Triterpenoid Saponins of Aquifoliaceous Plants. V.¹⁾ Ilexosides XV—XIX from the Barks of *Ilex crenata* THUNB.²⁾

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Five new saponins, ilexosides XV—XIX, were isolated from the fresh bark of *Ilex crenata*, and their structures were elucidated on the basis of chemical and physicochemical evidence. Ilexosides XV—XVII are 3,28-bisdesmosides of siarasinolic acid, whereas ilexosides XVIII and XIX are those of pomolic acid.

Keywords *Ilex crenata*; Aquifoliaceae; pentacyclic triterpene; ilexoside; pomolic acid; siarasinolic acid; bisdesmoside; saponin

In a previous paper, we reported the isolation and structures of six saponins from the fruit of *Ilex crenata* THUNB.¹⁾ Continuing with our study of the saponin constituents of this plant we now described the isolation and the structures of five new saponins from the bark of the title plant.

The 70% MeOH extract of the fresh bark (8 kg) of *Ilex crenata* THUNB. was subjected to Amberlite XAD-2 column chromatography to give a saponin fraction (45 g). Repeated separation of the saponin fraction by reversed-phase octadecyl silica (ODS) and/or ordinary-phase SiO₂ column chromatography furnished five new saponins, ilexosides XV (1, 0.54 g), XVI (2, 0.14 g), XVII (3, 0.04 g), XVIII (4, 0.12 g) and XIX (5, 0.13 g).

Ilexoside XV (1) was obtained as an amorphous powder and had the molecular formula C₄₇H₇₆O₁₈ as analyzed by positive fast atom bombardment mass spectrometry (FAB-MS) and carbon counts in the carbon-13 nuclear magnetic resonance (¹³C-NMR) spectrum. On acid hydrolysis, 1 afforded L-arabinose and D-glucose in the ratio of 1:2. The ¹H-NMR spectrum of 1 indicated the presence of seven tertiary methyl groups (δ 0.90, 0.99, 0.99, 1.15, 1.17, 1.30, 1.66), one trisubstituted olefinic proton (δ 5.52, brt), one α -arabinosyl unit [H-1: δ 4.76 (d, $J=7.5$ Hz)], and two β -glucosyl units [H-1: δ 5.37 (d, $J=7.5$ Hz), 6.36 (d, $J=8.0$ Hz)]. Compound 1 provided methyl siarasinolate (6)³⁾ on methanolysis. The electron impact mass spectrum (EI-MS) of 1 acetate showed fragment ion peaks due to a terminal hexosyl cation (m/z 331) and a hexosylpentosyl cation (m/z 547). The arabinosyl C-3 signal appeared at lower field by +9.5 ppm than that of ziyu-glucoside I (7)⁴⁾ because of the glycosylation shift,⁵⁾ demonstrating that a β -glucopyranosyl group is located at the C-3-OH of arabinose. Therefore, 1 was formulated as 3-*O*- β -D-glucopyranosyl (1 $\rightarrow$ 3)- α -L-arabinopyranosyl siarasinolic acid 28-*O*- β -D-glucopyranoside.

Ilexoside XVI (2), C₄₉H₇₈O₁₉, was obtained as an amorphous powder. The FAB-MS of 2 revealed a quasi-molecular ion peak at m/z 993 [M+Na]⁺, 42 mass units more than 1. The ¹H-NMR spectrum of 2 showed the presence of an acetyl group (3H, s at δ 2.29), one α -arabinosyl unit [H-1: δ 4.74 (d, $J=8.0$ Hz)], and two β -glucosyl units [H-1: δ 5.05 (d, $J=7.5$ Hz), 6.36 (d, $J=8.0$ Hz)]. On mild alkaline hydrolysis with 2% KOH, compound 2 afforded 1. A ¹H- and ¹³C-NMR spectral comparison of 2 with 1, revealed an acylation shift at the C₂ (position) [+1.40 ppm (H-2), +0.3 ppm (C-2), -2.6 ppm (C-1) and

-2.8 ppm (C-3)] of the arabinosyl moiety of 2. Therefore, in 2, the *O*-2 of the arabinosyl moiety at C-3 of the aglycone should be acetylated. Accordingly, ilexoside XVI was formulated as 3-*O*-[β -D-glucopyranosyl(1 $\rightarrow$ 3)]-2-*O*-acetyl- α -L-arabinopyranosyl siarasinolic acid 28-*O*- β -D-glucopyranoside.

