Cytotoxic Triterpenoid Saponins Acetylated with Monoterpenoid Acid from *Albizia julibrissin*

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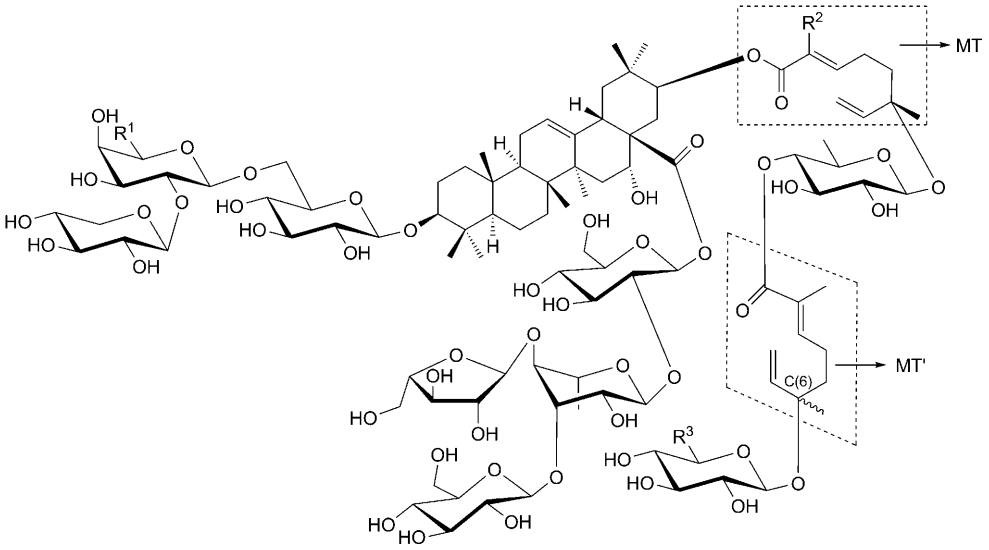
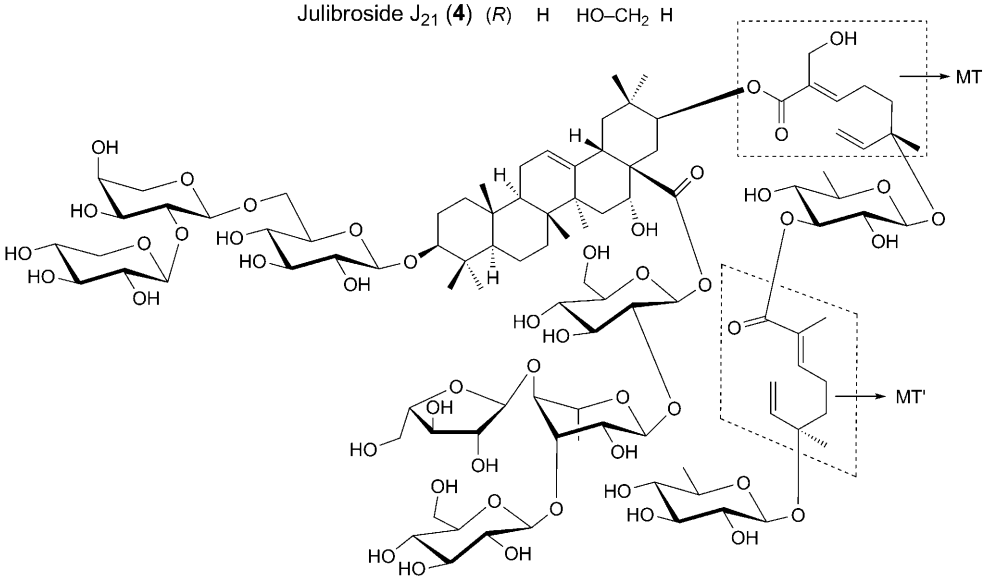
Three new triterpenoid saponins, named julibroside J_{16} (**2**), julibroside J_{17} (**3**), and julibroside J_{21} (**4**), each of which possesses an oleanane triterpenoid aglycone of acacic acid, two monoterpenoid acids, and nine sugar moieties, together with one known saponin, julibroside II (**1**), were isolated from the stem bark of *Albizia julibrissin* by chromatographic methods. Their structures were established by chemical and spectroscopic means. Saponins **1**, **2**, and **4** showed inhibitory activities against Bel 7402 human cancer cell line *in vitro*.

