, xylose and rhamnose. After separation of X to *β*-(Xa) and *α*-(Xb) anomers, the NMR spectra were carefully examined (Tables II and III). The ROE difference spectra of Xb measured in $CD_3OD$[5] by irradiation at the frequencies of the anomeric protons of the two rhamnopyranosyl groups, Ra-1H (*δ* 4.79) and Rb-1H (*δ* 4.95) showed NOE at the signals of Xa-2H (*δ* 3.46) (Fig. 2C) and Xa-3H (*δ* 3.74) (Fig. 2B), respectively. On irradiation at the signals of the anomeric protons of the xylopyranosyl groups, Xb-1H (*δ* 4.70), Xd-1H (*δ* 4.65) and Xe-1H (*δ* 4.52), NOE enhancement was observed at the signals of Ra-4H (*δ* 3.71) (Fig. 2D), Ra-3H (*δ* 3.97) (Fig. 2E) and Xd-3H (*δ* 3.50) (Fig. 2F), respectively. From these data, the structure of Xb was determined to be a methyl *O*-*β*-D-xylopyranosyl-(1→3)-*O*-*β*-D-xylopyranosyl-(1→3)-[*O*-*β*-D-xylopyranosyl-(1→4)]-

*O*-α-L-rhamnopyranosyl-(1→2)-[*O*-α-L-rhamnopyranosyl-(1→3)]-α-D-xylopyranoside, and Xa is its β anomer. The structure of IV was determined to be as shown in the Chart 1, and IV was named scaberoside $\mathrm{Hc}_1$. Compounds V and VI were identified as methyl esters of foetidissimoside A[2] and scaberoside $\mathrm{A}_2$,[1b] respectively, by direct comparison with authentic samples.

## Experimental[6]

**Extraction and Isolation of I—VI** The plant material was collected in Fukuoka prefecture in August, 1989. The air-dried ground part (2.3 kg) of *Aster scaber* THUNB. was percolated with $\mathrm{CHCl_3}$, 50% MeOH and $\mathrm{H_2O}$ successively. The 50% MeOH extract was concentrated to half the initial volume under reduced pressure, and combined with the $\mathrm{H_2O}$ extract, and the mixture was passed through a Diaion HP-20 column. The resin was washed with $\mathrm{H_2O}$ and 50% MeOH, then the crude glycoside fraction (41 g) was eluted with MeOH. The crude glycoside fraction was chromatographed on silica gel (eluant, EtOAc : MeOH : $\mathrm{H_2O}$, 7 : 2 : 0.5→5 : 4 : 1) to give seven fractions (frs. 1—7). Fractions 1—4 did not contain any triterpene glycoside. Fr. 5 was repeatedly chromatographed on silica gel (EtOAc : MeOH : $\mathrm{H_2O}$ : AcOH, 6 : 2 : 1 : 0.1→6 : 3 : 1 : 0.1) and ODS (Packed column RQ-2, 24 mm i.d. × 360 mm l., Fuji Gel Co., Ltd.; 35% MeCN/0.5% AcOH), and subjected to preparative HPLC (Capcell pak C18-AG120 Å, 20 mm i.d. × 250 mm l., Shiseido Co., Ltd.; 35% MeCN/0.5% AcOH). The fractions containing triterpene glycosides were treated with $\mathrm{CH_2N_2}$ and further subjected to silica gel chromatography (EtOAc : MeOH : $\mathrm{H_2O}$, 8 : 1 : 0.5→7 : 2 : 1) and preparative HPLC (Cosmosil $5\mathrm{C}_{18}$-AR, 20 mm i.d. × 250 mm l., Nacalai Tesque; 40% MeCN) to give I (155 mg), V (44 mg) and VI (36 mg). Fr. 6 was chromatographed on an ODS column (YMC-Gel ODS-A-120-230/70, YMC Co., Ltd.; 27—32% MeCN/0.5% AcOH) repeatedly, methylated with $\mathrm{CH_2N_2}$, and purified by preparative HPLC (Capcell pak; 51% acetone) to yield III (60 mg) and VI (260 mg). Fr. 7 was also subjected to ODS chromatography (YMC-Gel ODS-AQ-120-S50, YMC Co., Ltd.; 27—30% MeCN/0.5% AcOH) and preparative HPLC (Capcell pak; 47—54% acetone/0.5% AcOH) repeatedly, and treated with $\mathrm{CH_2N_2}$ followed by column chromatography on silica gel (EtOAc : MeOH : $\mathrm{H_2O}$, 8 : 1 : 0.5→7 : 2 : 1) and preparative HPLC (Cosmosil; 51% acetone) to give II (460 mg), III (640 mg) and IV (1.3 g).

