Oleanolic Triterpene Saponins from the Roots of *Panax bipinnatifidus*

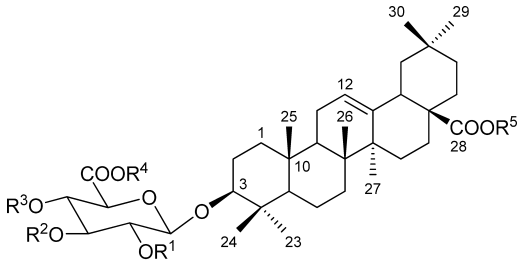
Nguyen Huu Tung,[a,b] Tran Hong Quang,[a,b] Nguyen Thi Thanh Ngan,[a] Chau Van Minh,[b] Bui Kim Anh,[c] Pham Quoc Long,[d] Nguyen Manh Cuong,[d] and Young Ho Kim*,[a]

[a] *College of Pharmacy, Chungnam National University; Daejeon 305–764, Korea:* [b] *Institute of Marine Biochemistry, Vietnam Academy of Science and Technology;* [c] *Institute of Chemistry, Vietnam Academy of Science and Technology; and* [d] *Institute of Natural Products Chemistry, Vietnam Academy of Science and Technology; 18 Hoang Quoc Viet, Caugiay, Hanoi, Vietnam.* Received June 16, 2011; accepted August 1, 2011; published online August 5, 2011

Ten oleanane-type saponins (1—10), including three new compounds, namely bifinosides A—C (1—3), were isolated from the roots of *Panax bipinnatifidus* Seem. Their structures were elucidated on the basis of chemical and spectroscopic methods.

Key words *Panax bipinnatifidus*; Araliaceae; oleanane triterpene; oleanolic acid; bifinoside

Panax bipinnatifidus Seem. (Araliaceae) is a hygrophilous and shade-enduring plant, preferring cool and wet climate conditions with an average temperature of about 12—15 °C. In nature, this plant is relatively rare and mostly found in the high mountainous region of Hoang Lien Son in the northwest of Vietnam. The root of *P. bipinnatifidus* has been used as a valuable tonic to increase mental and physical performance, improve thinking and memory, reduce cancer risk, and lower blood sugar in diabetics in the Vietnamese traditional medicine.[1)] To date, phytochemical studies on this plant have been not undertaken extensively. In our ongoing research on *Panax* plants, the presence of saponins in polar fractions of a methanol extract of this plant was suggested. From other plants of the same genus such as *P. ginseng* and *P. stipuleanatus*, many kinds of saponins have been identified.[2—5)] We therefore carried out a study of saponins of the title plant. This paper herein deals with the isolation and structural identification of ten saponins (**1**—**10**) from the root of *P. bipinnatifidus*.



Comp.	R^1	R^2	R^3	R^4	R^5
1:	Ara(p)	H	H	Me	H
2:	H	Xyl(1→6)glc	H	Me	H
3:	Xyl	Ara(p)	H	Me	Glc
4:	H	H	Ara(p)	Me	H
5:	H	H	H	Me	Glc
6:	Xyl	H	H	Me	H
7:	H	Glc	Ara(f)	H	H
8:	Xyl	H	H	Me	Glc
9:	Xyl	Ara(p)	H	H	Glc
10:	H	Glc	Ara(f)	Me	Glc

Me : methyl
Ara(f) : α-L-arabinofuranosyl
Ara(p) : α-L-arabinopyranosyl
Glc : β-D-glucopyranosyl
Xyl : β-D-xylopyranosyl

Fig. 1. Structures of Saponins **1**—**10**

Results and Discussion

The methanolic extract from the roots of *P. bipinnatifidus* was suspended in water and partitioned with CH_2Cl_2. The H_2O layer was subjected to Diaion HP-20 column chromatography, followed by various silica gel and C-18 reversed-phase columns to afford three new saponins, bifinosides A—C (**1**—**3**), and seven known compounds including narcissiflorine methyl ester (**4**),[6)] chikusetsusaponin IVa (**5**),[5)] pseudoginsenoside RP_1 methyl ester (**6**),[5)] stipuleanoside R_1 (**7**),[7)] pseudoginsenoside RT_1 methyl ester (**8**),[5)] momordin IIe (**9**),[8)] and stipuleanoside R_2 methyl ester (**10**),[5)] respectively (Fig. 1).