Ilexoside XVII (3), C₅₃H₈₆O₂₃, was obtained as an amorphous powder. The FAB-MS of 3 revealed a quasi-molecular ion peak at m/z 1113 [M+Na]⁺, 162 mass units more than 1. The ¹H- and ¹³C-NMR spectra of 3 showed similar patterns to those of 1 except for the region of hydroxymethine signals. Compound 3 afforded L-arabinose and D-glucose in the ratio of 1:3 on acid hydrolysis. The ¹H-NMR spectrum indicated the presence of one α -arabinosyl unit [H-1: δ 4.81 (d, $J=7.0$ Hz)] and three β -glucopyranosyl units [H-1: δ 5.31 (d, $J=7.5$ Hz), 5.52 (d, $J=8.0$ Hz), 6.36 (d, $J=8.0$ Hz)]. The EI-MS of 3 acetate showed fragment ion peaks due to a terminal hexosyl cation at (m/z 331) and a hexosyl(hexosyl)pentosyl cation (m/z 835). A ¹³C-NMR spectral comparison of 3 with 1 revealed a glycosylation shift (+6.8 ppm) at the C-2 signal (from δ 71.9 to 78.7) of the arabinopyranosyl moiety, indicating a β -glucopyranosyl group to be located at C-2 of arabinopyranosyl moiety. Therefore, 3 was formulated as 3-*O*-[β -D-glucopyranosyl(1 $\rightarrow$ 2)]-[β -D-glucopyranosyl(1 $\rightarrow$ 3)]- α -L-arabinopyranosyl siarasinolic acid 28-*O*- β -D-glucopyranoside.

Ilexoside XVIII (4) obtained as an amorphous powder, had the same molecular formula C₅₃H₈₆O₂₃ [FAB-MS, m/z 1113 (M+Na)⁺] as 3. Compound 4 afforded L-arabinose and D-glucose in the ratio of 1:3 on acid hydrolysis. The ¹H-NMR spectrum of 4 indicated the presence of six tertiary methyl groups (δ 0.88, 1.11, 1.18, 1.25, 1.41, 1.70), one secondary methyl group [δ 1.07 (d, $J=6.0$ Hz)], one trisubstituted olefinic proton (δ 5.56, brt), one α -arabinosyl unit [H-1: δ 4.74 (d, $J=7.5$ Hz)], and three β -glucosyl units [H-1: δ 5.32 (d, $J=7.5$ Hz), 5.51 (d, $J=7.5$ Hz), 6.29 (d, $J=7.5$ Hz)]. Treatment of 4 with crude cellulase gave pomolic acid (8)^{6,7)} as the aglycone. The EI-MS of 4 acetate showed the fragment ion peaks due to a terminal hexosyl cation (m/z 331) and a hexosyl(hexosyl)pentosyl cation (m/z 835). The carbon signals due to the sugar moieties are superimposable on those of 3, indicating that the sugar moieties are the same. Therefore, 4 was formulated as 3-*O*-[β -D-glucopyranosyl(1 $\rightarrow$ 2)]-[β -D-glucopyranosyl(1 $\rightarrow$ 3)]- α -L-arabinopyranosyl pomolic acid 28-*O*- β -D-glucopyranoside.

Chart 1

Ilexoside XIX (5), C₅₄H₈₆O₂₃ was obtained as an amorphous powder and afforded L-arabinose, D-glucose and D-xylose in the ratio of 1:2:1 on acid hydrolysis. The carbon signals due to the aglycone of 5 are superimposable on those of 4, indicating that 5 has the same aglycone as 4. The ¹H-NMR spectrum indicated the presence of an acetyl group (3H s, at δ 2.29), one α -arabinosyl unit [H-1: δ 4.66 (d, J =8.0 Hz)], two β -glucosyl units [H-1: δ 5.14 (d, J =6.5 Hz), 6.26 (d, J =8.0 Hz)], and one β -xylosyl unit [H-1: δ 5.06 (d, J =8.0 Hz)]. On enzymatic hydrolysis with crude hesperidinase, 5 provided prosapogenins I (10) and II (9).

