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TRITERPENE GLYCOSIDES OF *Hedera canariensis*. I. STRUCTURES OF GLYCOSIDES L-A, L-B_1, L-B_2, L-C, L-D, L-E_1, L-G_1, L-G_2, L-G_3, L-G_4, L-H_1, L-H_2, AND L-I_1 FROM THE LEAVES OF *Hedera canariensis*

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From the leaves of Algerian ivy Hedera canariensis *Willd. (fam. Aralaceae) we have isolated 13 triterpene glycosides: the 3-O-α-*L*-arabinopyranosides of oleanolic acid (A), of echinocystic acid (B_1), and of hederagenin (B_2); the 3-O-[O-α-*L*-rhamnopyranosyl-(1→2)-α-*L*-arabinopyranoside]s of oleanolic acid (C), of echinocystic acid (D), and of hederagenin (E_1); the 3-O-α-*L*-rhamnopyranoside 28-O-[O-α-*L*-rhamnopyranosyl-(1→4)-β-gentiobioside] of hederagenin (G_1); the 3-O-[O-α-*L*-rhamnopyranosyl-(1→2)-α-*L*-arabinopyranoside] 28-O-β-gentiobioside of hederagenin (G_3); the 3-O-[O-α-*L*-rhamnopyranosyl-(1→2)-α-*L*-arabinopyranoside] 28-O-[O-α-*L*-rhamnopyranosyl-(1→4)-β-gentiobioside]s of oleanolic acid (G_2), of echinocystic acid (H_1), and of hederagenin (H_2); the 3-O-[O-α-*L*-rhamnopyranosyl-(1→2)-β-D-glucopyranoside] 28-O-[O-α-*L*-rhamnopyranosyl-(1→4)-β-gentiobioside] of hederagenin (I_1); and the 3-O-[O-α-*L*-rhamnopyranosyl-(1→4)-O-gentiobiosyl)-O-(1→4)-α-*L*-rhamnopyranosyl-(1→2)-α-*L*-arabinopyranoside] of hederagenin (G_4). The structures of the substances isolated have been established on the basis of chemical transformations and ^{13}C NMR spectroscopy.*

The aim of the present series of investigations is a systematic study of the glycoside compositions of various organs of *Hedera canariensis* Willd. (synonyms *Hedera helix canariensis* DC., *H. algeriensis* Hibberd, *H. maderensis* C. Koch, *H. grandifolia* Hibberd, *H. azorica* Carr., and *H. canariensis* var. *azorica* Bean), fam. Araliaceae. Algerian ivy is distributed in the Azores, the Canary islands, the islands of Madeira, and parts of the West African littoral (Algeria, Morocco) and is widely cultivated as a decorative plant in many countries [1]. However, its glycoside composition has not been studied previously.

In the present paper we describe the isolation and identification of 13 triterpene glycosides from the leaves of Algerian ivy. TLC analysis of an alcoholic extract of the leaves showed the presence of nine groups of glycosides, L-A–L-I in order of increasing polarity. To isolate the glycosides, the dried and comminuted plant raw material was defatted and was then extracted with aqueous isopropanol. The preparative chromatographic separation of the extract into the glycoside fractions L-A–L-I was carried out on silica gel (SiO_2) with gradient elution by water-saturated mixtures of chloroform and ethanol. According to the results of TLC analysis, fractions L-A, L-C, and L-D consisted of individual glycosides, while the other fractions each contained several glycosides, the preparative separation of which was achieved on Silpearl microspherical silica gel with elution by water-saturated mixtures of chloroform and ethanol. The glycosides were additionally purified by the elimination of phenolic impurities on SiO_2 with elution by mixtures of chloroform and ethanol saturated with aqueous ammonia.

