New Oleanene Triterpenoid Saponins from *Madhuca longifolia*

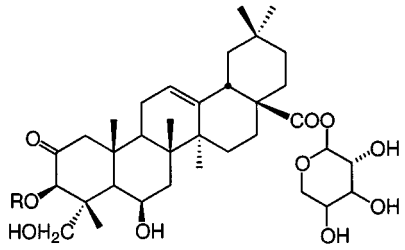
Kazuko Yoshikawa,*,† Masami Tanaka,† Shigenobu Arihara,† Bikas Chandra Pal,‡ Subodh Kumar Roy,‡ Eiko Matsumura,§ and Satoshi Katayama§

Faculty of Pharmaceutical Sciences, Tokushima Bunri University, Yamashiro-Cho, Tokushima 770-8514, Japan, Medicinal Chemistry Division, Indian Institute of Chemical Biology, 4 Raja S. C. Mullick Road, Jadavpur, Calcutta-700 032, India, and Laboratory of Cell Biology, Osaka University of Pharmaceutical Sciences, 4-20-1 Nasahara, Takatsuki Osaka, 569-1094, Japan

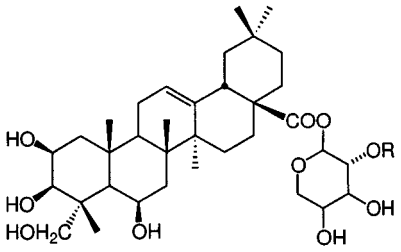
Received July 14, 2000

Four new oleanane-type triterpene glycosides, madlongisides A−D (**1**−**4**), were isolated from the seeds of *Madhuca longifolia*, and their structures were elucidated on the basis of extensive NMR experiments and chemical methods. Also obtained in this investigation were the known compounds mimusopside A, Mi-saponins A, B, and C, and 3-*O*-*β*-D-glucopyranosyl protobassic acid.

Madhuca longifolia (L.) Macbride (syn, *Bassia longifolia* L.) (Sapotaceae) is a tree widely distributed throughout India. The cake was reported to have insecticidal and piscicidal properties.[1] Previous phytochemical studies on this plant have revealed the presence of Mi-saponins A, B,[2] and C.[3] The methanolic extract of the seeds of this plant showed many additional saponin spots on TLC. Therefore, we initiated a phytochemical investigation of the saponins of this species. We have isolated four new oleanene saponins, madlongisides A (**1**), B (**2**), C (**3**), and D (**4**), along with five known oleanene saponins, mimusopside A,[4] Mi-saponins A,[2] B,[2] and C,[3] and 3-*O*-*β*-D-glucopyranosyl protobassic acid.[5−7] The structures of these compounds were established on the basis of extensive spectroscopic as well as chemical degradation.



