Chemistry of Natural Compounds, Vol. 37, No. 2, 2001

TRITERPENE GLYCOSIDES OF *Tetrapanax papyriferum*. II. ISOLATION AND STRUCTURE DETERMINATION OF GLYCOSIDES St-E_2, St-F_2, St-J_2, and St-K_2 FROM STEM BARK

V. G. Strigunov,[1] N. I. Grishkovets,[1]
N. V. Tolkacheva,[1] and A. S. Shashkov[2]

UDC 547.918:543.422

Stem bark of Tetrapanax papyriferum *yielded the new triterpene glycosides 3-O-[β-D-glucopyranosyl-(1→3)]-β-D-galactopyranosyl-(1→2)-O-α-L-arabinopyranosides of oleanolic and echinocystic acids and their 28-O-α-L-rhamnopyranosyl-(1→4)-O-β-D-glucopyranosyl-(1→6)-O-β-D-glucopyranosyl esters. Their structures were established using chemical and physicochemical methods.*

Key words: *Tetrapanax papyriferum*, Araliaceae, triterpene glycosides, new glycosides of oleanolic and echinocystic acids.

Triterpene glycoside fractions St-E, St-F, St-J, and St-K that were isolated by us earlier from leaves of *Tetrapanax papyriferum* [1] were treated with an ether solution of diazomethane, which increased the chromatographic mobility of one of the components in each fraction (designated St-E_1, St-F_1, St-J_1, and St-K_1) and left that of another unchanged (St-E_2, St-F_2, St-J_2, and St-K_2). Preparative separation of these glycoside pairs in each fraction was performed in silica gel with elution by $CHCl_3$—C_2H_5OH—H_2O.

Total acid hydrolysis of St-E_2 (**1**) produced arabinose, galactose, glucose, and the algycone oleanolic acid. The chromatographic mobility of **1** is consistent with the progenin obtained by total base hydrolysis of St-H_2, which we previously isolated from *Tetrapanax* stems [1]. We also identified **1** as the progenin of glycoside St-H_2 by comparing ^{13}C chemical shifts of atoms in the carbohydrate part of **1** and those of the carbohydrate chain on C-3 of the aglycone described earlier for St-H_2 [1]. The chemical shifts of C atoms in the aglycone of **1** agree with the literature values for 3-O-glycosylated oleanolic acid [2].

Thus, glycoside St-E_2 is the 3-O-[β-D-glucopyranosyl-(1→3)]-[β-D-galactopyranosyl-(1→2)]-O-α-L-arabinopyranoside of oleanolic acid. Glycoside St-E_2 is a new triterpene glycoside.

Total acid hydrolysis of St-F_2 (**2**) gave arabinose, galactose, glucose, and echinocystic acid. The chromatographic mobility of **2** is identical to that of the progenin of glycoside St-J_2 prepared by total base hydrolysis [2].

The ^{13}C NMR of **2** was analyzed as for that of glycoside **1**. The ^{13}C NMR spectrum of **2** differs from that of **1** only for the chemical shifts of several atoms in the aglycone, the signals of which are unambiguously assigned by comparing them with the literature data for 3-O-glycosylated echinocystic acid [2].

Thus, glycoside St-F_2 is the 3-O-[β-D-glucopyranosyl-(1→3)]-[β-D-galactopyranosyl-(1→2)]-O-α-L-arabinopyranoside of echinocystic acid and is also a new triterpene glycoside.

Total acid hydrolysis of glycoside St-J_2 (**3**) yields arabinose, galactose, glucose, rhamnose, and the aglycone oleanolic acid. The chromatographic mobility of **3** is the same as that for deacetylated glycoside St-H_2, which was prepared by mild ammonolysis [1]. Total base hydrolysis of **3** produces a progenin that is identical by TLC to **1**. The NMR of **3** was consistent with six monosaccharide units. The ^{13}C NMR spectrum of **3** was practically the same as that of St-H_2 [1] with the exception of the signals for C-4, C-5, and C-6 of the internal glucose (Glc''''') in the trisaccharide chain on C-28 of the aglycone.

---

1) N. I. Vernadskii Tavricheskii National University, 95007, Simferopol, ul. Yaltinskaya, 4; 2) N. D. Zelinskii Institute of Organic Chemistry, Russian Academy of Sciences, 117913, Moscow, B-334, Leninskii pr., 47. Translated from Khimiya Prirodnykh Soedinenii, No. 2, pp. 151-153, March-April, 2001. Original article submitted March 23, 2001.

