Chemistry of Natural Compounds, Vol. 37, No. 5, 2001

TRITERPENE GLYCOSIDES FROM *Tetrapanax papyriferum.* III. MINOR MONODESMOSIDE GLYCOSIDES FROM STEM BARK

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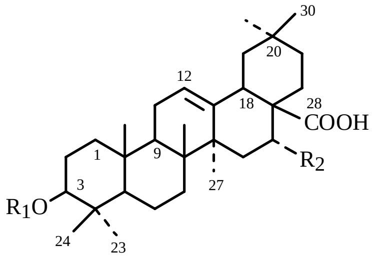
UDC 547.918:543.422

Minor monodesmoside triterpene glycosides St-A, St-B, St-C_1, St-D_1, St-C_2, and St-D_2 were isolated from stem bark of Tetrapanax papyriferum *C. Koch (Araliaceae). The structures of oleanolic and echinocystic acid 3-O-α-L-arabinopyranosides, oleanolic and echinocystic acid 3-O-β-D-glucopyranosyl-(1→3)-O-α-L-arabinopyranosides, and oleanolic and echinocystic acid 3-O-β-D-galactopyranosyl-(1→2)-O-α-L-arabinopyranosides, respectively, were proposed. Glycosides St-C_2, St-D_1, and St-D_2 are new triterpene glycosides. The structures of the isolated compounds were established using chemical methods and NMR spectroscopy.*

Key words: *Tetrapanax papyriferum*, Araliaceae, triterpene glycosides, oleanolic and echinocystic acid glycosides.

We reported previously methods for isolating and establishing the structure of triterpene glycosides from polar fractions of stem bark of *Tetrapanax papyriferum* C. Koch (Araliaceae) [1, 2]. The present article reports the structures of six less polar glycosides from fractions St-A through St-D.

Fractions St-A and St-B are pure compounds according to TLC in various solvent systems. Fractions St-C and St-D were separated into pure glycosides by preparative chromatography over silica gel with elution by $CHCl_3$—C_2H_5OH—H_2O solvent systems and afforded pairs of glycosides St-C_1 and St-C_2 and St-D_1 and St-D_2 with similar chromatographic mobilities. The chromatographic mobilities of all six glycosides decrease if solvents containing ammonia are used but do not change under alkaline-hydrolysis conditions. Therefore, these compounds have a free carboxylic group in the aglycone and are monodesmosides.



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	R_1	R_2
1	α-L-Ara*p*	H
2	α-L-Ara*p*	OH
3	β-D-Glc*p*-(1→3)-α-L-Ara*p*	H
4	β-D-Gal*p*-(1→2)-α-L-Ara*p*	H
5	β-D-Glc*p*-(1→3)-α-L-Ara*p*	OH
6	β-D-Gal*p*-(1→2)-α-L-Ara*p*	OH

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TABLE 1. ^{13}C Chemical Shifts for Aglycones of Glycosides St-C_1(**3**), St-C_2 (**4**), St-D_1 (**5**), and St-D_2(**6**) (δ, ppm, 0 = TMS, C_5D_5N)

C-atom	Compound				C-atom	Compound			
	3	**4**	**5**	**6**		**3**	**4**	**5**	**6**
1	39.0	39.0	39.1	39.0	**16**	23.6	23.6	74.3	74.2
2	26.4	26.5	26.5	26.5	**17**	47.2	47.1	49.4	49.3
3	88.8	88.9	89.0	89.0	**18**	41.6	41.7	41.3	41.3
4	39.6	39.7	39.6	39.6	**19**	46.4	46.4	47.1	47.1
5	56.1	56.0	56.0	56.1	**20**	30.7	30.6	30.6	30.7
6	18.7	18.6	18.5	18.6	**21**	34.1	33.9	35.8	35.8
7	33.2	33.1	33.4	33.3	**22**	32.6	32.5	31.9	31.8
8	40.0	40.1	40.2	40.1	**23**	28.2	28.2	28.1	28.1
9	48.2	48.2	47.3	47.2	**24**	16.7	16.6	16.7	16.7
10	37.0	37.2	37.0	37.0	**25**	15.5	15.6	15.6	15.6
11	23.8	23.9	24.0	23.8	**26**	17.5	17.5	17.6	17.7
12	122.7	122.9	122.6	122.6	**27**	25.9	25.8	27.0	27.1
13	144.1	144.2	144.3	144.3	**28**	176.5	176.4	175.9	176.0
14	42.1	42.2	41.9	42.0	**29**	33.0	32.9	33.0	33.0
15	28.4	28.2	36.1	36.0	**30**	23.7	23.7	24.9	24.8

TABLE 2. ^{13}C Chemical Shifts of Carbohydrates of Glycosides St-C_1 (**3**), St-C_2(**4**), St-D_1(**5**), and St-D_2 (**6**) (δ, ppm, 0 = TMS, C_5D_5N)

C-atom	Compound			
	3	**4**	**5**	**6**
		Ara		
1	106.9	104.6	107.1	104.8
2	71.5	81.2	71.6	81.1
3	83.9	73.3	83.8	73.5
4	69.0	68.2	69.0	68.4
5	66.7	64.1	66.6	64.1
		Gal		
1		106.6		106.8
2		73.7		73.5
3		75.2		75.3
4		69.7		69.7
5		76.8		76.7
6		61.6		61.5
		Glc		
1	105.9		105.7	
2	75.5		75.5	
3	78.1		78.2	
4	71.6		71.7	
5	78.4		78.5	
6	62.6		62.7	

Glycosides St-A (**1**) and St-B (**2**) contain arabinose according to total acid hydrolysis. The aglycones are oleanolic and echinocystic acids, respectively. They were identical to authentic samples of oleanolic and echinocystic acid 3-O-α-L-arabinopyranosides according to chromatographic mobilities and ^{13}C NMR spectra [3].