Scaberoside Ha Methyl Ester (I): A white powder. $[\alpha]_{\mathrm{D}}^{25}$ $-68.9°$ ($c=2.0$, MeOH). Positive ion high resolution (HR)-FAB-MS *m/z*: 1109.550 ($[\mathrm{M+Na}]^+$). $\mathrm{C_{54}H_{86}NaO_{22}}$ requires 1109.550. *m/z*: 447.147 ($[\mathrm{Xyl+2Rha+Na}]^+$). $\mathrm{C_{17}H_{28}NaO_{12}}$ requires 447.147. Negative ion FAB-MS *m/z*: 1085 ($[\mathrm{M-H}]^-$), 661 ($[\mathrm{prosapogenin-H}]^-$). $^1$H-NMR δ: aglycone moiety: 3.37 (dd, $J=4$, 12 Hz, $\mathrm{C_3}$-H), 5.60 (dd, $J=3$, 3 Hz, $\mathrm{C_{12}}$-H), 5.19 (br s, $\mathrm{C_{16}}$-H), 3.44 (dd, $J=4$, 14 Hz, $\mathrm{C_{18}}$-H), 1.26 ($\mathrm{C_{23}}$-H), 0.95 ($\mathrm{C_{24}}$-H), 0.86 ($\mathrm{C_{25}}$-H), 1.03 ($\mathrm{C_{26}}$-H), 1.78 ($\mathrm{C_{27}}$-H), 0.99 ($\mathrm{C_{29}}$-H), 1.13 ($\mathrm{C_{30}}$-H). Sugar moiety; shown in Table III. $^{13}$C-NMR: shown in Tables I and II. Coupling constant between anomeric C and H ($J_{\mathrm{C_1H_1}}$) of the ester-linked xylopyranosyl group (Xa): 174 Hz.

Scaberoside $\mathrm{Hb_1}$ Methyl Ester (II): A white powder. $[\alpha]_{\mathrm{D}}^{28}$ $-71.0°$ ($c=0.9$, MeOH). Positive ion HR-FAB-MS *m/z*: 1241.593 ($[\mathrm{M+Na}]^+$). $\mathrm{C_{59}H_{94}NaO_{26}}$ requires 1241.593. *m/z*: 579.190 ($[\mathrm{2Xyl+2Rha+Na}]^+$). $\mathrm{C_{22}H_{36}NaO_{16}}$ requires 579.190. Negative ion FAB-MS *m/z*: 1217 ($[\mathrm{M-H}]^-$), 661 ($[\mathrm{prosapogenin-H}]^-$). $^1$H-NMR δ: aglycone moiety: 3.36 (dd, $J=4$, 12 Hz, $\mathrm{C_3}$-H), 5.60 (dd, $J=3$, 3 Hz, $\mathrm{C_{12}}$-H), 5.19 (br s, $\mathrm{C_{16}}$-H), 3.44 (dd, $J=4$, 14 Hz, $\mathrm{C_{18}}$-H), 1.27 ($\mathrm{C_{23}}$-H), 0.96 ($\mathrm{C_{24}}$-H), 0.83 ($\mathrm{C_{25}}$-H), 1.03 ($\mathrm{C_{26}}$-H), 1.77 ($\mathrm{C_{27}}$-H), 0.99 ($\mathrm{C_{29}}$-H), 1.13 ($\mathrm{C_{30}}$-H). Sugar moiety: shown in Table III. $^{13}$C-NMR: shown in Tables I and II. $J_{\mathrm{C_1H_1}}$ of Xa: 174 Hz.

