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# SESQUITERPENE LACTONES AND NEW DITERPENOID ALKALOIDS FROM *Artemisia korshinskyi*

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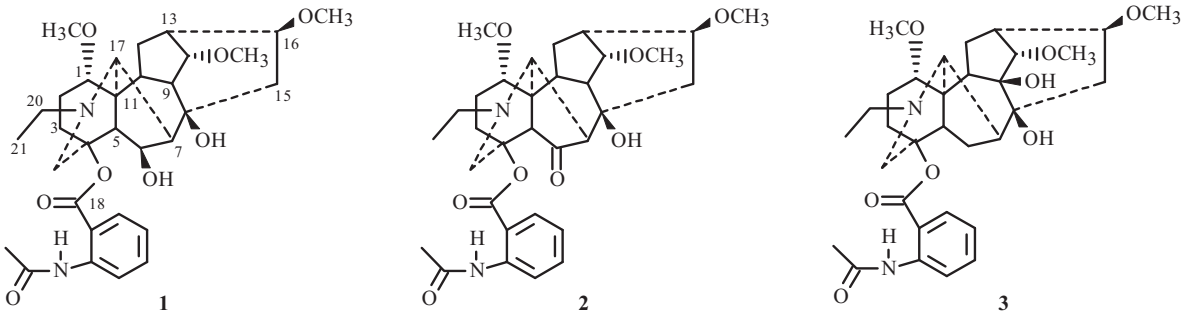
*New diterpenoid alkaloids that were called artekorine (**1**) and 6-ketoartekorine (**2**) and had the structures 1α,14α,16β-trimethoxy-4β-N-acetylanthroyloxy-6β,8β-dihydroxy-N-ethylaconitane (**1**) and 1α,14α,16β-trimethoxy-4β-N-acetylanthroyloxy-6-keto-8β-hydroxy-N-ethylaconitane (**2**) in addition to sesquiterpene lactones were isolated for the first time from a plant of the genus* Artemisia *L. (Asteraceae) during an investigation of the aerial part of* Artemisia korshinskyi *Krash. ex Poljakov. The structures of the diterpenoid alkaloids were established using spectral data and x-ray crystal structure analyses.*

**Keywords:** *Artemisia korshinskyi*, sesquiterpene lactones, diterpenoid alkaloids, artekorine, 6-ketoartekorine, XSA.

The plant *Artemisia korshinskyi* Krash. ex Poljakov (Asteraceae) is indigenous to Central Asia, grows as a small shrub of height 30–50 cm, and belongs to the subgenus and section Seriphidium (Bess.) Rouy [1]. Its habitat includes high-mountain deserts and icy patches.

We reported earlier on the isolation from the aerial part of this species of two eudesmanolides [2-acetoxy-3(4)-en-6$\beta$,11$\beta$(H)-eudesm-6,12-olide and 3-acetoxy-4(15)-en-5-hydroxy-6$\beta$,11$\beta$(H)-eudesm-6,12-olide] [2]. In continuation of research on the composition of secondary metabolites from the aerial part of *A. korshinskyi*, column chromatography of the $CHCl_3$ extract isolated known sesquiterpene lactones with the germacrane-type skeleton (herbolides A and B) in addition to previously unknown diterpene alkaloids that we called artekorine (**1**) and 6-ketoartekorine (**2**).




**1** **2** **3**

The isolated herbolides A and B were identified based on spectral data and were confirmed by x-ray crystal structure analyses (XSA) compared with data deposited in the CCDC database.

Artekorine (**1**) was a crystalline base, $C_{32}H_{44}N_2O_8$, mp 228–229°C (hexane:EtOAc). Its IR spectrum had absorption bands for stretching vibrations of OH (3513, 3447 $cm^{-1}$), amide NH (3293), ester (1703), amide carbonyl (1680), aromatic ring (1602, 1587, 1524), and ether (1141, 1099).

The PMR spectrum of **1** (Table 1) contained resonances for protons of *N*-ethyl, *N*-acetoxy, and three methoxyls. Weak-field resonances included four aromatic protons, the chemical shifts and splitting of which corresponded with acetylanthranilic acid. The NH proton of acetylanthranilic acid appeared as a broad 1H resonance at 10.96 ppm.

