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Triterpenoid Saponins of Aquifoliaceous Plants. VI.[1] Ilexosides XX—XXIV from the Bark of *Ilex crenata* THUNB.[2]

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Five new saponins, ilexosides XX—XXIV, were isolated from the fresh bark of *Ilex crenata*, and their structures were elucidated on the basis of chemical and physicochemical evidence. Ilexoside XX is the 3,28-bisdesmoside of siaresinolic acid, whereas ilexosides XXI—XXIV are those of 3*β*,19*α*,21*α*-trihydroxyurs-12-en-28-oic acid.

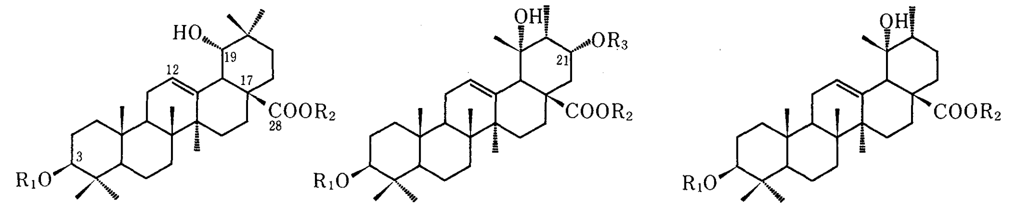
Keywords *Ilex crenata*; Aquifoliaceae; pentacyclictriterpene; ilexoside; 3*β*,19*α*,21*α*-trihydroxyurs-12-en-28-oicacid; 21*α*-hydroxypomolic acid; siaresinolic acid; bisdesmoside; saponin

In a previous paper, we have reported the isolation and structure determination of five saponins, ilexosides XV—XIX, from the fresh bark of *Ilex crenata* THUNB.[1] Ilexosides XV and XVII are 3,28-bisdesmosides of pomolic acid and ilexosides XVIII—XIX are those of siaresinolic acid. In the present communication, we wish to report the isolation and structure determination of five additional 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 and ordinary-phase column chromatography furnished five new saponins, ilexosides XX (**1**, 0.13 g), XXI (**2**, 0.1 g), XXII (**3**, 0.08 g), XXIII (**4**, 0.1 g) and XXIV (**5**, 0.04 g).

Ilexoside XX (**1**) was obtained as colorless needles and the relative molecular mass (M_r) was proposed to be 1206, as the deprotonated molecular ion was apparent at *m/z* 1205 in its fast atom bombardment mass spectrum (FAB-MS). The molecular formula of this compound was confirmed as $C_{58}H_{94}O_{28}$ by elemental analysis. A carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectral comparison of **1** with ilexoside XV (**6**), obtained in our previous investigation,[1] showed that **1** is also a glycoside of siaresinolic acid (**7**),[3] and varies structurally from **6** only in its saccharide moieties, though these sugar units are also affixed to the C-3 and C-28 positions. On acid hydrolysis, **1** gave L-arabinose, D-glucose, L-rhamnose and D-xylose in the ratio of 1 : 2 : 1 : 1. The proton magnetic resonance (^{1}H-NMR) spectrum of **1** indicated the presence of one α-arabinosyl unit [H-1; δ 4.80 (d, J=7.5 Hz)], two β-glucosyl units [H-1; δ 5.38 (d, J=8.0 Hz) and 6.16 (d, J=8.0 Hz)], one α-rhamnosyl unit [H-1, δ 6.54 s] and one β-xylosyl unit [H-1; δ 4.88 (d, J=7.5 Hz)]. The electron impact mass spectrum (EI-MS) of **1** acetate showed characteristic fragment ion peaks due to terminal pentosyl (*m/z* 259), deoxyhexosyl (*m/z* 273), hexosyl (*m/z* 331), pentosylhexosyl (*m/z* 547) and hexosyl (deoxyhexosyl)-pentosyl moieties (*m/z* 777). The linkages of the saccharide units to the aglycone unit of **1** were conveniently established by referring to the (^{13}C-NMR) data of ilexoside III (**8**).[4] The carbon signals due to the sugar moieties of **1** were superimposable on those of **8**, indicating that the sugar moieties are the same. Therefore, **1** was formulated as 3-*O*-β-D-glucopyranosyl (1→3)-α-L-arabinopyranosyl siaresinolic acid 28-*O*-[α-L-rhamnopyranosyl (1→2)]-[β-D-xylopyranosyl(1→6)]-β-D-glucopyranoside.

