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TRITERPENE GLYCOSIDES FROM *Hedera canariensis*. VI. STRUCTURE OF L-G_1, AND L-G_{1b} GLYCOSIDES FROM LEAVES OF CANARY IVY

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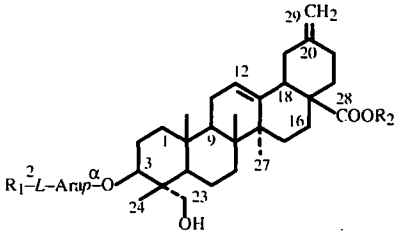
*Two new minor triterpene glycosides L-G_1, and L-G_{2b}, the 3-O-α-L-arabinopyranosyl-28-O-α-L-rhamnopyranosyl-(1→4)-O-β-D-gentiobiosyl and 3-O-α-L-rhamnopyranosyl-(1→2)-O-α-L-arabinopyranosyl-28-O-α-L-rhamnopyranosyl-(1→4)-O-(6-O-acetyl-β-D-glucopyranosyl)-(1→6)-O-β-D-glucopyranosyl esters of 30-norhederagenin, respectively, are isolated from the leaves of canary ivy (*Hedera canariensis *Willd.). The structures of the glycosides are found by chemical methods and ^1H and ^{13}C NMR spectroscopy.*

We recently isolated glycosides of 30-norhederagenin, which have previously been found only in *Akebia quinata* (Lardizabalaceae) [1], from the leaves of *Hedera canariensis* (Araliaceae) [2]. In the present article, we describe the isolation and structure determination of two more minor saponins with this aglycone, the glycosides L-G_1, (**1**) and L-G_{1b} (**2**). Glycosides **1** and **2** were found in the fraction L-G_1, the preparation of which we previously described [3]. Careful TLC analysis of fraction L-G_1 on plates with Merck high-efficiency $60F_{254}$ silica gel revealed that **1** and **2** were present in addition to the previously identified glycosides L-G_1 and L-G_{1a}. The glycosides **1** and **2** were isolated by preparative chromatography of fraction L-G_1 on Silpearl high-efficiency microspherical silica gel by elution with chloroform—ethanol—water.

Total acid hydrolysis of **1** and **2** produced only one aglycone, identical by TLC in various solvent systems to 30-norhederagenin, the aglycone of glycosides L-E_2 and L-H_3 [2], which were isolated from the leaves of canary ivy. The carbohydrate composition of **1** and **2** that was established by total acid hydrolysis consists of identical monosaccharide residues, arabinose, glucose, and rhamnnose.



	R_1	R_2
1	H	← β-*D*-Glc*p*-(6← 1)-β-*D*-Glc*p*-(4← 1)-α-*L*-Rha*p*
2	α-*L*-Rha*p* →	← β-*D*-Glc*p*-(6← 1)-β-*D*-Glc*p*-(4← 1)-α-*L*-Rha*p* ↑6 OAc
3	H	H
4	α-*L*-Rha*p* →	H
5	α-*L*-Rha*p* →	← β-*D*-Glc*p*-(6← 1)-β-*D*-Glc*p*-(4← 1)-α-*L*-Rha*p*

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Alkaline hydrolysis of **2** produces progenin **4**, which is identical in chromatographic mobility (TLC) to L-E_2, 30-norhederagenin 3-O-α-L-rhamnopyranosyl-(1→2)-O-α-L-arabinopyranoside [2]. Arabinose and 30-norhederagenin were identified by TLC in the acid hydrolysate of the progenin from **1** (**3**). Thus, progenin 3 is apparently 30-norhederagenin 3-O-α-L-arabinopyranoside.

Mild alkaline hydrolysis of **2** produces glycoside **5**, which is identical to L-H_3 from the leaves of canary ivy [2], 30-norhederagenin 3-O-α-L-rhamnopyranosyl-(1→2)-O-α-L-arabinopyranosyl-28-O-α-L-rhamnopyranosyl-(1→4)-O-β-D-glucopyranosyl-(1→6)-O-β-D-glucopyranoside. Such changes in **2** upon treatment with an aqueous-alcohol solution of ammonia partially define its structure and suggest the presence of at least one acyl group.

The ^{1}H NMR spectrum of **1** contains signals for the anomeric protons of one arabinose unit, two glucose units, and one rhamnose unit. Furthermore, the chemical shifts of the ^{13}C atoms in the carbohydrate chains of **1** coincide completely with those in the literature [4] for the fragments α-*L*-Ara*p* → and β-*D*-Glc*p*-(6←1)-β-*D*-Glc*p*-(4←1)-α-*L*-Rha*p*. Signals in the PMR spectra of **1** and **2** were assigned on the basis of COSY spectra and are given in the Experimental section.

The presence of signals for five anomeric protons in the PMR spectrum of **2** and the nature of the splitting for the remaining backbone protons confirm that **2** contains five monosaccharide units (two each of rhamnose and glucose and one of arabinose). Furthermore, the spectrum contains one additional 3-proton singlet (1.91 ppm) in the region characteristic of acetates (1.80-2.20 ppm).

