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TRITERPENE GLYCOSIDES FROM *Kalopanax septemlobum*. VII. MINOR GLYCOSIDES FROM STEMS OF *Kalopanax septemlobum* VAR. *maximowiczii* AND *Kalopanax septemlobum* VAR. *typicum*

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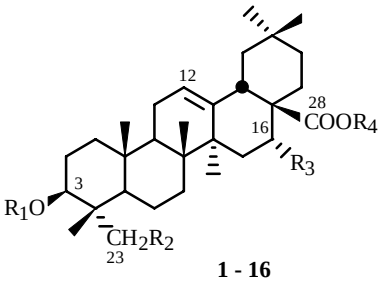
*Sixteen triterpene glycosides, three of which were new, hederagenin 28-*O-β-*D-glucuronopyranosyl ester and 28-*O-β-*D-gentiobiosyl ester and oleanolic acid 3-*O-α-*L-arabinopyranoside, were isolated from stem bark of* Kalopanax septemlobum. *The glycoside contents in stem bark of two varieties,* maximowiczii *and* typicum, *were compared.*

Key words: *Kalopanax septemlobum* var. *maximowiczii*, *Kalopanax septemlobum* var. *typicum*, Araliaceae, triterpene glycosides, hederagenin glycosides, oleanolic and echinocystic acid glycosides.

We described previously [1] the isolation and structure determination of the principal triterpene glycosides from stem bark of the two varieties *Kalopanax septemlobum* (Thunb.) Koidz. var. *maximowiczii* (Van Houte) Hara and *K. septemlobum* var. *typicum* (Nakai) Pojark. Herein we report results from an investigation of the minor glycosides from stem bark of these two varieties.

Fraction B, which was isolated from stems of both varieties, contained pure glycoside B (**1**) (Table 1). Fraction C in variety *typicum* contained two glycosides with similar chromatographic mobilities, minor C_1 (**2**) and predominant C_2 (**3**). This fraction contained only **3** in variety *maximowiczii* [1]. Analogously, fractions E and F in variety *typicum* contained the glycoside pairs E_1 (**4**) and E_2 (**5**) and F_1 (**6**) and F_2 (**7**) whereas these fractions for variety *maximowiczii* contained only **4** and **7**. Fraction G of variety *maximowiczii* contained pure glycoside G (**9**); of variety *typicum*, the glycoside pair G_1 (**8**) and G_2 (**10**). Fraction H of variety *typicum* contained the principal glycoside H_1 (**11**) [1] and two minor glycosides H_2 (**12**) and H_3 (**13**). Analogously, fraction I of variety *typicum* contained the principal glycoside I_2 (**15**) [1] and another minor glycoside I_1 (**14**). Separation of total glycosides from stem bark of variety *maximowiczii* gave fractions A-J and the minor glycoside K (**16**).



1 - 16

	R_1	R_2	R_3	R_4
1[b]:	H	OH	H	←Glc
2[b]:	Rha→ ^{2}Ara→	H	OH	H
3:	Rha→ ^{2}Ara→	OH	H	H
4[a]:	H	OH	H	←Glc^6 ←Glc
5[a]:	Ara→	H	H	←Glc^6 ←Glc
6[b]:	Rha→ ^{2}Ara→	OH	H	←Glc
7:	H	OH	H	←Glc^6 Glc^4 Rha
8[a]:	H	OH	H	←GlcUA
8a:	H	OH	H	←GlcUA-6-O-Me
9[b]:	Xyl→ ^{3}Rha→ ^{2}Ara→	OH	H	←Glc
10[b]:	Ara→	OH	H	←Glc^6 ←Glc
11:	Ara→	OH	H	←Glc^6 ←Glc^4 ←Rha
12:	Rha→ ^{2}Ara→	H	H	←Glc^6 ←Glc^4 ←Rha
13[b]:	Rha→ ^{2}Ara→	OH	H	←Glc^6 ←Glc
14[b]:	Rha→ ^{2}Ara→	H	OH	←Glc^6 ←Glc^4 ←Rha
15:	Rha→ ^{2}Ara→	OH	H	←Glc^6 ←Glc^4 ←Rha
16:	Glc→ ^{4}Xyl→ ^{3}Rha→ ^{2}Ara→	OH	H	←Glc^6 ←Glc^4 ←Rha