Bifinoside A (**1**), a white amorphous powder, has the molecular formula $C_{42}H_{66}O_{13}$ as determined by high resolusion-electrospray ionization-time-of-flight-mass spectrometry (HR-ESI-TOF-MS) experiment (Found at *m/z* $[M+H]^+$ 779.4596, Calcd for $C_{42}H_{67}O_{13}$ 779.4582). Acid hydrolysis of **1** liberated oleanolic acid and sugar components of D-glucuronic acid and L-arabinose as confirmed by gas chromatography (GC) analysis. The ^{1}H-NMR spectrum of the aglycon moiety of **1** showed seven tertiary methyl groups at δ 0.75, 0.78, 0.86, 0.88, 0.89, 0.98, and 1.10, that correlated in the heteronuclear multiple quantum coherence (HMQC) experiments with the carbon signals at δ 17.7, 15.9, 33.6, 24.0, 16.5, 28.2, and 26.4, respectively (Tables 1—3). A further feature was the signal at δ 5.16 (1H, t, J=5.4 Hz), typical of H-12 of Δ^{12} oleanene skeleton, which was further confirmed by the presence of the signals at δ 123.7 (C-12) and 145.2 (C-13) in the ^{13}C-NMR spectrum.[7,9)] A signal at δ 181.9 and the carbon resonances of ring D in the ^{13}C-NMR spectrum similar to those of oleanolic acid suggested the occurrence of a free carboxylic group at the C-28 position. Furthermore, the glycosylated 3β-hydroxy oleanolic acid was proposed as the presence of a secondary alcoholic function from the signal at δ 3.07 (1H, dd, J=11.4, 4.2 Hz), which correlated in the HMQC spectrum with the downfield carbon signal at δ 91.3.

The ^{1}H- and ^{13}C-NMR spectra of **1** showed the presence of two anomeric protons at δ 4.36 (d, J=5.2 Hz) and 4.44 (d, J=7.8 Hz) and carbons at δ 105.6 and 106.3. Additionally, the appearance of a methoxy proton at δ 3.70 (3H, s), which correlated with the carbon signal at δ 52.8 in the HMQC spectrum and with the carbon resonance at δ 171.2 in the

* To whom correspondence should be addressed. e-mail: yhk@cnu.ac.kr

Table 1. ^{13}C-NMR Data (δ, CD_3OD) for Bifinosides A—C (**1**—**3**)

Carbon	**1**	**2**	**3**	Carbon	**1**	**2**	**3**
Aglycone				Sugar moiety	3-GluAMe (I)	3-GluAMe (I)	3-GluAMe (I)
1	39.8	39.8	39.9	1	105.6	105.8	105.8
2	27.1	27.1	27.1	2	82.7	74.7	79.6
3	91.3	91.9	91.8	3	77.6	86.5	86.5
4	40.3	40.4	40.7	4	71.2	70.0	71.6
5	57.1	57.1	57.1	5	77.8	77.9	76.1
6	19.3	19.3	19.3	6	171.2	171.0	170.9
7	33.8	33.8	33.1	$COO\underline{C}H_3$	52.8	52.9	52.9
8	40.6	40.6	40.4		Ara(p) (II)	Glc (II)	Xyl (II)
9	48.8	48.8	49.8	1	106.3	105.0	104.5
10	37.9	37.9	37.9	2	72.9	74.7	76.1
11	24.5	24.5	24.6	3	74.8	78.3	78.2
12	123.7	123.6	123.8	4	67.2	71.6	71.1
13	145.2	145.2	144.8	5	64.3	79.6	66.9
14	42.9	42.9	42.9	6		67.9	
15	28.9	28.9	28.9			Xyl (III)	Ara(p) (III)
16	24.1	24.1	24.0	1		104.5	104.9
17	47.7	47.7	48.0	2		76.1	72.9
18	42.8	42.8	42.6	3		78.1	74.6
19	47.3	47.3	47.2	4		71.5	67.9
20	31.6	31.6	31.4	5		66.9	64.9
21	34.9	34.9	34.1				28-Glc (IV)
22	34.0	34.0	33.1	1			95.6
23	28.2	28.2	28.3	2			73.9
24	16.5	16.6	16.0	3			78.6
25	15.9	16.0	16.6	4			71.4
26	17.7	17.7	17.7	5			78.2
27	26.4	26.4	26.5	6			62.4
28	181.9	181.9	178.0				
29	33.6	33.6	33.5				
30	24.0	24.0	23.9				

Table 2. ^{1}H-NMR Data (δ, CD_3OD) of the Aglycon Moieties of Bifinosides A—C (**1**—**3**)[a]