Ilexoside XXI (**2**), $C_{41}H_{66}O_{14}\cdot 2H_2O$ was obtained as a white powder. Its EI-MS showed ion peaks at *m/z* 470, 426, 280, 262, 244, 208 and 199, which indicate that the aglycone is an amyrin derivative having one hydroxyl in the A/B rings and one esteric carboxyl and two hydroxyls in the D/E rings.[5,6] A deprotonated ion peak at *m/z* 781 ascribable to $[M-H]^-$ in its negative FAB-MS showed that the M_r was 782, *i.e.*, 16 mass units more than that of ziyu-glycoside I (**9**)[7] obtained from *Sanguisorba officinalis*. Acid hydrolysis



	R1	R2
ilexoside XX (**1**)	-Ara$\overset{3}{-}$Glc	-Glc$\overset{6}{-}$Xyl $\vert_2$ Rha
ilexoside XV (**6**)	-Ara$\overset{3}{-}$Glc	-Glc
7	-H	-H

	R1	R2	R3
ilexoside XXI (**2**)	-Ara	-Glc	-H
ilexoside XXII (**3**)	-Ara	-H	-Glc
ilexoside XXIII (**4**)	-Ara$\overset{3}{-}$Glc	-Glc	-H
ilexoside XXIV (**5**)	-Ara$\overset{3}{-}$Glc $\vert_2$ Ac	-Glc	-H

	R1	R2
ilexoside X (**8**)	-Ara$\overset{3}{-}$Glc	-Glc$\overset{6}{-}$Xyl $\vert_2$ Rha
9	-Ara	-Glc

Ara : α-L-arabinopyranosyl
Glc : β-D-glucopyranosyl
Rha : α-L-rhamnopyranosyl
Xyl : β-D-xylopyranosyl

Fig. 1

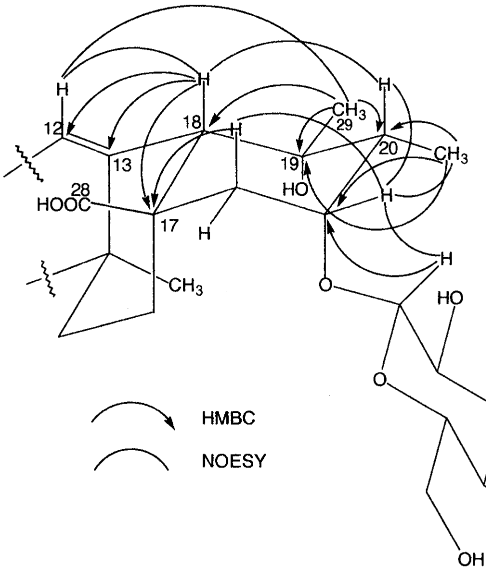


Fig. 2. HMBCs and NOEs Observed in Compound **3**

Table I. ^{13}C-NMR Spectral Data for Aglycone Moieties of Compounds **1**—**6** and **9** (Pyridine-d_5, δ-Values)