Prosapogenin I (10), C₄₃H₆₈O₁₄, obtained as colorless needles, afforded L-arabinose and D-glucose in the ratio of 1:1 on acid hydrolysis. The ¹H-NMR spectrum indicated the presence of an acetyl group (3H s, at δ 2.27). The EI-MS of 10 acetate showed the fragment ion peaks due to a terminal hexosyl cation (m/z 331) and a hexosylpentosyl cation (m/z 547). The carbon signals due to the sugar moiety at C-3 of the aglycone are superimposable on those of 2, indicating that these compounds have the same sugar moiety at C-3. Accordingly, prosapogenin I is formulated as structure 10.

Prosapogenin II (9), C₄₈H₇₆O₁₈ provided L-arabinose, D-glucose and D-xylose in the ratio of 1:1:1 on acid hydrolysis. The EI-MS of 9 acetate showed fragment ion peaks due to a terminal pentosyl cation (m/z 259), a pentosylhexosyl cation (m/z 547) and pentosylhexosylpentosyl cation (m/z 763). The glucopyranosyl C-2 signal appeared at lower field by +6.9 ppm than that of 7 because of the glycosylation shift, demonstrating that a β -xylopyranosyl group is located at the C-2-OH of glucose. Therefore, prosapogenin II is formulated as structure 9.

The EI-MS of 5 acetate showed the fragment ion peaks due to a terminal pentosyl cation (m/z 259) and a hexosyl cation (m/z 331), a pentosylhexosyl cation (m/z 547) and a pentosylhexosylpentosyl cation (m/z 763). A ¹³C-NMR spectral comparison of 5 with 9 revealed a glycosylation shift (-3.4 ppm) at C-28 of 5, indicating that the glucopyranosyl unit is linked to C₂₈-OH. Hence, 5 was formulated as 3-*O*- β -D-xylopyranosyl(1 $\rightarrow$ 2)- β -D-glucopyranosyl(1 $\rightarrow$ 3)-2-*O*-acetyl- α -L-arabinopyranosyl pomolic

acid 28-*O*- β -D-glucopyranoside.

Experimental

Melting points were measured with a Yanagimoto micromelting point apparatus and are uncorrected. Optical rotations were taken on a JASCO DIP-140 digital polarimeter. ¹H-(400 MHz) and ¹³C-(100 MHz) NMR spectra were recorded on a JEOL GX-400 spectrometer in pyridine-*d*₅ solution using tetramethylsilane (TMS) as an internal standard. Chemical shifts are given in δ (ppm) and coupling constants (J values) are given in hertz (Hz). The following abbreviations are used: s=singlet, d=doublet, t=triplet, m=multiplet and br=broad. The EI and FAM-MS were measured with a JEOL JMS-PX303 mass spectrometer. High performance liquid chromatography (HPLC) was carried out with a Waters ALC/GPC 244 instrument. For column chromatography, Silica gel 60 (230–400 mesh, Merck) was used. Thin layer chromatography (TLC), precoated Silica gel 60F-254 (Merck) was used.

Extract and Isolation of Compounds 1–5 Fresh bark (8 kg) of *Ilex crenata* was extracted with 70% MeOH and the MeOH extract, obtained after removal of the solvent under reduced pressure, was passed through an Amberlite XAD-2 column and eluted with MeOH. Crude saponins (45 g) obtained by evaporation of the MeOH eluate were chromatographed with Servachrome XAD-2 (eluted with 30–70% MeOH) to give five fractions, fr. I–V, in order of elution. Fr. V (1.6 g) was chromatographed on silica gel with CHCl₃–MeOH–H₂O (25:8:0.5) to give 2 (0.14 g) and 5 (0.13 g). Fraction IV (18.4 g) was separated into six fractions, fr. IVa–IVf, by Sephadex LH-20 (MeOH). Fraction IVc (3.0 g) was chromatographed on silica gel and purified by repeated HPLC (ODS, 35% CH₃CN) to give 1 (0.54 g) and 4 (0.12 g). Fraction III (0.6 g) was chromatographed on silica gel with BuOH–AcOEt–H₂O (4:1:5, upper layer) to give 3 (0.04 g).