[a], new compounds; [b], first observed in *Kalopanax* spp.; Rha, α-L-Rha; Ara, α-L-Ara*p*; Xyl, β-D-Xyl; Glc, β-D-Glc*p*; GlcUA, β-D-GlcUA*p*

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TABLE 1. Distribution of Glycosides **1-16** in Stem Bark of *Kalopanax septemlobum* by Varieties *maximowiczii* and *typicum*

Fraction (glycoside)	Compound	*K. septemlobum* var. *maximowiczii*	*K. septemlobum* var. *typicum*	Fraction (glycoside)	Compound	*K. septemlobum* var. *maximowiczii*	*K. septemlobum* var. *typicum*
A		+	+	G	**9**	+	-
B	**1**	+	+	G_2	**10**	-	+
C_1	**2**	-	+	H_1	**11**	+	+
C_2	**3**	+	+	H_2	**12**	-	+
D		+	-	H_3	**13**	-	+
E_1	**4**	+	+	I_1	**14**	-	+
E_2	**5**	-	+	I_2	**15**	+	+
F_1	**6**	-	+	J		+	-
F_2	**7**	+	+	K	**16**	+	-
G_1	**8**	-	+				

TABLE 2. ^{13}C Chemical Shifts (δ, ppm, 0 = TMS, C_5D_5N) in Aglycons of **1-16**

C atom	**2**	**3**	**1, 4, 7, 8**	**5, 12**	**14**	**6, 9-11, 13, 15, 16**	C atom	**2**	**3**	**1, 4, 7, 8**	**5, 12**	**14**	**6, 9-11, 13, 15, 16**
1	38.9	39.0	38.9	39.0	39.0	39.0	16	74.8	23.7	22.7	23.4	74.4	23.4
2	26.4	26.2	27.7	26.6	26.5	26.3	17	48.9	46.6	47.1	47.1	49.1	47.0
3	88.9	81.1	73.5	88.8	89.0	81.5	18	41.3	42.0	41.8	41.7	41.2	41.7
4	39.3	43.6	42.9	39.6	39.4	43.6	19	47.2	46.4	46.3	46.3	47.0	46.2
5	56.2	47.7	48.6	56.0	56.2	47.6	20	30.9	30.9	30.8	30.8	30.7	30.8
6	18.6	18.2	18.7	18.7	18.5	18.6	21	36.1	34.2	34.0	34.1	35.9	34.0
7	33.4	32.8	32.9	33.2	33.4	32.8	22	32.5	33.2	32.6	32.6	32.1	32.6
8	39.8	39.8	40.0	39.9	40.0	40.0	23	28.1	64.0	67.8	28.2	28.0	64.2
9	47.2	48.2	48.2	48.1	47.2	48.2	24	16.9	14.0	13.2	17.0	16.9	14.0
10	37.1	36.9	37.3	37.1	37.0	36.9	25	15.5	16.1	16.2	15.7	15.7	16.3
11	23.8	23.8	23.9	23.9	23.8	23.9	26	17.4	17.5	17.6	17.6	17.5	17.9
12	122.6	122.6	123.0	122.9	122.9	122.9	27	27.2	26.2	26.2	26.1	27.1	26.2
13	144.7	144.8	144.2	144.2	144.6	144.2	28	180.3	180.2	176.6	176.7	176.2	176.6
14	42.1	42.2	42.2	42.2	42.0	42.2	29	33.2	33.2	33.2	33.2	33.1	33.1
15	36.1	28.3	28.3	28.3	36.0	28.3	30	24.6	23.8	23.7	23.7	24.6	23.7

Columns in Tables 2-5 give average chemical shifts.