Introduction. – *Albizia julibrissin* DURAZZ (Leguminosae) is a plant widely distributed all over the world. In China, its stem bark, named '*He Huan Pi*' in Chinese, has been used as sedative agent for hundreds of years. As a traditional Chinese medicine, it is recorded in Chinese Pharmacopoeia as a sedative agent and an anti-inflammatory drug to treat injuries from falls and remove carbuncles [1]. The isolation and structure elucidation of some complicated triterpenoid saponins from this plant have been already reported by our research group, and some of them displayed marked inhibitory activities against some cancer cell lines *in vitro* [2–19]. Continuing our study on bioactive constituents of the stem bark of *A. julibrissin*, three new minor triterpenoid saponins, named julibroside J_{16} (**2**), julibroside J_{17} (**3**), julibroside J_{21} (**4**), along with one known triterpenoid saponin, julibroside II (**1**), were isolated, and the screening tests of inhibitory activity against human cancer cell lines *in vitro* showed that saponins **1**, **2**, and **4** displayed good inhibitory activities against Bel 7402 cancer cell line. Here, we report the isolation, characterization, and cytotoxic activities of the four saponins.

Results and Discussion. – The 95% EtOH extract of the stem bark of *A. julibrissin* was partitioned successively between H_2O and $CHCl_3$, AcOEt, and BuOH. The BuOH extract was subjected to column chromatography on D_{101} macroporous resin, *Sephadex LH-20*, normal-phase silica gel, reversed-phase (RP) silica gel, and then repeated preparative HPLC to give compounds **1**–**4**.



	C(6)	R^1	R^2	R^3
Julibroside II (**1**)	(*S*)	Me	Me	Me
Julibroside J_{16} (**2**)	(*R*)	Me	Me	Me
Julibroside J_{21} (**4**)	(*R*)	H	HO–CH_2	H



Julibroside J_{17} (**3**)

Compound **1** was obtained as a white powder, and showed positive *Molish* and *Liebermann–Burchard* reactions. By comparison of its ^{1}H- and ^{13}C-NMR data with those published in [20], **1** was established as julibroside II.

Compound **2** was obtained as a white powder. It showed positive *Molish* and *Liebermann–Burchard* reactions. The MALDI-TOF-MS (positive-ion mode) showed *quasi*-molecular-ion peaks at *m/z* (relative intensity) 2177.9 (56), 2178.9 (100), 2179.9 (45), 2180.9 (10, $[M+Na]^+$). The ^{1}H- and ^{13}C-NMR spectra of **2** were very similar to those of **1**, except for the ^{1}H- and ^{13}C-NMR signals (*Table 1*) of the monoterpenoid acid group MT′. A comparison of the ^{1}H- and ^{13}C-NMR data of **2** with those of **1** revealed that the ^{1}H-NMR signals of H–C(7) and Me(10) of the MT′ group of **2** underwent a downfield shift of 0.11 and an upfield shift of 0.11 ppm, while the ^{13}C-NMR signals of C(5) and C(10) of the MT′ group of **2** underwent an upfield shift of 1.7 and a downfield shift of 0.9 ppm, respectively. The results were quite similar to the ^{1}H- and ^{13}C-NMR data of a pair of diastereoisomeric saponins with different configuration at C(6) of the MT′ group, *i.e.*, julibroside J_1 and julibroside J_9 [8], indicating that **1** and **2** were a pair of diastereoisomeric saponins with different configuration at C(6) of the MT′ group. Therefore, **2** was characterized as the diastereoisomer of **1** with an (*R*)-configuration at C(6) of the MT′ group, and its structure was established to be 3-*O*-[*β*-D-xylopyranosyl-(1→2)-*β*-D-fucopyranosyl-(1→6)-*β*-D-glucopyranosyl]-21-*O*-((2*E*,6*S*)-2,6-dimethyl-6-*O*-{4-*O*-[((2*E*,6*R*)-2,6-dimethyl-6-*O*-*β*-D-quinovopyranosylocta-2,7-dienoyl)-*β*-D-quinovopyranosyl]}octa-2,7-dienoyl)acacic acid 28-*O*-*β*-D-glucopyranosyl-(1→3)-[*α*-L-arabinofuranosyl-(1→4)]-*α*-L-rhamnopyranosyl-(1→2)-*β*-D-glucopyranosyl ester. Compound **2** was a new compound and named Julibroside J_{16}.