A comparison of the ^{13}C NMR spectra of L-H_3 [2] and **2** shows that the latter spectrum contains two additional signals with chemical shifts 21.4 and 171.7 ppm. These are assigned to signals of C-atoms in the –CO–CH_3 moiety. This confirms that **2** contains one O-acetyl group. An analysis of the magnitudes of the chemical shifts and the effects of acetylation on ^{1}H and ^{13}C NMR spectra of carbohydrate chains [3] proves that the acetyl group is localized on C-6 of the inner Glc″″ unit.

Signals for the C-atoms of the aglycones of **1** and **2** were assigned by comparing their spectrum with the spectra of L-E_2 and L-H_3 [2]. The chemical shifts for the C-atoms of the aglycones are identical. This completely confirms the nature of the aglycone in **1** and **2**.

Thus, **1** and **2** are 30-norhederagenin 3-O-α-*L*-arabinopyranosyl-28-O-α-*L*-rhamnopyranosyl-(1→4)-O-β-*D*-gentiobiosyl and 3-O-α-*L*-rhamnopyranosyl-(1→2)-O-α-*L*-arabinopyranosyl-28-O-α-*L*-rhamnopyranosyl-(1→4)-O-(6-O-acetyl-β-*D*-glucopyranosyl)-(1→6)-O-β-*D*-glucopyranosyl ethers, respectively. The isolated glycosides of 30-norhederagenin are new compounds.

EXPERIMENTAL

Common procedures and hydrolysis methods have been described previously [3, 4]. The isolation of fraction L-G_1 has been described [3].

NMR spectra were obtained on Bruker WM-250 and AM-400 instruments. Solutions of glycosides in pyridine-D_5 were used.

Fraction L-G_1 (600 mg) was separated by column chromatography on Silpearl (Czech Republic) silica gel by elution with $CHCl_3$-ethanol (2:1) saturated with water. Yields were L-G_1, 350 mg; L-$G_{1'}$, 30 mg; L-G_{1a}, 150 mg; L-G_{1b}, 15 mg.

Glycoside L-$G_{1'}$ (1). The total acid hydrolysate of **1** contained rhamnose, arabinose, glucose, and 30-norhederagenin according to TLC.

Alkaline hydrolysis of **1** gives the progenin **3**. Acid hydrolysis of **3** produces arabinose and 30-norhederagenin, which were identified by TLC with authentic samples.

^{1}H NMR spectrum of **1** (δ, ppm, 0 = TMS, C_5D_5N): 4.92 (d, H-1′, $J_{1,2}$ = 7.5), 4.38 (dd, H-2′, $J_{2,3}$ = 9.0), 4.02 (dd, H-3′, $J_{3,4}$ = 3.2), 4.1-4.3 (m, H-4′), 4.23 (dd, H-5e′, $J_{4,5e}$ = 3.2, $J_{5a,5e}$ = 10.5), 3.6-3.75 (m, H-5a′), 6.11 (d, H-1″, $J_{1,2}$ = 8.5), 4.08 (t, H-2″, $J_{2,3}$ = 9.0), 4.1-4.3 (m, H-3″, H-4′″), 4.00 (m, H-5″), 4.63 (H-6A″), 4.28 (H-6B″), 4.91 (d, H-1′″, $J_{1,2}$ = 8.0), 3.90 (dd, H-2′″, $J_{2,3}$ = 9.0), 4.08 (t, H-3′″, $J_{3,4}$ = 9.0), 4.29 (t, H-4′″, $J_{4,5}$ = 9.0), 3.58 (m, H-5′″), 4.16 (H-6A′″), 4.01 (H-6B′″), 5.76 (d, H-1″″, $J_{1,2}$ = 1.5), 4.65 (dd, H-2″″, $J_{2,3}$ = 3.5), 4.53 (dd, H-3″″, $J_{3,4}$ = 9.5), 4.29 (t, H-4″″, $J_{4,5}$ = 9.5), 4.87 (m, H-5″″), 1.64 (d, H-6″″, $J_{5,6}$ = 6.5), 3.01 (dd, H-3, $J_{2e,3}$ = 3.8, $J_{2a,3}$ = 14.0), 5.39 (t, H-12, $J_{11,12}$ = 3.5), 3.03 (dd, H-18, $J_{18,19e}$ = 5.0, $J_{18,19e}$ = 13.5), 2.46 (t, H-19a, $J_{19a,19e}$ = 14.0), 4.1-4.3 (m, H-23A), 3.6-3.75 (m, H-23B), 4.70 (m, H-29A), 4.65 (m, H-29B), 1.12, 1.01, 0.91, 0.84 (all s, 4 CH_3).

The ^{13}C NMR spectrum of **1** is listed in Tables 1 and 2.