The complete acid hydrolysis of glycosides L-A (**1**), L-B_1 (**2**) and L-B_2 (**3**) showed the presence in them of one and the same monosaccharide — arabinose — and, respectively, the aglycons oleanolic acid (**14**), echinocystic acid (**15**), and hederagenin (**16**). The treatment of these glycosides with an ethereal solution of diazomethane converted them into methyl esters, while alkaline hydrolysis caused no changes whatever. Consequently, in (**1**–**3**) the arabinose residue was attached at

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TABLE 1. Chemical Shifts of the ^{13}C Atoms of the Aglycon Moieties of Glycosides L-A (**1**), -B_1 (**2**), -B_2 (**3**), -C (**4**), -D (**5**), -E_1 (**6**), -G_1 (**7**), -G_2 (**8**), -G_3 (**9**), -G_4 (**10**), -H_1 (**11**), -H_2 (**12**), and -I_1 (**13**) and of Oleanolic Acid (**14**), Echinocystic Acid (**15**), and Hederagenin (**16**) (δ, ppm, 0 — TMS; C_5D_5N)

C atom	Compound								
	14	1, 4	8	15	2, 5	11	16	3,6,10	7,9,12,13
1	39.0	38.7	38.8	38.9	38.9	39.0	38.8	38.9	38.9
2	28.1	26.5	26.5	28.0	26.4	26.5	27.7	26.0	26.0
3	78.1	88.7	88.7	78.0	88.9	89.0	73.6	82.0	82.1
4	39.4	39.5	39.5	39.3	39.3	39.4	42.9	43.5	43.5
5	55.9	56.0	55.9	55.8	56.2	56.2	48.8	47.2	47.7
6	18.8	18.5	18.5	18.8	18.6	18.5	18.5	18.3	18.3
7	33.3	33.3	33.1	33.5	33.4	33.4	33.0	33.0	32.9
8	39.8	39.8	39.9	39.8	39.8	40.0	39.8	39.8	40.0
9	48.2	48.0	48.0	47.2	47.2	47.2	48.2	48.2	48.3
10	37.4	37.0	36.9	37.3	37.1	37.0	37.3	36.9	37.0
11	23.8	23.8	23.7	23.7	23.8	23.8	23.7	23.8	23.9
12	122.5	122.5	122.6	122.4	122.6	122.9	122.4	122.8	122.9
13	144.9	144.8	144.1	144.9	144.7	144.6	144.8	144.8	144.2
14	42.2	42.2	42.1	42 0	42.1	42.0	42.2	42.1	42.2
15	28.4	28.3	28.2	36.0	36.1	36.0	28.4	28.3	28.4
16	23.8	23.8	23.5	74.6	74.8	74.6	23.7	23.8	23.5
17	46.7	46.7	47.0	48.8	48.9	49.1	46.6	46.7	47.1
18	42.1	42.0	41.8	41.3	41.3	41.2	42.0	42.0	41.8
19	46.6	46.6	46.3	47.2	47.2	47.0	46.5	46.5	46.3
20	31.0	30.9	30.8	30.9	30.9	30.7	30.9	30.9	30.8
21	34.3	34.3	34.0	36.0	36.1	35.9	34.3	34.3	34.1
22	33.3	33.3	32.7	32.7	32.5	32.1	33.3	33.2	32.6
23	28.8	28.2	28.2	28.7	28.1	28.0	68.3	64.4	64.6
24	16.5	17.0	16.9	16.5	16.9	16.9	13.1	13.7	13.8
25	15.5	15.5	15.5	15.6	15.5	15.7	16.0	16.1	16.3
26	17.4	17.4	17.5	17.4	17.4	17.5	17.3	17.4	17.6
27	26.2	26.3	26.1	27.1	27.2	27.1	26.1	26.2	26.2
28	180.2	180.1	176.5	179.8	180.3	176.2	180.1	180.2	176.6
29	33.3	33.3	33.1	33.3	33.2	33.1	33.3	33.2	33.2
30	23.8	23.8	23.7	24.7	24.6	24.6	23.7	23.8	23.8

Note: Here and in Table 2 the columns covering more than one compound give averaged values differing from those for the individual compounds by not more than $\pm$(0.1-0.2) ppm.