Ilexoside XV (1) Amorphous powder, [α]_D +13.4° (c =5.0, MeOH). FAB-MS m/z : 951 [(M+Na)⁺, C₄₇H₇₆O₁₈: 928]. ¹H-NMR δ : 0.90, 0.99, 0.99, 1.15, 1.17, 1.30, 1.66 (3H, each, s, *tert*-CH₃ $\times$ 7), 3.33 (1H, dd, J =11.0, 4.0 Hz, H-3), 3.53 (1H, brs, H-18), 3.59 (1H, d, J =3.0 Hz, H-19), 4.76 (1H, d, J =7.5 Hz, H-1 of Ara), 5.37 (1H, d, J =7.5 Hz, H-1 of Glc), 5.52 (1H, brt, H-12), 6.36 (1H, d, J =8.0 Hz, H-1 of esteric Glc). ¹³C-NMR: Tables I and II.

Ilexoside XVI (2) Amorphous powder, [α]_D +21.8° (c =1.0, MeOH). FAB-MS m/z : 993 [(M+Na)⁺, C₄₉H₇₈O₁₉: 970]. ¹H-NMR δ : 0.86, 0.90, 0.99, 1.13, 1.13, 1.17, 1.66 (3H, each, s, *tert*-CH₃ $\times$ 7), 2.29 (3H, s, acetyl), 3.20 (1H, dd, J =11.0, 4.0 Hz, H-3), 3.52 (1H, brs, H-18), 3.60 (1H, d, J =3.0 Hz, H-19), 4.74 (1H, d, J =8.0 Hz, H-1 of Ara), 5.05 (1H, d, J =8.0 Hz, H-1 of Glc), 5.51 (1H, brt, H-12), 5.99 (1H, dd, J =10.0, 8.0 Hz, H-2 of Ara), 6.33 (1H, d, J =8.0 Hz, H-1 of esteric Glc). ¹³C-NMR: Tables I and II.

Ilexoside XVII (3) Amorphous powder, [α]_D +56.2° (c =1.2, MeOH). FAB-MS m/z : 1113 [(M+Na)⁺, C₅₃H₈₆O₂₃: 1090]. ¹H-NMR δ : 0.87, 0.99, 1.12, 1.13, 1.17, 1.25, 1.65 (3H, each, s, *tert*-CH₃ $\times$ 7), 3.24 (1H, dd, J =10.0, 4.0 Hz, H-3), 3.53 (1H, brs, H-18), 3.60 (1H, d, J =3.0 Hz, H-19), 4.81 (1H, d, J =7.0 Hz, H-1 of Ara), 5.31 (1H, d, J =7.5 Hz, H-1 of Glc), 5.52 (1H, d, J =8.0 Hz, H-1 of Glc), 5.59 (1H, brt, H-12), 6.36 (1H, d, J =8.0 Hz, H-1 of esteric Glc). ¹³C-NMR: Tables I and II.

Ilexoside XVIII (4) Amorphous powder, [α]_D +3.9° (c =0.8, MeOH). FAB-MS m/z : 1113 [(M+Na)⁺, C₅₃H₈₆O₂₃: 1090]. ¹H-NMR δ : 0.88, 1.11, 1.18, 1.25, 1.41, 1.70 (3H, each, s, *tert*-CH₃ $\times$ 6), 1.07 (3H, d, J =6.0 Hz, 30-CH₃), 2.93 (1H, brs, H-18), 3.24 (1H, dd, J =11.0, 4.0 Hz, H-3), 4.74 (1H, d, J =7.5 Hz, H-1 of Ara), 5.32 (1H, d, J =7.5 Hz, H-1 of Glc), 5.51 (1H, d, J =7.5 Hz, H-1 of Glc), 5.56 (1H, brt, H-12), 6.29 (1H, d, J =7.5 Hz, H-1 of esteric Glc). ¹³C-NMR: Tables I and II.

Ilexoside XIX (5) Amorphous powder, [α]_D +10.2° (c =5.0, MeOH). FAB-MS m/z : 1125 [(M+Na)⁺, C₅₄H₈₆O₂₃: 1102]. ¹H-NMR δ : 0.87, 0.92, 1.08, 1.17, 1.41, 1.76 (3H, each, s, *tert*-CH₃ $\times$ 6), 1.09 (3H, d, J =6.5 Hz, 30-CH₃), 2.29 (3H, s, acetyl), 2.92 (1H, brs, H-18), 3.17 (1H, dd, J =10.5, 5.5 Hz, H-3), 4.66 (1H, d, J =8.0 Hz, H-1 of Ara), 5.06 (1H, d, J =8.0 Hz, H-1 of Xyl), 5.14 (1H, d, J =7.0 Hz, H-1 of Glc), 5.56 (1H, brt, H-12), 5.96 (1H, dd, J =10.0, 8.0 Hz, H-2 of Ara), 6.26 (1H, d, J =8.0 Hz, H-1 of esteric Glc). ¹³C-NMR: Tables I and II.