	1	**2**	**3**	**4**	**5**	**6**	**9**
C-1	38.9	38.9	38.9	38.9	38.9	38.7	39.2
C-2	26.9	26.7	26.7	26.8	26.7	26.7	26.9
C-3	88.9	88.8	88.7	88.8	89.3	88.8	89.0
C-4	39.8	39.6	39.6	39.7	39.4	39.7	39.7
C-5	56.2	55.5	55.9	55.9	55.9	56.0	56.2
C-6	18.9	18.7	18.6	18.7	18.8	18.8	19.0
C-7	32.9	33.7	33.8	33.7	33.8	33.1	33.7
C-8	40.3	40.4	40.1	40.4	40.5	40.3	40.8
C-9	48.4	47.7	47.7	47.7	47.9	48.4	48.0
C-10	37.3	37.0	37.0	37.0	37.1	37.2	37.3
C-11	24.3	24.0	24.0	24.1	24.1	24.2	24.3
C-12	124.2	128.8	128.2	128.8	129.0	123.4	128.7
C-13	144.4	138.5	139.0	138.5	138.6	144.4	139.4
C-14	42.5	42.2	42.3	42.2	42.4	42.2	42.3
C-15	29.7	29.7	29.4	29.7	29.8	29.0	29.3
C-16	28.1	28.6	28.7	28.6	28.7	28.0	26.4
C-17	46.9	48.4	47.8	48.3	48.5	46.5	48.8
C-18	44.9	54.9	54.2	54.9	54.9	44.7	54.6
C-19	81.4	75.4	74.8	75.4	75.5	81.1	73.0
C-20	35.6	42.6	43.2	42.6	42.7	35.6	42.3
C-21	29.3	73.0	78.0	73.0	73.1	29.1	26.9
C-22	33.6	44.2	38.5	44.2	44.2	33.2	37.8
C-23	28.3	28.2	28.2	28.2	28.1	28.2	28.5
C-24	17.1	17.0	17.0	17.0	17.0	16.9	17.1
C-25	15.8	15.8	15.7	15.8	15.8	15.6	15.8
C-26	17.7	17.5	17.4	17.5	17.7	17.6	17.7
C-27	24.7	23.7	23.4	23.9	23.9	24.7	24.8
C-28	177.4	176.4	180.2	176.5	176.9	177.3	177.0
C-29	28.9	27.0	27.5	27.0	27.0	28.8	27.3
C-30	25.2	14.2	13.4	14.3	14.4	25.0	16.8

of **2** afforded L-arabinose and D-glucose in the ratio of 1 : 1. Its ^{1}H-NMR spectrum indicated the presence of one α-arabinosyl unit [H-1, δ 4.80 (d, $J=7.2$ Hz)] and one β-glucosyl unit [H-1, δ 6.30 (d, $J=8.4$ Hz)]. A ^{13}C-NMR spectral comparison of **2** with **9** showed that **2** is also a glycoside of a pomolic acid analogue that varies structurally from **9** only its E ring, and that the sugar units are affixed to the C-3 and C-28 position.

Table II. ^{13}C-NMR Spectral Data for Sugar Moieties of Compounds **1**—**5**, **8** and **9** (Pyridine-d_5, δ-Values)