Scaberoside $\mathrm{Hb_2}$ Methyl Ester (III): Colorless needles from $\mathrm{H_2O}$–MeOH, mp 271 °C. $[\alpha]_{\mathrm{D}}^{25}$ $-64.0°$ ($c=0.7$, MeOH). Positive ion HR-FAB-MS *m/z*: 1373.635 ($[\mathrm{M+Na}]^+$). $\mathrm{C_{64}H_{102}NaO_{30}}$ requires 1373.635. *m/z*: 711.232 ($[\mathrm{3Xyl+2Rha+Na}]^+$). $\mathrm{C_{27}H_{44}NaO_{20}}$ requires 711.232. Negative ion FAB-MS *m/z*: 1349 ($[\mathrm{M-H}]^-$), 661 ($[\mathrm{prosapogenin-H}]^-$). $^1$H-NMR δ: aglycone moiety: 3.36 (dd, $J=4$, 12 Hz, $\mathrm{C_3}$-H), 5.60 (dd, $J=3$, 3 Hz, $\mathrm{C_{12}}$-H), 5.18 (br s, $\mathrm{C_{16}}$-H), 1.28 ($\mathrm{C_{23}}$-H), 0.97 ($\mathrm{C_{24}}$-H), 0.82 ($\mathrm{C_{25}}$-H), 1.01 ($\mathrm{C_{26}}$-H), 1.77 ($\mathrm{C_{27}}$-H), 0.99 ($\mathrm{C_{29}}$-H), 1.14 ($\mathrm{C_{30}}$-H). Sugar moiety: shown in Table III. $^{13}$C-NMR: shown in Tables I and II. $J_{\mathrm{C_1H_1}}$ of Xa: 170 Hz.

Scaberoside $\mathrm{Hc_1}$ Methyl Ester (IV): Colorless needles from $\mathrm{H_2O}$–MeOH, mp 238—240 °C. $[\alpha]_{\mathrm{D}}^{22}$ $-74.7°$ ($c=1.0$, MeOH). Positive ion HR-FAB-MS *m/z*: 1505.676 ($[\mathrm{M+Na}]^+$). $\mathrm{C_{69}H_{110}NaO_{34}}$ requires 1505.677. *m/z*: 843.274 ($[\mathrm{4Xyl+2Rha+Na}]^+$). $\mathrm{C_{32}H_{52}NaO_{24}}$ requires 843.274. Negative ion FAB-MS *m/z*: 1481 ($[\mathrm{M-H}]^-$), 661 ($[\mathrm{prosapogenin-H}]^-$). $^1$H-NMR δ: aglycone moiety: 3.37 (dd, $J=4$, 12 Hz, $\mathrm{C_3}$-H), 5.60 (dd, $J=3$, 3 Hz, $\mathrm{C_{12}}$-H), 5.17 (br s, $\mathrm{C_{16}}$-H), 3.44 (dd, $J=4$, 14 Hz, $\mathrm{C_{18}}$-H), 1.28 ($\mathrm{C_{23}}$-H), 0.98 ($\mathrm{C_{24}}$-H), 0.85 ($\mathrm{C_{25}}$-H), 1.04 ($\mathrm{C_{26}}$-H), 1.77 ($\mathrm{C_{27}}$-H), 0.99 ($\mathrm{C_{29}}$-H), 1.15 ($\mathrm{C_{30}}$-H). Sugar moiety: shown in Table III. $^{13}$C-NMR: shown in Tables I and II. $J_{\mathrm{C_1H_1}}$ of Xa: 172 Hz.

