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TRITERPENE GLYCOSIDES FROM *Kalopanax septemlobum*. III. GLYCOSIDES D_2, I_1, AND K_1 FROM LEAVES OF *Kalopanax septemlobum* VAR. *maximowiczii* INTRODUCED IN CRIMEA

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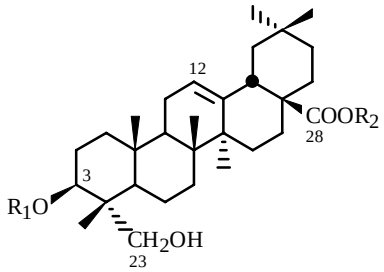
The new caffeylated triterpene glycosides hederagenin 3-O-(6-O-caffeyl-β-D-glucopyranosyl)-(1→4)-O-β-D-xylopyranosyl-(1→3)-O-α-L-rhamnopyranosyl-(1→2)-O-β-L-arabinopyranoside and its 28-O-α-L-rhamnopyranosyl-(1→4)-β-D-glucopyranosyl-(1→6)-O-β-D-glucopyranosyl and 28-O-α-L-rhamnopyranosyl-(1→4)-O-6-O-acetyl-β-D-glucopyranosyl-(1→6)-O-β-D-glucopyranosyl esters were isolated from leaves of Kalopanax septemlobum *var.* maximowiczii *introduced in Crimea. The structures of these compounds were established using chemical methods and NMR spectroscopy.*

Key words: *Kalopanax septemlobum* var. *maximowiczii*, Araliaceae, triterpene glycosides, hederagenin glycosides.

We have previously described the chromatographic analysis of glycoside D, K, and I fractions from leaves of *Kalopanax septemlobum* var. *maximowiczii* and the method for preparing them [1]. It was shown that they contained acidic glycosides because they formed chromatographic bands with characteristic "tails" and contain acyl groups according to two-dimensional (2D) TLC [2].

Treatment of fraction D, consisting according to TLC of two glycosides D_1 and D_2 (**1**), with CH_2N_2 in ether and subsequent chromatographic separation produced the methyl ester of D_2 (**1a**). The method for isolating glycoside I_1 (**2**) has been reported [1]. It was purified of accompanying I_2 by treatment with CH_2N_2 in ether and additional chromatography of the methyl ester of I_1 (**2a**) over silica gel. Glycoside K_1 (**3**) was prepared by chromatographic purification of glycoside K, which was described by us earlier [3]. It was additionally purified by esterification with CH_2N_2 and chromatography of the methyl ester (**3a**).



1 - 3

	R_1	R_2
1:	Caff-O→^{6}β-D-Glc*p*→^{4}β-D-Xyl*p*→^{3}α-L-Rha*p*→^{2}α-L-Ara*p*→	H
1a:	3′,4′-di-Me-Caff-O→^{6}β-D-Glc*p*→^{4}β-D-Xyl*p*→^{3}α-L-Rha*p*→^{2}α-L-Ara*p*→	Me
2:	Caff-O→^{6}β-D-Glc*p*→^{4}β-D-Xyl*p*→^{3}α-L-Rha*p*→^{2}α-L-Ara*p*→←β-D-Glc*p*^{6}	←β-D-Glc*p*^{6} ←OAc)^4 ←α-L-Rha*p*
2a:	3′,4′-di-Me-Caff-O→^{6}β-D-Glc*p*→^{4}β-D-Xyl*p*→^{3}α-L-Rha*p*→^{2}α-L-Ara*p*→	←β-D-Glc*p*^{6} ←(β-D-Glc*p*^{6} ←OAc)^4 ←α-L-Rha*p*
3:	Caff-O→^{6}β-D-Glc*p*→^{4}β-D-Xyl*p*→^{3}α-L-Rha*p*→^{2}α-L-Ara*p*→←β-D-Glc*p*^{6}	←β-D-Glc*p*^{4} ←α-L-Rha*p*
3a:	3′,4′-di-Me-Caff-O→^{6}β-D-Glc*p*→^{4}β-D-Xyl*p*→^{3}α-L-Rha*p*→^{2}α-L-Ara*p*→	←β-D-Glc*p*^{6} ←β-D-Glc*p*^{4} ←α-L-Rha*p*