	1	**2**	**3**	**4**	**5**	**8**	**9**
Inner Ara							
3-*O*-C-1	107.4	107.5	107.5	107.4	104.9	107.3	107.2
3-*O*-C-2	71.9	72.9	72.9	71.9	72.4	71.9	73.0
3-*O*-C-3	84.0	74.6	74.7	84.1	81.3	84.1	74.6
3-*O*-C-4	69.2	69.6	69.6	69.3	69.6	69.1	69.4
3-*O*-C-5	67.0	66.8	66.8	67.0	67.2	67.0	66.4
Terminal Glc (1→3)							
C-1	106.1			106.4	106.5	106.3	
C-2	75.6			75.7	74.6	75.7	
C-3	78.6			78.7	78.5	78.6	
C-4	71.6			71.5	71.6	71.5	
C-5	78.2			78.4	78.3	78.3	
C-6	62.7			62.7	62.7	62.6	
21-*O*-Glc							
C-1			101.3				
C-2			75.1				
C-3			78.9				
C-4			71.8				
C-5			78.6				
C-6			62.9				
Inner Glc							
28-*O*-C-1	95.1	96.0		96.0	96.1	94.9	95.5
28-*O*-C-2	79.4	74.1		74.1	74.0	79.6	74.2
28-*O*-C-3	75.6	79.3		79.3	79.4	75.7	79.0
28-*O*-C-4	71.0	71.3		71.2	71.3	71.0	71.6
28-*O*-C-5	77.6	78.9		78.9	78.8	77.6	79.0
28-*O*-C-6	69.2	62.4		62.3	62.4	69.3	62.7
Terminal Xyl (1→6)							
C-1	105.5					105.6	
C-2	74.7					74.8	
C-3	77.8					78.1	
C-4	71.2					71.0	
C-5	67.0					67.1	
Terminal Rha (1→2)							
C-1	101.5					101.3	
C-2	72.5					72.5	
C-3	72.2					72.2	
C-4	73.8					73.8	
C-5	70.0					69.7	
C-6	18.9					18.8	
Acetyl					21.7 170.0		

In the ^{1}H-detected miltiple-bond heteronuclear multiple quantum coherence (HMBC) experiment, the quaternary carbon at δ 75.4 (C-19), bearing an oxygen atom, gave cross peaks with the methine at δ 3.09 (C-18), and the methyl signals at δ 1.44 (Me-29) and 1.39 (Me-30). The methyl at C-30 further showed cross peaks with the methine carbon at δ 42.6 (C-20) and that bearing an oxygen atom at δ 73.0 (C-21). The methine proton, linked to the carbon at δ 73.0, appeared as a broad singlet ($W_{1/2}=6$ Hz) at δ 4.08 showing the hydroxy group to be α (axial). Additional information on the stereochemistry in the E ring was obtained from nuclear Overhauser effect (NOE) difference measurements. NOEs were observed between H-20 (δ 1.59) and both H-18 (δ 3.09) and H$_\beta$-22 (δ 4.08). Hence, the aglycone of **2** was formulated as 3β, 19α, 21α-trihydroxyurs-12-en-28-oic acid. Accordingly, **2** was formulated as 3-*O*-α-L-arabinopyranosyl 3β,19α,21α-trihydroxyurs-12-en-28-oic acid 28-*O*-β-D-glucopyranoside.

Ilexoside XXII (**3**), obtained as colorless needles, had the same molecular formula $C_{41}H_{66}O_{14}$ [FAB-MS, *m/z* 781 $(M-H)^-$] as **2**. The ^{1}H- and ^{13}C-NMR spectra of **3** showed similar patterns to those of **2** except for those ascribable to the E ring, demonstrating a glucosyl group to be absent at C-28. A ^{13}C-NMR spectral comparison of **3** with **2** revealed glycosylation and deglycosylation shifts[8] at the C-21 position (+5.0 ppm from δ 73.0 to 78.0) and C-28 position (−3.8 ppm from δ 180.2 to 176.4), respectively, implying that a β-glucopyranosyl group is joined to the C-21-OH in the former. Additional information on the sugar linkage to the aglycone was obtained from HMBC and nuclear Overhauser and exchange spectroscopy (NOESY) experiments (Fig. 2). Therefore, **3** was formulated as 3-*O*-α-L-arabinopyranosyl 21-*O*-β-D-glucopyranosyl 3β,19α,21α-trihydroxyurs-12-en-28-oic acid.