TABLE 1. Chemical Shifts of ^{13}C Atoms in Aglycones of St-E_2 (**1**), St-F_2 (**2**), St-J_2 (**3**) and St-K_2 (**4**) (δ, ppm, 0 = TMS, C_5D_5N)

C-atom	Compound			
	1	**2**	**3**	**4**
1	38.8	38.9	38.9	39.1
2	26.4	26.3	26.5	26.5
3	88.8	88.8	88.9	89.1
4	39.5	39.3	39.6	39.5
5	55.9	56.2	56.0	56.2
6	18.6	18.5	18.5	18.5
7	33.3	33.4	33.1	33.3
8	39.9	39.8	40.0	40.2
9	48.2	47.2	48.0	47.1
10	37.1	37.1	36.9	37.0
11	23.7	23.8	23.5	23.9
12	122.5	122.6	122.8	122.9
13	144.8	144.7	144.2	144.6
14	42.2	42.1	42.1	42.0
15	28.3	36.3	28.2	36.1
16	23.8	74.8	23.4	74.3
17	46.6	48.9	47.1	49.2
18	42.0	41.4	41.8	41.1
19	46.5	47.4	46.2	47.2
20	30.9	31.0	30.7	30.8
21	34.3	36.3	33.9	36.1
22	33.4	32.6	32.8	32.2
23	28.1	28.1	28.2	28.0
24	17.0	16.9	16.8	16.9
25	15.6	15.5	15.5	15.7
26	17.4	17.5	17.7	17.5
27	26.2	27.5	26.0	27.2
28	180.1	180.4	176.5	176.1
29	33.2	33.3	33.0	33.1
30	23.9	24.7	23.8	24.6

The C-4, C-5 and C-6 signals of this glucose were assigned unambiguously by comparison with the literature values for the unacetylated trisaccharide fragment *β*-Glc*p*←^{6}*β*-Glc*p*←^{4}*α*-Rha*p* [2]. Furthermore, the ^{13}C NMR spectrum of **3** lacks characteristic signals of acetyl ^{13}C atoms.

Thus, glycoside St-J_2 is the 28-O-α-L-rhamnopyranosyl-(1→4)-O-*β*-D-glucopyranosyl-(1→6)-O-*β*-D-glucopyranosyl ester of the 3-O-[*β*-D-glucopyranosyl-(1→3)]-[*β*-D-galactopyranosyl-(1→2)]-O-*α*-L-arabinopyranoside of oleanolic acid and is a new triterpene glycoside.

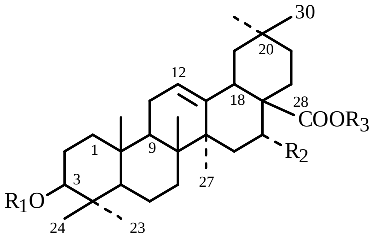
Total acid hydrolysis of glycoside St-K_2 (**4**) gives arabinose, galactose, glucose, rhamnose, and echinocystic acid.

The chromatographic mobility of **4** is the same as that of the deacetylated glycoside St-J_2, which was prepared by mild ammonolysis [1]. Total base hydrolysis of **4** gave the progenin, which was identical to **2**.

The ^{13}C NMR of **4** was analyzed analogously to that of **3** by comparing the spectra of **2** and **3** and glycoside St-J_2. It was found that glycoside St-K_2 is the 28-O-*α*-L-rhamnopyranosyl-(1→4)-O-*β*-D-glucopyranosyl-(1→6)-O-*β*-D-glucopyranosyl ester of the 3-O-[*β*-D-glucopyranosyl-(1→3)]-[*β*-D-galactopyranosyl-(1→2)]-*α*-L-arabinopyranoside of oleanolic acid and is also a new triterpene glycoside.