Compound **3** was obtained as a white powder, and showed positive *Molish* and *Liebermann–Burchard* reactions. The FAB-MS (positive-ion mode) exhibited *quasi*-molecular-ion peaks at *m/z* (relative intensity) 2179.8, 2180.8 (100), 2181.8 ($[M+Na]^+$), which were identical to those of julibroside J_1 [2][9]. The ^{1}H- and ^{13}C-NMR spectra of **3** were also quite similar to those of julibroside J_1, except for those assignable to the inner quinovose moiety. A detailed comparison of ^{13}C-NMR data of the inner quinovose of **3** with those of the terminal quinovose of **3** or J_1 showed upfield shifts of 2.8 and 1.9 ppm for C(2) and C(4), respectively, and a downfield shift of 1.4 ppm for C(3), suggesting that the outer monoterpenoid acid was linked to the inner quinovose *via* the OH group at C(3). This was further supported by a marked *triplet* H-atom signal at *δ*(H) 5.82 in the ^{1}H-NMR spectrum of **3**, which was a typical signal of H–C(3) of inner quinovose due to the esterification at C(3) [3]. Accordingly, the structure of **3** was identified as 3-*O*-[*β*-D-xylopyranosyl-(1→2)-*α*-L-arabinopyranosyl-(1→6)-*β*-D-glucopyranosyl]-21-*O*-((2*E*,6*S*)-2-(hydroxymethyl)-6-methyl-6-*O*-{3-*O*-[(2*E*,6*R*)-2,6-dimethyl-6-*O*-*β*-D-quinovopyranosylocta-2,7-dienoyl]}-*β*-D-quinovopyranosylocta-2,7-dienoyl)acacic acid 28-*O*-*β*-D-glucopyranosyl-(1→3)-[*α*-L-arabinofuranosyl-(1→4)]-*α*-L-rhamnopyranosyl-(1→2)-*β*-D-glucopyranosyl ester. Compound **3** was a new compound and named julibroside J_{17}.

Compound **4**, an amorphous powder, showed positive *Molish* and *Liebermann–Burchard* reactions. *Quasi*-molecular-ion peaks at *m/z* (relative intensity) 2166.1 (49), 2167.1 (100), 2168.1 (29, $[M+Na]^+$) were observed in the MALDI-TOF-MS spectrum (positive-ion mode), which were consistent with a formula of $C_{100}H_{158}O_{49}$. The ^{1}H-NMR revealed characteristic signals of seven angular Me groups at *δ*(H) 1.86, 1.28, 1.15, 1.06, 1.04, 1.00, 0.96 (7*s*, each 3 H); nine anomeric H-atom signals at *δ*(H) 6.24 (*s*), 6.03 (*d*, *J* = 7.6), 5.88 (*s*), 5.31 (*d*, *J* = 7.9), 5.14 (br. *s*), 4.98 (*d*, *J* = 6.3), 4.87 (*d*, *J* = 7.4), 4.82 (*d*, *J* = 7.6), and 4.80 (*d*, *J* = 7.5), an olefinic H-atom signal at *δ*(H) 5.61

Table 1. *^{13}C-NMR Data of* **1**–**4** (in (D_5)pyridine; δ in ppm)