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TABLE 1. PMR Spectra of Diterpenoid Alkaloids **1**–**3** (400 MHz, $CDCl_3$, 0 = HMDSO, δ, ppm, J/Hz)

| Protons | **1** | **2** | **3** |
|---|---|---|---|
| N-$CH_2$-$C\underline{H}_3$ | 1.04 (3H, t, J = 7.06) | 1.09 (3H, t, J = 7.14) | 1.08 (3H, t, J = 7.14) |
| NH-CO-$C\underline{H}_3$ | 2.17 (3H, s) | 2.16 (3H, s) | 2.17 (3H, s) |
| 17-H | 3.00 (1H, d, J = 1.88) | 2.64 (1H, br.s) | 2.94 (1H, br.s) |
| 1-$OCH_3$ | 3.23 (3H, s) | 3.28 (3H, s) | 3.24 (3H, s) |
| 14-$OCH_3$ | 3.27 (3H, s) | 3.28 (3H, s) | 3.25 (3H, s) |
| 16-$OCH_3$ | 3.35 (3H, s) | 3.31 (3H, s) | 3.35 (3H, s) |
| 14$\beta$-H | 3.66 (1H, t, J = 4.61) | 3.56 (1H, t, J = 4.60) | 3.38 (1H, dd, J = 4.86; 1.0) |
| 6$\alpha$-H | 4.53 (1H, d, J = 7.0) | – | – |
| Ar-H-3′ | 8.00 (1H, dd, J = 1.72; 8.06) | 8.03 (1H, dd, J = 1.67; 8.08) | 7.88 (1H, dd, J = 1.58; 8.15) |
| 4′ | 7.44 (1H, ddd, J = 1.73; 7.35; 8.79) | 7.43 (1H, ddd, J = 1.67; 7.10; 7.82) | 7.44 (1H, ddd, J = 1.71; 7.28; 7.52) |
| 5′ | 7.00 (1H, ddd, J = 1.29; 7.34; 8.35) | 7.03 (1H, ddd, J = 1.25; 7.38; 8.50) | 6.97 (1H, ddd, J = 1.14; 7.28; 8.00) |
| 6′ | 8.60 (1H, dd, J = 1.51; 8.85) | 8.55 (1H, dd, J = 1.25; 8.64) | 8.60 (1H, dd, J = 1.15; 8.42) |
| Ar-NH | 10.96 (1H, br.s) | 10.71 (1H, br.s) | 11.01 (1H, br.s) |

Spectral data indicated that **1** was a diterpenoid alkaloid with the lycoctonine skeleton and contained acetylanthranilic acid. Its spectra were similar to those of lappaconitine (**3**) (Table 1).

The identical empirical formulas and functional groups of **1** and **3** and the similarity of their spectral data indicated that they were structural isomers that differed in the location of the substituents. The PMR spectrum of **1** differed from that of **3** (Table 1) by the fact that the C14-$\beta$-proton resonance appeared as a triplet with splitting constant 4.61 Hz. This indicated that **1** did not have substituents in the C9 and C13 positions. Furthermore, a 1H doublet (J = 7 Hz) from the C6 $\alpha$-proton geminal to a hydroxy group was found at 4.53 ppm. This was consistent with a C6 $\beta$-hydroxyl in **1**.

All this suggested that **1** was a structural isomer of **3** with respect to the location of the hydroxyl on the lycoctonine skeleton. This was reflected in the reported structures of **1** and **3**.

6-Ketoartekorine (**2**) was isolated during rechromatography of mother liquor of **1**. It was a crystalline base of formula $C_{32}H_{42}N_2O_8$, mp 212–213°C (hexane). Its IR spectrum had absorption bands for OH (3507, 3316 $cm^{-1}$), amide NH (2923), carbonyl in a five-membered ring (1743), ester (1701), and amide (1684) carbonyls, aromatic ring (1589, 1526, 1448), and ether (1266, 1088).

The PMR spectrum of **2** exhibited resonances for *N*-ethyl, *N*-acetoxy, three methoxyls, and four aromatic protons of acetylanthranilic acid. The NH resonance of acetylanthranilic acid appeared at 10.71 ppm as a broad 1H singlet.

A comparison of the IR and PMR spectra of diterpenoid alkaloids **1** and **2** (Table 1) showed that they were similar.

