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Isolation and Characterization of Saponins from *Castanospermum australe* CUNN. *et* FRASER

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Three new triterpenoid saponins, their methyl esters designated as castaralesides F (1), G (2) and H (3), were isolated from the fresh leaves of *Castanospermum australe*. The structures of these three saponins were elucidated on the basis of chemical and spectral data as 3β-*O*-[β-galactopyranosyl-(1→4)-β-glucuronopyranosyl]-2β,23-dihydroxyolean-12-en-28-oic acid; 3β-*O*-[α-rhamnopyranosyl-(1→4)-β-galactopyranosyl-(1→2)-β-glucuronopyranosyl]-2β,28-dihydroxyolean-12-ene; and 3β-*O*-[α-rhamnopyranosyl-(1→4)-β-xylopyranosyl-(1→2)-β-glucuronopyranosyl]-2β,28-dihydroxyolean-12-ene.

Keywords *Castanospermum australe*; Fabaceae; triterpenoid saponin; castaraleside F; castaraleside G; castaraleside H

We have previously reported[1] the isolation and structural determination of two saponins from the fresh leaves of *Castanospermum australe* CUNN. *et* FRASER (Fabaceae). This paper deals with the isolation and structure elucidation of three new oleanane-type triterpenoid saponins designated as castaralesides F (**1**), G (**2**) and H (**3**).

The saponins were methylated with diazomethane, and the methylated glycosidic mixture (containing castaralesides F, G and H) was subjected to a combination of silica gel chromatographies and reversed phase high performance liquid chromatography (HPLC) which afforded three compounds in a pure form as methyl esters (**1a**, **2a** and **3a**).

The castaraleside F methyl ester (**1a**) was obtained as a gummy mass. Compound **1a** showed an $[M-H]^-$ ion at m/z 839 in the negative ion FAB-MS, and the molecular formula, $C_{43}H_{68}O_{16}$, was obtained by high resolution fast atom bombardment-mass spectrum (FAB-MS). Other peaks in FAB-MS (negative ion mode) showed fragmentation due to the stepwise loss of sugar moities at m/z 677 $[M-H-\text{galactose}]^-$ and 501 $[\text{aglycone moiety}]^-$. Compound **1a** was composed of one mole each of glucuronic acid methyl ester and galactose, as well as bayogenin, on the basis of the chemical degradation and spectroscopic data mentioned below. The ^{1}H-nuclear magnetic resonance (^{1}H-NMR) spectrum of **1a** indicated the presence of an oleanane-type triterpene, which was shown by six tertiary methyl singlets of bayogenin (δ 0.89, 6H; 0.92, 3H; 1.20, 3H; 1.37, 3H; 1.60, 3H), and another at C-28 (δ 3.82) due to the methyl ester of bayogenin.[1] The characteristic signal due to the H-5 of glucuronic acid was exhibited at δ 4.53 (1H, d, $J=9.0$ Hz) and a signal due to a carbomethoxyl group of glucuronic acid at δ 3.70 (3H, s).[2] The olefinic proton signal appeared at δ 5.38 (1H, triplet), and two anomeric protons appeared at δ 5.28 (1H, d, $J=8.0$ Hz glucuronic acid) and 5.03 (1H, d, $J=8.0$ Hz, galactose). The H-3 proton of the aglycone moiety furnished a doublet at δ 4.32 ($J=3.6$ Hz). A quartet at δ 4.76 ($J=3.3$ Hz) is due to the H-2 of the aglycone moiety. Further evidence of glycosidic moiety and sugars was obtained through a detailed proton decoupling experiment, COSY-45° and C–H COSY spectrum.

The ^{13}C-NMR (Table I) signals of two anomeric carbons were observed at δ 105.0 and 106.3, and the signal at δ 83.0 due to the C-3 of the aglycone was shifted downfield ($\Delta+6$ ppm) in comparison with that of bayogenin. This glycosylation shift indicates that the sugar is attached to the C-3 position.[2] Standard gas chromatographic (GC) sugar analysis on the alditol acetate of the acid hydrolysed product of compound **1a** showed galactose. Compound **1a** was treated with $NaBH_4$, and the reduction product (**1b**) was hydrolysed; glucuronic acid and galactose were detected in a molar ratio of 1 : 1 by alditol acetate analysis.[3]

The anomeric configurations of galactose and glucuronic acid were both determined to be β according to the J values of their proton signals. In order to determine the sugar sequence and the position of sugar linkage, a differential nuclear Overhauser enhancement (NOE) spectral experiment was performed. When the signals at δ 5.28 and 5.03 (anomeric protons of glucuronic acid and galactose) were irradiated, NOEs were observed at a signal due to the H-3 of the aglycone and the H-4 of glucuronic acid, respectively. This experiment clearly provides evidence that the galactosyl-(1→4)-glucuronic acid unit is attached to the C-3 of bayogenin.