	1	**2**	**3**	**4**		**1**	**2**	**3**	**4**		**1**	**2**	**3**	**4**
C(1)	39.0	39.0	39.0	39.6	*MT′*					C(4)	77.2	77.1	75.0	76.8
C(2)	26.9	26.8	26.6	26.9	C(1)	167.8	167.8	168.2	167.8	C(5)	70.2	70.3	70.370.2	
C(3)	88.4	88.4	88.8	88.7	C(2)	128.6	128.6	128.3	127.6	C(6)	18.5	18.8	18.7	18.6
C(4)	39.7	39.7	39.6	40.1	C(3)	144.2	143.5	143.7	143.7	Qui′				
C(5)	56.1	56.1	56.1	56.0	C(4)	23.8	23.6	23.7	23.6	C(1)	99.4	99.2	99.2	
C(6)	18.9	18.4	18.8	18.4	C(5)	40.4	38.7	38.7	38.5	C(2)	75.6	75.5	75.4	
C(7)	33.6	33.7	33.7	33.6	C(6)	79.8	79.4	79.5	79.4	C(3)	78.4	78.5	78.4	
C(8)	40.2	40.2	40.2	40.4	C(7)	144.4	144.4	144.3	144.3	C(4)	77.0	77.0	76.9	
C(9)	47.2	47.2	47.2	47.1	C(8)	114.8	114.2	114.1	114.1	C(5)	72.6	72.7	72.7	
C(10)	37.2	37.2	37.2	37.1	C(9)	12.8	12.7	12.7	12.6	C(6)	18.9	18.8	18.8	
C(11)	23.9	23.9	23.5	23.7	C(10)	23.9	24.8	24.7	24.6	Xyl				
C(12)	123.0	123.1	123.1	123.1	*3-Sugars*					C(1)				100.1
C(13)	143.4	143.5	143.4	143.3	Glc					C(2)				75.4
C(14)	42.1	42.1	42.1	42.0	C(1)	106.8	106.7	106.7	106.7	C(3)				78.6
C(15)	35.9	36.0	36.0	35.9	C(2)	76.8	76.1	76.1	76.8	C(4)				70.8
C(16)	73.9	73.9	73.9	73.8	C(3)	78.4	78.5	78.4	78.4	C(5)				66.9
C(17)	51.7	51.7	51.7	51.6	C(4)	72.2	72.3	72.3	72.6	*28-Sugars*				
C(18)	40.9	41.0	41.0	40.9	C(5)	77.2	77.3	77.5	77.2	Glc′				
C(19)	47.9	47.9	48.0	47.9	C(6)	70.1	69.6	69.6	69.5	C(1)	95.7	95.7	95.7	95.6
C(20)	35.4	35.4	35.5	35.4	Fuc					C(2)	76.9	76.9	76.9	76.8
C(21)	77.1	77.1	77.2	77.0	C(1)	103.4	103.4			C(3)	77.6	77.5	78.4	78.1
C(22)	36.5	36.5	36.4	36.4	C(2)	82.2	82.1			C(4)	71.2	71.2	71.9	71.2
C(23)	28.3	28.3	28.3	28.2	C(3)	75.4	75.5			C(5)	79.1	79.0	79.0	79.0
C(24)	17.2	17.2	17.1	17.1	C(4)	71.8	72.6			C(6)	62.0	62.1	62.1	62.0
C(25)	15.9	15.9	15.9	15.8	C(5)	71.3	71.9			Rha				
C(26)	17.4	17.4	17.4	17.3	C(6)	17.3	17.2			C(1)	101.8	101.8	101.8	101.7
C(27)	27.4	27.3	27.3	27.2	Ara					C(2)	70.6	70.7	70.6	70.5
C(28)	174.5	174.5	174.4	174.4	C(1)			102.3	102.2	C(3)	82.0	82.0	82.1	82.0
C(29)	29.2	29.2	29.2	29.2	C(2)			80.3	80.3	C(4)	79.1	79.0	79.0	78.9
C(30)	19.2	19.2	19.2	19.1	C(3)			72.6	72.5	C(5)	69.2	69.1	69.2	69.1
MT					C(4)			67.4	67.4	C(6)	18.9	18.8	18.8	18.8
C(1)	167.8	167.8	167.6	167.5	C(5)			64.3	64.2	Araf				
C(2)	128.0	128.0	133.8	133.8	Xyl					C(1)	111.1	111.1	111.1	111.1
C(3)	142.3	142.3	145.2	145.2	C(1)	107.0	106.8	106.2	106.2	C(2)	84.5	84.4	84.4	84.4
C(4)	23.6	23.6	23.7	23.5	C(2)	75.8	75.4	75.4	75.6	C(3)	78.5	78.5	78.4	78.4
C(5)	40.5	40.6	41.0	40.9	C(3)	78.2	78.2	77.9	77.8	C(4)	85.5	85.6	85.5	85.4
C(6)	79.5	79.8	79.8	79.7	C(4)	70.9	70.8	70.9	70.8	C(5)	62.6	62.6	62.6	62.5
C(7)	144.2	144.0	142.8	143.9	C(5)	67.2	67.2	67.3	67.2	Glc″				
C(8)	115.1	115.0	115.1	115.0	*21-Sugars*					C(1)	105.8	105.8	105.7	105.7
C(9)	12.7	12.8	56.6	56.3	Qui					C(2)	75.3	75.2	75.4	75.3
C(10)	23.7	23.6	23.9	23.9	C(1)	99.4	99.4	99.3	99.2	C(3)	78.5	78.5	78.4	78.4
					C(2)	75.7	75.7	72.6	75.4	C(4)	71.4	71.8	71.9	71.8
					C(3)	75.8	75.7	79.8	75.6	C(5′)	78.4	78.5	78.2	78.4
										C(6)	62.8	62.9	62.9	62.8

(br. *s*, H–C(12)), and two monoterpenoid acid groups, suggesting that **4** was an oleanane triterpenoid saponin containing two monoterpenoid acids and nine sugar residues. In the ^{13}C-NMR spectrum of **4**, the signals for aglycone, two monoterpenoid acids, and sugar residues were in good agreement with those of julibroside J_1 [2][9], except for the outside sugar residue at C(21), indicating that the sugar residue at C(21) of **3** is not quinovose. This sugar was finally determined to be xylose by a comparison of its ^{1}H- and ^{13}C-NMR data with those of xylose moiety in julibroside J_{20} [5], and this was further confirmed by 2D-NMR spectra, including TOCSY, ^{13}C,^{1}H-COSY, and HMBC. Therefore, the structure of **4** was characterized as (3-*O*-[β-D-xylopyranosyl-(1 → 2)-α-L-arabinopyranosyl-(1 → 6)-β-D-glucopyranosyl]-21-*O*-((2*E*,6*S*)-2-(hydroxymethyl)-6-methyl-6-*O*-{4-*O*-[(2*E*,6*R*)-2,6-dimethyl-6-*O*-(β-D-xylopyranosylocta-2,7-dienoyl)]}-β-D-quinovopyranosylocta-2,7-dienoyl)acacic acid 28-*O*-β-D-glucopyranosyl-(1 → 3)-[α-L-arabinofuranosyl-(1 → 4)]-α-L-rhamnopyranosyl-(1 → 2)-β-D-glucopyranosyl ester. Compound **4** was a new compound and named julibroside J_{21}.