1 R=H
2 R=Glucosyl



3 R=H
4 R=Rhamnosyl

Madlongiside A (**1**) was obtained as an amorphous solid. The molecular formula was deduced as $C_{35}H_{54}O_{10}$ from a $[M - H]^-$ peak observed at *m*/*z* 633 in the negative FABMS and from its DEPT ^{13}C NMR data. The IR spectrum showed hydroxy (3420 cm^{-1}) and carbonyl group (1720 cm^{-1}) absorptions. The EIMS showed an ion peak at *m*/*z* 502 $[M - 132]^+$ and other characteristic peaks at *m*/*z* 254 and 248 due to loss of the sugar, H transfer, and retro Diels−Alder fission, which suggested the occurrence of three hydroxy and one carbonyl group in the A/B rings and one carboxy group in the C/D rings on the amyrin skeleton.[8] The ^{13}C NMR spectrum showed 35 signals, of which 30 were assigned to a triterpenoid moiety and five to a pentose sugar moiety. The ^1H NMR spectrum showed the presence of six methyl signals, a vinylic proton, an isolated oxymethylene, and an isolated methylene. The ^{13}C NMR signals at *δ* 122.8 and 143.7 were ascribable to C-12 and C-13 and confirmed the Δ^{12} oleanene skeleton.[9] A signal at *δ* 176.4 and the carbon resonances of ring D and E suggested the occurrence of a glycosylated COOH at C-28.[9] Assignments of the significant proton and carbon resonances of the aglycon were made using $^1H-^1H$ COSY, HMQC, HMBC, and ROESY. In the ^{13}C NMR spectrum of **1**, the carbonyl (*δ* 212.6) and the shifted C-1 (+17.0 ppm) and C-3 (+4.6 ppm) signals compared well with those of hederagenin[10] and indicated the carbonyl group to be at C-2. In the HMBC experiment, the methylene protons (C-1) at *δ* 2.35 and 2.61 gave cross-peaks with the carbonyl carbon at *δ* 212.6 (C-2), the oxymethine carbon (C-3) at *δ* 78.5, the methine carbon (C-5) at *δ* 47.9, the methine carbon at *δ* 48.6 (C-9), and quaternary carbon at *δ* 43.7 (C-10). The oxymethine proton at *δ* 5.32 (H-3) gave further cross-peaks with the methylene carbon at *δ* 56.0 (C-1), the carbonyl carbon at *δ* 212.6 (C-2), the quaternary carbon at *δ* 50.8 (C-4), the methine carbon at *δ* 47.9 (C-5), oxymethylene carbon at *δ* 65.2 (C-23), and the methyl carbon at *δ* 15.8 (C-24). Hence, the aglycon of **1** was formulated as 3*β*,6*β*,23-trihydroxy-2-oxo-olean-12-ene-28-oic acid (2-oxouncargenin A), a new triterpenoid sapogenin. Acid hydrolysis of **1** afforded L-arabinose, which was confirmed by specific rotation using chiral detection by HPLC analysis.[11] The H-1 and H-2 vicinal coupling constant (5.8 Hz) for arabinose indicated that this sugar occurred in **1** as the α-anomeric in $^4C_1$ configuration.[12] Accordingly, **1** was formulated as 3*β*,6*β*,23-trihydroxy-2-oxo-olean-12-ene-28-oic acid (2-oxouncargenin A) 28-*O*-α-L-arabinopyranoside.

The negative FABMS of madlongiside B (**2**) revealed a deprotonated molecular ion peak at *m*/*z* 795 $[M - H]^-$, 162 mass units more than that of **1**. Acid hydrolysis of **2**

* To whom correspondence should be addressed. Tel.: 88-622-9611. Fax: 88-655-3057. E-mail: yosikawa@ph.bunri-u.ac.jp.
† Tokushima Bunri University.
‡ Indian Institute of Chemical Biology.
§ Osaka University of Pharmaceutical Sciences.

10.1021/np000351r CCC: $19.00
Published on Web 10/28/2000

afforded L-arabinose and D-glucose. The ^{1}H and ^{13}C NMR spectra of **2** indicated the presence of α-arabinopyranosyl and β-glucopyranosyl units. A ^{13}C NMR comparison of **2** with **1** showed a 9.5 ppm glycosilation shift[13,14] of C-3, demonstrating that the second sugar linkage was at C-3-OH. HMBC correlations between H-1 of glucose and C-3, and H-1 of arabinose and C-28, suggested that the glucosyl and arabinosyl units were located at C-3 and C-28, respectively. Accordingly, **2** was formulated as 3-*O*-β-D-glucopyranosyl-3β,6β,23-trihydroxy-2-oxo-olean-12-ene-28-oic acid (2-oxouncargenin A) 28-*O*-α-L-arabinopyranoside.

Madlongiside C and D were identified as compounds **3** and **4**, respectively, previously obtained from the enzymatic hydrolysis of Mi-saponin A, isolated from the seed kernels of *Madhuca longifolia* by Kitagawa et al.[2] As far as we know, full assignments of the proton and carbon resonances of **3** and **4** have not been reported previously. Madlongisides C and D are described here for the first time from a natural source and with complete NMR data.

The compounds madlongiside A−D (**1**−**4**) were all tested for activity against Kato III cells.[15] No activity was observed in this assay.