the C-3 atom of the aglycon in each case. This was additionally confirmed by analyzing the chemical shifts of the signals of the ^{13}C atoms of the aglycon moieties of (**1**−**3**) in comparison with the free aglycons (**14**−**16**) (Table 1). This showed a considerable positive α-effect (8.5-11 ppm) on the C-3 atoms of the aglycons and a negative β-effect (−1.6 ppm) on the C-2 atoms. With respect to their chromatographic mobilities in various solvent systems and the magnitudes of their specific rotations, compounds (**1**−**3**) were identical with authentic specimens of the 3-O-α-*L*-arabinosides of oleanolic acid, of echinocystic acid, and of hederagenin. These glycosides have been detected previously in the leaves and fruit of *Hedera helix* L. [2, 3] and in the leaves, buds, and fruit of *Fatsia japonica* (Thunb.) Decne et Planch. [4-6].

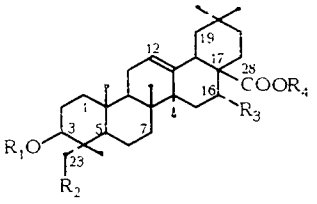
The carbohydrate compositions, types of aglycons and positions of the carbohydrate residues were determined similarly for glycosides L-C (**4**), L-D (**5**), and L-E_1 (**6**), which, from their TLC behavior and ^{13}C NMR spectra, proved to be identical with the 3-O-[O-α-*L*-rhamnopyranosyl-(1→2)-α-*L*-arabinopyranosides of oleanolic and echinocystid acids and of hederagenin, respectively. We have previously found these glycosides in *H. helix* [2] and *H. taurica* [7-9], while glycoside (**6**) has been detected in many other plants of the Aralaceae family [10].

According to the results of complete acid hydrolysis, the carbohydrate components of glycosides L-G_1 (**7**), L-G_2 (**8**), L-G_3 (**9**), and L-G_4 (**10**) consisted of rhamnose, arabinose, and glucose, while the aglycons were oleanolic acid in (**8**) and hederagenin in (**7**), (**9**) and (**10**). It was established by alkaline hydrolysis that (**7**−**9**) were bisdesmosidic glycosides, and the progenins obtained by cleaving the acyl glycosidic bonds at the carboxy groups of the aglycons were identical, respectively, with glycosides (**3**), (**4**), and (**6**) described above. According to TLC and ^{13}C NMR spectra, the glycosides (**7**), (**8**), and (**9**), themselves, were identical with the 3-O-α-*L*-arabinopyranoside 28-O-[O-α-*L*-rhamnopyranosyl-(1→4)-β-gentiobioside] of hederagenin, the 3-O-[O-α-*L*-rhamnopyranosyl-(1→2)-α-*L*-arabinopyranoside] 28-O-[O-α-*L*-rhamnopyranosyl-(1→4)-β-genti-

TABLE 2. Chemical Shifts of the ^{13}C Atoms of the Carbohydrate Moieties of Glycosides L-A (**1**), -B_1 (**2**), -B_2 (**3**), -C (**4**), -D (**5**), -E_1 (**6**), -G_1 (**7**), -G_2 (**8**), -G_3 (**9**), -G_4 (**10**), -H_1 (**11**), -H_2 (**12**), and -I_1 (**13**) (δ, ppm. 0 — TMS; C_5D_5N)

C atom	Compound								
	1, 2	3, 7	4, 5, 8, 11	6, 9, 12	10	13	9	7, 8, 11–13	10
	Ara′	Ara′	Ara′	Ara′	Ara′	Glc′	Glc‴	Glc‴	Glc‴
1	105.3	106.7	104.8	104.3	104.4	104.7	95.7	95.8	106.4
2	72.8	73.1	76.0	75.9	76.1	79.8	73.8	74.0	75.9
3	74.6	74.8	73.8	74.5	74.5	77.7	78.7	78.7	78.6
4	69.4	69.7	68.7	69.4	69.3	72.2	71.3	70.8	71.4
5	66.7	66.8	64.7	65.6	65.7	78.0	78.0	78.1	77.3
6						62.8	69.8	69.3	70.2
			Rha″	Rha″	Rha″	Rha″	Glc⁗	Glc⁗	Glc⁗
1			101.8	101.7	101.4	101.7	105.2	104.9	105.3
2			72.4	72.4	71.9	72.3	75.2	75.4	75.5
3			72.6	72.6	72.6	72.6	78.2	76.5	76.4
4			74.0	74.2	85.0	74.2	71.8	78.4	78.2
5			69.9	69.8	68.2	69.7	78.3	77.2	77.2
6			18.6	18.5	18.7	18.8	62.9	61.4	61.4
								Rha⁗′	Rha⁗′
1								102.8	102.7
2								72.6	72.6
3								72.8	72.8
4								73.9	74.0
5								70.4	70.4
6								18.6	18.6