The presence in the IR spectrum of **2** of an absorption band for carbonyl in a five-membered ring (1743) and the absence in the PMR spectrum of a resonance for the C6$\alpha$ proton geminal to a secondary hydroxyl signified that the isolated diterpenoid alkaloid **2** was 6-ketoartekorine.

X-ray crystal structure analyses (XSA) of **1** and **2** were performed in order to establish unambiguously their structures. It was noticed in the preliminary stages of the XSA that the crystal structures of these alkaloids were similar because their unit-cell constants had similar values in the range 0.07–0.23 Å and they crystallized in the same trigonal space group $P3_12_1$, which is atypical of natural compounds (see Experimental).

Figure 1 shows the x-ray molecular structures of **1** and **2** in the same projection and compared with that of **3** [3]. The molecule of **1** had the lycoctonine skeleton with functional groups located as follows: OMe groups on C1 and C14 with the $\alpha$-orientation; OH groups on C6 and C8 and an OMe group on C16 with the $\beta$-orientation. The acetylanthranilic acid was bonded to C4 and had the $\beta$-orientation. Therefore, **1** was an isomer of lappaconitine that differed from it by the location of one hydroxyl.

The lycoctonine skeleton of **1** was a hexacyclic framework of four six-membered (A, C, E, F) and two five-membered (B, D) rings. Six-membered rings A and C in **1** had ideal chair conformations (deviation of atoms from the plane of four atoms was less than ±0.02 Å). Ring E had a boat conformation (±0.03 ) but was more planar on the side of C16 (deviations of C14 and C16 from the plane of four atoms were 0.70 and 0.23 Å). Heterocycle F was a twist-chair. Five-membered rings B and D had envelope conformations. The O–C=O (±0.03 Å) and $H\underline{N}COCH_3$ (±0.01 Å) planes were slightly rotated (by 6.8° and 11.2°, respectively) relative to the plane of the aromatic ring (±0.02 Å). The lengths of single $Csp^3$–$Csp^3$ bonds varied over the broad range 1.513(3)–1.575(3) Å although the C–O bonds were stable in the range 1.413–1.437 Å [except for C8–O6, 1.452(3) Å]. In general the bond lengths and angles agreed well with those in the other related alkaloid **3** [3].

TABLE 2. Geometric Parameters of Intramolecular H-bonds in **1** (d, distance; D, donor; A, acceptor)

| D-H…A | d (D...A), Å | d (D-H), Å | d (H...A), Å | <(DHA), deg. |
|---|---|---|---|---|
| O5-H...O6 | 2.708 (2) | 1.10 (3) | 1.69 (3) | 153 (2) |
| O6-H...O7 | 2.813 (2) | 0.85 (3) | 2.15 (3) | 135 (2) |
| N2-H...O2 | 2.686 (2) | 0.80 (2) | 2.00 (3) | 144 (3) |