Experimental Section

General Experimental Procedures. Melting points were measured with a Yanagimoto micromelting point apparatus and are uncorrected. Optical rotations were taken on a JASCO DIP-360 polarimeter. IR spectra were recorded on a JASCO FT/IR-5300, and NMR spectra were run on Varian UNITY 600 and/or a JEOL GSX-400 spectrometer in C_5D_5N solution, using TMS as internal standard. NMR experiments included ^{1}H−^{1}H COSY, HMQC, HMBC, TOCSY, and ROESY. Coupling constants (*J* values) are given in hertz. The FABMS (Xe gun, 10 kV, triethylene glycol as the matrix) was measured on a JEOL JMS-HX-100 mass spectrometer. HPLC separations were performed with a Hitachi HPLC system (L-6200 Pump, L-4000 UV).

Plant Material. The seeds of *Madhuca longifolia* (L.) Macbride were collected in June 1998 from Jadavpur, Calcutta, India, and identified by Dr. N. D. Paria, Department of Botany, University of Calcutta. A voucher specimen is deposited in the Herbarium of this Institute.

Extraction and Isolation. The air-dried seeds (2.2 kg) of *M. longifolia* were defatted with petroleum ether (boiling point range 60−80 °C) and then extracted with MeOH by percolation. The MeOH extract was evaporated to dryness *in vacuo*. The residue (180 g) was suspended in water and extracted successively with EtOAc and *n*-BuOH (3 × 1L, each). Solutions were evaporated to dryness *in vacuo* to provide EtOAc-soluble (22 g), *n*-BuOH-soluble (65 g), and water-soluble portions (90 g). An aliquot (20 g) of *n*-BuOH-soluble portion was chromatographed on silica gel (500 g) eluting with $CHCl_3$−MeOH (9:1, 4:1, 7:3, 3:2) and afforded fractions I (1.50 g), II (1.92 g), III (2.75 g), and IV (3.80 g). Fraction I was purified by repeated CC over silica gel eluting with $CHCl_3$−MeOH (4:1) to afford crude madlongisides A (20 mg) and C (30 mg), which were purified further by HPLC on ODS with 65% MeOH to furnish madlongiside A (**1**, 7 mg) and C (**3**, 10 mg), respectively. Fraction II was also purified by chromatography over silica gel eluting with $CHCl_3$−MeOH (7:3) to yield madlongisides B (**2**, 10 mg) and D (**4**, 0.15 g) and 3-*O*-β-D-glucopyranosyl protobassic acid (0.25 g). Similarly, chromatography over silica gel of fractions III and IV eluting with $CHCl_3$−MeOH (3:2) and (1:1) yielded mimusopside A (0.36 g), Mi-saponins A (0.19 g) and B (1.1 g), and crude Mi-saponin C (0.37 g). Preparative HPLC of the last compound on ODS with 24% CH_3CN furnished Mi-saponin C (0.1 g).