obioside] of oleanolic acid, and the 3-O-[O-α-*L*-rhamnopyranosyl-(1→2)-α-*L*-arabinopyranoside] 28-O-β-gentiobioside of hederagenin. We have recently found glycosides of analogous structures in *H. helix* [2] and *H. taurica* [7-9], and they have also been detected in many other plants [10].



	R_1	R_2	R_3	R_4
1.	*L*-Ara$_p$ (1→α)	H	H	H
2.	*L*-Ara$_p$ (1→α)	H	OH	H
3.	*L*-Ara$_p$ (1→α)	OH	H	H
4.	*L*-Rha$_p$ (1→2α) *L*-Ara$_p$ (1→α)	H	H	H
5.	*L*-Rha$_p$ (1→2α) *L*-Ara$_p$ (1→α)	H	OH	H
6.	*L*-Rha$_p$ (1→2α) *L*-Ara$_p$ (1→α)	OH	H	H
7.	*L*-Ara$_p$ (1→α)	OH	H	*D*-Glc$_p$ (1→β) 6→β *D*-Glc$_p$ 4→α *L*-Rha$_p$
8.	*L*-Rha$_p$ (1→2α) *L*-Ara$_p$ (1→α)	H	H	*D*-Glc$_p$ (1→β) 6→β *D*-Glc$_p$ 4→α *L*-Rha$_p$
9.	*L*-Rha$_p$ (1→2α) *L*-Ara$_p$ (1→α)	OH	H	*D*-Glc$_p$ (1→β) 6→β *D*-Glc$_p$
10.	*L*-Rha$_p$ (1→2α) *L*-Ara$_p$ (1→α) 4←β *D*-Glc$_p$ 6→β *D*-Glc$_p$ 4→α *L*-Rha$_p$	OH	H	H
11.	*L*-Rha$_p$ (1→2α) *L*-Ara$_p$ (1→α)	H	OH	*D*-Glc$_p$ (1→β) 6→β *D*-Glc$_p$ 4→α *L*-Rha$_p$
12.	*L*-Rha$_p$ (1→2α) *L*-Ara$_p$ (1→α)	OH	H	*D*-Glc$_p$ (1→β) 6→β *D*-Glc$_p$ 4→α *L*-Rha$_p$
13.	*L*-Rha$_p$ (1→2α) *D*-Glc$_p$ (1→β)	OH	H	*D*-Glc$_p$ (1→β) 6→β *D*-Glc$_p$ 4→α *L*-Rha$_p$
14.	H	H	H	H
15.	H	H	OH	H
16.	H	OH	H	H

Glycoside L-G_4 (**10**) did not change under the conditions of alkaline hydrolysis but was methylated by diazomethane, which confirmed its monodesmosidic nature and the presence of the carbohydrate chain at the C-3 atom of the aglycon. According to its TLC behavior and its ^{13}C NMR spectrum, (**10**) was identical with helicoside L-6d from the leaves of *H. helix*

[11], which is hederagenin 3-O-[O-α-*L*-rhamnopyranosyl-(1→4)-O-β-gentiobiosyl-(1→4)-O-α-*L*-rhamnopyranosyl-(1→2)-α-*L*-arabinopyranoside].