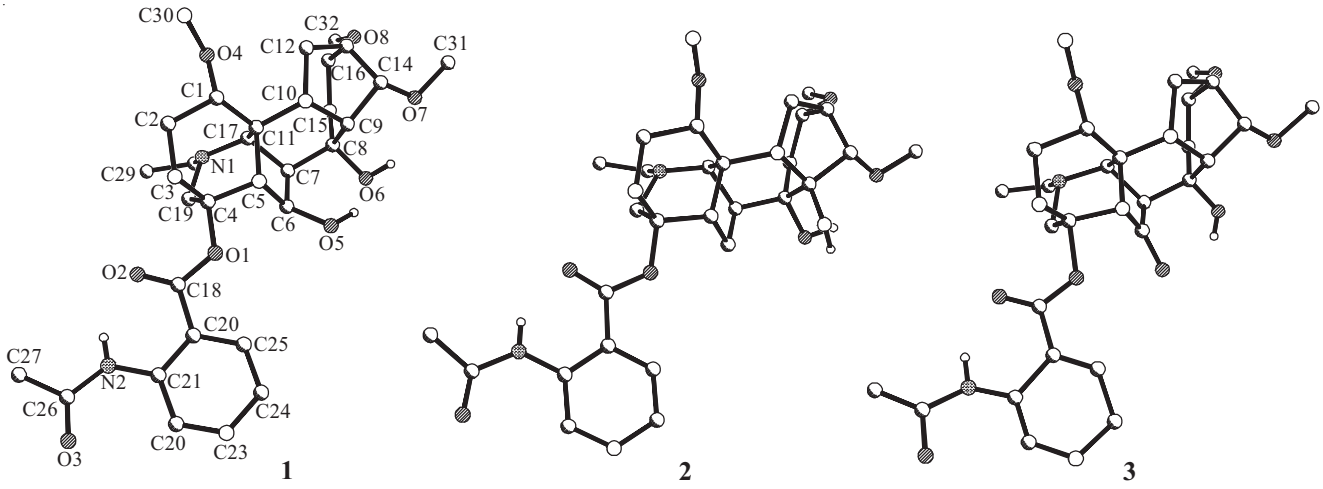


Fig. 1. Molecular structures of diterpenoid alkaloids **1**-**3** (only H atoms forming intramolecular H-bonds are shown).

The mutual location of functional groups in the carbon skeleton and the $-NHCOCH_3$ group with the active H on the benzene ring enabled intramolecular H-bonds of the N–H…O and O–H…O types to form. Among these, the N2–H…O2 H-bond forming a six-membered pseudoring was especially notable. Other intramolecular H-bonds were formed by O5–H…O6–H…O7–Me. Table 2 presents characteristic parameters of these bonds, which were analogous to intramolecular H-bonds involving hydroxyls, methoxyls, and NH groups that were observed in **3** (Fig. 1) [3].

An XSA was used to establish unambiguously the structure of **2**. However, the amount of isolated compound did not enable us to grow and collect single crystals of suitable quality for the x-ray experiment. As a result, the statistical dataset of reflections obtained from a very thin crystal was weak (see Experimental). The structure of **2** could not be solved using a dataset of reflections by direct methods in automatic and manual (with variation of values and initial reflections) mode. Therefore, we utilized the isostructural nature of the crystals of these alkaloids. Circumventing direct methods, the coordinates of non-hydrogen atoms for the structure of **1** were refined by a least-squares method (LSM) using the dataset of reflections for the crystal of **2**. It was noticed during the LSM refinement process that the *a priori* fixed lycoctonine skeleton (molecular framework of **1**) was in general retained in the crystal structure of **2**. New distinct peaks did not appear in a difference electron-density synthesis. The molecular fragment consisting of four atoms (C5, C6, C7, and O5) began to acquire a planar configuration (Fig. 1) during the refinement. Also, the C6–O5 bond distance [1.24(2) Å] became closer to that of a double bond. Thus, the final structure of **2** that was refined by the LSM confirmed that **2** had the artekorine skeleton with a ketone in the 6-position. This was confirmed by IR and PMR spectral data.

The high value of the agreement factor and the weak statistics did not enable the molecular geometry of **2** to be analyzed in more detail. However, the conformations of the rings in the lycoctonine skeleton of **2** were practically preserved, as shown in Fig. 1. They were the same as those observed in **1** and **3**, despite the presence of the C6 ketone. The placement of hydroxyls, methoxyls, and the *N*-acetylanthranilic acid group relative to the lycoctonine skeleton agreed in general with those in **1**. Therefore, the nature of the intramolecular H-bond in **2** was also retained. H-bonds were formed between N2H…O2 (2.63 Å) and O6H…O7 (2.84 Å). However, the alternative bond involving the ketone C6=O5…H–O6 (3.00 Å) was also possible for the latter because the positions of H atoms in the structure of **2** were not determined experimentally.

Intermolecular H-bonds were not observed in the crystal structures of **1** and **2** because all active H atoms were blocked by intramolecular H-bonds. The molecules were situated at van-der-Waals distances from each other.