Thus, the structure of castaraleside F (**1**) was elucidated as 3β-*O*-[β-galactopyranosyl-(1→4)-β-glucuronopyranosyl]-2β,3β,23-trihydroxyolean-12-en-28-oic acid.

Castaraleside G methyl ester (**2a**) was obtained as a white gummy mass having $[\alpha]^{20}$ $+32.2°$ ($c=0.90$, MeOH). It was subjected to FAB-MS (negative ion mode) which exhibited a deprotonated molecular ion peak $[M-H]^-$ at m/z 941, and peaks at m/z 795 $[M-H-146]^-$, 633 $[M-H-146-162]^-$ and 457 $[M-H-146-162-176]^-$, corresponding to the subsequent loss of rhamnose, galactose and glucuronic acid methyl ester moiety, respectively. This indicated that rhamnose is the terminal sugar. Furthermore, FAB-MS (positive ion mode) measurement showed a molecular ion peak at m/z 965 $[M+Na]^+$. High resolution MS in a negative ion mode

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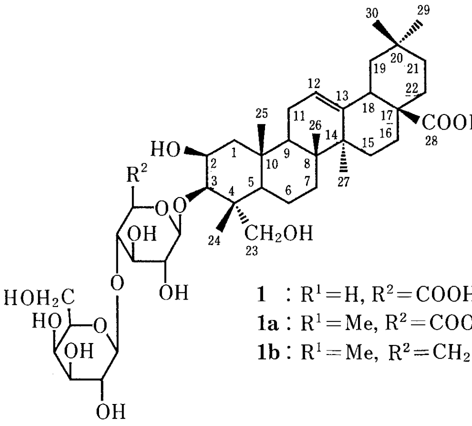
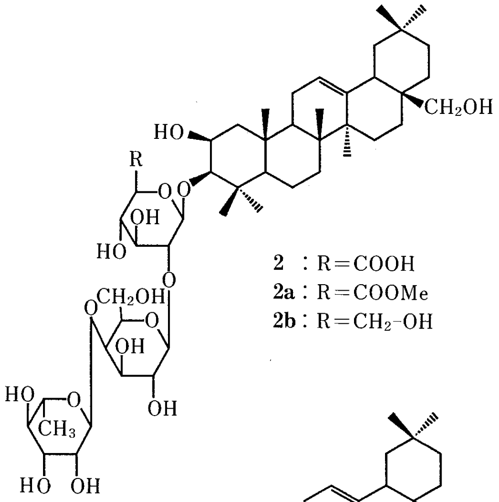
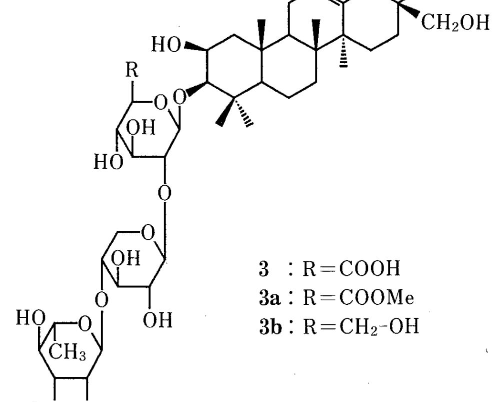


1 : $R^1=H, R^2=COOH$
1a : $R^1=Me, R^2=COOMe$
1b : $R^1=Me, R^2=CH_2\text{-}OH$



2 : $R=COOH$
2a : $R=COOMe$
2b : $R=CH_2\text{-}OH$



3 : $R=COOH$
3a : $R=COOMe$
3b : $R=CH_2\text{-}OH$

indicated a molecular peak at *m*/*z* 941.5170, and its molecular formula corresponds to $C_{48}H_{78}O_{18}$.

Compound **2a** was reduced with $NaBH_4$, and the product (**2b**) was hydrolysed. GC analysis of the alditol acetates indicated the formation of glucitol acetates,[3] galactitol acetate and rhamnitol acetate in a molar ratio of 1 : 1 : 1. Consequently, the presence of glucuronic acid, galactose and rhamnose was established in the glycoside molecule.