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TABLE 1. ^{13}C Chemical Shifts (C_5D_5N, δ, ppm, 0 = TMS) of Aglycon Parts of Glycosides **1**-**3** and **1a**-**3a**

C atom	**1**	**1a**	**2**, **2a**, **3**, **3a***	C atom	**1**	**1a**	**2**, **2a**, **3, 3a***
1	39.0	39.0	39.1	17	46.6	47.0	47.0
2	26.2	26.2	26.4	18	42.0	41.9	41.7
3	81.1	81.1	81.1	19	46.4	46.2	46.2
4	43.6	43.6	43.6	20	30.9	30.9	30.8
5	47.7	47.7	47.7	21	34.2	34.1	34.0
6	18.2	18.2	18.2	22	33.2	32.9	32.6
7	32.8	32.8	32.8	23	64.0	64.0	64.0
8	39.8	39.8	39.9	24	14.2	14.2	14.2
9	48.2	48.2	48.2	25	16.1	16.1	16.2
10	36.9	36.9	36.9	26	17.4	17.4	17.6
11	23.8	23.8	23.9	27	26.3	26.3	26.1
12	122.6	122.6	123.0	28	180.2	178.1	176.5
13	144.8	144.8	144.1	29	33.2	33.2	33.1
14	42.2	42.2	42.2	30	23.8	23.8	23.8
15	28.3	28.2	28.3	$O\text{-}CH_3$		51.7	
16	23.7	23.8	23.4				

*Average chemical shifts are given for these compounds. Deviations for individual compounds are less than ±0.1 ppm for ^{13}C atoms and ±0.05 ppm for ^{1}H.

Total acid hydrolysis found in **1**-**3** hederagenin and the sugars glucose, xylose, rhamnose, and arabinose. Alkaline hydrolysis of **1**-**3** afforded hederagenin 3-O-β-D-glucopyranosyl-(1→4)-O-β-D-xylopyranosyl-(1→3)-O-α-L-rhamnopyranosyl-(1→2)-O-α-L-arabinopyranoside, which was isolated by us previously from *Kalopanax septemlobum* [3]. This established preliminarily the structure of the carbohydrate chain on C-3 of the aglycon in **1**-**3**. Mild alkaline hydrolysis of **1** afforded the same progenin. However, it became obvious that another acyl fragment was present in the carbohydrate chain on C-3 of the aglycon because an acylglycoside bond was not cleaved under these conditions. Mild alkaline hydrolysis of **2** and **3** afforded the same 3-O-β-D-glucopyranosyl-(1→4)-O-β-D-xylopyranosyl-(1→3)-O-α-L-rhamnopyranosyl-(1→2)-O-α-L-arabinopyranosyl-28-O-α-L-rhamnopyranosyl-(1→4)-β-D-glucopyranosyl-(1→6)-O-β-D-glucopyranosyl ester of hederagenin [3]. Hence, the structures of the carbohydrate chains on C-3 and C-28 of the aglycon were established. However, the nature and location of the acyl groups in **2** and **3** were unclear.

The nature of the aglycon in **1**-**3** was established by analysis of chemical shifts of C atoms in the one-dimensional ^{13}C NMR spectra. For **1**, these were identical to those of 3-O-glycosylated hederagenin [4]; for **2** and **3**, 3,28-di-O-glycosylated hederagenin [4]. Table 1 lists the chemical shifts of ^{13}C atoms in NMR subspectra of the aglycons in **1**-**3**.

The structures of the carbohydrate parts in **1**-**3** were confirmed and the nature and location of the acyl groups were established by using various versions of 1D and 2D NMR spectroscopy. Since the carbohydrate chain on C-3 of the aglycon is the same in **1**-**3** according to the results of alkaline hydrolysis, we confirmed its structure first by analyzing 2D COSY, TOCSY, and HSQC spectra of **1a** and comparing them with those for 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]. This revealed that the chemical shifts of the C and H atoms of xylose, rhamnose, and arabinose were practically the same. However, those of the terminal glucose unit experienced typical α-effects of acylation, namely, +1.9 ppm for C-6 and +0.5 ppm for H-6, and β-effects of acylation of -2.6 ppm for C-5 and +0.18 ppm for H-5. This indicates that an acyl group is located on the C-6 hydroxyl of this monosaccharide unit.