**Determination of Sugar Species and Their Absolute Configurations** A glycoside (*ca.* 3 mg) was dissolved in 1 N HCl–MeOH (1 ml) and heated at 95 °C for 2 h. The acidic solution was neutralized with $\mathrm{Ag_2CO_3}$ and the precipitates were centrifuged off. The supernatant was concentrated and the residue was trimethylsilylated with trimethylsilylimidazole, and checked by GLC. The GLC conditions were as follows: column, Shimadzu HiCap-CBP-1 (50 m × 0.2 mm i.d.); column oven temperature, 200 °C; injection port temperature, 290 °C; carrier gas, He (linear velocity, 20 cm/s); split ratio, 1/110; make-up gas, He (50 ml/min). Determination of the absolute configuration was performed according to the method reported by Hara *et al.*[7] A glycoside (5—10 mg) was hydrolyzed in 1 N HCl (1 ml) at 95 °C for 2 h. The acidic solution was neutralized in the same manner as described above. The hydrolysate was suspended in $\mathrm{H_2O}$ and extracted with $\mathrm{CHCl_3}$ to remove the aglycone. The aqueous layer was concentrated and the residue was dissolved in pyridine (0.2 ml). After addition of a pyridine solution (0.4 ml) of L-cysteine methyl ester hydrochloride (0.06 mol/l), the mixture was warmed at 60 °C for 1 h. The solvent was blown off under an $\mathrm{N_2}$ stream, and the residue was trimethylsilylated and checked by GLC. The identification was performed by comparison of the retention time with that of an authentic sugar sample. The absolute configuration of glucuronic acid was determined in the same way after $\mathrm{NaBH_4}$ reduction of VII to methyl echinocystate 3-*O*-β-glucopyranoside. The GC conditions for the determination of the absolute configurations of the component monosaccharides were the same as those described above except for the column oven temperature (250 °C). The results are presented in the text.

**Selective Cleavage of the Ester Glycoside Linkage** Selective cleavage of the ester-linked sugar moiety was performed according to the method reported by Ohtani *et al.*[4] Compound II (340 mg) and anhydrous LiI (700 mg) were dissolved in a mixture of MeOH (3 ml) and 2,6-lutidine (6 ml). The reaction solution was heated at 180 °C for 3 h, then diluted with 50% MeOH and passed through an Amberlite MB-3 column. The eluate was concentrated to dryness, and the residue was dissolved in MeOH and treated with $\mathrm{CH_2N_2}$. The reaction mixture was chromatographed on silica gel (EtOAc : MeOH : $\mathrm{H_2O}$ = 8 : 2 : 0.5) to give a prosapogenin methyl ester (VII, 113 mg) and an anomeric mixture (VIII, 105 mg) of a methyl glycoside.

Prosapogenin Methyl Ester (VII): A white powder. $[\alpha]_{\mathrm{D}}^{24}$ $-16.6°$ ($c=1.0$, MeOH). Positive ion FAB-MS *m/z*: 699 ($[\mathrm{M+Na}]^+$). $^1$H-NMR δ: aglycone moiety: 3.40 (2H, $\mathrm{C_3}$-H and $\mathrm{C_{18}}$-H were overlapped), 5.53 (dd, $J=3$, 3 Hz, $\mathrm{C_{12}}$-H), 5.01 (br s, $\mathrm{C_{16}}$-H), 1.30 ($\mathrm{C_{23}}$-H), 0.99 ($\mathrm{C_{24}}$-H), 0.90 ($\mathrm{C_{25}}$-H), 0.87 ($\mathrm{C_{26}}$-H), 1.79 ($\mathrm{C_{27}}$-H), 1.02 ($\mathrm{C_{29}}$-H), 1.10 ($\mathrm{C_{30}}$-H). Sugar moiety: shown in Table III. $^{13}$C-NMR: shown in Tables I and II.

VIII: A white powder. Positive ion FAB-MS *m/z*: 611 ($[\mathrm{M+Na}]^+$). Negative ion FAB-MS *m/z*: 587 ($[\mathrm{M-H}]^-$), 455, 441, 309, 163. Compound VIII was chromatographed on preparative HPLC to give a β-anomer (VIIIa, 47 mg) and an α anomer (VIIIb, 44 mg) as white powder.

VIIIa: $[\alpha]_{\mathrm{D}}^{28}$ $-67.2°$ ($c=2.4$, MeOH). $^1$H-NMR: shown in Table III. $^{13}$C-NMR: shown in Table II.