Ilexoside XXIII (**4**), $C_{47}H_{76}O_{19}$ was obtained as a white powder. The FAB-MS of **4** revealed a quasi-molecular ion peak at *m*/*z* 943 $[M-H]^-$, 162 mass units more than that of **3**. On acid hydrolysis, **4** afforded L-arabinose and D-glucose in the ratio of 1 : 2. The ^{1}H-NMR spectrum indicated the presence of one α-arabinosyl unit [H-1, δ 4.79 (d, J=7.0 Hz)] and two β-glucosyl units [H-1, δ 5.37 (d, J=8.0 Hz), and 6.29 (d, J=8.5 Hz)]. A ^{13}C-NMR spectral comparison of **4** with **2**, showed that **4** was also a glycoside of 21α-hydroxypomolic acid, varying structurally from **2** only in its saccharide moieties, and that these sugar units were also affixed to the C-3 and C-28 positions. The arabinosyl C-3 signal of **4** appeared at lower field by +9.4 ppm than that of **2** because of the glycosylation shift, indicating a β-glucopyranosyl group to be located at C-3 of arabinose. Therefore, **4** was formulated as 3-*O*-β-D-glucopyranosyl(1→3)-α-L-arabinopyranosyl 3β,19α,21α-trihydroxyurs-12-en-28-oic acid 28-*O*-β-D-glucopyranoside.

Ilexoside XXIV (**5**) was obtained as a white powder. The FAB-MS of **5** revealed a quasi-molecular ion peak at *m*/*z* 985 $[M-H]^-$, 42 mass units more than that of **4**. The ^{1}H-NMR spectrum of **5** showed the presence of an acetyl group (3H, s, at δ 2.30), one α-arabinosyl unit [H-1, δ 4.76 (d, J=7.5 Hz)], and two β-glucosyl units [H-1, δ 5.08 (d, J=8.0 Hz) and 6.31 (d, J=8.5 Hz)]. On mild alkaline hydrolysis with 2% KOH, compound **5** afforded **4**. A ^{1}H- and ^{13}C-NMR spectral comparison of **5** with **4** revealed an acylation shift at the C_2 position [+1.59 ppm (H-2), +0.5 ppm (C-2), −2.5 ppm (C-1) and −2.8 ppm (C-3)] of the arabinosyl moiety of **5**. Therefore, in **5**, the hydroxy group at the 2-position of the arabinosyl moiety should be acetylated. Therefore, **5** was formulated as 3-*O*-[β-D-glucopyranosyl(1→3)]-2-*O*-acetyl-α-L-arabinopyranosyl 3β,19α,21α-trihydroxyurs-12-en-28-oic acid 28-*O*-β-D-glucopyranoside.

Ilexosides XXI—XXIV are the first naturally occurring analogues of pomolic acid having a hydroxy group at the C-21 position.

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. ^{1}H-(400 or 600 MHz) and ^{13}C-(100 or 150 MHz) NMR spectra were recorded on a JEOL GX-400 or Varian UNITY600 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 FAB-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. For 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 eluated 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, frs. I—V in order of elution. Fraction V (1.6 g) was chromatographed on silica gel with $CHCl_3$–MeOH–H_2O (25 : 8 : 0.5) to give **5** (0.04 g). Fraction III (6 g) was separated into six fractions, frs. IIIa—f by Sephadex LH-20 chromatography (MeOH). Fraction IIIb (0.3 g) was chromatographed on silica gel with BuOH–AcOEt–H_2O (4 : 1 : 5, upper layer) to give **1** (0.13 g). Fraction IIIc (2 g) was chromatographed on silica gel with $CHCl_3$–MeOH–H_2O (25 : 6 : 0.5) to give **2** (0.1 g) and **3** (0.08 g). Fraction IVd (1 g) was chromatographed on silica gel with $CHCl_3$–MeOH–H_2O (25 : 8 : 0.5) to give **4** (0.1 g).