After assigning the signals for the carbohydrate part of **1a**, it was determined that the overall ^{13}C NMR spectrum contained a signal for the C atom of the aglycon C-28 carboxyl at 178.1 ppm in addition to a signal for a carbonyl C atom at 167.4 ppm and two additional signals for methoxyl C atoms at 55.9 and 56.0 ppm (and yet another methoxyl C atom on aglycon C-28 at 51.7 ppm). These additional methoxyls corresponded in the PMR spectrum to 3H singlets at 3.74 and 3.81 ppm (methoxyl on C-28 at 3.61 ppm). Furthermore, the spectral region from 110 to 160 ppm contained another eight C signals. According to ^{13}C NMR with APT-testing, three of these signals belonged to quaternary C atoms; the others, to tertiary ones.

The magnitude of the chemical shift for the additional carbonyl C atom indicated that a carboxylate carbonyl was conjugated either to a double bond or to an aromatic ring. This model corresponded with the signals at 110-160 ppm, which could be those of aromatic or olefinic C atoms. Several signals in this region suggested that an aromatic ring was present. Furthermore, they included two phenolic OH groups because only they could be easily methylated by CH_2N_2 in ether and gave signals for C and H atoms of two methoxyls, the chemical shifts of which corresponded to phenol-methyl ethers [5]. Furthermore, the PMR spectrum of **1a** contained in the region of olefinic and aromatic protons (from 6 to 8 ppm) four groups of signals that integrated for five protons. The structure of the acyl fragment was then fully established using special NMR methods. Thus, two 1H doublets at 6.63 and 7.97 ppm with overall spin—spin coupling constant (SSCC) 15.9 Hz were observed in the range 6-8 ppm. The 2D COSY spectrum confirmed the coupling between them and demonstrated that they form an isolated spin system because neither of them had cross peaks with other protons.

The 2D HSQC spectrum located the signals for the corresponding C atoms at 116.1 and 145.6 ppm. The magnitudes of the chemical shifts for these C and H atoms, the nature of the splitting of the corresponding protons, and the value of the SSCC led to the conclusion that they form an asymmetrically substituted *trans*-olefinic R–CH=CH–R′ fragment. The C atoms bound directly to the olefinic C atoms in the R and R′ groups were quaternary because the olefinic H atoms lacked any SSCC and cross peaks with other H atoms in the COSY spectrum.

Two other groups of signals in the PMR spectrum of **1a** at 7.19 (2H multiplet) and 6.91 ppm (1H doublet) with SSCC 8.8 Hz had a common cross peak and also formed an isolated spin system according to the COSY spectrum. Since all these protons should be aromatic according to the magnitude of the chemical shifts and the logic of the preceding discussion, the nature of the splitting for the proton at 6.91 ppm and the magnitude of its SSCC led to the conclusion that one of the protons at 7.19 ppm was located in the *o*-position relative to it (J_{ortho} = 8.8 Hz); the other, in the *p*-position (J_{para} ~ 0 Hz). Because the chemical shifts of the two protons at 7.19 were very similar, it was impossible to analyze the nature of their splitting or establish their mutual positions. However, the HSQC spectrum showed signals for C atoms bound to them at 111.1 and 123.3 ppm. The signal for the C atom bound to the proton with δ 6.91 ppm was located at 112.2 ppm.

Three more of the aforementioned quaternary C atoms of the acyl fragment should also be aromatic. It was also obvious that two of them should be bound to phenolic OH groups. Because quaternary atoms were bound to the CH groups of the R–CH=CH–R′ fragment found above, one of them, the carboxyl C, was conjugated to a double bond. The other was the remaining third quaternary C atom of the aromatic ring.