H	**1**	**2**	**3**
1	0.93, 1.56, 2H[b]	0.93, 1.57, 2H[b]	0.92, 1.57, 2H[b]
2	1.60, 1.77, 2H[b]	1.61, 1.77, 2H[b]	1.62, 1.76, 2H[b]
3	3.07, 1H, dd (11.4, 4.2)	3.08, 1H, dd (11.4, 4.2)	3.10, 1H, dd (11.4, 4.2)
4			
5	0.78, 1H, dd (12.0, 4.2)	0.78, 1H, dd (12.0, 4.2)	0.78, 1H, dd (12.0, 4.2)
6	1.36, 1.53, 2H[b]	1.36, 1.54, 2H[b]	1.36, 1.54, 2H[b]
7	1.15, 1.26, 2H[b]	1.15, 1.26, 2H[b]	1.15, 1.26, 2H[b]
8			
9	1.54, 1H[b]	1.54, 1H[b]	1.53, 1H[b]
10			
11	1.48, 1.88, 2H[b]	1.48, 1.88, 2H[b]	1.48, 1.88, 2H[b]
12	5.16, 1H, t (5.4)	5.17, 1H, t (5.4)	5.18, 1H, t (5.4)
13			
14			
15	1.02, 1.72, 2H[b]	1.02, 1.72, 2H[b]	1.04, 1.74, 2H[b]
16	1.80—1.91, 2H[b]	1.80—1.90, 2H[b]	1.80—1.91, 2H[b]
17			
18	2.82, 1H, dd (12.6, 4.2)	2.80, 1H, dd (12.6, 4.2)	2.82, 1H, dd (12.6, 4.2)
19	1.10, 1.65, 2H[b]	1.10, 1.65, 2H[b]	1.12, 1.67, 2H[b]
20			
21	1.17, 1.36, 2H[b]	1.17, 1.36, 2H[b]	1.18, 1.36, 2H[b]
22	1.49, 1.71, 2H[b]	1.49, 1.71, 2H[b]	1.50, 1.71, 2H[b]
23	0.98, 3H, s	0.98, 3H, s	0.99, 3H, s
24	0.89, 3H, s	0.88, 3H, s	0.89, 3H, s
25	0.78, 3H, s	0.77, 3H, s	0.78, 3H, s
26	0.75, 3H, s	0.74, 3H, s	0.73, 3H, s
27	1.10, 3H, s	1.10, 3H, s	1.10, 3H, s
28			
29	0.86, 3H, s	0.85, 3H, s	0.86, 3H, s
30	0.88, 3H, s	0.88, 3H, s	0.88, 3H, s

a) Assignments were established by HMQC, DQF-COSY, and HMBC spectra. *J* values (in Hz) are given in parentheses. *b*) Multiplicities not assigned due to overlapped signals.

Table 3. ^{1}H-NMR Data (δ, CD_3OD) of the Sugar Moieties of Bifinosides A—C (**1**—**3**)[a]

H	**1**	**2**	**3**
	GluAMe (I)	GluAMe (I)	GluAMe (I)
1	4.44, 1H, d (7.8)	4.46, 1H, d (7.8)	4.46, 1H, d (7.2)
2	3.56, 1H[b]	3.48, 1H[b]	3.64, 1H, t (7.8)
3	3.48, 1H[b]	3.69, 1H[b]	3.71, 1H[b]
4	3.42, 1H[b]	3.78, 1H[b]	3.58, 1H[b]
5	3.81, 1H[b]	3.83, 1H[b]	3.85, 1H[b]
6			
$COOC\underline{H}_3$	3.70, 3H, s	3.70 s	3.72, 3H, s
	Ara(p) (II)	Glc (II)	Xyl (II)
1	4.36, 1H, d (5.2)	4.70, 1H, d (7.8)	4.75, 1H, d (7.2)
2	3.50, 1H[b]	3.26, 1H[b]	3.10, 1H[b]
3	3.42, 1H[b]	3.30, 1H[b]	3.39, 1H[b]
4	3.71, 1H[b]	3.34, 1H[b]	3.42, 1H[b]
5	3.34, 3.75, 2H[b]	3.62, 1H[b]	3.60, 3.87, 2H[b]
6		3.60, 1H[b]	
		3.85, 1H, dd(11.4, 5.4)	
		Xyl (III)	Ara(p) (III)
1		4.41, 1H, d (7.2)	4.52, 1H, d (4.8)
2		3.12, 1H[b]	3.56, 1H[b]
3		3.24, 1H[b]	3.48, 1H[b]
4		3.40, 1H[b]	3.78, 1H[b]
5		3.13, 3.72, 2H[b]	3.12, 3.75, 2H[b]
			Glc (IV)
1			5.34, 1H, d (7.8)
2			3.29, 1H[b]
3			3.32, 1H[b]
4			3.40, 1H[b]
5			3.42, 1H[b]
6			3.63, 1H[b]
			3.80, 1H, d (12.0, 5.4)

a) Assignments were established by HMQC, DQF-COSY, and HMBC spectra. *J* values (in Hz) are given in parentheses. *b*) Multiplicities not assigned due to overlapped signals.