The ^1H-NMR of the methyl ester of **2a** exhibited three signals of anomeric protons at δ 5.19 (d, $J=8.0$ Hz), 5.81 (d, $J=7.9$ Hz) and 6.30 (br s, Rha-1). The characteristic doublet signal at δ 1.78 ($J=6.1$ Hz) is assignable to a methyl group in the rhamnose moiety. The signals at δ 5.81 and 6.30 (s) indicate the presence of a β-linked methyl glucuronopyranosyl group from the *J* value and an α-linked rhamnopyranosyl group from the δ value,[4] respectively. Another anomeric proton at δ 5.19 (d) represents the β-configuration of the galactose moiety. The methyl of glucuronic acid (methyl ester) was displayed as a singlet at δ 3.70. The seven methyls of the aglycone were found at δ 0.72 (H-25), 0.90 (H-24), 1.01 (H-29), 1.23 (H-26), 1.27 (H-30), 1.31 (H-23) and 1.45 (H-27). A triplet-like signal of H-12 was observed at δ 5.31. The characteristic signal of H-18 was observed at δ 3.39 (dd, $J=14.0$, 4.0 Hz).[5]

The ^{13}C-NMR was indicative of the skeletal structure of castaraleside G methyl ester (**2a**), showing the presence of 48 carbon atoms inclusive of three sugar molecules. The carbon signals of C-28 at δ 62.9, C-12 at δ 122.6 and C-13 at δ 144.8 and angular methyl groups of the genin at δ 28.7 (C-23), 15.6 (C-24), 17.1 (C-25), 18.3 (C-26), 18.3 (C-27), 33.4 (C-29) and 24.1 (C-30) were assigned to an oleanane-type skeleton. The signals for anomeric carbon atoms were displayed at δ 101.8, 102.4 and 105.4. The δ assignments for C-3 at 91.4, glucuronic acid C-2 at 78.3 and galactose C-4 at 77.8 were shifted downfield due to the glycosidic linkages.[6] Signals for the methyl of rhamnose, the methyl of glucuronic acid, and that of C-23 appeared at δ 18.9, 52.09 and 28.7, respectively.

Based on all of this spectral evidence, the structure of castaraleside G (**2**) is determined to be 3β-*O*-[α-rhamnopyranosyl-(1→4)-β-galactopyranosyl-(1→2)-β-glucuronopyranosyl]-2β,3β,28-trihydroxyolean-12-ene.

Castaraleside H methyl ester (**3a**) was obtained as a gummy mass. The ^1H- and ^{13}C-NMR spectra of compounds **3a** and **2a** suggested the presence of the same genin, 2β,3β-28-trihydroxyolean-12-en, with a different type of trioside unit: glucuronic acid attached to the aglycone and the terminal rhamnose, but xylose or galactose in the intermediate position in **3a** and **2a** respectively. The gas chromatographic sugar analysis of alditol acetates of the acid hydrolysate product of **3a** displayed glucitol acetate, xylitol acetate and rhamnitol acetate in a molar ratio of 1 : 1 : 1. Thus, **3a** was confirmed to retain glucuronic acid, xylose and rhamnose.

The FAB-MS in the negative ion mode of compound **3a** exhibited a characteristic molecular ion at *m*/*z* 911 $[M-H]^-$. The negative ion FAB-MS spectrum showed three ion peaks at *m*/*z* 765, 633 and 457 ascribable to the loss of rhamnose, xylose and glucuronic acid methyl ester moieties, respectively. The high resolution electron impact mass spectrum of the aglycone of compound **3a** exhibited a prominent ion at *m*/*z* 458.3752 with an elemental composition of $C_{30}H_{50}O_3$, indicating *retro* Diels–Alder cleavage, characteristic of a Δ^{12}-oleanane skeleton.[7] Other ions appeared at *m*/*z* 234 ($C_{16}H_{26}O$), 203 ($C_{15}H_{23}$) and 133 ($C_{10}H_{13}$). The presence of a CH_2OH group in the part containing rings D and E was indicated by the appearance of a characteristic fragment ion at *m*/*z* 234.1995 ($C_{16}H_{26}O$), which had the highest intensity (49.2%). The FAB-MS (positive ion mode) exhibited a molecular ion peak at *m*/*z* 935 $[M+Na]^+$, corresponding to the molecular formula $C_{47}H_{76}O_{17}$.