According to the results of acid hydrolysis, the carbohydrate compositions of glycosides L-H_1 (**11**) and L-H_2 (**12**) were the same, consisting of rhamnose, arabinose, and glucose, while the aglycons were echinocystic acid and hederagenin, respectively. The progenins obtained from (**11**) and (**12**) by alkaline hydrolysis were identical with glycosides (**5**) and (**6**) described above. From its TLC behavior and ^{13}C NMR spectrum, glycoside (**11**) was identical with echinocystic acid 3-O-[O-α-*L*-rhamnopyranosyl-(1→2)-α-*L*-arabinopyranoside] 28-O-[O-α-*L*-rhamnopyranosyl-(1→4)-β-gentiobioside], which we have found previously in the leaves of *H. helix* and *H. taurica* [12]. Glycoside (**12**) was identical with hederagenin 3-O-[O-α-*L*-rhamnopyranosyl-(1→2)-α-*L*-arabinopyranoside] 28-O-[O-α-*L*-rhamnopyranosyl-(1→4)-β-gentiobioside], which has been found in all the ivy species studied and in a number of other plants of the Aralaceae family [10, 12].

From the results of acid hydrolysis we found rhamnose, glucose, and hederagenin as components of glycoside L-I_1 (**13**). The alkaline hydrolysis of (**13**) gave a progenin identical with glycoside St-D_2 from *H. taurica* stems, with the structure of hederagenin 3-O-[O-α-*L*-rhamnopyranosyl-(1→2)-β-*D*-glucopyranoside], while, according to its TLC behavior and ^{13}C NMR spectrum, glycoside (**13**) itself was identical with tauroside St-I_2 from *H. taurica* stems [13], which is hederagenin 3-O-[O-α-*L*-rhamnopyranosyl-(1→2)-β-*D*-glucopyranoside] 28-O-[O-α-*L*-rhamnopyranosyl-(1→4)-β-gentiobioside].

It has not been possible to identify glycosides L-E_2, L-F, L-H_3, L-I_2, and L-I_3 with known glycosides from *H. helix* and *H. taurica*, and the determination of their structures is continuing.

EXPERIMENTAL

PMR spectra were obtained on a Bruker WM-250 instrument (62.9 MHz for ^{13}C atoms) in deuteropyridine. Specific rotations were measured on a SU-4 saccharimeter at 589 nm.

TLC monitoring was conducted on Silufol plates in the following solvent systems: chloroform–methanol–water (100:40:7) and (100:30:5), and chloroform–methanol–25% ammonia (100:50:15), (100:40:10), and (100:30:6). The glycosides and aglycons were detected with a 10% alcoholic solution of tungstophosphoric acid, and sugars with acid aniline phthalate followed by the heating of the chromatograms. Preparative separation was conducted on silica gels L (40-100 mμ) and Silpearl (Czechoslovakia).

Complete acid hydrolysis was achieved with a 2 N CF_3COOH solution in aqueous dioxane (1:1) at 100°C for 2 h. Alkaline hydrolysis was conducted with 10% KOH in aqueous methanol (1:1) at 100°C for 2 h, followed by treatment with 1 N aqueous H_2SO_4 to give a weak acid reaction and extraction of the progenins with butanol.

Leaves of Algerian ivy *Hedera canariensis* Willd. cv. *Variegata hort.*, obtained from the collection of living plants in the Botanical Garden of the Botanical Institute, Russian Academy of Sciences, in an amount of 32 g dry weight were comminuted and defatted with chloroform–benzene (7:3) (3 × 300 ml); the glycosides were extracted with 90% aqueous isopropanol (5 × 300 ml), and evaporation of the extract gave 8.0 g of dry residue. The total extractive substances so obtained were separated on 1 kg of SiO_2 with elution by water-saturated chloroform–ethanol (10:1→1:1). This yielded the glycoside fractions L-A (50 mg), L-B (50 mg), L-C (70 mg), L-D (200 mg), L-E (2.0 g), L-F (150 mg), L-G (400 mg), L-H (2.5 g) and L-I (1.5 g).