Methanolysis of 1 A solution of 1 (70 mg) in 1N HCl–MeOH (2 ml) was heated at 70°C for 2 h. After work-up as in a usual manner, the crude aglycone (25 mg) was recrystallized from MeOH to give methyl siaresinolate (6) (20 mg), mp 181–183°C (lit.³), mp 184–186°C, [α]_D +46.0° (c =1.0, CHCl₃) (lit.³) +45.0°. EI-MS m/z : 486 (M)⁺. ¹H-NMR (CDCl₃) δ : 0.67, 0.77, 0.90, 0.95, 0.96, 1.00, 1.24 (3H, each, s, *tert*-CH₃ $\times$ 7), 3.20 (1H, dd, J =11.0, 4.0 Hz, H-3), 3.10 (1H, brs, H-18), 3.33

TABLE I. ^{13}C -NMR Spectral Data for Aglycone Moieties of Compounds 1—6, 8, 9 and 10 in Pyridine- d_5 (100 MHz)

	1	2	3	4	5	6	8	9	10
C- 1	38.7	38.6	38.7	39.1	38.9	38.8	38.9	38.6	38.6
C- 2	26.7	26.6	26.6	26.8	26.7	28.1	28.0	27.2	27.2
C- 3	88.8	89.1	89.0	89.5	89.3	78.2	78.2	89.1	89.1
C- 4	39.7	39.4	39.7	39.9	39.4	39.3	39.3	39.4	39.3
C- 5	56.0	55.9	56.0	56.1	56.0	56.0	55.8	55.8	55.8
C- 6	18.8	18.8	18.7	18.9	18.9	18.9	18.9	18.7	18.7
C- 7	33.1	33.1	33.1	33.6	33.7	33.2	33.6	33.5	33.5
C- 8	40.3	40.7	40.2	40.8	40.7	40.0	40.3	40.4	40.4
C- 9	48.4	48.4	48.3	47.9	47.9	47.3	47.7	47.7	47.7
C-10	37.2	37.2	37.2	37.1	37.1	37.5	37.3	37.0	37.0
C-11	24.2	24.3	24.2	24.2	24.3	24.1	24.0	24.0	24.0
C-12	123.4	123.4	123.4	128.6	128.6	123.3	128.1	128.1	128.0
C-13	144.4	144.3	144.3	139.4	139.4	144.3	139.9	140.0	140.0
C-14	42.2	42.2	42.1	42.3	42.3	42.1	42.1	42.1	42.4
C-15	29.0	29.1	29.0	29.4	29.5	29.0	29.2	29.3	29.6
C-16	28.0	28.1	28.0	26.3	26.3	28.1	26.6	26.5	26.5
C-17	46.5	46.6	46.5	48.8	48.9	46.4	48.2	48.3	48.3
C-18	44.7	44.7	44.6	54.6	54.6	44.6	54.5	54.6	54.6
C-19	81.1	81.2	81.0	72.7	72.3	81.0	72.7	72.7	72.7
C-20	35.6	35.6	35.6	42.2	42.3	35.6	42.3	42.2	42.1
C-21	29.1	29.1	29.1	26.8	26.9	29.0	27.0	27.2	29.2
C-22	33.2	33.3	33.2	37.9	38.0	33.2	37.4	38.6	38.5
C-23	28.2	28.1	28.0	28.2	28.3	28.2	28.7	28.0	28.0
C-24	16.9	16.8	16.7	16.9	16.9	16.5	16.7	16.8	16.8
C-25	15.6	15.5	15.5	15.8	15.8	15.5	15.5	15.5	15.4
C-26	17.6	17.6	17.6	17.6	17.6	17.4	17.1	17.2	17.2
C-27	24.7	24.8	24.7	24.8	24.8	24.7	24.6	24.8	24.8
C-28	177.3	177.3	177.3	177.4	177.4	178.7	180.6	180.8	180.7
C-29	28.8	28.9	28.8	27.1	27.2	28.8	26.8	27.2	27.1
C-30	25.0	25.0	24.9	16.9	16.9	24.9	16.4	16.8	16.8
COOCH ₃						51.7			

(1H, d, $J=3.0\text{ Hz}$, H-19), 3.62 (3H, s, COOMe), 5.46 (1H, brt, H-12). ^{13}C -NMR: Table I.