heteronuclear multiple bond correlation (HMBC) spectrum, suggested the presence of glucuronate methyl ester (GluAMe) moiety. Complete assignments of all the proton resonances in each sugar unit were achieved by double-quantum filtered correlation spectroscopy (DQF-COSY), HMQC, and HMBC spectra (Tables 1—3). In the HMBC experiment, the anomeric signal at δ 4.44 (H-$1_{GluAMe(I)}$) showed a long-range correlation with the signal at δ 91.3 (C-3), indicating that glucuronyl moiety is directly linked to the triterpene structure at C-3. Subsequently, the arabinose unit linked to the GluAMe segment was at H-$2_{GluAMe(I)}$ on the basis of the HMBC spectrum, in which the two anomeric protons at δ 4.36 (H-$1_{Ara(II)}$) and 4.44 (H-$1_{GluAMe(I)}$) correlated with the same carbon C-$2_{GluAMe(I)}$ at δ 82.7. Consequently, bifinoside A (**1**) was characterized as oleanolic acid 3-*O*-α-L-arabinopyranosyl(1→2)-β-D-glucuronopyranoside-6-*O*-methyl ester.

Bifinoside B (**2**), also a white amorphous power, revealed a quasi-molecular ion peak $[M+Na]^+$ at *m/z* 963.4913 in its HR-ESI-TOF-MS spectrum. Acid hydrolysis of **2** afforded oleanolic acid and sugar components of D-glucuronic acid, D-glucose, and D-xylose. The ^{1}H- and ^{13}C-NMR spectra showed the presence of oleanolic acid, the same aglycon moiety as saponin **1**, which was glycosylated at C-3 as the downfield shift at δ 91.9, and the occurrence of three anomeric signals [δ_H 4.41$_{Xyl(III)}$ (d, J=7.2 Hz), 4.70$_{Glc(II)}$ (d, J=7.8 Hz), 4.46$_{GluAMe(I)}$ (d, J=7.8 Hz), and δ_C 104.5, 105.0, 105.8, respectively]. The sugar sequence was proposed by HMBC spectrum after assignments of the protons and the carbons by a combination of HMQC and COSY data, starting from the anomeric proton of each sugar unit (Tables 1—3). Accordingly, H-$1_{GluAMe(I)}$ (δ 4.46) gave a correlation with the C-3 at δ 91.9, and a cross peak between H-$1_{Glc(II)}$ (δ 4.70) and C-$3_{GluAMe(I)}$ (δ 86.5) was revealed. Additionally, a cross peak between H-$1_{Xyl(III)}$ (δ 4.41) and C-$6_{Glc(II)}$ (δ 67.9) was also observed. Hence, bifinoside B (**2**) was concluded to be oleanolic acid 3-*O*-[β-D-xylopyranosyl(1→6)-β-D-glucopyranosyl](1→3)-β-D-glucuronopyranoside-6-*O*-methyl ester.