Triterpenoid saponins **1**–**4** were assayed for inhibitory activity against human cancer cell lines (H-60, PC-3 MIE-8, BGC823, MDA-MB-435, Bel-7402, and Hela) *in vitro*, and saponins **1**, **2**, and **4** showed good inhibitory activities against Bel 7402 human cancer cell line (*Table 2*).

Table 2. *The Cytotoxic Activity* [%] *of* **1**–**4** *against Bel-7402*

c [μg/ml]	**1**	**2**	**3**	**4**
1	75.7	5.8	– 1.7	3.8
10	85.6	63.8	29.9	65.6
100	91.9	72.4	74.3	76.6

Experimental Part

General. HPLC Grade MeCN was purchased from *Fisher Scientific* (Fair Lawn, NJ). Deionized H_2O was purifed by *Milli-Q* system (Bedford, MA). MeOH, $CHCl_3$, THF, and BuOH for purification were of anal. grade from *Beijing Reagent Company* (Beijing, P. R. China). Column chromatography (CC): macroporous resin D_{101} (*Nankai University Chemical Factory*), silica gel (SiO_2, 10–40 μm, 200–300 mesh; *Qingdao Marine Chemical Factory*), *Sephadex LH-20* (*Pharmacia*), and *RP* C_{18} silica gel (100–200 mesh; *Pharmacia*) were used. HPLC: *1*) a *Gilson* automatic system for prep. HPLC with an *Alltima* C_{18} column (5 μm, 60 Å pore size, 22 × 250 mm i.d. and 10 μm, 60 Å pore size, 22 × 250 mm i.d.), or *2*) a *Waters 600* semiprep. HPLC with a μ*Bondpak* C_{18} column (6 μm, 60 Å pore size, 7.8 × 300 mm i.d.). Optical rotations: *AA-10R Automatic Polarimeter* (*GA Optical Activity LTD*). IR Spectra: *Perkin-Elmer 983* FT-IR instrument; KBr disks. 1D- and 2D-NMR spectra: *Bruker AM 500* or *Varian-300* instruments at 295 K, δ in ppm relative to Me_4Si and *J* in Hz. FAB-MS: *ZABspec* mass spectrometer. MALDI-TOF-MS: *Bruker Autoflex III* mass spectrometer.

Plant Material. Dried stem bark of *A. julibrissin* was purchased from *Mianyang Medicinal Company* of Sichuan Province in October 1995 and identified by Prof. *Jun-Hua Zheng* (School of Pharmaceutical Sciences, Peking University Health Science Center). A vouch specimen has been deposited with the Department of Natural Medicines, School of Pharmaceutical Sciences, Peking University Health Science Center.

Extraction and Isolation. Air-dried powdered stem bark (13.5 kg) was extracted with 95% EtOH. The EtOH residue (1140 g) was suspended in H_2O and extracted successively with $CHCl_3$, AcOEt, and BuOH. The BuOH-soluble part was dissolved in MeOH, then poured into acetone dropwise. The precipitate was chromatographyed over D_{101} macroporous resin column, eluting with gradient solvent

system (100% $H_2O \rightarrow 100\%$ MeOH). The MeOH part (248 g) was subjected to CC (SiO_2; gradient $CHCl_3$/MeOH/H_2O 100:0:0 → 6:4:1) to afford 68 fractions (500 ml/Fr.). *Frs. 41–43* were decolorized by active charcoal in MeOH to give a white powder (22.5 g). The white powder was further subjected to repeated CC (*Sephadex LH-20* and *RP C-18* silica gel) and prep. HPLC to give **1** (17.0 mg), **2** (29.7 mg), **3** (14.5 mg), and **4** (64.8 mg).