Ilexoside XX(1) Colorless needles from MeOH, mp 231—233 °C, $[\alpha]_D$ −19.4° (c=4.2, MeOH). FAB-MS *m*/*z*: 1205$[(M-H)^-]$. *Anal.* Calcd for $C_{58}H_{94}O_{28}\cdot 4H_2O$: C, 54.45; H, 8.04. Found: C, 54.30; H, 8.12. ^{1}H-NMR (400 MHz) δ: 0.91, 0.96, 1.02, 1.11, 1.13, 1.24, and 1.66 (3H each, s, *tert*-$CH_3 \times 7$), 1.76 (3H, d, J=6.0 Hz), 3.31 (1H, dd, J=11.0, 4.0 Hz, H-3), 3.48 (1H, br s, H-18), 3.56 (1H, d, J=3.0 Hz, H-19), 4.80 (1H, d, J=7.5 Hz, H-1 of Ara), 4.88 (1H, d, J=7.5 Hz, H-1 of Xyl), 5.38 (1H, d, J=8.0 Hz, H-1 of Glc), 5.52 (1H, br t, H-12), 6.16 (1H, d, J=8.0 Hz, H-1 of esteric Glc), 6.54 (1H, s, H-1 of Rha). ^{13}C-NMR: Tables I and II.

Ilexoside XXI (2) A white powder, $[\alpha]_D$ +8.6° (c=2.7, MeOH). FAB-MS *m*/*z*: 781 $[(M-H)^-]$. *Anal.* Calcd for $C_{41}H_{66}O_{14}\cdot 2H_2O$: C, 60.13; H, 8.61. Found: C, 60.01; H, 8.82. ^{1}H-NMR (400 MHz) δ: 0.93, 0.99, 1.20, 1.28, 1.44, and 1.69 (3H each, s, *tert*-$CH_3 \times 6$), 1.39 (3H, d, J=6.8 Hz), 1.59 (1H, m, H-20), 2.12 (1H, dd, J=14.0, 3.0 Hz, H_β-22), 2.44 (1H, ddd, J=14.0, 3.0, 3.0 Hz, H_β-16), 2.60 (1H, dd, J=14.0, 2.5 Hz, H_α-22), 3.09 (1H, s, H-18), 3.18 (1H, ddd, J=14.0, 14.0, 3.0 Hz, H_α-16), 3.34 (1H, dd, J=11.8, 4.2 Hz, H-3), 4.08 (1H, m, H-21), 4.80 (1H, d, J=7.2 Hz, H-1 of Ara), 5.62 (1H, br t, H-12), 6.30 (1H, d, J=8.4 Hz, H-1 of esteric Glc). ^{13}C-NMR: Tables I and II.

Ilexoside XXII (3) Colorless needles from MeOH, mp 238—239 °C, $[\alpha]_D$ −0.9° (c=2.2, MeOH). FAB-MS *m*/*z*: 781 $[(M-H)^-]$. *Anal.* Calcd for $C_{41}H_{66}O_{14}\cdot 21/2H_2O$: C, 59.47; H, 8.64. Found: C, 59.58; H, 8.36. ^{1}H-NMR (600 MHz) δ: 0.88, 0.94, 1.07, 1.24, 1.35, and 1.70 (3H each, s, *tert*-$CH_3 \times 6$), 1.39 (3H, d, J=6.8 Hz), 1.85 (1H, m, H-20), 2.14 (1H, dd, J=14.5, 3.0 Hz, H_β-22), 2.51 (1H, ddd, J=14.5, 3.5, 3.5 Hz, H_β-16), 2.87 (1H, dd, J=14.5, 3.5 Hz, H_α-22), 3.18 (1H, s, H-18), 3.23 (1H, ddd, J=14.5, 14.5, 3.5 Hz, H_α-16), 3.34 (1H, dd, J=11.8, 4.2 Hz, H-3), 4.53 (1H, m, H-21), 4.77 (1H, d, J=7.8 Hz, H-1 of Ara), 5.61 (1H, br t, H-12), 5.06 (1H, d, J=7.8 Hz, H-1 of Glc). ^{13}C-NMR: Tables I and II.

