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TRITERPENE GLYCOSIDES OF *Scheffleropsis angkae*. I. STRUCTURE OF GLYCOSIDES L-B_1, L-B_2, L-H_1, AND L-H_2

A. S. Stolyarenko,[1] V. I. Grishkovets,[1] N. N. Arnautov,[2] S. V. Iksanova,[3] and V. Ya. Chirva[1]

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The structures of four triterpene glycosides from the leaves of Scheffleropsis angkae *(Araliaceae) are found by chemical methods and NMR spectroscopy to be the 3-O-α-L-arabinopyranosides of oleanic and ursolic acids and their 28-O-α-L-rhamnopyranosyl-(1→4)-O-β-gentiobiosyl esters, which are designated L-B_1, L-B_2, L-H_1, and L-H_2, respectively. The glycoside L-H_2 is new.*

Key words: *Scheffleropsis angkae*, triterpene glycosides, ursolic acid 3-O-α-L-arabinopyranosyl-28-O-α-L-rhamnopyranosyl-(1→4)-O-β-gentiobioside.

Scheffleropsis angkae (Craib.) Grushv. et N. Skvorts. is a large evergreen plant that grows in the tropical regions of southeastern Asia. It is a representative of the oligotypic genus *Scheffleropsis* Ridl. (Araliaceae), which is related to the genus *Schefflera* Forst. and often included in it [1]. The glycoside composition of this plant has not been previously studied.

We found 11 groups of glycosides in the TLC of an alcohol extract of the leaves of shefflera. We designated them L-A through L-K in the order of increasing polarity. Of these, L-F, L-G, L-H, and L-K predominated. The chromatographic mobility of the glycosides did not change after treatment of the alcohol extract of the leaves with aqueous ammonia. This suggested that partially acetylated glycosides, which are often observed in plants of the Araliaceae family, were absent [2].

The triterpene glycosides were isolated by defatting the ground starting material with a C_6H_6—$CHCl_3$ mixture and extracting exhaustively with aqueous isopropanol. The alcohol extract was evaporated. The solid was dissolved in butanol and washed with aqueous ammonia to remove substantial quantities of phenolic glycosides. The purified glycosides were separated by chromatography on silica gel with elution by $CHCl_3$—$(CH_3)_2CHOH$—H_2O to give glycoside fractions from L-A to L-K. Fractions L-B and L-H according to TLC analysis were pure glycosides. The determination of their structures is described in the present article.

The chromatographic mobilities of L-B (**1**) and authentic oleanolic acid 3-O-α-L-arabinopyranoside coincide in various solvent systems. However, the colors of the spots are different if phosphotungstic acid or sulfuric acid mixed with an excess of *p*-hydroxybenzaldehyde is used. This suggests that the isolated glycoside is a glycoside of isomeric ursolic acid or a mixture of arabinopyranosides of these two aglycones, which was recently found by us in the glycosides of *Tupidanthus calyptratus* [3] and has been found in a number of other plants of the Araliaceae family: *Aralia decaisneana* [4] and *Schefflera octophylla* [5].

The ^{13}C NMR spectrum of **1**, which we have previously reported [3], was studied in detail in order to resolve this issue. Signals of all C atoms of the unsubstituted residue of α-L-arabinopyranose and the 3-O-substituted residues of oleanolic and ursolic acids were identified in the spectrum. The ratio of glycosides of these aglycones, L-B_1 (**1a**) and L-B_2 (**1b**), which was estimated from the integrated intensities of the well resolved peaks for C-8, C-25, C-28, etc., is about 3:2. The facts that base hydrolysis does not change **1** and an ether solution of CH_2N_2 methylates **1** provide additional confirmation that the sugar is localized on C-3.

Thus, L-B is a chromatographically inseparable mixture of 3-O-α-L-arabinopyranosides of oleanolic and ursolic acids. The arabinoside of ursolic acid was isolated previously from *Sanquisorba officinalis* [6]; the arabinoside of oleanolic acid, from many representatives of Araliaceae and other plants of other families [2].

1) V. I. Vernadskii Tavricheskii National University, 95007, Simferopol', ul. Yaltinskaya, 4; 2) Botanical Garden of the Botanical Institute, Russian Academy of Sciences, 197376, St. Petersburg, ul. prof. Popova, 2; 3) Institute of Organic Chemistry, Ukrainian National Academy of Sciences, 253660, Kiev, ul. Murmanskaya, 5. Translated from Khimiya Prirodnykh Soedinenii, No. 2, pp. 136-138, March-April, 2000. Original article submitted April 3, 2000.