Glycosides **2**, **12**, and **14-16** were identified using TLC and authentic samples isolated and described previously from *Hedera taurica* [2] and *K. septemlobum* [3]. Their structures were also confirmed by comparing their ^{13}C NMR spectra with those in the literature [2-4]. We note that the glycosides of echinocystic acid (**2** and **14**) were observed for the first time in representatives of the genus *Kalopanax*.

The aglycon of **1**, **6**, and **9** is hederagenin according to total acid hydrolysis. The hydrolysates contained glucose for **1**, **6**, and **9**; rhamnose and arabinose for **6** and **9**; and xylose for **9**. Alkaline hydrolysis of **1** produced hederagenin; of **6**, **3**; of **9**, hederagenin 3-*O*-β-D-xylopyranosyl-(1→3)-*O*-α-L-rhamnopyranosyl-(1→2)-*O*-α-L-arabinopyranoside [1]. After assigning signals in the ^{13}C NMR spectra of **1**, **6**, and **9** for the aglycon and carbohydrate chain on aglycon C-3, a comparison with the literature [3] showed that an additional glucopyranose was present on aglycon C-28. Its chemical shifts agreed with those in the literature [5]. Thus, **1**, **6**, and **9** were hederagenin 28-*O*-β-D-glucopyranosyl ester, 3-*O*-α-L-rhamnopyranosyl-(1→2)-*O*-α-L-arabinopyranoside, and 3-*O*-β-D-xylopyranosyl-(1→3)-*O*-α-L-rhamnopyranosyl-(1→2)-*O*-α-L-arabinopyranoside, respectively. Glycosides **1** and **6** were found for the first time in the genus *Kalopanax*; **9**, in the family Araliaceae, being previously observed only in *Decaisnea fargensii* (Lardizabalaceae) [6].

TABLE 3. ^{13}C Chemical Shifts (δ, ppm, 0 = TMS, C_5D_5N) in Carbohydrates of **2**, **5**, **12**, and **14**

C atom	Substituent on atom			
	C-3		C-28	
	5	**2**, **12**, **14**	**5**	**12**, **14**
	Ara-	Ara-	-Glc-	-Glc-
1	107.1	104.9	95.7	95.7
2	72.8	76.0	73.9	73.9
3	74.5	73.8	78.7	78.7
4	69.3	68.7	70.9	70.8
5	66.4	64.7	78.0	78.3
6			69.4	69.2
		-Rha	-Glc	-Glc-
1		101.8	105.2	104.8
2		72.4	75.2	75.4
3		72.6	78.4	76.5
4		74.0	71.6	78.5
5		70.0	78.4	77.2
6		18.6	62.7	61.3
				-Rha
1				102.8
2				72.6
3				72.8
4				74.1
5				70.4
6				18.6

Total acid hydrolysis of **4**, **10**, and **13** produced hederagenin; of **5**, oleanolic acid. Alkaline hydrolysis of **4** produced hederagenin; of **5** and **10**, oleanolic acid and hederagenin, respectively, 3-*O*-α-L-arabinopyranosides; of **13**, **3**. After assigning signals in the ^{13}C NMR spectra of **4**, **5**, **10**, and **13** for the aglycon and carbohydrate chain on aglycon C-3, a comparison with the literature [3, 4] revealed that two hexoses were present. Their chemical shifts were compared with literature [7] and identified them as the disaccharide ←β-D-Glc*p*^{6}←β-D-Glc*p* (gentiobiose). The structure of the β-D-gentiobiosyl group for **4** and **5** was also confirmed by 2D spectral analyses (COSY, TOCSY, and HSQC), as described by us several times previously. Thus, **4**, **5**, **10**, and **13** are 28-*O*-β-D-gentiobiosyl esters of hederagenin, oleanolic acid and hederagenin 3-*O*-α-L-arabinopyranosides, and hederagenin 3-*O*-α-L-rhamnopyranosyl-(1→2)-*O*-α-L-arabinopyranoside, respectively. Glycosides **10** and **13** were observed in *Kalopanax* species for the first time. Compounds **4** and **5** are new triterpene glycosides.