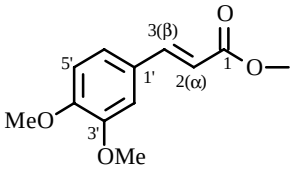
Thus, the aromatic ring contained three substituents. These were acrylic acid residue (–CH=CH–COOH) and two phenolic hydroxyls. However, their location could be different and still satisfy the mutually established location of the aromatic protons. This question was answered and the mutual bonding of the fragments in the acyl substituent was confirmed conclusively by analyzing the 2D HMBC spectrum.

The signal for the carboxyl C atom at 167.4 ppm gave rise in the HMBC spectrum to cross peaks with protons of the double bond, very strong with that at 7.97 ppm and much weaker with that at 6.63 ppm. Because correlations in the HMBC spectrum are most effective through three chemical bonds, the proton with δ 6.63 ppm was located on the α-C atom; with δ 7.97 ppm, on the β-C atom relative to the carboxyl group. The signals of the corresponding C atoms at 166.1 ppm (α-C) and 145.6 ppm (β-C), which were found earlier using the HSQC spectrum, were unambiguously assigned. The α-proton gave rise to a strong cross peak with the quaternary C atom at 127.9 ppm. Obviously this was the quaternary aromatic atom C-1′ that was bound to the β-C atom of the acrylic acid. The β-proton gave rise to strong cross peaks with tertiary C atoms at 111.1 and 123.3 ppm. These were C-2′ and C-6′ of the aromatic ring. The protons with δ 7.19 ppm bound to these atoms gave rise in the HMBC spectrum to a cross peak with one quaternary C atom at 152.1 ppm. Therefore, this was C-4′ with the phenolic OH group. Aromatic C-1′ (δ 127.9 ppm) produced a cross peak through three bonds with the proton at 6.91 ppm. Thus, this proton and the corresponding C atom (δ 112.2 ppm) lay in the *m*-position relative to C-1′, i.e., atoms H-5′ and C-5′. Proton H-5′ (δ 6.91 ppm) produced a cross peak through three bonds with a quaternary C atom at 150.1 ppm. This identified it as C-3′ with a phenolic OH group. Proton H-5′ gave a weak cross peak (through two bonds) with C-6′ at 123.3 ppm. This resolved the initial ambiguity about the mutual assignment of the signals for C-2′ and C-6′ that was due to the overlap of the signals for their protons. The cross peaks through three bonds for the methoxyl protons (δ 3.81 and 3.74) and quaternary C atoms at 150.1 and 152.1 ppm, respectively, confirmed that the O–CH_3 groups were located on these atoms and that the assignments for C-3′ and C-4′ were correct.

TABLE 2. Chemical Shifts and SSCC (C_5D_5N, δ, ppm, 0 = TMS, J/Hz) for ^{13}C and ^{1}H Atoms in *trans*-Caffeic Acid in **1-3** and **1a-3a**

^{13}C atom	**1-3***	**1a-3a***	^{1}H atom	**1-3***	SSCC	**1a-3a***	SSCC
1	167.6	167.4	1	-		-	
2 (α)	114.7	116.1	2 (α)	6.52	$J_{2,3}$ = 15.8	6.63 d	$J_{2,3}$ = 15.9
3 (β)	146.2	145.6	3 (β)	7.92	$J_{2,3}$ = 15.8	7.97 d	$J_{2,3}$ = 15.9
1′	126.6	127.9	1′	-		-	
2′	115.8	111.1	2′	7.47 d	$J_{2',6'}$ = 2.0	7.19 m	
3′	144.1	150.1	3′	-		-	
4′	144.1	152.1	4′	-		-	
5′	116.7	112.2	5′	7.15 m		6.91 d	$J_{5',6'}$ = 8.8
6′	122.2	123.3	6′	7.06 dd	$J_{5,6}$ = 8.1	7.19 m	
(3′)-O-CH_3		56.0	(3′)-O-CH_3			3.81 s	
(4′)-O-CH_3		55.9	(4′)-O-CH_3			3.74 s	

Thus, the methylated acyl fragment was (*E*)-3-(3,4-dimethoxyphenyl)-2-propenoic acid or *trans*-3,4-dimethoxycinnamic acid.