Julibroside II (=α-L-*Arabinofuranosyl-(1 → 4)-[β-*D-*glucopyranosyl-(1 → 3)]-α-*L-*rhamnopyranosyl-(1 → 2)-1-*O-*[(3β,16α,21β)-21-({(*2E,6S*)-6-[(4-*O-*{(*2E,6S*)-6-[(β-*D-*quinovopyranosyl)oxy]-2,6-dimethylocta-2,7-dienoyl}-β-*D-*quinovopyranosyl)oxy]-2,6-dimethylocta-2,7-dienoyl}oxy)-16-hydroxy-28-oxo-3-{[β-*D-*xylopyranosyl-(1 → 2)-β-*D-*fucopyranosyl-(1 → 6)-β-*D-*glucopyranosyl]oxy}olean-12-en-28-yl]-β-*D-*glucopyranose*; **1**). White powder. IR (KBr): 3406, 2918, 1700, 1639, 1382, 1256, 1072. ^{1}H-NMR ((D$_5$)pyridine): 7.05 (*t*, *J* = 6.4, H−C(3$_{MT'}$)); 6.91 (*t*, *J* = 7.2, H−C(3$_{MT}$)); 6.26 (*s*, H−C(1$_{araf}$)); 6.24 (*dd*, *J* = 11.0, 17.7, H−C(7$_{MT}$)); 6.21 (*dd*, *J* = 11.0, 17.4, H−C(7$_{MT'}$)); 6.07 (*d*, *J* = 7.6, H−C(1$_{glc'}$)); 5.92 (*s*, H−C(1$_{rha}$)); 5.64 (br. *s*, H−C(12)); 5.47 (*d*, *J* = 17.4, H−C(8b$_{MT'}$)); 5.44 (*d*, *J* = 17.7, H−C(8b$_{MT}$)); 5.33 (*d*, *J* = 8.2, H−C(1$_{glc''}$)); 5.28 (*d*, *J* = 11.0, H−C(8a$_{MT'}$)); 5.23 (*d*, *J* = 11.0, H−C(8a$_{MT}$)); 5.10 (*d*, *J* = 7.0, H−C(1$_{xyl}$)); 5.01 (*d*, *J* = 7.9, H−C(1$_{fuc}$)); 4.94 (*d*, *J* = 7.5, H−C(1$_{glc}$)); 4.87 (*d*, *J* = 7.5, H−C(1$_{qui}$), H−C(1$_{qui'}$)); 1.91 (*s*, Me(27)); 1.89 (*s*, Me(9$_{MT}$)); 1.85 (*s*, Me(9$_{MT'}$)); 1.77 (*d*, *J* = 6.0, Me(6$_{rha}$)); 1.60 (*d*, *J* = 5.5, Me(6$_{qui'}$)); 1.55 (*s*, Me(10$_{MT}$), Me(10$_{MT'}$)); 1.50 (*d*, *J* = 6.5, Me(6$_{fuc}$)); 1.36 (*d*, *J* = 6.0, Me(6$_{qui}$)); 1.33 (*s*, Me(23)); 1.19 (*s*, Me(26)); 1.09 (*s*, Me(30)); 1.06 (*s*, Me(29)); 1.01 (*s*, Me(24)); 0.99 (*s*, Me(25)). ^{13}C-NMR: see *Table 1*.