TABLE 3. Principal Crystallographic Parameters and X-ray Structure Characteristics for **1**, **2**, and **3**

| Parameter | **1** | **2** | **3** [3] |
|---|---|---|---|
| Molecular formula | $C_{32}H_{44}N_2O_8$ | $C_{32}H_{42}N_2O_8$ | $C_{32}H_{44}N_2O_8$ |
| MW, g/mol | 584.69 | 582.68 | 584.69 |
| System | Trigonal | Trigonal | Trigonal |
| Space group | P $3_12_1$ | P $3_12_1$ | P $3_12_1$ |
| $Z$ | 6 | 6 | 6 |
| $a$, Å | 10.6385 (15) | 10.7613 (8) | 10.8074 (6) |
| $b$, Å | 10.6385 (15) | 10.7613 (8) | 10.8084 (6) |
| $c$, Å | 44.298 (9) | 44.541 (4) | 44.179 (2) |
| $\alpha$ | 90.00 | 90.00 | 90.00 |
| $\beta$ | 120.00 | 120.00 | 120.00 |
| $\gamma$ | 90.00 | 90.00 | 90.00 |
| $V$, Å$^3$ | 4341.8 (12) | 4467.0 (6) | 4479.1 (2) |
| $\rho$, g/cm$^3$ | 1.342 | 1.300 | |
| Crystal size, mm | 0.26 × 0.18 × 0.06 | 0.20 × 0.40 × 0.02 | |
| Scan range 2θ | 2.21 ≤ θ ≤ 27.50° | 4.74 ≤ θ ≤ 76.79° | |
| $\mu_{exp}$, cm$^{-1}$ | 0.096 | 0.763 | |
| Number of reflections | 6625 | 5436 | |
| Number of reflections with $I > 2\sigma$ (I) | 5140 | 1577 | |
| $R_1$ ($I > 2\sigma$ (I) and total) | 0.0485 (0.0616) | 0.1453 (0.2659) | |
| W$R_2$ | 0.1097 (0.1150) | 0.3358 (0.4015) | |
| GOOF | 0.970 | 1.562 | |
| Electron-density difference peaks, eÅ$^{-3}$ | 0.36 and –0.29 | 0.32 and –0.35 | |
| CCDC | 252386 | | |

Thus, sesquiterpene germacrane-type lactones (herbolides A and B) and the new diterpenoid alkaloids artekorine (**1**) and 6-ketoartekorine (2) were isolated from the aerial part of *A. korshinskyi*. It was established unambiguously that **1** isolated from this plant was a structural isomer of **3** with respect to the location of a hydroxyl and had the structure 1$\alpha$,14$\alpha$,16$\beta$-trimethoxy-4$\beta$-*N*-acetylanthroyloxy-6$\beta$,8$\beta$-dihydroxy-*N*-ethylaconitane. The other new alkaloid was the 6-ketone derivative of artekorine (**2**) and had the structure 1$\alpha$,14$\alpha$,16$\beta$-trimethoxy-4$\beta$-*N*-acetylanthroyloxy-6-keto-8$\beta$-hydroxy-*N*-ethylaconitane.

In conclusion, it should be noted that diterpenoid alkaloids had not been isolated until now from plants of the genus *Artemisia* L. The principal secondary metabolites of these plants are known to be nitrogen-free terpenoids [4], among which sesquiterpene lactones dominate in a quantitative sense [5–7]. According to the literature, an analogy was observed in plants of the genus *Inula* L. (Asteraceae), which also produce mainly nitrogen-free terpenoids [4]. However, sesquiterpene lactones and diterpenoid alkaloids with the lycoctonine skeleton that contained an anthranilic acid moiety were isolated from the species *I. royleana* DC. growing high in the Himalayas [8–10].

It was found that the biosynthesis of the diterpenoid alkaloids and sesquiterpene lactones took the isoprenoid pathway. Therefore, they are considered pseudoalkaloids [11]. The isoprenoid pathway for biosynthesis of diterpenoid alkaloids was examined experimentally [12–14]. It was demonstrated that the biogenetic precursor and the structural basis of the C-18 diterpenoid alkaloids (including artekorine and 6-ketoartekorine isolated by us) was a rearranged carbon skeleton of the tetracyclic diterpenoid caurane [13], the biosynthesis of which involved cyclization of geranyl-geranyl-pyrophosphate [11].

The biosynthesis of tetracyclic caurane-type diterpenoids is known to involve all flowering plants because they form the structural basis of gibberellin plant phytohormones [15].

It could be assumed from the foregoing that the biosynthesis of diterpenoid alkaloids, e.g., in plants of the family Asteraceae, is evidently sporadic in nature despite the presence of their biogenetic precursors in all flowering plants. Their biosynthesis may occur in response to extreme environmental factors so that they provide additional chemical protection for the plant [16].