Alkaline Hydrolysis of 2 Compound 2 (30 mg) was stirred with 2% KOH in 50% EtOH (2 ml) at room temperature for 1 h, then the reaction mixture was neutralized with Amberlite IRC-50 and filtered. The filtrate was chromatographed on a silica gel column with $\text{CHCl}_3\text{--MeOH--H}_2\text{O}$ (25:8:0.5) giving 1 (25 mg).

Enzymatic Hydrolysis of 4 A solution of 4 (50 mg) and crude cellulase (50 mg, Sigma) in EtOH- H_2O (1:9) and 0.01 M NaH_2PO_4 buffer (pH 4.0) (4 ml each) was incubated for 72 h at 37°C. After cooling, the reaction mixture was concentrated to dryness. The residue was chromatographed on a silica gel column with $\text{CHCl}_3\text{--MeOH--H}_2\text{O}$ (25:4:0.5) to give pomolic acid (8) (10 ml), colorless needles from MeOH, mp 298–300°C, $[\alpha]_D^{25} + 55.1^\circ$ ($c=0.7$, tetrahydrofuran (THF)). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3400 (br, OH), 1690 (C=O), 1045, 1025. FAB-MS: m/z 473 [(M+H) $^+$, $\text{C}_{36}\text{H}_{46}\text{O}_4$: 472], 495 [(M+Na) $^+$, $\text{C}_{36}\text{H}_{46}\text{O}_4$: 472]. EI-MS m/z 472 (M^+), 454 ($\text{M--H}_2\text{O}$) $^+$, 410 ($\text{M}^+ - \text{H}_2\text{O} - \text{CO}_2$), 264, 246, 208, 201, 190, 175. ^1H -NMR δ : 0.92, 1.04, 1.11, 1.24, 1.47, 1.73 (3H, each, s, *tert*-CH₃ $\times$ 6), 1.13 (3H, d, $J=6.5\text{ Hz}$, 30-CH₃), 3.05 (1H, brs, H-18), 3.45 (1H, dd, $J=10.4, 5.5\text{ Hz}$, H-3), 5.62 (1H, brt, H-12). ^{13}C -NMR: Table I.

Enzymatic Hydrolysis of 5 A solution of 5 (0.1 g) and crude hesperidinase (0.1 g, Tanabe) in EtOH- H_2O (1:9) and 0.01 M NaH_2PO_4 buffer (pH 4.0) (4 ml each) was incubated for 24 h at 37°C. After cooling, the reaction mixture was concentrated to dryness. The residue was chromatographed on a silica gel column with $\text{CHCl}_3\text{--MeOH--H}_2\text{O}$ (25:8:0.5) to give prosopogenin I (9) (20 mg) and II (10) (25 mg). 9, colorless needles from MeOH, mp 285–287°C, $[\alpha]_D^{25} + 23.7^\circ$ ($c=3.1$, MeOH). FAB-MS m/z : 963 [(M+Na) $^+$, $\text{C}_{48}\text{H}_{76}\text{O}_{18}$: 940]. ^1H -NMR δ : 0.82, 0.90, 1.07, 1.09, 1.44, 1.74 (3H, each, s, *tert*-CH₃ $\times$ 6), 1.13 (3H, d, $J=6.0\text{ Hz}$, 30-CH₃), 2.29 (3H, s, acetyl), 3.04 (1H, brs, H-18), 3.18 (1H, dd, $J=10.5, 5.5\text{ Hz}$, H-3), 4.65 (1H, d, $J=8.0\text{ Hz}$, H-1 of Ara), 5.07 (1H, d, $J=8.0\text{ Hz}$, H-1 of Xyl), 5.14 (1H, d, $J=8.0\text{ Hz}$, H-1 of Glc), 5.59 (1H, brt, H-12), 5.97 (1H, dd, $J=9.5, 8.0\text{ Hz}$, H-2 of Ara). ^{13}C -NMR: Tables I and II. 10, colorless needles from MeOH, mp 295–297°C, $[\alpha]_D^{25} + 11.6^\circ$ ($c=1.0$, MeOH). FAB-MS m/z : 831 [(M+Na) $^+$, $\text{C}_{43}\text{H}_{68}\text{O}_{14}$: 808]. ^1H -NMR δ : 0.82,