Julibroside J$_{16}$ (=α-L-*Arabinofuranosyl-(1 → 4)-[β-*D-*glucopyranosyl-(1 → 3)]-α-*L-*rhamnopyranosyl-(1 → 2)-1-*O-*[(3β,16α,21β)-21-({(*2E,6S*)-6-[(4-*O-*{(*2E,6R*)-6-[(β-*D-*quinovopyranosyl)oxy]-2,6-dimethylocta-2,7-dienoyl}-β-*D-*quinovopyranosyl)oxy]-2,6-dimethylocta-2,7-dienoyl}oxy)-16-hydroxy-28-oxo-3-{[β-*D-*xylopyranosyl-(1 → 2)-β-*D-*fucopyranosyl-(1 → 6)-β-*D-*glucopyranosyl]oxy}olean-12-en-28-yl]-β-*D-*glucopyranose*; **2**). White powder. $[\alpha]_D^{20} = -35.8$ (*c* = 0.70, MeOH). IR (KBr): 3403, 2924, 1701, 1640, 1383, 1276, 1072, 637. ^{1}H-NMR ((D$_5$)pyridine): 7.08 (*t*, *J* = 6.4, H−C(3$_{MT'}$)); 6.88 (*t*, *J* = 7.0, H−C(3$_{MT}$)); 6.24 (*s*, H−C(1$_{araf}$)); 6.32 (*dd*, *J* = 11.0, 17.7, H−C(7$_{MT}$)); 6.18 (*dd*, *J* = 10.8, 17.4, H−C(7$_{MT'}$)); 6.04 (*d*, *J* = 8.0, H−C(1$_{glc'}$)); 5.88 (*s*, H−C(1$_{rha}$)); 5.60 (br. *s*, H−C(12)); 5.44 (*d*, *J* = 17.7, H−C(8b$_{MT'}$)); 5.43 (*d*, *J* = 17.4, H−C(8b$_{MT}$)); 5.31 (*d*, *J* = 7.8, H−C(1$_{glc''}$)); 5.28 (*d*, *J* = 11.0, H−C(8a$_{MT'}$)); 5.20 (*d*, *J* = 10.8, H−C(8a$_{MT}$)); 5.06 (*d*, *J* = 7.0, H−C(1$_{xyl}$)); 4.99 (*d*, *J* = 7.6, H−C(1$_{fuc}$)); 4.92 (*d*, *J* = 7.5, H−C(1$_{glc}$)); 4.84 (*d*, *J* = 7.6, H−C(1$_{qui}$)); 4.81 (*d*, *J* = 7.2, H−C(1$_{qui'}$)); 1.92 (*s*, Me(27)); 1.88 (*s*, Me(9$_{MT}$)); 1.85 (*s*, Me(9$_{MT'}$)); 1.75 (*d*, *J* = 5.8, Me(6$_{rha}$)); 1.58 (*d*, *J* = 6.0, Me(6$_{qui'}$)); 1.51 (*s*, Me(10$_{MT}$)); 1.48 (*d*, *J* = 5.6, Me(6$_{fuc}$)); 1.44 (*s*, Me(10$_{MT'}$)); 1.34 (*d*, *J* = 5.8, Me(6$_{qui}$)); 1.28 (*s*, Me(23)); 1.15 (*s*, Me(26)); 1.09 (*s*, Me(30)); 1.04 (*s*, Me(29)); 1.01 (*s*, Me(24)); 0.97 (*s*, Me(25)). ^{13}C-NMR: see *Table 1*. MALDI-TOF-MS (pos.): 2177.9 (56), 2178.9 (100), 2179.9 (45), 2180.9 (10, $[M + Na]^+$).

Julibroside J$_{17}$ (=α-L-*Arabinofuranosyl-(1 → 4)-[β-*D-*glucopyranosyl-(1 → 3)]-α-*L-*rhamnopyranosyl-(1 → 2)-1-*O-*[(3β,16α,21β)-21-{[(*2E,6S*)-6-[(3-*O-*{(*2E,6R*)-6-[(β-*D-*quinovopyranosyl)oxy]-2,6-dimethylocta-2,7-dienoyl}-β-*D-*quinovopyranosyl)oxy]-2-(hydroxymethyl)-6-methylocta-2,7-dienoyl]oxy}-16-hydroxy-28-oxo-3-{[β-*D-*xylopyranosyl-(1 → 2)-α-*L-*arabinopyranosyl-(1 → 6)-β-*D-*glucopyranosyl]-oxy}olean-12-en-28-yl]-β-*D-*glucopyranose*; **3**). White powder. $[\alpha]_D^{20} = -30.5$ (*c* = 0.73, MeOH). IR (KBr): 3407, 2928, 1692, 1639, 1561, 1411, 1284, 1072. ^{1}H-NMR ((D$_5$)pyridine): 7.03 (*t*, *J* = 6.8, H−C(3$_{MT}$)); 7.02 (*t*, *J* = 6.8, H−C(3$_{MT'}$)); 6.28 (*dd*, *J* = 10.9, 17.4, H−C(7$_{MT'}$)); 6.25 (*s*, H−C(1$_{araf}$)); 6.11 (*dd*, *J* = 11.0, 17.6, H−C(7$_{MT}$)); 6.04 (*d*, *J* = 7.8, H−C(1$_{glc'}$)); 5.88 (*s*, H−C(1$_{rha}$)); 5.82 (*t*, *J* = 9.1, H−C(3$_{qui}$)); 5.62 (br. *s*, H−C(12)); 5.34 (*d*, *J* = 17.4, H−C(8b$_{MT'}$)); 5.31 (*d*, *J* = 7.4, H−C(1$_{glc''}$)); 5.28 (*d*, *J* = 17.6, H−C(8b$_{MT}$)); 5.18 (*d*, *J* = 10.9, H−C(8a$_{MT'}$)); 5.16 (br. *s*, H−C(1$_{arap}$)); 5.14 (*d*, *J* = 11.0, H−C(8a$_{MT}$)); 4.98 (*d*, *J* = 7.4, H−C(1$_{xyl}$)); 4.87 (*d*, *J* = 7.6, H−C(1$_{glc}$)); 4.83 (*d*, *J* = 7.8, H−C(1$_{qui}$)); 4.79 (*d*, *J* = 7.6, H−C(1$_{qui'}$)); 4.71 (*s*, CH$_2$(9$_{MT}$)); 1.87 (*s*, Me(27)); 1.84 (*s*, Me(9$_{MT'}$)); 1.75 (*d*, *J* = 5.8, Me(6$_{rha}$)); 1.59 (*d*, *J* = 5.5, Me(6$_{qui}$)); 1.55 (*d*, *J* = 5.3, Me(6$_{qui'}$)); 1.48 (*s*, Me(10$_{MT}$)); 1.42 (*s*, Me(10$_{MT'}$)); 1.28 (*s*, Me(23)); 1.15 (*s*, Me(26)); 1.08 (*s*, Me(30)); 1.03 (*s*, Me(29)); 1.01 (*s*, Me(24)); 0.95 (*s*, Me(25)). ^{13}C-NMR: see *Table 1*. FAB-MS (pos.): 2179.8, 2180.8 (100), 2181.8 ($[M + Na]^+$).