## EXPERIMENTAL

IR spectra were recorded on a PerkinElmer 2000 IR-Fourier spectrometer (KBr pellets). NMR spectra were recorded in $CDCl_3$ with HMDSO (0 ppm) internal standard for $^1$H on a Unity-400+ spectrometer at 400 MHz operating frequency.

Spectra were recorded at room temperature on the δ-scale. TLC used Silufol UV254 chromatographic plates and glass plates with a thin layer of silica gel with detection by $I_2$ vapor, $NH_3$ vapor, a UV lamp at 254 and 365 nm, vanillin solution (1%) in conc. $H_2SO_4$, and Dragendorff's solution. Melting points of isolated compounds were determined in glass capillaries on an Electrothermal Mel-Temp® instrument (Barnstead/Thermolyne, USA).

**Plant Material.** The species was identified by Cand. Biol. Sci. V. Bakanova, Inst. Bot., AS, RUz, by comparison of collected herbarium specimens with herbarium *A. korshinskyi* preserved in the Central Herbarium of Uzbekistan (combined herbariums of Tashkent State Univ. and Inst. Bot., AS, RUz).

**Extraction and Isolation.** The aerial part of *A. korshinskyi* (4.5 kg) collected during budding and at the start of flowering between the Kashkasu and Asku Rivers (at 3900–4300 m elevation) 10–12 km from Kyzylrabat, Murgab Region, Republic of Tajikistan, was extracted thoroughly with $CHCl_3$ (raw material:extractant ratio 1:7). The evaporated $CHCl_3$ extract was worked up with alcohol (60%). The resulting precipitate was filtered off. Compounds were extracted (3×) by $CHCl_3$ from an aqueous alcohol solution. The $CHCl_3$ was distilled off to afford a light-brown thick mass (137 g) that was chromatographed over KSK silica gel (1:20 ratio) with elution successively by hexane and then solvent systems (gradient with increasing latter) hexane:EtOAc (9:1→1:1), EtOAc, EtOAc:MeOH (9:1→1:1). The eluate volume was 400 mL.

**Herbolide A**, $C_{17}H_{24}O_4$, mp 162–163°C (EtOH), was isolated from eluates 22–25 (hexane:EtOAc, 9:1), yield 4.61 g.

IR spectrum (KBr, ν, $cm^{-1}$): 3507, 3426, 2995, 2937, 2867, 1769 (γ-lactone C=O), 1721 (ester C=O), 1661 (C=C stretching), 1458, 1434, 1387, 1371, 1319, 1244 (C=C bending), 1213, 1185, 1165, 1145, 1129, 1080, 1048, 1017, 959, 894, 870, 854, 820, 796, 766, 717, 681, 642, 616, 591, 567, 535, 488, 463, 416.

PMR spectrum (400 MHz, $CDCl_3$, HMDSO = 0, δ, ppm, J/Hz): 1.23 (3H, d, J = 6.98, H-13), 1.41 (3H, dd, J = 1.4, 0.7, H-14), 1.65 (3H, d, J = 0.7, H-15), 1.78 (1H, ddd, J = 8.81, 3.12, 5.69, H-3a), 1.83 (1H, d, J = 6.66, H-8a), 1.84 (1H, dd, J = 6.45, 9.92, H-7), 1.96 (1H, dq, J = 11.04, 2.37, 7.20, 5.48, H-3b), 1.97 (3H, s, OAc), 2.15-2.30 (4H, m, H-2, H-8b, H-11), 4.50 (2H, m, H-9, H-6), 5.05 (1H, dd, J = 6.98, 4.09, H-5), 5.10 (1H, m, H-1). The spectral data agreed with the literature [17].

**Herbolide B**, $C_{17}H_{24}O_5$, mp 209°C (EtOH), was isolated from eluates 39–44 (hexane:EtOAc 7:1), yield 3.80 g.

IR spectrum (KBr, ν, $cm^{-1}$): 3507, 3422, 3013, 2978, 2938, 2874, 1760 (γ-lactone C=O), 1719 (ester C=O), 1674 (C=C stretching), 1464, 1394, 1374, 1379, 1348, 1328, 1251 (C=C bending), 1236, 1220, 1211, 1191, 1182, 1166, 1131, 1107, 1089, 1055, 1033, 1017, 981, 962, 930, 913, 896, 858, 841, 824, 803, 721, 686, 642, 614, 580, 568, 555, 498, 475, 460, 414.