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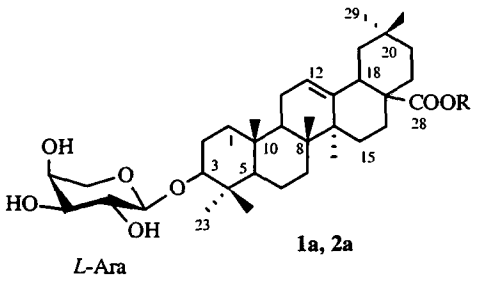
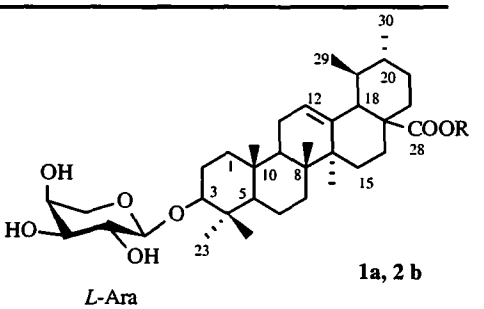
TABLE 1. ^{13}C Chemical Shifts in Glycosides B_1 (**1a**), B_2 (**1b**), H_1 (**2a**), and H_2 (**2b**) (δ, ppm, 0 = TMS, C_5D_5N)

C atom	Compound				C atom	Compound			
	1a	1b	2a	2b		1a	1b	2a	2b
					Ara ′				
1	38.9	39.1	38.9	39.1	1	107.1	107.1	107.0	107.0
2	26.6	26.6	26.5	26.5	2	72.8	72.8	72.7	72.7
3	88.8	88.8	88.8	88.8	3	74.5	74.5	74.4	74.4
4	39.6	39.6	39.5	39.5	4	69.3	69.3	69.2	69.2
5	56.0	56.0	55.9	55.9	5	66.4	66.4	66.3	66.3
6	18.6	18.6	18.5	18.5	Glc ″				
7	33.3	33.6	33.1	33.5	1			95.5	95.5
8	39.9	40.1	39.9	40.1	2			73.8	73.8
9	48.1	48.1	48.1	48.0	3			78.6	78.6
10	37.2	37.0	37.0	36.9	4			70.8	70.9
11	23.8	23.7	23.7	23.7	5			77.8	77.7
12	122.6	125.7	122.6	126.1	6			69.2	69.4
13	144.8	139.3	144.1	138.4	Glc ‴				
14	42.2	42.6	42.1	42.5	1			104.5	104.5
15	28.4	28.7	28.3	28.7	2			75.1	75.1
16	23.8	25.0	23.4	24.6	3			76.4	76.4
17	46.7	48.0	47.0	48.4	4			78.5	78.5
18	42.0	53.6	41.7	53.2	5			76.9	76.9
19	46.6	39.4	46.3	39.1	6			61.4	61.4
20	31.0	39.4	30.7	39.3	Rha ⁗				
21	34.3	31.2	34.0	30.8	1			102.6	102.6
22	33.3	37.5	32.5	36.7	2			72.3	72.3
23	28.3	28.3	28.3	28.3	3			72.6	72.6
24	16.9	16.9	16.9	16.9	4			73.8	73.8
25	15.7	15.7	15.6	15.7	5			70.2	70.2
26	17.4	17.4	17.5	17.6	6			18.3	18.3
27	26.2	24.0	26.0	23.8					
28	180.2	179.9	176.5	176.3					
29	33.3	17.5	33.1	17.3					
30	23.9	21.4	23.7	21.2					



1a, 2a

L-Ara



1a, 2 b

L-Ara

1a, 1b: R=H

2a, 2b: R=←$^{\beta}$*D*-Glc*p*←$^{6\beta}$*D*-Glc*p*←$^{4\alpha}$*L*-Rha*p*

According to total acid hydrolysis, L-H (**2**) contains arabinose, rhamnose, and glucose. CH_2N_2 does not methylate L-H. Base hydrolysis gives the progenin, which was identified by chromatographic mobility and the color of the spots using various reagents as glycoside L-B, which was described above. This is consistent with **2** being a bisdesmoside and partially determines its structure.

The TLC chromatographic mobility in various solvent systems of L-H is identical to that of oleanolic acid 3-O-α-L-

arabinopyranosyl-28-O-α-L-rhamnopyranosyl-(1→4)-O-β-gentiobioside [7]. However, like for L-B, the color of the spots differs somewhat.

The ^{13}C NMR spectrum of **2** confirmed that it is also a mixture of glycosides of isomeric aglycones (oleanolic and ursolic acids). The signals of the glycoside atoms were completely assigned as before [3] and are listed in Table 1. The ratio of isomeric glycosides (**2a** and **2b**), like for **1**, was approximately 3:2. Signals not belonging to aglycone atoms in the ^{13}C NMR spectrum of **2** were unambiguously assigned to α-L-arabinopyranose and the trisaccharide residue α-L-rhamnopyranosyl-(1→4)-O-β-gentiobiose, which is usually present in aralia glycosides and is bonded through an acylglycoside bond to the aglycone according to the literature [8].