According to the results of TLC analysis, fractions L-A, L-C, and L-D were individual glycosides, while the other fractions were mixtures of glycosides having close chromatographic mobilities. Fractions L-B and L-E were separated into the individual glycosides L-B_1, L-B_2, L-E_1, and L-E_2 by rechromatography on Silpearl with elution by water-saturated chloroform–ethanol (10:1→2:1), and fractions L-G, L-H, and L-I into the individual glycosides L-G_1, L-G_2, L-G_3, L-G_4, L-H_1, L-H_2, L-H_3, L-I_1, L-I_2, and L-I_3 by elution with water-saturated chloroform–ethanol (2:1→1:1).

Additional purification of the glycosides by the elimination of phenolic impurities was achieved by chromatography on SiO_2 with elution by chloroform–ethanol (10:1→1:1) saturated with 10% NH_4OH. As a result we obtained the glycosides L-A_1(10 mg), L-B_1 (20 mg), L-B_2 (30 mg), L-C (35 mg), L-D (75 mg), L-E_1 (700 mg), L-E_2 (50 mg), L-F (55 mg), L-G_1 (35 mg), L-G_2 (60 mg), L-G_3 (30 mg), L-G_4 (20 mg), L-H_1 (100 mg), L-H_2 (1.5 g), L-H_3 (70 mg), L-I_1 (10 mg), L-I_2 (20 mg), L-I_3 (40 mg).

Glycoside L-A (1), $[\alpha]_D$+50° (*c* 0.3; CH_3OH); lit. $[\alpha]_D$+53.1° (CH_3OH) [5]. In an acid hydrolysate of (**1**) we identified arabinose and oleanolic acid (**14**). According to TLC and the ^{13}C NMR spectrum, (**1**) was identical with an authentic specimen of oleanolic acid 3-O-α-*L*-arabinopyranoside [2]. The identification of compounds (**2**–**13**) was achieved similarly.

Glycoside L-B_1 (2), $[\alpha]_D$+38° (*c* 0.5; CH_3OH); lit. $[\alpha]_D$+42.1° (CH_3OH) [5]. An acid hydrolysate of (**2**) contained arabinose and echinocystic acid (**15**). Glycoside (**2**) was identical with echinocystic acid 3-O-α-*L*-arabinopyranoside [2].

Glycoside L-B_2, (3), $[\alpha]_D$+75° (*c* 1.0; C_5D_5N); lit. $[\alpha]_D$+82.1° (C_5D_5N) [6]. An acid hydrolysate of (**3**) contained arabinose and hederagenin (**16**). Glycoside (**3**) was identical with hederagenin 3-O-α-*L*-arabinopyranoside [2].

Glycoside L-C (4), $[\alpha]_D$+11° (*c* 0.5; CH_3OH); lit. $[\alpha]_D$+10.9° (CH_3OH) [15]. An acid hydrolysate of (**4**) contained arabinose, rhamnose, and (**14**). Glycoside (**4**) was identical with oleanolic acid 3-O-[O-α-*L*-rhamnopyranosyl-(1→2)-α-*L*-arabinopyranoside] [2].

Glycoside L-D (5), $[\alpha]_D$−25° (*c* 1.2; C_5D_5N); lit. $[\alpha]_D$−29.9° (C_5D_5N) [9]. An acid hydrolysate of (**5**) contained arabinose, rhamnose, and (**15**). Glycoside (**5**) was identical with echinocystic acid 3-O-[O-α-*L*-rhamnopyranosyl-(1→2)-α-*L*-arabinopyranoside] [2].

Glycoside L-E_1 (6), $[\alpha]_D$+9° (*c* 1.0; C_2H_5OH); lit. $[\alpha]_D$+7° (C_2H_5OH) [7]. An acid hydrolysate of (**6**) contained rhamnose, arabinose, and (**16**). Glycoside (**6**) was identical with hederagenin 3-O-[O-α-*L*-rhamnopyranosyl-(1→2)-α-*L*-arabinopyranoside] [2].