The aglycon hederagenin and the sugars rhamnose and glucose were found in **7**. Alkaline hydrolysis of **7** gave hederagenin, which is consistent with the presence of a single carbohydrate chain bonded to the aglycon carboxyl group.

The ^{13}C NMR spectrum of **7** showed that it contained the typical trisaccharide ←β-D-Glc*p*^{6}←β-D-Glc*p*^{4}←α-L-Rha*p* [3, 5, 7]. This glycoside was isolated previously from bark of *K. pictus* [8].

The chromatographic behavior of **8** (bands with tails) suggested that this glycoside was acidic in nature. This was also confirmed by the significant increase in the chromatographic mobility in solvent systems with HCOOH [9]. Total acid hydrolysis of **8** gave the aglycon hederagenin and glucuronic acid. Alkaline hydrolysis of **8** also produced hederagenin. This indicated that glucuronic acid was located on the aglycon carboxyl group. Compound **8** was purified further by chromatography by converting it to the methyl ester (**8a**) by treatment with CH_2N_2 in ether [10].

The ^{13}C NMR spectrum of **8a** showed after assigning signals for the aglycon (by comparison with **1**, **4**, and **7**) an additional seven C atoms, one of which at 52.0 ppm was the C of the added –O–CH_3 group. The remaining six signals belonged undoubtedly to the glucuronic acid. Taking into account the chemical shifts, two of them were assigned unambiguously to the C-6 carboxyl (170.2 ppm) and anomeric C-1 (95.6 ppm).

TABLE 4. ^{13}C Chemical Shifts (δ, ppm, 0 = TMS, C_5D_5N) in Carbohydrates of **1**, **3**, **4**, **6-11**, **13**, **15**, and **16**

C atom	Substituent on aglycon atom							
	C-3				C-28			
	10, **11**	**3**, **6**, **13**, **15**	**9**	**16**	**8a**	**1**, **6**, **9**	**4**, **10**, **13**	**7**, **11**, **15**, **16**
	-Ara	-Ara-	-Ara-	-Ara-	-GlcUA	-Glc	-Glc-	-Glc-
1	106.3	104.3	104.8	104.6	95.6	95.8	95.7	95.7
2	72.5	75.9	75.1	75.4	73.7	74.2	73.9	73.9
3	74.8	74.5	75.2	74.9	78.1	78.9	78.7	78.7
4	69.4	69.3	69.9	69.6	73.0	71.1	70.9	70.8
5	66.0	65.5	66.4	66.0	77.8	79.4	78.0	78.1
6					170.2	62.3	69.4	69.2
-O-CH_3					52.0			
		-Rha	-Rha-	-Rha-			-Glc	-Glc-
1		101.7	101.3	101.4			105.2	104.8
2		72.3	72.0	71.9			75.2	75.4
3		72.5	82.8	82.9			78.5	76.6
4		74.2	73.0	72.9			71.5	78.4
5		69.8	69.6	69.7			78.4	77.2
6		18.6	18.5	18.6			62.6	61.3
			-Xyl	-Xyl-				-Rha
1			107.5	107.0				102.8
2			75.6	75.3				72.6
3			78.4	76.2				72.8
4			71.1	78.0				74.0
5			67.4	64.9				70.4
6								18.6
				-Glc				
1				103.6				
2				74.4				
3				78.1				
4				71.7				
5				78.8				
6				62.7				

The remaining signals for C-2—C-5 were assigned by analyzing 2D spectra. Starting with a doublet for anomeric H-1 at 6.29 ppm in the COSY spectrum, signals for H-2—H-5 were assigned. The nature of the splitting of the signals and the SSCCs confirmed unambiguously that the carbohydrate was β-glucuronopyranose. Next signals for C-2—C-5 were assigned using the 2D HSQC spectrum. The assignments compared well with the literature values for β-D-glucuronoyranosyl bonded to C-3 of the aglycon [5, 11] except for the C-1 and C-2 signals. Naturally, this is explained by the change of the ordinary glycoside bond (with a hydroxyl at C-3 of the aglycon) to the acylglycoside (at C-28 of the aglycon). Thus, **8** is hederagenin 28-*O*-β-D-glucuronopyranosyl ester and is a new triterpene glycoside. Furthermore, the presence of β-D-glucuronopyranosyl on the aglycon carboxyl group was observed for the first time in natural triterpene glycosides.