The ^{13}C-NMR spectrum of **3a** was also compatible with the structure of the methyl ester of 2β,3β,28-trihydroxy-

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Table I. ^{13}C-NMR Chemical Shifts of Compounds **1a**, **2a** and **3a**

Carbon	1a	2a	3a
C-1	44.4	43.9	44.4
C-2	71.1	71.3	70.9
C-3	83.0	91.4	91.2
C-4	43.0	42.4	42.4
C-5	48.4	56.2	56.5
C-6	17.9	21.5	21.2
C-7	32.8	33.29[a)]	33.2
C-8	39.8	40.8	40.0
C-9	47.0	47.8	47.8
C-10	37.0	36.5	36.6
C-11	23.4	23.1	23.0
C-12	123.1	122.9	122.6
C-13	144.2	144.8	144.8
C-14	42.1	42.3	42.3
C-15	28.0	26.4	26.4
C-16	23.9	28.6	28.6
C-17	46.9	38.0	38.0
C-18	41.8	45.3	45.4
C-19	46.0	46.8	46.8
C-20	30.8	30.9	30.9
C-21	33.9	33.32[a)]	33.4
C-22	32.8	33.29[a)]	33.2
C-23	64.8	28.7	28.7
C-24	14.9	15.8	15.6
C-25	17.3	17.0	17.1
C-26	17.2	18.5	18.3
C-27	26.3	25.7	18.3
C-28	178.0	63.7	62.9
C-29	33.1	33.32[a)]	33.4
C-30	23.7	24.1	24.1
$COOCH_3$	51.6		
Sugar moiety: glucuronic acid			
1′	105.0	105.4	105.4
2′	74.4	78.3	79.5
3′	76.0	76.9	77.7
4′	82.3	75.6	74.4
5′	75.1	76.5	78.3
6′	170.0	170.3	170.4
$COOCH_3$	52.5	52.1	52.0
Sugar moiety: galactose			
1″	106.3	102.4	—
2″	74.6	72.3	—
3″	78.5	76.64[b)]	—
4″	71.6	77.8	—
5″	78.2	76.69[b)]	—
6″	62.5	61.7	—
Sugar moiety: xylose			
1″			102.6
2″			75.6
3″			76.8
4″			78.6
5″			66.9
Sugar moiety: rhamnose			
1‴		101.8	102.3
2‴		72.8	72.3
3‴		73.6	72.8
4‴		74.4	73.6
5‴		69.4	69.5
6‴		18.9	18.9

a—b) Assignments may be interchanged.

olean-12-ene and the three units of sugar moieties, *i.e.* glucuronic acid methyl ester, xylose and rhamnose. In sugar moieties, signals due to the C-2′ of glucuronic acid and C-4″ of xylose, shifted downfield to δ 79.5 and 78.6, respectively, suggesting 1$\rightarrow$2 and 1$\rightarrow$4 linkages, and glucuronic acid attached to the aglycone. C-3 of the aglycone moiety was observed at δ 91.2, and also underwent a large downfield shift because of the attachment of a glucuronic acid moiety.[2)]

On the basis of the foregoing spectral evidence for **3a** and of alditol acetate analysis, the structure of castaraleside H (**3**) could be represented as 3β-*O*-[α-rhamnopyranosyl-(1$\rightarrow$4)-β-xylopyranosyl-(1$\rightarrow$2)-β-glucuronopyranosyl]-2β,3β,28-trihydroxyolean-12-ene.

These three new saponins from *Castanospermum australe* are being reported for the first time.

Experimental

Optical rotations were measured with a JASCO DIP-140 digital polarimeter. Mass spectra (MS) were obtained from Varian MAT-112 (EI-MS), and Varian MAT-312 (positive and negative ion) FAB-MS. ^{1}H-NMR and ^{13}C-NMR were recorded with Bruker AM-300 and Bruker AM-400 (300, 400; 75.43, 100.6 MHz, respectively) and JEOL (500, 125.65 MHz, respectively) spectrometers. The experiments involving proton and carbon magnetic resonance included DEPT-NMR (distortionless enhancement by polarization transfer), COSY-45, 2D-J-resolved, HeteroCOSY (C-H correlations) and differential NOE spectral measurements. Chemical shifts are given on a δ (ppm) scale with tetramethylsilane (TMS) as an internal standard.