Madlongiside A (1): colorless needles; mp 202−204 °C; $[\alpha]^{25}_D$ +34.5° (*c* 0.8, MeOH); IR (dry film) ν_{max} 3420 (OH), 1720 (C=O) cm^{-1}; ^{1}H NMR (400 MHz, C_5D_5N) δ 0.89 (3H, s, H_3-29), 0.95 (3H, s, H_3-30), 1.21 (3H, s, H_3-27), 1.51 (3H, s, H_3-24), 1.64 (3H, s, H_3-25), 1.68 (3H, s, H_3-26), 2.35 (1H, d, *J* = 12.0, H-1α), 2.58 (1H, br s, H-5α), 2.61 (1H, d, *J* = 12.0, H-1β), 3.32 (1H, dd, *J* = 13.0, 4.0 Hz, H-18), 3.91 (1H, dd, *J* = 11.0, 2.0 Hz, H-5 of ara), 4.12 (1H, d, *J* = 11.0 Hz, H_2-23), 4.25 (1H, d, *J* = 11.0 Hz, H_2-23), 4.32 (1H, m, H-3 of ara), 4.41 (1H, dd, *J* = 10.0, 3.5 Hz, H-5 of ara), 4.45 (1H, m, H-4 of ara), 5.07 (1H, s, H-3), 5.18 (1H, s, H-6), 5.52 (1H, dd, *J* = 3.0, 3.0 Hz, H-12), 6.27 (1H, d, *J* = 5.8 Hz, H-1 of ara); ^{13}C NMR (100 MHz, C_5D_5N) δ 212.6 (s, C-2), 176.4 (s, C-28), 143.7 (s, C-13), 122.8 (d, C-12), 78.5 (d, C-3), 67.6 (d, C-6), 65.2 (t, C-23), 56.0 (t, C-1), 50.8 (s, C-4), 48.6 (d, C-9), 47.9 (d, C-5), 47.4 (s, C-17), 46.5 (t, C-19), 43.7 (s, C-10), 43.1 (s, C-14), 42.0 (d, C-18), 41.1 (t, C-7), 40.0 (s, C-8), 34.4 (t, C-21), 33.4 (q, C-29), 33.0 (t, C-22), 31.2 (s, C-20), 28.6 (t, C-15), 26.4 (q, C-27), 24.4 (t, C-16), 24.2 (q, C-30), 23.6 (t, C-11), 18.9 (q, C-26), 18.8 (q, C-25), 15.8 (q, C-24), Ara: 96.0 (d, C-1), 74.1 (d, C-3), 71.5 (d, C-2), 68.4 (d, C-4), 66.5 (t, C-5); FABMS *m/z* [M − H]$^-$ 663; EIMS *m/z* 472 (4.0), 426 (5.9), 254 (2.0), 248 (100), 233 (11.0). 219 (6.5), 203 (95), 202 (10.0), 189 (13.5), 133 (22.0), 119 (13.3), 105 (12.9); *anal*. C 64.02%, H 8.71%, calcd for $C_{35}H_{54}O_{10}\cdot H_2O$, C, 64.39%, H 8.65%.

Madlongiside B (2): colorless needles; mp 212−214 °C; $[\alpha]^{25}_D$ +15.7 (*c* 1.5, MeOH); IR (dry film) ν_{max} 3400 (OH), 1735, 1710 (C=O) cm^{-1}; ^{1}H NMR (600 MHz, C_5D_5N) δ 0.88 (3H, s, H_3-29), 0.94 (3H, s, H_3-30), 1.22 (3H, s, H_3-27), 1.14 (2H m, H-15α, H-21β), 1.25 (1H, m, H-19α), 1.34 (1H, ddd, *J* = 13.5, 13.5, 4.0 Hz, H-21α), 1.59 (3H, s, H_3-24), 1.60 (3H, s, H_3-25), 1.68 (3H, s, H_3-26), 1.74 (2H, m, H-16α, H-19α), 1.85 (1H, dd, *J* = 12.0, 3.0 Hz, H-7β), 1.90 (2H, m, H-11α, H-16β), 1.97 (1H, m, H-7α), 1.98 (1H, ddd, *J* = 12.0, 12.0, 3.0 Hz, H-22β), 2.03 (1H, dd, *J* = 12.0, 3.0 Hz, H-22α), 2.16 (2H, m, H-9α, H-11β), 2.25 (1H, d, *J* = 12.0 Hz, H-1α), 2.35 (1H, ddd, *J* = 13.5, 13.5, 3.5 Hz, H-15β), 2.48 (1H, d, *J* = 12.0 Hz, H-1β), 2.50 (1H, br s, H-5α), 3.29 (1H, dd, *J* = 14.0, 4.0 Hz, H-18), 3.90 (1H, dd, *J* = 9.5, 2.5 Hz, H-5 of ara), 3.90 (1H, m, H-5 of glc), 4.05 (1H, dd, *J* = 9.0, 8.0 Hz, H-2 of glc), 4.11 (1H, d, *J* = 11.0 Hz, H_2-23), 4.15 (1H, dd, *J* = 9.0, 9.0 Hz, H-3 of glc), 4.22 (1H, dd, *J* = 9.5, 9.0 Hz, H-4 of glc), 4.34 (1H, m, H-3 of ara), 4.35 (1H, dd, *J* = 12.0, 4. 5 Hz, H-6 of glc), 4.39 (1H, d, *J* = 11.0 Hz, H_2-23), 4.40 (1H, dd, *J* = 9.5, 3.0 Hz, H-5 of ara), 4.42 (1H, dd, *J* = 12.0, 2. 5 Hz, H-6 of glc), 4.45 (1H, m, H-4 of ara), 4.58 (1H, dd, *J* = 7.5, 6.0 Hz, H-2 of ara), 5.13 (1H, br s, H-6), 5.23 (1H, d, *J* = 8.0 Hz, H-1 of glc), 5.32 (1H, s, H-3), 5.49 (1H, dd, *J* = 3.0, 3.0 Hz, H-12), 6.26 (1H, d, *J* = 6.0 Hz, H-1 of ara); ^{13}C NMR (125 MHz, C_5D_5N) δ 210.5 (s, C-2), 176.4 (s, C-28), 143.7 (s, C-13), 122.8 (d, C-12), 82.8 (d, C-3), 67.6 (d, C-6), 64.4 (t, C-23), 56.8 (t, C-1), 51.2 (s, C-4), 48.6 (d, C-9), 48.4 (d, C-5), 47.4 (s, C-17), 46.4 (t, C-19), 43.4 (s, C-10), 43.1 (s, C-14), 42.0 (d, C-18), 41.1 (t, C-7), 40.0 (s, C-8), 34.4 (t, C-21), 33.4 (q, C-29), 33.0 (t, C-22), 31.2 (s, C-20), 28.6 (t, C-15), 28.6 (t, C-15), 26.5 (q, C-27), 24.2 (t, C-11), 24.0 (q, C-30), 23.6 (t, C-16), 18.9 (q, C-25), 18.7 (q, C-26), 16.3 (q, C-24), Ara: 96.0 (d, C-1), 74.1 (d, C-3), 71.5 (d, C-2), 68.4 (d, C-4), 66.5 (t, C-5), Glc: 104.3 (d, C-1), 78.5 (d, C-5), 78.0 (d, C-3), 74.9 (d, C-2), 71.4 (d, C-4), 62.4 (d, C-6); FABMS *m/z* [M − H]$^-$ 795, [M − H − ara]$^-$ 663; *anal*. C 60.46%, H 7.98%, calcd for $C_{41}H_{64}O_{15}\cdot H_2O$, C, 60.43%, H 8.16%.