Julibroside J$_{21}$ (=α-L-*Arabinofuranosyl-(1 → 4)-[β-*D-*glucopyranosyl-(1 → 3)]-α-*L-*rhamnopyranosyl-(1 → 2)-1-*O-*[(3β,16α,21β)-21-{[(*2E,6S*)-6-[(-4-*O-*{(*2E,6R*)-2,6-dimethyl-6-[(β-*D-*xylopyranosyl)oxy]-octa-2,7-dienoyl}-β-*D-*quinovopyranosyl)oxy]-2-(hydroxymethyl)-6-methylocta-2,7-dienoyl]oxy}-16-hydroxy-28-oxo-3-{[β-*D-*xylopyranosyl-(1 → 2)-α-*L-*arabinopyranosyl-(1 → 6)-β-*D-*glucopyranosyl]oxy}-

*olean-12-en-28-yl]-β-*D*-glucopyranose*; **4**). White powder. $[\alpha]_D^{20} = -39.4$ ($c = 0.71$, MeOH). IR (KBr): 3410, 2927, 1692, 1640, 1383, 1281, 1074. ^{1}H-NMR ((D$_5$)pyridine): 7.05 (*t*, *J* = 7.2, H−C(3$_{MT'}$)); 7.02 (*t*, *J* = 7.0, H−C(3$_{MT}$)); 6.30 (*dd*, *J* = 11.1, 17.5, H−C(7$_{MT'}$)); 6.24 (*s*, H−C(1$_{araf}$)); 6.17 (*dd*, *J* = 8.9, 18.3, H−C(7$_{MT}$)); 6.03 (*d*, *J* = 7.6, H−C(1$_{glc'}$)); 5.88 (*s*, H−C(1$_{rha}$)); 5.61 (br. *s*, H−C(12)); 5.44 (*d*, *J* = 18.3, H−C(8b$_{MT}$)); 5.31 (*d*, *J* = 7.9, H−C(1$_{glc''}$)); 5.31 (*d*, *J* = 17.6, H−C(8b$_{MT'}$)); 5.19 (*d*, *J* = 8.9, H−C(8a$_{MT}$)); 5.18 (*d*, *J* = 11.1, H−C(8a$_{MT'}$)); 5.14 (br. *s*, H−C(1$_{arap}$)); 4.98 (*d*, *J* = 6.3, H−C(1$_{xyl}$)); 4.87 (*d*, *J* = 7.4, H−C(1$_{glc}$)); 4.82 (*d*, *J* = 7.6, H−C(1$_{qui}$)); 4.80 (*d*, *J* = 7.5, H−C(1$_{xyl'}$)); 4.71 (*s*, CH$_2$(9$_{MT}$)); 1.92 (*s*, H−C(9$_{MT'}$)); 1.86 (*s*, Me(27)); 1.75 (*d*, *J* = 5.5, Me(6$_{rha}$)); 1.49 (*s*, Me(10$_{MT}$)); 1.46 (*s*, Me(10$_{MT'}$)); 1.33 (*d*, *J* = 6.1, Me(6$_{qui}$)); 1.28 (*s*, Me(23)); 1.15 (*s*, Me(26)); 1.06 (*s*, Me(30)); 1.04 (*s*, Me(29)); 1.00 (*s*, Me(24)); 0.96 (*s*, Me(25)). ^{13}C-NMR: see *Table 1*. MALDI -TOF MS (pos.): 2166.1 (49), 2167.1 (100), 2168.1 (29, $[M + Na]^+$).

Evaluation of Inhibitory Activity of **1**–**4** *against Human Cancer Cell Lines.* Triterpenoid saponins **1**–**4** were assayed for inhibitory activity against human cancer cell lines (H-60, PC-3MIE-8, BGC823, MDA-MB-435, Bel-7402, and Hela) *in vitro*, and saponins **1**, **2**, and **4** showed good inhibitory activity against Bel 7402 human cancer cell line (*Table 2*).

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