The abbreviations used for NMR data are as follows: s, singlet; d, doublet; dd, double doublet; t, triplet; q, quartet; br, broad; m, multiplet. Gas chromatography (GC) was run on a Hitachi G-3000 gas chromatograph with a flame ionization detector; conditions: column, Supelco capillary column SPB 2380, 0.25 mm × 30 m; column temperature, 250 °C; carrier gas, N_2.

1) Isolation The leaves of *Castanospermum australe* were collected from Aram Bagh Garden, Karachi, in October, 1987. The identity of the plant material was carried out by Prof. S.I. Ali, Department of Botany, University of Karachi. An authentic voucher specimen has been deposited in the Botanical Herbarium of the University of Karachi. Fresh leaves (6 kg) of the plant were soaked in MeOH, kept at room temperature for one week, and this procedure was repeated thrice. The combined methanolic extract was evaporated under reduced pressure. The dark brown material (142 g), so obtained, was suspended in water, then partitioned first with hexane and thereafter with EtOAc. The aqueous portion was extracted several times with presaturated *n*-BuOH. The *n*-BuOH fractions were combined together and evaporated under a high vacuum. TLC of the *n*-BuOH extract displayed a mixture of variable saponin constituents on spraying with ceric sulphate (10% w/v in 10% H_2SO_4). and vanillin reagents (1% w/v in 10% H_2SO_4).

The crude saponin mixture, obtained on evaporation of *n*-BuOH, was subjected to methylation. To a solution of crude saponin (10 g) in MeOH was added an ethereal solution of CH_2N_2 (in excess), and the mixture kept overnight at room temperature. Removal of the solvent from the reaction mixture furnished the methylated saponins.

The methylated saponins were subjected to column chromatography on silica gel, and the separation afforded four fractions, I—IV. Fraction III was eluted with $CHCl_3$–MeOH (75 : 25) and reloaded on a fine silica gel column (400#size). The constituents were eluted with a $CHCl_3$–MeOH–H_2O–benzene (7.5 : 2 : 0.25 : 1) solvent to provide castaraleside F methyl ester (**1a**) (17 mg). Fraction IV was eluted with $CHCl_2$–MeOH (1 : 1) and was again subjected to column chromatography by using fine silica gel (400#size). It was eluted with $CHCl_3$–MeOH–H_2O–benzene (6.5 : 3.0 : 0.5 : 1.0) to furnish castaraleside G methyl ester (**2a**) (7 mg) and castaraleside H methyl ester (**3a**) (5.7 mg).

Castaraleside F Methyl Ester (1a) Gummy mass. $[\alpha]^{20}$: +32.2°

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(c=0.90, MeOH). ^{1}H-NMR (500 MHz, C_5D_5N) δ: 0.89 (6H, s, H-26, 29), 0.92 (3H, s, H-30), 1.20 (3H, s, H-24), 1.37 (3H, s, H-25), 1.60 (3H, s, H-27), 3.19 (1H, dd, J=14.0, 4.0 Hz, H-18), 3.70 (3H, s, glu A-Me), 3.82 (3H, s, 28-Me), 3.98 (1H, t, J=9.3 Hz, H-2″), 4.18 (1H, dd, J=9.3, 4.0 Hz, H-3″), 4.09 (1H, t, J=8.5 Hz, H-2′), 4.20 (1H, t, J=8.5 Hz, H-3′), 4.3 (1H, d, J=3.6 Hz, H-3), 4.43 (1H, t, J=8.5 Hz, H-4′), 4.53 (1H, d, J=9.0 Hz, H-5′), 5.03 (1H, d, J=8.0 Hz, H-1″), 5.28 (1H, d, J=8.0 Hz, H-1′). ^{13}C-NMR (CD_3OD, 75 MHz): Table I. FAB-MS (negative) m/z: 839 $[M-H]^-$, 677 $[M-H-Gal]^-$, 501 $[M-\text{aglycone moiety}]^-$. HR-MS m/z: 839.4410 (M^+-H, Calcd for $C_{43}H_{67}O_{16}$: 839.4429).