Madlongiside C (3): colorless needles; mp 196−198 °C; $[\alpha]^{25}_D$ +32.0° (*c* 1.2, MeOH); IR (dry film) ν_{max} 3400 (OH), 1735 (C=O) cm^{-1}; ^{1}H NMR (400 MHz, C_5D_5N) δ 0.89 (3H, s, H_3-29), 0.95 (3H, s, H_3-30), 1.23 (3H, s, H_3-27), 1.73 (3H, s, H_3-26), 2.06 (3H, s, H_3-24), 2.29 (3H, s, H_3-25), 2.41 (1H, br s, H-5α), 3.30 (1H, dd, *J* = 13.0, 4.0 Hz, H-18), 3.91 (1H, dd, *J* = 11.0, 2.0 Hz, H-5 of ara), 4.05 (1H, d, *J* = 11.0 Hz, H_2-23), 4.32 (1H, m, H-3 of ara), 4.34 (1H, d, *J* = 4.0 Hz, H-3), 4.36 (1H, d, *J* = 11.0, H_2-23), 4.39 (1H, m, H-5 of ara), 4.42 (1H, m, H-4 of ara), 4.59 (2H, m, H-2, H-2 of ara), 5.16 (1H, br s, H-6), 5.56 (1H, dd, *J* = 3.0, 3.0 Hz, H-12), 6.28 (1H, d, *J* = 5.8 Hz, H-1 of ara); ^{13}C NMR (100 MHz, C_5D_5N) δ 176.5 (s, C-28), 143.6 (s, C-13), 123.0 (d, C-12), 73.2 (d, C-3), 72.1 (d, C-2), 67.9 (d, C-6), 67.4 (t, C-23), 49.4 (d, C-5), 49.3 (d, C-9), 47.8 (t, C-1), 47.5 (s, C-17), 46.5 (t, C-19), 43.9 (s, C-4), 43.1 (s, C-14), 42.1 (d, C-18), 41.4 (t, C-7), 39.7 (s, C-8), 37.4 (s, C-10), 34.4 (t, C-21), 33.4 (q, C-29), 33.0 (t, C-22), 31.2 (s, C-20), 28.5 (t, C-15), 26.5 (q, C-27), 24.4 (t, C-11), 24.0 (q, C-30), 23.5 (t, C-16), 19.4 (q,