Total acid hydrolysis of St-C_1 (**3**) has indicated that it contains arabinose, glucose, and the aglycone oleanolic acid. Partial acid hydrolysis of **3** gave oleanolic acid and its 3-O-α-L-arabinopyranoside, which defines the sequence of monosaccharides in **3**. The chromatographic mobility of **3** was the same as that of oleanolic acid 3-O-β-D-glucopyranosyl-(1→3)-O-α-L-arabonopyranoside, glycoside L-E_1 from leaves of *Scheffleropsis angkae* [4]. The fact that the chemical shifts in the ^{13}C NMR spectra of compound **3** and L-E_1 were identical has confirmed that they are identical.

Glycoside St-C_2 (**4**) contains arabinose, galactose, and oleanolic acid according to total acid hydrolysis. Partial acid hydrolysis of **4**, like for **3**, produced oleanolic acid and oleanolic acid 3-O-α-L-arabinopyranoside. This defined the bonding sequence of monosaccharides in the carbohydrate chain of **4**. The ^{13}C NMR spectrum of **4** was compared with those in the literature [1, 5] and enabled signals for the terminal galactopyranose and 2-substituted arabinopyranose to be identified. Furthermore, the chemical shifts of ^{13}C atoms in the carbohydrate part of **4** are identical to those of ^{13}C atoms in the disaccharide fragment β-D-Gal*p*-(1→2)-α-L-Ara*p*- bonded to C-3 of the baccharane-type aglycone with ring A and B structures that are identical to oleanolic acid in actinostemmoside F from *Actinostemma lobatum* [6]. Chemical shifts of ^{13}C atoms in the aglycone part of **4** and **3** are analogous and correspond with 3-O-glycosylated oleanolic acid [3].

Thus, glycoside St-C_2 is oleanolic acid 3-O-β-D-galactopyranosyl-(1→2)-O-α-L-arabinopyranoside, a new triterpene glycoside.

The structures of St-D_1 (**5**) and St-D_2 (**6**) were established analogously to those of **3** and **4**. Thus, **5** contains monosaccharides arabinose and glucose according to total acid hydrolysis; **6**, arabinose and galactose. The aglycone in both compounds is echinocystic acid. The triterpene products of partial acid hydrolysis of **5** and **6** were identical and were identified by TLC as echinocystic acid and its 3-O-α-L-arabinopyranoside. This established the bonding sequence of monosaccharides in the carbohydrate parts of both glycosides.

Comparison of the ^{13}C NMR spectra of **5** and **6** with those of **3** and **4** and literature data [4-6] has shown that the carbohydrate parts of **5** and **6** are identical with those of **3** and **4**. The chemical shifts of ^{13}C atoms in the aglycones of **5** and **6** corresponded with 3-O-glycosylated echinocystic acid [3]. This suggested the structures of echinocystic acid 3-O-β-D-glucopyranosyl-(1→3)-O-α-L-arabinopyranoside and 3-O-β-D-galactopyranosyl-(1→2)-O-α-L-arabinopyranoside for St-D_1 and St-D_2, respectively. Both these compounds are also new triterpene glycosides. Apparently glycosides **5** and **6**, like **2**, are degradation products of St-I_2 whereas **1**, **3**, and **4** come from St-H_2, the principal glycosides of stem bark of *Tetrapanax* that we previously isolated [2].

EXPERIMENTAL

General comments and isolation methods of St-A through St-D fractions have been published [1].

Glycosides St-A and St-B (**1** and **2**, respectively) from crude fractions St-A and St-B were purified by rechromatography over silica gel with elution by water-saturated $CHCl_3$—C_2H_5OH (5:1) to afford **1** (20 mg) and **2** (17 mg).

Fractions St-C (38 mg) and St-D (30 mg) were separated chromatographically over silica gel with elution by water-saturated $CHCl_3$—C_2H_5OH (2:1) to afford pure glycosides St-C_1 (20 mg), St-C_2 (16 mg), St-D_1 (15 mg), and St-D_2 (13 mg) (**3-6**, respectively).

Total acid hydrolysis of **1-6** produced arabinose in **1** and **2**, glucose and arabinose in **3** and **5**, galactose and arabinose in **4** and **6**, and the aglycones oleanolic acid in **1**, **3**, and **4** and echinocystic acid in **2**, **5**, and **6**. Partial acid hydrolysis of **3** and **4** gave oleanolic acid and its 3-O-α-L-arabinopyranoside; of **5** and **6**, echinocystic acid and its 3-O-α-L-arabinopyranoside. ^{13}C NMR data for **3-6** are listed in Tables 1 and 2.

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