TABLE II. ^{13}C -NMR Spectral Data for Sugar Moieties of Compounds 1—5, 7, 9 and 10 in Pyridine- d_5 (100 MHz)

	1	2	3	4	5	7	9	10
Inner Ara								
C-1	107.5	104.9	104.4	104.4	104.0	107.2	103.9	104.8
C-2	71.9	72.2	78.7	78.5	71.7	73.0	71.5	72.2
3-O-C-3	84.1	81.3	83.3	83.5	81.8	74.6	81.7	81.3
C-4	69.4	69.6	68.8	68.8	69.5	69.4	69.4	69.5
C-5	67.0	67.1	66.1	66.1	66.9	66.4	66.7	67.1
Terminal Glc (1→3)								
C-1	106.4	106.4	105.5	105.6	105.2		105.1	106.5
C-2	75.7	74.6	75.3	75.3	83.2		83.4	74.6
C-3	78.7	78.4	78.5	78.5	78.5		78.4	78.4
C-4	71.6	71.6	71.5	71.5	71.0		71.1	71.6
C-5	78.4	78.4	78.3	78.2	78.2		78.2	78.4
C-6	62.7	62.8	62.5	62.5	62.5		62.5	62.8
Terminal Glc (1→2) or Xyl (1→2)								
C-1			105.1	105.1	106.4		106.5	
C-2			76.2	76.1	76.0		76.1	
C-3			77.6	77.9	78.2		78.2	
C-4			72.4	72.3	71.1		71.1	
C-5			77.5	77.3	67.4		67.3	
C-6			63.2	63.2				
Glc								
C-1	95.9	95.9	95.9	96.0	96.0	95.5		
C-2	74.2	74.2	74.2	74.0	74.1	74.2		
28-O-C-3	79.3	79.3	79.4	79.3	79.3	79.0		
C-4	71.1	71.2	71.1	71.3	71.3	71.6		
C-5	79.0	78.9	79.0	78.8	78.9	79.0		
C-6	62.2	62.4	62.2	62.4	62.5	62.7		
Acetyl								
		21.6			22.0		21.7	21.5
		170.0			170.0		169.7	169.9

0.89, 1.08, 1.13, 1.44, 1.75 (3H, each, s, *tert*-CH₃ $\times$ 6), 1.12 (3H, d, $J=6.0\text{ Hz}$, 30-CH₃), 2.27 (3H, s, acetyl), 3.06 (1H, brs, H-18), 3.21 (1H, dd, $J=10.5, 5.5\text{ Hz}$, H-3), 4.73 (1H, d, $J=7.5\text{ Hz}$, H-1 of Ara), 5.18 (1H, d, $J=7.5\text{ Hz}$, H-1 of Glc), 5.56 (1H, brt, H-12), 6.03 (1H, dd, $J=9.0, 8.0\text{ Hz}$, H-2 of Ara). ^{13}C -NMR: Tables I and II.

Identification of Component Sugars of 1—5, 9 and 10 A solution of each compound (3–4 mg) in 5% H_2SO_4 in 50% EtOH was heated at 100°C for 3 h. The reaction mixture was diluted with water, neutralized with Amberlite IR-45 and concentrated *in vacuo* to dryness. The mole ratio and enantiomeric character (D or L) of each sugar were determined by using RI detection (Waters 410) and chiral detection (Shodex OR-1), respectively, in HPLC (Shodex RSpak DC-613, 75% CH_3CN , 1 ml/min, 70°C) by comparison with authentic sugars (10 mM each of L-Ara, D-Glc and D-Xyl). These sugars gave the following peaks: D-(+)-Xyl; 5.75 min, L-(+)-Ara; 6.2 min, D-(+)-Glc; 7.38 min.

Acetylation of 1—5, 9 and 10 Each compound (1–2 mg) was acetylated with Ac_2O -pyridine (each 0.1 ml) at room temperature overnight. Work-up as usual gave a colorless oils in each case, IR $\nu_{\text{max}}^{\text{CCl}_4}$ cm^{-1} : 1760–1750, 1230–1220, 1030–1025.

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