C-26), 19.1 (q, C-25), 16.6 (q, C-24), Ara: 96.0 (d, C-1), 74.1 (d, C-3), 71.5 (d, C-2), 68.3 (d, C-4), 66.4 (t, C-5); FABMS *m*/*z* [M − H] $^-$ 635; *anal*. C 64.35%, H 9.11%, calcd for $C_{35}H_{56}O_{10}\cdot H_2O$, C, 64.20%, H 8.93%.

Madlongiside D (4): colorless needles; mp 230−232 °C; $[\alpha]^{25}_D$ −12.9° (*c* 1.8, MeOH); IR (dry film) ν_{max} 3410 (OH), 1740 (C=O) cm^{-1}; ^{1}H NMR (600 MHz, C_5D_5N) δ 0.89 (3H, s, H_3-29), 0.98 (3H, s, H_3-30), 1.14 (1H, ddd, J = 11.0, 3.5 3.5 Hz, H-21β), 1.24 (3H, s, H_3-27), 1.29 (1H, dd, J = 15.5. 5.5 Hz, H-19β), 1.35 (3H, m, H-1α, H-15α, H-21α), 1.73 (1H, ddd, J = 11.0, 3.5, 3.5 Hz, H-22α), 1.69 (3H, s, H_3-26), 1.84 (1H, dd, J = 15.5, 15.5 Hz, H-19α), 1.91 (1H, dd, J = 12.0, 6.0, Hz, H-9α), 1.92 (1H, br s, H-5α), 2.00 (2H, m, 7β, 22β), 2.03 (3H, s, H_3-24), 2.08 (1H, m, 7α), 2.11 (1H, ddd, J = 12.0, 6.0, 3.5 Hz, H-11α), 2.26 (1H, m, 15β), 2.27 (3H, s, H_3-25), 2.36 (1H, ddd, J = 12.0, 12.0, 6.0 Hz, H-11β), 2.40 (1H, dd, J = 14.5, 2.5 Hz, H-1β), 3.33 (1H, dd, J = 15.5, 5.0 Hz, H-18), 3.91 (1H, dd, J = 11.0, 3.5 Hz, H-5 of ara), 4.01 (1H, d, J = 10.0 Hz, H_2-23), 4.30 (1H, dd, J = 9.5, 9.5 Hz, H-4 of rha), 4.32 (1H, J = 4.0 Hz, H-3), 4.34 (1H, d, J = 10.0 Hz, H_2-23), 4.38 (1H, m, H-4 of ara), 4.50 (3H, m, H-3, H-5 of ara, H-5 of rha), 4.54 (1H, dd, J = 9.5, 3.5 Hz, H-3 of rha), 4.62 (2H, m, H-2, H-2 of ara), 5.14 (1H, dd, J = 3.0, 3.0 Hz, H-6), 5.56 (1H, dd, J = 3.5, 3.5 Hz, H-12), 5.96 (1H, br s, H-1 of rha), 6.43 (1H, d, J = 4.0 Hz, H-1 of ara); ^{13}C NMR (125 MHz, C_5D_5N) δ 176.3 (s, C-28), 143.6 (s, C-13), 123.0 (d, C-12), 73.3 (d, C-3), 72.1 (d, C-2), 68.1 (d, C-6), 67.5 (t, C-23), 49.4 (d, C-5 and C-9), 47.7 (t, C-1), 47.7 (s, C-17), 46.6 (t, C-19), 43.9 (s, C-4), 43.1 (s, C-14), 42.1 (d, C-18), 41.2 (t, C-7), 39.7 (s, C-8), 37.4 (s, C-10), 34.5 (t, C-21), 33.5 (q, C-29), 33.1 (t, C-22), 31.2 (s, C-20), 28.8 (t, C-15), 26.5 (q, C-27), 24.4 (t, C-11), 24.1 (q, C-30), 23.5 (t, C-16), 19.4 (q, C-25), 18.9 (q, C-26), 16.5 (q, C-24), Ara: 93.8 (d, C-1), 75.3 (d, C-2), 71.7 (d, C-3), 67.2 (d, C-4), 64.2 (t, C-5), Rha: 101.6 (d, C-1), 74.1 (d, C-4), 72.8 (d, C-2 and C-3), 70.6 (d, C-5), 19.1 (q, C-6); FABMS *m*/*z* [M − H]$^-$ 781, [M − H − ara − rha]$^-$ 503; *anal*. C 61.12%, H 8.81%, calcd for $C_{41}H_{66}O_{14}\cdot H_2O$, C, 61.48%, H 8.56%.