The structure of the acyl fragment in **1a** was established completely. However, there was some question about the origin of **1**. Either both phenolic hydroxyls were not methylated in the native glycoside, which corresponded to a caffeic group (3,4-dihydroxycinnamic) acid, or one of them was methylated, i.e., the acyl fragment could be ferulic (4-hydroxy-3-methoxycinnamic) or hesperetic (isoferulic, 3-hydroxy-4-methoxycinnamic) acid. This question was easily resolved by analyzing survey PMR and ^{13}C NMR spectra. Thus, the signals for the methoxyl protons in these spectra (3.5-4.0 ppm) and the methoxyl C atoms (55-57 ppm) were absent. This precludes the presence of ferulic or isoferulic acids and unambiguously defines the native acyl fragment as *trans*-caffeic acid. The signals of caffeic acid in **1** were completely assigned in analogy to that described above and in Table 2.

The caffeic acid esterified the primary-alcohol group of the terminal glucose. This was established not only from the aforementioned acylation effects compared with the nonacylated glycoside, 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], but also by the observation in the HMBC spectrum of a cross peak between the carboxyl C of caffeic acid (167.4 ppm) and one of the H-6 protons (δ 5.06 ppm) of the terminal glucose.

Thus, **1** was hederagenin 3-O-(6-O-caffeyl-β-D-glucopyranosyl)-(1→4)-O-β-D-xylopyranosyl-(1→3)-O-α-L-rhamnopyranosyl-(1→2)-O-α-L-arabinopyranoside and is a new triterpene glycoside. Table 3 lists the chemical shifts of ^{1}H and ^{13}C atoms for the carbohydrate parts of **1** and **1a**.

The PMR and ^{13}C NMR spectra of **2a** and **3a** were compared with those of **1a** and exhibited the same signals for the caffeylated tetrasaccharide fragment and additional signals that were easily and unambiguously assigned by analyzing the chemical shifts as previously described [1, 3] as the acetylated trisaccharide fragment α-L-Rha*p*→^{4}(AcO→^{6}β-D-Glc*p*)→^{6}β-D-Glc*p*→ in **2a** and the trisaccharide fragment α-L-Rha*p*→^{4}β-D-Glc*p*→^{6}β-D-Glc*p*→ in **3a**. The lack of native methylated phenolic groups in **2** and **3** (Table 3) was confirmed by analyzing their PMR spectra which, like for **1**, lacked signals for O–CH_3 groups.

TABLE 3. Chemical Shifts (C_5D_5N, δ, ppm, 0 = TMS) for ^{13}C and ^{1}H Atoms in Carbohydrate Parts of **1-3** and **1a-3a**

^{13}C atom	**1-3, 1a-3a***	^{1}H atom	**1-3, 1a-3a***	^{13}C atom	**2**	^{1}H atom	**2**	^{13}C atom	**3**	^{1}H atom	**3**
Ara-1	104.6	Ara-1	5.05	Glc-1	95.6	Glc-1	6.19	Glc-1	95.7	Clc-1	6.15
2	75.4	2	4.52	2	73.9	2	4.09	2	73.8	2	4.09
3	75.0	3	4.02	3	78.7	3	4.18	3	78.6	3	4.20
4	69.6	4	4.12	4	70.9	4	4.21	4	70.8	4	4.28
5	66.0	5e	3.66	5	78.1	5	4.10	5	78.0	5	4.06
		5a	4.23	6	69.4	6A	4.64	6	69.4	6A	4.62
						6B	4.32			6B	4.29
Rha-1	101.4	Rha-1	6.23	Glc-1	104.7	Glc-1	4.98	Glc-1	104.9	Glc-1	4.95
2	71.9	2	4.81	2	75.1	2	3.92	2	75.3	2	3.90
3	83.2	3	4.66	3	76.4	3	4.10	3	76.5	3	4.09
4	72.9	4	4.42	4	79.3	4	4.07	4	78.4	4	4.30
5	69.6	5	4.65	5	73.8	5	3.82	5	77.1	5	3.62
6	18.4	6	1.55	6	63.7	6A	4.62	6	61.3	6A	4.17
				-OAc	20.6	6B	4.52			6B	4.04
					170.6	-OAc	1.93				
Xyl-1	107.2	Xyl-1	5.21	Rha-1	103.0	Rha-1	5.50	Rha-1	102.8	Rha-1	5.75
2	75.3	2	4.02	2	72.4	2	4.57	2	72.5	2	4.64
3	75.9	3	4.10	3	72.6	3	4.45	3	72.7	3	4.50
4	77.8	4	4.23	4	73.9	4	4.29	4	73.9	4	4.29
5	65.0	5e	4.33	5	70.7	5	4.80	5	70.4	5	4.86
		5a	3.60	6	18.5	6	1.68	6	18.6	6	1.65
Glc-1	103.6	Glc-1	4.99								
2	73.8	2	4.00								
3	77.8	3	4.17								
4	71.4	4	4.07								
5	76.2	5	4.12								
6	64.6	6A	5.06								
		6B	4.72								