Glycoside L-G_1 (7), $[\alpha]_D$+4° (*c* 0.9; C_5D_5N); lit. $[\alpha]_D$+3.6° (C_5D_5N) [12]. An acid hydrolysate of (**7**) contained rhamnose, arabinose, glucose, and (**16**). A progenin of (**7**) obtained by alkaline hydrolysis was identified by TLC as (**3**). Glycoside (**7**) was identical with hederagenin 3-O-α-*L*-rhamnopyranoside 28-O-[O-α-*L*-rhamnopyranosyl-(1→4)-β-gentiobioside] [2].

Glycoside L-G_2 (8), $[\alpha]_D$−30° (*c* 2.0; CH_3OH); lit. $[\alpha]_D$−28.8° (CH_3OH) [12]. An acid hydrolysate of (**8**) contained rhamnose, arabinose, glucose, and (**14**). The progenin of (**8**) was identical with (**4**). Glycoside (**8**) was identified as oleanolic acid 3-O-[O-α-*L*-rhamnopyranosyl-(1→2)-α-*L*-arabinopyranoside] 28-O-[O-α-*L*-rhamnopyranosyl-(1→4)-β-gentiobioside] [2].

Glycoside L-G_3 (9), $[\alpha]_D$−10° (*c* 0.5; C_5D_5N); lit. $[\alpha]_D$−8.2° (C_5D_5N) [12]. An acid hydrolysate of (**9**) contained rhamnose, arabinose, glucose, and (**16**). According to TLC a progenin from (**9**) was identical with (**6**). Glycoside (**9**) was identified as hederagenin 3-O-[O-α-*L*-rhamnopyranosyl-(1→2)-α-*L*-arabinopyranoside] 28-O-β-gentiobioside [2].

Glycoside L-G_4 (10), $[\alpha]_D$ 0° (*c* 0.2; C_5D_5N). An acid hydrolysate of (**10**) contained rhamnose, arabinose, glucose, and (**16**). Glycoside (**10**) was identified as hederagenin 3-O-[O-α-*L*-rhamnopyranosyl-(1→4)-O-β-gentiobiosyl-(1→4)-O-α-*L*-rhamnopyranosyl-(1→2)-α-*L*-arabinopyranoside [11].

Glycoside L-H_1 (11), $[\alpha]_D$−35° (*c* 1.0; C_5D_5N); lit $[\alpha]_D$−34.9° (C_5D_5N) [12]. An acid hydrolysate of (**11**) contained rhamnose, arabinose, glucose, and (**15**). According to TLC a progenin of (**11**) was identical with (**5**). Glycoside (**11**) was identified as echinocystic acid 3-O-[O-α-*L*-rhamnopyranosyl-(1→2)-α-*L*-arabinopyranoside] 28-O-[O-α-*L*-rhamnopyranosyl-(1→4)-β-gentiobioside] [2].

Glycoside L-H_2 (12), $[\alpha]_D$−12° (*c* 1.0; C_5D_5N); lit. $[\alpha]_D$−14.9° (C_5D_5N) [12]. An acid hydrolysate of (**12**) contained rhamnose, arabinose, glucose, and (**16**). According to TLC a progenin from (**16**) was identical with (**6**). Glycoside (**12**) was identified as hederagenin 3-O-[O-α-*L*-rhamnopyranosyl-(1→2)-α-*L*-arabinopyranoside] 28-O-[O-α-*L*-rhamnopyranosyl-(1→4)-β-gentiobioside] [2].

Glycoside L-I_1 (13), $[\alpha]_D$−11° (*c* 0.5; C_5D_5N); lit $[\alpha]_D$−10° (C_5D_5N) [13]. An acid hydrolysate of (**13**) contained rhamnose, glucose, and (**16**). According to TLC a progenin from (**13**) was identical with hederagenin 3-O-[O-α-*L*-rhamnopyranosyl-(1→2)-α-*L*-glucopyranoside]. Glycoside (**13**) was identified as hederagenin 3-O-[O-α-*L*-rhamnopyranosyl-(1→2)-α-*L*-glucopyranoside] 28-O-[O-α-*L*-rhamnopyranosyl-(1→4)-β-gentiobioside] [13].

The ^{13}C NMR spectra of (**1**−**16**) are given in Tables 1 and 2.

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