Identification of Component Sugar of Madlongisides A−D (1−4). A solution of each compound (2−3 mg) in 5% H_2SO_4−dioxane (1:1) was heated at 100 °C for 3 h. The reaction mixture was diluted with H_2O, neutralized with Amberlite IRA-35, and evaporated *in vacuo* to dryness. The identification and the D or L configuration of each sugar was determined by using RI detection (Waters 410) and chiral detection (Shodex OR-1) by HPLC (Shodex RSpak NH_2P-50 4D column, CH_3CN−H_2O−H_3PO_4, 95:5:1, 1 mL/min, 47 °C) by comparison with an authentic sugar (10 mmol each of D-glc, L-ara, and L-rha). The sugar portion gave the following peaks: L-(+)-rha 6.40 min; L-(+)-ara 10.80 min; D-(+)-glc 20.70; ara from **1** and **3**, ara and glc from **2**, ara and rha from **4**.

References and Notes

(1) Sastri, M. N. *The Wealth of India Raw Materials*; CSIR: New Delhi, 1962; Vol. 6, p 207.
(2) Kitagawa, I.; Inada, A.; Yoshioka, I.*Chem. Pharm. Bull*. **1975**, *23*, 2268−2278.
(3) Kitagawa, I.; Shirakawa, K.; Yoshikawa, M. *Chem. Pharm. Bull*. **1978**, *26*, 1100−1110.
(4) Sahu, N. P. *Phytochemistry* **1996**, *41*, 883−886.
(5) Kitagawa, I.; Inada, A.; Yoshioka, I.; Somanthan, R.; Sultanbawa, M. U. S. *Chem. Pharm. Bull*. **1972**, *20*, 630−632.
(6) Yoshioka, I.; Inada, A.; Kitagawa, I. *Tetrahedron* **1974**, *30*, 707−714.
(7) Jiang, Y.; Ali, A. O.; Guillaume, D.; Weinger, B.; Anton, R. *Phytochemistry* **1994**, *35*, 1013−1015.
(8) Karliner, J.; Djerassi, C. *J. Org. Chem*. **1966**, *31*, 1945−1956.
(9) Mahato, S. B.; Kundu, A. P. *Phytochemistry* **1994**, *37*, 1517−1575.
(10) Takemoto T.; Arihara S.; Yoshikawa K.; Kusumoto K.; Hayashi T. *Yakugaku Zasshi* **1984**, *103*, 246−255.
(11) Yoshikawa, K.; Satou, Y.; Tokunaga, Y.; Tanaka, M.; Arihara, S. *J. Nat. Prod*. **1998**, *61*, 440−445.
(12) Ishii, H.; Kitagawa, I.; Matsushita, K.; Shirakawa, K.; Tori, K.; Tozyo, T.; Yoshikawa, M.; Yoshimura, Y. *Tetrahedron Lett*. **1981**, *22*, 1529−1532.
(13) Tori, K.; Seo, S.; Sakurai, K.; Tomita, Y. *Tetrahedron Lett*. **1977**, 179−182.
(14) Kasai, R.; Ogiwara, M.; Asakawa, J.; Mizutani, K.; Tanaka, O. *Tetrahedron* **1979**, *35*, 1427−1432.
(15) Mosmann, T. *J. Immunol. Methods* **1983**, *65*, 55−63.

NP000351R