Castaraleside G Methyl Ester (2a) $[\alpha]^{20}$: +114.9° (c=0.74, MeOH). ^{1}H-NMR (500 MHz, C_5D_5N) δ: 0.72 (3H, s, H-25), 0.90 (3H, s, H-24), 1.01 (3H, s, H-29), 1.23 (3H, s, H-26), 1.27 (3H, s, H-30), 1.31 (3H, s, H-23), 1.45 (3H, s, H-27), 1.78 (3H, d, J=6.1 Hz, Rha-Me), 3.70 (3H, s, glu A–Me), 3.39 (1H, dd, J=14.0, 4.0 Hz, H-18), 4.53 (1H, d, J=9.0 Hz, H-5′), 5.19 (1H, d, J=8.0 Hz, H-1′), 5.31 (1H, t-like, H-12), 5.81 (1H, d, J=7.9 Hz, H-1″), 6.31 (1H, s, H-1‴). ^{13}C-NMR (CD_3OD, 75.0 MHz): Table I. FAB-MS (positive) m/z: 965 $[M+Na]^+$; FAB-MS (negative) m/z: 941 $[M-H]^-$, 795 $[M-H-Rha]^-$, 633 $[M-H-Rha-Gal]^-$, 457 [aglycone moiety]$^-$. HR-MS m/z: 941.5170 (M^+-H, Calcd for $C_{48}H_{77}O_{18}$: 941.5189).

Castaraleside H Methyl Ester (3a) Gummy mass. $[\alpha]^{20}$: +43.3° (c=0.15, MeOH). ^{1}H-NMR (500 MHz, C_5D_5N) δ: 0.78 (3H, s, H-25), 0.98 (3H, s, H-24), 1.00 (3H, s, H-29), 1.22 (3H, s, H-26), 1.29 (3H, s, H-30), 1.30 (3H, s, H-23), 1.54 (3H, s, H-27), 1.81 (3H, d, J=6.1 Hz, Rha-Me), 3.75 (3H, s, glu A–Me), 5.31 (1H, t-like, H-12), 5.00 (1H, d, J=7.6 Hz, H-1″), 5.71 (1H, d, J=8.5 Hz, H-1′), 4.10 (1H, t, J=7.6 Hz, H-2′), 3.90 (1H, d, J=11.8 Hz, H-5″), 3.41 (dd, J=14.0, 4.0 Hz, H-18). ^{13}C-NMR (CD_3OD, 75.0 MHz): Table I. FAB-MS positive ion: m/z 935 $[M+Na]^+$; FAB-MS negative ion: m/z 911 $[M-H]^-$, 765 $[M-H-Rha]^-$, 633 $[M-H-Rha-Xyl]^-$, 457 [aglycone moiety]$^-$. HR-MS m/z: 911.4998 (M^+-H, Calcd for $C_{47}H_{75}O_{17}$: 911.5004).

2) Sugar Analysis Each methyl ester (**1a**—**3a**) (0.5 mg) was treated with $NaBH_4$ (1 mg) in MeOH (0.2 ml) for 15 h at room temperature. The reaction mixture was passed through a short column packed with a Mitsubishi Diaion HP-20, and the adsorbed material was eluted with MeOH after washing the resin with H_2O. The MeOH eluate gave **1b**—**3b**. A solution of each compound (**1a**—**3a** and **1b**—**3b**) (0.5 mg) in dioxane–5% H_2SO_4 aq. (1 : 1) (0.2 ml) was heated at 100 °C for 1 h. The reaction mixture was passed through an Amberlite IR-45 column, the eluate was concentrated, and the residue was treated with $NaBH_4$ (1 mg) in H_2O (0.2 ml) at room temperature for 1 h. The reduced product was passed through an Amberlite IR-120 column, and the eluate was concentrated to dryness. H_3BO_3 was removed by co-distillation with MeOH and the residue was acetylated with Ac_2O–Py (1 : 1) (0.1 ml) at 100 °C for 1 h. Alditol acetates were detected by GC: Galactitol acetate from **1a**; galactitol acetate–glucitol acetate (1 : 1) from (**1b**); rhamnitol acetate–galactitol acetate (1 : 1) from **2a**; rhamnitol acetate–galactitol acetate–glucitol acetate (1 : 1 : 1) from **2b**; rhamnitol acetate–xylitol acetate (1 : 1) from **3a**; rhamnitol acetate–xylitol acetate–glucitol acetate (1 : 1 : 1) from **3b**. GC conditions: column, Supelco SP-2380 capillary column (0.25 mm × 30 m); column temperature, 250 °C; carrier gas, N_2; t_R, rhamnitol acetate 4.9 min, xylitol acetate 7.2 min, galactitol actate 10.1 min, glucitol acetate 11.8 min.

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