We note that most minor glycosides from stem bark differ from the principal ones by the presence on the carboxyl group of a gentiobiose unit, a single glucose, or even glucuronic acid instead of the typical trisaccharide ←Glc^6←Glc^4←Rha. We have previously noted [1] significant qualitative differences in the content of the principal glycosides in stem bark of both varieties. The distribution of the minor glycosides were consistent with these differences and confirmed our previous chemotaxonomic conclusions about the need to raise the rank of these varieties to the species level [4].

TABLE 5. ^{1}H Chemical Shifts (δ, ppm, 0 = TMS, C_5D_5N, J/Hz) in Carbohydrates of **4**, **5**, and **8a**

Substituent on aglycon C-3		Substituent on aglycon C-28			
H atom	**5**	H atom	**4**, **5**	H atom	**8a**
	Ara-		Glc-		-GlcUA
1	4.94	1	6.19	1	6.29 (d, $J_{1,2}$ = 7.9)
2	4.38	2	4.09	2	4.22 (t, $J_{2,3}$ = 8.0)
3	4.05	3	4.18	3	4.27 (t, $J_{3,4}$ = 9.0)
4	4.21	4	4.29	4	4.45 (t, $J_{4,5}$ = 9.0)
5e	4.22	5	4.05	5	4.59 d
5a	3.73	6A	4.66	(6)-O-CH_3	3.61 s
		6B	4.29		
			-Glc		
		1	4.97		
		2	3.95		
		3	4.14		
		4	4.14		
		5	3.83		
		6A	4.42		
		6B	4.30		

EXPERIMENTAL

General comments have been published [3].

Isolation of Glycosides. Air-dried root bark (200 g) of *K. septemlobum* var. *maximowiczii* that was collected in Nikitskii Botanical Garden was thoroughly ground and treated with benzene (4 × 1000 mL). The defatted solid was extracted with isopropanol (80%, 4 × 1000 mL). The combined extracts were evaporated to afford total extracted compounds (23.5 g) that were dissolved in water-saturated butanol (500 mL) and washed with aqueous NH_3 (4%, 3 × 500 mL). Evaporation of the butanol layer afforded purified total glycosides (11.2 g). Glycosides from stem bark of *K. septemlobum* var. *typicum* were extracted by the same scheme to afford purified total glycosides (10.3 g).

Separation of Glycosides from *K. septemlobum* var. *maximowiczii*. Total glycosides (11.2 g) were chromatographed over silica gel L (500 g, 40-100 μm) with gradient elution by water-saturated $CHCl_3$:C_2H_5OH (7:1→1:1) to afford glycoside fractions A (502 mg), B (395 mg), C (480 mg), D (615 mg), E (254 mg), F (425 mg), G (162 mg), H (370 mg), I (3.4 g), J (4.5 mg), and K (106 mg). Additional chromatographic purification of these in water-saturated $CHCl_3$:C_2H_5OH solvent systems of corresponding polarities produced pure glycosides A (314 mg) [1], **1** (269 mg), **3** (351 mg), D (455 mg) [1], **4** (127 mg), **7** (216 mg), **9** (127 mg), **11** (138 mg), **15** (3.1 g), J (4.2 g) [1], and **16** (46 mg).

Separation of Glycosides from *K. septemlobum* var. *typicum*. Total glycosides (10.3 g) were chromatographed over silica gel L (500 g, 40-100 μm) with gradient elution by water-saturated $CHCl_3$:C_2H_5OH (7:1→1:1) to afford glycoside fractions A (310 mg), B (347 mg), C (665 mg), E (127 mg), F (462 mg), G (249 mg), H (335 mg), and I (7.1 g).