Bifinoside C (**3**), again a white amorphous power, showed a quasi-molecular ion peak $[M+H]^+$ at *m/z* 1073.5554 in the HR-ESI-TOF-MS spectrum. The acid hydrolysis of this saponin liberated oleanolic acid and sugar components of D-glucuronic acid, L-arabinose, D-glucose, and D-xylose based on results of the GC analysis. Four anomeric signals were observed in the ^{13}C-NMR spectrum at δ 95.6, 104.5, 104.9, and 105.8 and at δ 4.46 (1H, d, J=7.2 Hz), 4.52 (1H, d, J=4.8 Hz), 4.75 (1H, d, J=7.2 Hz), and 5.34 (1H, J=7.8 Hz) in the ^{1}H-NMR spectrum. Furthermore, DQF-COSY and HMQC experiments allowed the sequential assignments of resonances for each sugar, starting from the anomeric proton signals (Tables 1—3). On the other hand, the HMBC spectrum showed the presence of a sugar chain at the C-3 and a monosaccharide unit at the C-28. The sequence of the monosaccharide chain at C-3 was further also defined by the HMBC spectrum, in which cross peaks of H-$1_{GluAMe(I)}$ (δ 4.46)/C-3 (δ 91.8), H-$1_{Xyl(II)}$ (δ 4.75)/C-$2_{GluAMe(I)}$ (δ 79.6), and H-$1_{Ara(III)}$ (δ 4.52)/C-$3_{GluAMe(I)}$ (δ 86.5) were observed; and the C-28 position of the triterpene aglycone was glycosylated with the D-glucopyranosyl upon the HMBC correlation of H-$1_{Glc(IV)}$ (δ 5.34)/C-28 (δ 178.0). On the basis of these findings, bifinoside C (**3**) was identified as 28-*O*-β-D-glucopyranosyloleanolic acid 3-*O*-β-D-xylopyranosyl(1→2)-[α-L-arabinopyranosyl(1→3)]-β-D-glucuronopyranoside-6-*O*-methyl ester.

To the best of our knowledge, there has very limited report on chemical constituents of *P. bipinnatifidus*. The current study has taken well part in research of phytochemical components of the title plant, which is rich in various oleanane-type saponins. In the view of *Panax* genus, *P. ginseng* (Asian ginseng), *P. quinquefolium* (American ginseng), and *P. vietnamensis* among the most used medicinal plants have been well documented with majority of dammarane-type glycosides.[10—14] Besides, the other species, *P. stipuleanatus* was dominated by oleanane-type saponins.[5] This result can have a significant chemotaxonomical meaning in the further studies for classification of the *Panax* species.

Experimental

General Procedures Optical rotations were obtained using a DIP-360 digital polarimeter (Jasco, Easton, U.S.A.). IR spectra were measured using a Perkin-Elmer 577 spectrometer (Perkin Elmer, Waltham, U.S.A.). NMR spectra were recorded on Bruker DRX 600 NMR spectrometers (Bruker, Billerica, U.S.A.). HR-ESI-TOFMS experiments utilized a JEOL AccuT-OF^{TM} LC mass spectrometer (Jeol, Tokyo, Japan). GC (Shimadzu-2010, Kyoto, Japan) using a DB-05 capillary column (0.5 mm i.d.×30 m) [column temperature, 210 °C; detector temperature, 300 °C; injector temperature, 270 °C; He gas flow rate, 30 ml/min (splitting ratio: 1/20)] was used for sugar determination. Column chromatography (CC) was performed on silica gel (70—230, 230—400 mesh, Darmstadt, Germany), YMC RP-18 resins (30—50 μm, Fuji Silysia Chemical Ltd., Aichi, Japan), and HP-20 Diaion (Mitshubishi Chemical, Tokyo, Japan). TLC was performed on Kieselgel 60 F_{254} (1.05715; Merck) or RP-18 F_{254s} (Merck) plates. Spots were visualized by spraying with 10% aqueous H_2SO_4 solution, followed by heating.

Plant Material The roots of *P. bipinnatifidus* were collected in Sapa, Laocai, Vietnam and were taxonomically identified by botanist Ngo Van Trai (Institute of Medicinal Materials, Hanoi, Vietnam). A voucher specimen (VHKC-0370) was deposited at the Herbarium of INPC, Vietnam.

Extraction and Isolation The air-dried roots of *P. bipinnatifidus* (0.5 kg) were extracted in MeOH, using Soxhlet extraction apparatus (2 l, 12 h), and extracts were concentrated *in vacuo* to dryness. The obtained MeOH residue (85 g) was suspended in H_2O (0.5 l), then partitioned with CH_2Cl_2 (0.5 l×3) to obtain CH_2Cl_2-soluble fraction (10 g) and the water layer, which was subjected to a Diaion HP-20 column eluted with a gradient of MeOH in H_2O (25, 50, 75, 100% MeOH, v/v) to give four fractions (fr. 1.1—1.4). Next, fr. 1.3 (23 g) was fractionated on a silica gel column with a gradient of CH_2Cl_2–MeOH (10 : 1—1 : 1) to furnish five fractions (fr. 2.1—2.5). Fr. 2.1 (600 mg) was repeatedly chromatographed on a silica gel column with $CHCl_3$–MeOH–H_2O (6 : 1 : 0.1), followed by reversed-phase columns eluted with MeOH–H_2O (4 : 1, 5 : 1) to obtain compounds **1** (5.4 mg), **4** (3.5 mg), **5** (10.0 mg), and **6** (13.0 mg), respectively.