Ilexoside XXIII (4) A white powder, $[\alpha]_D$ +14.2° (c=3.9, MeOH). FAB-MS *m*/*z*: 943 $[(M-H)^-]$. *Anal.* Calcd for $C_{47}H_{76}O_{19}\cdot 4H_2O$: C, 55.50; H, 8.32. Found: C, 55.61; H, 8.48. ^{1}H-NMR (400 MHz) δ: 0.92, 1.00, 1.12, 1.30, 1.40, and 1.71 (3H each, s, *tert*-$CH_3 \times 6$), 1.39 (3H, d, J=6.5 Hz), 1.60 (1H, m, H-20), 2.12 (1H, dd, J=14.0, 3.0 Hz, H_β-22), 2.44 (1H, ddd, J=14.0, 3.0, 3.0 Hz, H_β-16), 2.65 (1H, dd, J=14.0, 2.5 Hz, H_α-22), 3.09 (1H, s, H-18), 3.17 (1H, ddd, J=14.0, 14.0, 3.0 Hz, H_α-16), 3.24 (1H, dd, J=12.0, 4.0 Hz, H-3), 4.10 (1H, m, H-21), 4.79 (1H, d, J=7.0 Hz, H-1 of Ara), 5.37 (1H, d, J=8.0 Hz, H-1 of Glc), 5.61 (1H, br t, H-12), 6.29 (1H, d, J=8.5 Hz, H-1 of esteric Glc). ^{13}C-NMR: Tables I and II.

Ilexoside XXIV (5) A white powder, $[\alpha]_D$ +28.0° (c=0.4, MeOH). FAB-MS *m*/*z*: 985 $[(M-H)^-]$. *Anal.* Calcd for $C_{49}H_{78}O_{20}\cdot 5H_2O$: C, 54.63; H, 8.23. Found: C, 54.77; H, 8.46. ^{1}H-NMR (400 MHz) δ: 0.89, 0.92, 1.13, 1.20, 1.40, and 1.72 (3H each, s, *tert*-$CH_3 \times 6$), 1.39 (3H, d, J=7.5 Hz), 1.60 (1H, m, H-20), 2.13 (1H, dd, J=14.0, 3.0 Hz, H_β-22), 2.30 (3H, s, acetyl), 2.45 (1H, ddd, J=14.0, 3.0, 3.0 Hz, H_β-16), 2.64 (1H, dd, J=14.0, 2.5 Hz, H_α-22), 3.09 (1H, s, H-18), 3.18 (1H, ddd, J=14.0, 14.0, 3.0 Hz, H_α-16), 3.22 (1H, dd, J=11.0, 4.0 Hz, H-3), 4.10 (1H, m, H-21), 4.76 (1H, d, J=7.5 Hz, H-1 of Ara), 5.08 (1H, d, J=8.0 Hz, H-1 of Glc), 5.62 (1H, br t, H-12), 6.04 (1H, dd, J=9.5, 8.5 Hz, H-2 of Ara), 6.31 (1H, d, J=8.5 Hz, H-1 of esteric Glc). ^{13}C-NMR: Tables I and II.

Identification of Component Sugars of 1—5 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 HPLC (Shodex RSpak DC-613, 75% CH_3CN, 1 ml/min, 70 °C) by using refraction index detection (Waters 410) and chiral detection (Shodex OR-1), respectively, with authentic sugars (10 mmol each of L-Ara, D-Glc, L-Rha and D-Xyl) as standards. These sugars gave the following peaks: L-(−)-Rha; 4.8, D-(+)-Xyl; 5.75 min, L-(+)-Ara; 6.2 min, D-(+)-Glc; 7.38 min.

Alkaline Hydrolysis of 5 Compound **5** (15 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 $CHCl_3$–MeOH–H_2O (25 : 8 : 0.5), giving **4** (10 mg).

Acetylation of 1 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 oil in each case. IR $\nu_{\max}^{CCl_4}$: 1750, 1230, 1025.

References and Notes

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