Additional chromatographic purification of fractions A and B in water-saturated $CHCl_3$:C_2H_5OH solvent systems of corresponding polarities produced pure glycosides A (180 mg) [1] and **1** (117 mg). Fraction C (665 mg) was rechromatographed over silica gel "Silpearl" (250 g) with elution by water-saturated $CHCl_3$:C_2H_5OH (6:1) to give **2** (112 mg) and **3** (157 mg). Fraction E (127 mg) was rechromatographed over silica gel (150 g) with elution by water-saturated $CHCl_3$:C_2H_5OH (4:1) to give **4** (55 mg) and **5** (12 mg). Fraction F (462 mg) was rechromatographed over silica gel (150 g) with elution by water-saturated $CHCl_3$:C_2H_5OH (4:1) to give **6** (30 mg) and **7** (94 mg). Fraction G (249 mg) was rechromatographed over silica gel (200 g) with elution by water-saturated $CHCl_3$:C_2H_5OH (3:1) to give **8** (40 mg) and **10** (35 mg). Fraction H (335 mg) was rechromatographed over silica gel (250 g) with elution by water-saturated $CHCl_3$:C_2H_5OH (2:1) to give **11** (60 mg), **12** (65 mg), and **13** (63 mg). Fraction I (7.1 g) was rechromatographed over silica gel (450 g) with elution by water-saturated $CHCl_3$:C_2H_5OH (1:1) to give **14** (78 mg) and **15** (6.2 g).

The total acid hydrolysates of **5** and **12** contained according to TLC oleanolic acid and the sugars glucose, rhamnose, and arabinose. Alkaline hydrolysis of **5** produced oleanolic acid 3-*O*-α-L-arabinopyranoside [12] and glycoside **12**, oleanolic acid 3-*O*-α-L-rhamnopyranosyl-(1→2)-*O*-α-L-arabinopyranoside [3].

Total acid hydrolysis of **2** and **14** gave the aglycon, echinocystic acid, and the sugars rhamnose and arabinose in **2** and **14** in addition to glucose in **14**. Alkaline hydrolysis of **2** and **14** gave echinocystic acid 3-*O*-α-L-rhamnopyranosyl-(1→2)-*O*-α-L-arabinopyranoside [2].

The total acid hydrolysates of **1**, **3**, **4**, **6**-**11**, **13**, **15**, and **16** contained according to TLC hederagenin and the sugars glucuronic acid in **8**; glucose in **1** and **4**; rhamnose and arabinose in **3**; arabinose and glucose in **10**; rhamnose and glucose in **7**; rhamnose, arabinose, and glucose in **6**, **11**, **13**, and **15**; and xylose, rhamnose, arabinose, and glucose in **9** and **16**. Alkaline hydrolysis of **1**, **4**, **7**, and **8** produced hederagenin; of **10** and **11**, hederagenin 3-*O*-α-L-arabinopyranoside [1, 3]; of **6**, **13** and **15**, **3**; of **9**, hederagenin 3-*O*-β-D-xylopyranosyl-(1→3)-*O*-α-L-rhamnopyranosyl-(1→2)-*O*-α-L-arabinopyranoside [1, 3, 4]; of **16**, hederagenin 3-*O*-β-D-glucopyranosyl-(1→4)-*O*-β-D-xylopyranosyl-(1→3)-*O*-α-L-rhamnopyranosyl-(1→2)-*O*-α-L-arabinopyranoside [3, 4].

Table 1 gives the distributions of **1**-**16** in stem bark of the two varieties of *K. septemlobum*. Table 2 lists chemical shifts of the aglycon in ^{13}C NMR spectra of **1**-**16**. Tables 3 and 4 list chemical shifts of carbohydrates in ^{13}C NMR spectra of **1**-**16**. Table 5 lists chemical shifts of carbohydrate ^{1}H atoms in PMR spectra of **4**, **5**, and **8a**.

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