Fr. 2.2 (2.3 g) and fr. 2.3 (2.4 g) were combined due to their similar TLC profiles, and then subjected to a silica gel column with $CHCl_3$–MeOH–H_2O (4 : 1 : 0.1) to furnish eleven sub-fractions (fr. 3.1—3.11). Next, fr. 3.2 (140 mg) was purified on a RP column with MeOH–H_2O (5 : 1) to yield compounds **2** (15.0 mg) and **7** (4.5 mg). Similarly, fr. 3.4 (220 mg) was chromatographed over a RP column with MeOH–H_2O (4 : 1) to yield compound **8** (160 mg). Fr. 3.7 (280 mg) was further purified on a RP column with MeOH–H_2O to afford compounds **3** (45 mg) and **9** (18 mg). Finally, compound **10** (75 mg) was obtained from fr. 3.9 (250 mg) by mean of RP column chromatography with the elution of MeOH–H_2O (4 : 1).

Bifinoside A (**1**): White amorphous powder; $[\alpha]_D^{20}$ +8.0° (c=0.4, MeOH); IR (KBr): ν_{max} 3426, 2942, 1732, 1618, 1252, 1060 cm^{-1}; ^{1}H-NMR (CD_3OD, 600 MHz) and ^{13}C-NMR (CD_3OD, 150 MHz): see Tables 1—3; HR-ESI-TOF-MS: *m/z* 779.4596 $[M+H]^+$ (Calcd for $C_{42}H_{67}O_{13}$, 779.4582).

Bifinoside B (**2**): White amorphous powder; $[\alpha]_D^{20}$ +6.4° (c=0.4, MeOH); IR (KBr): ν_{max} 3424, 2940, 1731, 1618, 1250, 1059 cm^{-1}; ^{1}H-NMR (CD_3OD, 600 MHz) and ^{13}C-NMR (CD_3OD, 150 MHz): see Tables 1—3; HR-ESI-TOF-MS: *m/z* 963.4913 $[M+Na]^+$ (Calcd for $C_{48}H_{76}O_{18}Na$, 963.4929).

Bifinoside C (**3**): White amorphous powder; $[\alpha]_D^{20}$ +18.6° (c=0.7, MeOH); IR (KBr): ν_{max} 3428, 2946, 1718, 1624, 1248, 1054 cm^{-1}; ^{1}H-NMR (CD_3OD, 600 MHz) and ^{13}C-NMR (CD_3OD, 150 MHz): see Tables 1—3;

HR-ESI-TOFMS: *m/z* 1073.5554 $[M+H]^+$ (Calcd for $C_{53}H_{85}O_{22}$, 1073.5533).

Acid Hydrolysis and Sugar Determination of Bifinosides A—C (1—3) A solution of each (3.0 mg) in 2 M HCl (5.0 ml) was heated under reflux for 4 h. Then, the reaction mixture was concentrated *in vacuo* to dryness. The residue was extracted with CH_2Cl_2 and H_2O (5 ml×3). The organic portion was concentrated and examined on TLC [Silica gel plates with the mobile phase systems of $CHCl_3$–EtOAc (7 : 1) and hexane–acetone (2 : 1) comparing with oleanolic acid (*Rf* 0.52, 0.45)]. Next, the sugar residue, obtained by concentration of the water layer, was examined on TLC [Merck cellulose plate with the mobile phase system of benzene/*n*-butanol/pyridine/water (1 : 5 : 3 : 3)] and GC (as tetramethylsilane (TMS) ethers according to the reported method).[2,4] TLC: *Rf* 0.22 (GluA) observed for all three hydrolysates and the others: 0.34 (Ara) for **1**; 0.30 (Glc) and 0.38 (Xyl) for **2**; 0.30 (Glc), 0.34 (Ara), and 0.38 (Xyl) for **3** in comparison with authentic sugars (Sigma-Aldrich). GC: t_R (min): 4.46 (L-arabinose) for **1**; 8.21 (D-xylose) and 14.12 (D-glucose) for **2**; 4.46 (L-arabinose), 8.21 (D-xylose), and 14.12 (D-glucose) for **3**, which were in consistent with t_R data of the standard sugars after being treated in the similar manner [4.46 (L-arabinose), 4.90 (D-arabinose), 8.21 (D-xylose), 8.66 (L-xylose), 14.12 (D-glucose), 14.25 (L-glucose)].

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