Thus, **2** and **3** were 28-O-α-L-rhamnopyranosyl-(1→4)-O-6-O-acetyl-β-D-glucopyranosyl-(1→6)-O-β-D-glucopyranosyl and 28-O-α-L-rhamnopyranosyl-(1→4)-β-D-glucopyranosyl-(1→6)-O-β-D-glucopyranosyl esters of hederagenin 3-O-(6-O-caffeyl-β-D-glucopyranosyl)-(1→4)-O-β-D-xylopyranosyl-(1→3)-O-α-L-rhamnopyranosyl-(1→2)-O-α-L-arabinopyranoside and are new triterpene glycosides. Triterpene glycosides with a caffeyl moiety were previously observed only in *Clematis tibetana* (Ranunculaceae) [6].

EXPERIMENTAL

General comments have been published [1].

Isolation and Purification of Glycosides. Fraction D [1] (610 mg) was chromatographed over silica gel with elution by water-saturated $CHCl_3$:isopropanol (5:1) to afford glycosides D_1 (250 mg) and D_2 (**1**, 270 mg). Crude **1** (170 mg) was dissolved in CH_3OH (10 mL) and esterified by adding an excess of CH_2N_2 in ether [7]. The methylation product was purified by chromatography over silica gel with elution by water-saturated $CHCl_3$:isopropanol (8:1) to afford pure **1a** (100 mg).

Glycoside I_1 (**2**, 150 mg) [1] was dissolved in CH_3OH (10 mL) and esterified by adding an excess of CH_2N_2 in ether. The resulting **2a** was purified by chromatography over silica gel with elution by water-saturated $CHCl_3$:isopropanol (4:1) to afford pure **2a** (90 mg).

Fraction K [2] was separated by chromatography and purified to afford K_1 (100 mg). It was additionally purified by esterification with an excess of CH_2N_2 and chromatography of the resulting methyl ester over silica gel with elution by water-saturated $CHCl_3$:isopropanol (2:1) to afford pure **3a** (80 mg).

Structure Determination of Glycosides. Total acid hydrolysates of **1**-**3** contained hederagenin and the sugars glucose, xylose, rhamnose, and arabinose. Alkaline hydrolysis of **1**-**3** afforded 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], which was identified by TLC with an authentic specimen. Mild alkaline hydrolysis of **1** gave the same product. Mild alkaline hydrolysis of **2** and **3** gave the 3-O-β-D-glucopyranosyl-(1→4)-O-β-D-xylopyranosyl-(1→3)-O-α-L-rhamnopyranosyl-(1→2)-O-α-L-arabinopyranosyl-28-O-α-L-rhamnopyranosyl-(1→4)-β-D-glucopyranosyl-(1→6)-O-β-D-glucopyranosyl ester of hederagenin [3], which was identified by comparison with an authentic specimen.

Table 1 gives the chemical shifts of ^{13}C atoms in the NMR spectra of the aglycon parts of **1**-**3** and **1a**-**3a**. Tables 2 and 3 give the chemical shfits of ^{13}C and ^{1}H atoms in the carbohydrate fragments and acyl parts.

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