TABLE 1. Chemical Shifts for ^{13}C Atoms in Carbohydrates of Glycoside L-$G_{1'}$ (1) and L-G_{1b} (2) (δ, ppm, 0 = TMS, C_5D_5N)

C-atom	Compound		C-atom	Compound	
	1	2		1	2
	Ara′	Ara′		Glc″	Glc‴
1	106.7	104.5	1	96.1	96.0
2	73.1	76.0	2	74.0	74.1
3	74.8	74.0	3	78.6	78.7
4	69.7	69.3	4	70.8	71.0
5	67.0	65.4	5	78.2	78.3
			6	69.4	69.6
		Rha″		Glc‴	Glc⁗
1		101.0	1	104.9	105.0
2		72.3	2	75.3	75.3
3		72.6	3	76.6	76.5
4		74.4	4	78.5	79.5
5		70.0	5	77.2	74.0
6		18.8	6	61.2	64.1
			-CO-CH_3		171.7
			-CO-CH_3		21.4
				Rha⁗	Rha⁗′
			1	102.8	103.0
			2	72.5	72.6
			3	72.8	72.7
			4	74.0	74.0
			5	70.8	71.0
			6	18.8	18.8

TABLE 2. Chemical Shifts of ^{13}C Atoms in Aglycones of Glycosides L-$G_{1'}$ (1) and L-G_{1b} (2) (δ, ppm, 0 = TMS, C_5D_5N)

C-atom	Compound		C-atom	Compound	
	1	2		1	2
1	39.3	39.2	16	24.0	24.0
2	26.6	26.5	17	47.3	47.4
3	81.3	81.3	18	47.7	47.8
4	43.7	43.6	19	42.0	41.9
5	47.8	47.6	20	148.6	148.6
6	18.5	18.5	21	30.2	30.2
7	33.2	33.4	22	37.7	37.8
8	40.0	40.1	23	64.1	64.0
9	48.3	48.4	24	14.2	14.1
10	37.1	37.1	25	16.3	16.4
11	24.0	24.1	26	17.7	17.8
12	123.2	123.1	27	26.5	26.4
13	143.7	143.7	28	176.3	176.4
14	42.4	42.4	29	107.6	107.6
15	28.5	28.6			

Glycoside L-G_{1b} (2). The total acid hydrolysate of **2** contained rhamnose, arabinose, glucose, and 30-norhederagenin. Alkaline hydrolysis of **2** gave progenin **4**, which was identical by TLC to L-E_2 from canary ivy [2]. Mild alkaline hydrolysis

of **2** gave **5**, which was identical by TLC to L-H_3 [2].

^{1}H NMR spectrum of **2** (δ, ppm, 0 = TMS, C_5D_5N): 5.10 (d, H-1′, $J_{1,2}$ = 6.0), 4.50 (dd, H-2′, $J_{2,3}$ = 7.0), 4.10 (dd, H-3′, $J_{3,4}$ = 3.5), 4.19 (m, H-4′), 3.70 (dd, H-5a′, $J_{5a,4}$ = 2.0), 4.27 (dd, H-5e′, $J_{5e,4}$ = 4.0, $J_{5a,5e}$ = 10.0), 6.12 (d, H-1″, $J_{1,2}$ = 1.5), 4.70 (dd, H-2″, $J_{2,3}$ = 3.5), 4.60 (dd, H-3″, $J_{3,4}$ = 9.5), 4.27 (t, H-4″, $J_{4,5}$ = 9.5), 4.62 (m, H-5″), 1.59 (d, H-6″, $J_{5,6}$ = 6.5), 6.08 (d, H-1′″, $J_{1,2}$ = 8.0), 3.95 (t, H-2′″, $J_{2,3}$ = 8.5), 4.01 (t, H-3′″, $J_{3,4}$ = 9.0), 4.16 (t, H-4′″, $J_{4,5}$ = 9.0), 4.00 (m, H-5′″), 4.55 (H-6A′″), 4.23 (H-6B′″), 4.86 (d, H-1″″, $J_{1,2}$ = 8.0), 3.83 (t, H-2″″, $J_{2,3}$ = 8.5), 3.92-4.04 (m, H-3″″, H-4″″), 3.67 (m, H-5″″), 4.49 (H-6A″″), 4.39 (H-6B″″), 5.40 (d, H-1′″″, $J_{1,2}$ = 1.5), 4.50 (dd, H-2′″″, $J_{2,3}$ = 3.5), 4.40 (dd, H-3′″″, $J_{3,4}$ = 9.0), 4.23 (t, H-4′″″, $J_{4,5}$ = 9.5), 4.69 (m, H-5′″″, $J_{5,6}$ = 6.5), 1.52 (d, H-6′″″), 5.38 (t, H-12, $J_{11,12}$ = 3.5), 3.04 (dd, H-18, $J_{18,19e}$ = 5.0, $J_{18,19a}$ = 13.5), 2.45 (t, H-19a, $J_{19a,19e}$ = 14.0), 4.05 (d, H-23A), 3.71 (d, H-23B, $J_{23A,23B}$ = 11.0), 4.71 (m, H-29A), 4.65 (m, H-29B), 1.11, 0.99, 0.92, 0.83 (all s, 4 CH_3), 1.91 (s, –$COCH_3$).

The ^{13}C NMR of **2** is listed in Tables 1 and 2.

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