TABLE 2. Chemical Shifts of ^{13}C Atoms in Carbohydrates of St-E_2 (**1**), St-F_2 (**2**), St-J_2 (**3**), St-K_4 (**4**) (δ, ppm, 0 = TMS, C_5D_5N)

C-atom	Compound			
	1	**2**	**3**	**4**
Ara′				
1	104.7	104.8	104.8	104.8
2	77.4	77.3	77.3	77.4
3	82.6	82.7	82.5	82.6
4	68.0	68.0	68.1	68.0
5	65.1	65.0	64.9	65.1
Gal′′				
1	104.5	104.6	104.6	104.5
2	73.1	73.2	73.3	73.1
3	75.2	75.3	75.1	75.3
4	69.6	69.7	69.8	69.7
5	76.2	76.2	76.3	76.2
6	61.8	61.6	61.7	61.7
Glc′′′				
1	104.5	104.5	104.5	104.6
2	75.0	75.2	75.1	75.1
3	77.9	78.0	77.9	78.1
4	71.5	71.4	71.5	71.5
5	78.0	78.1	78.0	78.1
6	62.6	62.4	62.5	62.5
Glc′′′′				
1			95.5	95.7
2			73.8	73.9
3			78.6	78.6
4			70.8	70.8
5			77.8	77.9
6			69.3	69.4
Glc′′′′′				
1			104.5	104.4
2			75.1	75.0
3			76.4	76.5
4			78.5	78.4
5			77.0	76.9
6			61.4	61.5
Rha′′′′′′				
1			102.6	102.8
2			72.3	72.4
3			72.5	72.6
4			73.9	74.0
5			70.2	70.4
6			18.3	18.3



1 - 4

	R$_1$	R$_2$	R$_3$
1:	$\beta\text{Glc}p''' \xrightarrow{3} \alpha\text{Ara}p' \rightarrow$ $2\uparrow$ $\beta\text{Gal}p''$	H	H
2:	$\beta\text{Glc}p''' \xrightarrow{3} \alpha\text{Ara}p' \rightarrow$ $2\uparrow$ $\beta\text{Gal}p''$	OH	H
3:	$\beta\text{Glc}p''' \xrightarrow{3} \alpha\text{Ara}p' \rightarrow$ $2\uparrow$ $\beta\text{Gal}p''$	H	$\leftarrow \beta\text{Glc}p'''' \xleftarrow{6} \beta\text{Glc}p''''' \xleftarrow{4} \alpha\text{Rha}p''''''$
4:	$\beta\text{Glc}p''' \xrightarrow{3} \alpha\text{Ara}p' \rightarrow$ $2\uparrow$ $\beta\text{Gal}p''$	OH	$\leftarrow \beta\text{Glc}p'''' \xleftarrow{6} \beta\text{Glc}p''''' \xleftarrow{4} \alpha\text{Rha}p''''''$

EXPERIMENTAL

General comments and the method for isolating glycoside fractions have been published [1].

Fractions St-E, St-F, St-J, and St-K were dissolved in a minimal amount of CH_3OH, treated with an excess of diazomethane in ether, held for 30 min, evaporated to dryness, and separated by chromatography on silica gel with elution by water-saturated $CHCl_3$—C_2H_5OH (2:1) to give pure glycosides St-E$_1$ (35 mg), St-E$_2$ (80 mg), St-F$_1$ (65 mg), St-F$_2$ (42 mg), St-J$_1$ (50 mg), St-J$_2$ (55 mg), St-K$_1$ (70 mg), and St-K$_2$ (36 mg).

Glycoside St-E$_2$ (1). Total acid hydrolysis of **1** gives arabinose, galactose, glucose, and oleanolic acid. ^{13}C NMR data for **1** appear in Tables 1 and 2.

Glycoside St-F$_2$ (2). Total acid hydrolysis of **2** gives arabinose, galactose, glucose, and echinocystic acid. ^{13}C NMR data for **2** appear in Tables 1 and 2.

Glycoside St-J$_2$ (3). Total acid hydrolysis of **3** gives arabinose, galactose, glucose, rhamnose, and oleanolic acid. Total base hydrolysis of **3** gives the progenin, which is identical to that of glycoside **1**. ^{13}C NMR data appear in Tables 1 and 2.

Glycoside St-K$_2$ (4). Total acid hydrolysis of **4** gives arabinose, galactose, glucose, rhamnose, and echinocystic acid. Total base hydrolysis of **4** gives the progenin, which is identical to that of glycoside **2**. ^{13}C NMR data appear in Tables 1 and 2.

REFERENCES

1. V. I. Grishkovets, V. S. Strigunov, A. S. Shashkov, and V. Ya. Chirva, *Khim. Prir. Soedin.*, 147 (2001).
2. V. I. Grikhkovets, D. Yu. Sidorov, L. A. Yakovishin, N. N. Arnautov, A. S. Shashkov, and V. Ya. Chirva, *Khim. Prir. Soedin.*, 377 (1996).