Thus, glycoside L-H is a chromatographically inseparable mixture of L-H_1 and L-H_2, 3-O-α-L-arabinopyranosyl-28-O-α-L-rhamnopyranosyl-(1→4)-O-β-gentiobiosides of oleanolic and ursolic acids.

Glycoside L-H_1 has already been isolated from plants of the Araliaceae family [2] whereas glycoside L-H_2 is a new triterpene glycoside.

EXPERIMENTAL

NMR Spectra were obtained on a Varian VXR-300 (300 MHz for ^1H and 75 MHz for ^{13}C) instrument in C_5D_5N.

TLC Monitoring was performed on Silufol, Polygram, or Merck plates using $CHCl_3$—CH_3OH—H_2O (100:40:7) and (100:30:5) and $CHCl_3$—CH_3OH—NH_4OH (25%) (100:40:10), (100:30:6), and (100:20:3). Glycosides and aglycones were detected by phosphotungstic acid (10%) or *p*-hydroxybenzaldehyde (10%) and H_2SO_4 (2%) in alcohol; sugar, by acidic aniline phthalate. Chromatograms were heated to 100-150°C after treatment with the detecting reagent. Preparative separation and purification were carried out on silica gel L (40-100 μm).

Total acid hydrolysis for determining sugars was carried out using 2 N CF_3COOH in water—dioxane (1:1) at 100°C for 2 h. Total acid hydrolysis for determining aglycones was performed in 1 N H_2SO_4 in water—methanol (1:1) under the same conditions with subsequent extraction of the aglycone with $CHCl_3$.

Base hydrolysis was carried out with 10% KOH in water—methanol (1:1) for 2 h with subsequent neutralization by 1 N H_2SO_4 until the solution was weakly acidic and extraction of the progenins by butanol.

Methylation of free carboxyls in the glycosides was effected by adding an excess of an ether solution of CH_2N_2 to a solution of the glycoside in methanol.

Isolation and Purification. Leaves of *Scheffleropsis angkae* that were obtained from a collection of live plants at the Botanical Garden of the Botanical Institute of the Russian Academy of Sciences (44 g dry mass) were ground and defatted by C_6H_6—$CHCl_3$ (1:1, 4×300 ml). Glycosides were extracted by 80% isopropanol (3×700 ml). Evaporation of the solution under vacuum gave a dry solid (10 g) that was dissolved in water-saturated butanol (300 ml) and washed with aqueous NH_3 (2.5%, 3×100 ml). The butanol layer was evaporated to give the dry glycosides (5.9 g). Chromatographic separation on silica gel using gradient elution by water-saturated $CHCl_3$—isopropanol (100:23 → 100:65) gave 11 fractions: L-A (0.31 g), L-B (0.25 g), L-C (1.14 g), L-D (0.09 g), L-E (0.15 g), L-F (1.13 g), L-G (1.55 g), L-H (0.97 g), L-I (0.35 g), L-J (0.12 g), L-K (0.80 g).

Fraction B (250 mg) was chromatographed on silica gel using $CHCl_3$—$(CH_3)_2CHOH$—NH_4OH (25%) (100:20:3) to purify it of a significant quantity of lipid-like impurities. This yielded pure **1** (60 mg). Analogous rechromatography of L-H (970 mg) with elution by $CHCl_3$—$(CH_3)_2CHOH$—NH_4OH (25%) (10:4:1) gave pure **2** (680 mg).

Glycoside L-B (**1**, chromatographically inseparable **1a** and **1b**). The total acid hydrolysate of **1** contained arabinose and oleanolic and ursolic acids according to TLC.

PMR of **1** (300 MHz, C_5D_5N, ppm, J, Hz): 5.35 (pt, $W_{1/2}$ = 7, H-12), 4.65 (d, $J_{1,2}$ = 7, H-1′), 4.30 (t, $J_{2,3}$ = 7, H-2′), 4.21 (m, H-4′), 4.19 (d, H-5e′), 4.05 (dd, $J_{3,4}$ = 1.5, H-3′), 3.70 (dd, $J_{5a,4}$ = 2.5, $J_{5a,5e}$ = 13.5, H-5a′).

Content: 0.15% by mass.

Glycoside L-H (**2**, chromatographically inseparable **2a** and **2b**). The total acid hydrolysate of **2** contained arabinose, glucose, rhamnose, and oleanolic and ursolic acids.

PMR of **2** (300 MHz, C_5D_5N, ppm, J, Hz): 6.07 (d, $J_{1,2}$ = 8, H-1″ in **2a**), 6.02 (d, $J_{1,2}$ = 8, H-1″ in **2b**), 5.67 (s, H-1‴), 5.29 (pt, $W_{1/2}$ = 7, H-12), 1.54 (d, $J_{5,6}$ = 5.5, H-6‴).

Content: 1.5% by mass.

For the ^{13}C NMR spectra of **1a-2b**, see Table 1.

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