VIIIb: $[\alpha]_{\mathrm{D}}^{29}$ $-22.7°$ ($c=2.2$, MeOH). $^1$H-NMR: shown in Table III. $^{13}$C-NMR: shown in Table II.

Compounds III (520 mg) and IV (990 mg) were treated in the same way as described for II to give a prosapogenin methyl ester (VII, 174 mg from III and 336 mg from IV) and anomeric mixtures, IX (from III, 407 mg) and X (from IV, 278 mg). Compounds IX and X were also separated to β anomer (IXa, 73 mg; Xa, 135 mg) and α anomer (IXb, 90 mg; Xb, 188 mg).

IX: A white powder. Positive ion FAB-MS *m/z*: 743 ($[\mathrm{M+Na}]^+$). Negative ion FAB-MS *m/z*: 719 ($[\mathrm{M-H}]^-$), 587, 573, 455, 441, 309, 163.

IXa: $[\alpha]_{\mathrm{D}}^{23}$ $-84.7°$ ($c=0.8$, MeOH). $^1$H-NMR: shown in Table III. $^{13}$C-NMR: shown in Table II.

IXb: $[\alpha]_{\mathrm{D}}^{24}$ $-28.2°$ ($c=0.8$, MeOH). $^1$H-NMR: shown in Table III. $^{13}$C-NMR: shown in Table II.

X: A white powder. Positive ion FAB-MS *m/z*: 875 ($[\mathrm{M+Na}]^+$). Negative ion FAB-MS *m/z*: 851 ($[\mathrm{M-H}]^-$), 719, 705, 587, 573, 455, 441, 309, 163.

Xa: $[\alpha]_D^{23}$ $-81.6°$ ($c=0.7$, MeOH). $^1$H-NMR: shown in Table III. $^{13}$C-NMR: shown in Table II.

IXb: $[\alpha]_D^{24}$ $-36.4°$ ($c=0.8$, MeOH). $^1$H-NMR: shown in Table III: $^{13}$C-NMR: shown in Table II.

**Permethylation of IX and GC-CI-MS Analysis of Component Methylated Sugars** A glycoside (5—10 mg) was methylated according to Hakomori's method,[8)] and the reaction product was purified by silica gel column chromatography. The thin-layer-chromatographically homogeneous product was dissolved in 1 N HCl–MeOH and heated at 95 °C for 2 h. The reaction mixture was neutralized with $Ag_2CO_3$, acetylated with $Ac_2O$–pyridine and checked by GC-CI-MS. Identification of the component sugars was performed by comparison of the retention time and fragment pattern with those of authentic samples. GC-CI-MS conditions: GC part: column, 2% OV-17 on Uniport HP (80—100 mesh) packed in a glass column (3 mm i.d. × 1.0 m l.); column oven temperature, 130→190 °C (elevation rate, 3 °C/min); carrier gas, He (20 ml/min); injection port temperature, 250 °C. CI-MS part: reagent gas, isobutane (pressure, less than $1.5 \times 10^{-5}$ Torr); ionization source temperature, 270 °C; ionization energy, 150 eV; scan range, *m/z*: 100—400; scan interval, 4 s.

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### References and Notes

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5) The $C_2$-H signals of xylopyranosyl groups overlapped and could not be assigned when the NMR spectra were measured in pyridine-$d_5$ solution.

6) The instruments used in this work were as follows: Yanaco micro melting point apparatus (melting points), JASCO DIP-360 digital polarimeter (specific rotation), JEOL JNM GX-400 spectrometer ($^1$H- and $^{13}$C-NMR spectra), JEOL HX-110 spectrometer (MS), Shimadzu GC-8APF gas chromatograph (GC), Shimadzu GC-MS-6020 gas chromatograph-mass spectrometer and GC-MS-PAK 500 FDG data analyzer (GC-CI-MS). All melting points are uncorrected. NMR spectra were measured in pyridine-$d_5$ solution unless otherwise stated, and chemical shifts are expressed in the $\delta$ scale using tetramethylsilane as an internal standard.

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