PMR spectrum (400 MHz, $CDCl_3$, HMDSO = 0, δ, ppm, J/Hz): 1.18 (3H, s, H-14), 1.21 (3H, d, J = 6.98, H-13), 1.40 (1H, dq, J = 4.94, 11.28, 2.04, 1.44, H-7), 1.77 (3H, s, H-15), 1.78 (3H, m, H-2, H-3a), 2.02 (1H, m, J = 12.36, 5.05, 8.52, H-11), 2.03 (3H, s, OAc), 2.17 (1H, m, J = 1.40, 7.20, 2.36, H-8a), 2.20 (1H, dq, J = 5.05, 2.69, 6.88, 0.64, H-8b), 2.32 (1H, td, J = 12.57, 13.00, 5.26, H-3b), 2.75 (1H, dd, J = 2.25, 11.18, H-1), 4.20 (1H, dd, J = 9.67, 2.36, H-9), 4.32 (1H, dd, J = 7.84, 1.07, 9.03, H-6), 5.10 (1H, dd, J = 1.08, 10.0, H-5). The spectral data agreed with the literature [17].

**Artekorine (1α,14α,16β-trimethoxy-4β-*N*-acetylanthroyloxy-6β,8β-dihydroxy-*N*-ethylaconitane) (1).** Diterpenoid alkaloid, $C_{32}H_{44}N_2O_8$, mp 228–229°C (hexane:EtOAc), was isolated from eluates 52–59 (hexane:EtOAc 4:1), yield 9.37 g.

IR spectrum (KBr, ν, $cm^{-1}$): 3513, 3447, 2930, 2872, 2814, 1703, 1680, 1587, 1524, 1443, 1374, 1271, 1099, 764. Table 1 lists the PMR spectrum.

**6-Ketoartekorine (1α,14α,16β-trimethoxy-4β-*N*-acetylanthroyloxy-6-keto-8β-hydroxy-*N*-ethylaconitane (2).** Diterpenoid alkaloid, $C_{32}H_{42}N_2O_8$, mp 212–213°C (hexane), was isolated by rechromatography of condensed mother liquors of eluates 52–59 (hexane:EtOAc 4:1), yield 0.21 g.

IR spectrum (KBr, ν, $cm^{-1}$): 3507, 3317, 2924, 2846, 1743, 1701, 1684, 1589, 1526, 1448, 1367, 1266, 1088, 760. Table 1 lists the PMR spectrum.

**X-ray crystal structure analyses (XSA)** of **1** and **2** used single crystals shaped as thin six-sided plates. Single crystals of **2** of optimal dimensions and quality for the XSA could not be grown. The XSA of **1** was performed on a six-sided plate-like transparent single crystal at 110 K. Intensities of independent reflections were measured on a Bruker Smart 1K CCD automated diffractometer (Mo Kα-radiation, graphite monochromator, ω-scanning). Unit-cell constants of **1** were determined and refined on an Xcalibur Ruby CCD diffractometer (Oxford Diffraction) using Cu Kα-radiation (300 K, graphite monochromator). A three-dimensional dataset of reflections was obtained on the same diffractometer (dataset of reflections for **2** was collected from two experiments).

Absorption corrections were applied semi-empirically using the SADABS program [18], the maximum and minimum transmission coefficients were 1.000 and 0.677; for **2**, using the multi-scan program [19], the maximum and minimum

transmission coefficients were 1.000 and 0.442. Table 3 presents the principal experimental XSA parameters and refinement calculations for the structures of **1** and **2** and those of **3** for comparison [3].

The structure of **1** was solved by direct methods using the SHELXTL Plus 5.0 software [20]. All non-hydrogen atoms were refined by anisotropic full-matrix LSM (over $F^2$). Positions of H atoms in the structure of **1** were found in a difference Fourier synthesis and refined with fixed isotropic thermal parameters $U_{iso} = nU_{eq}$, where n = 1.5 for methyls and 1.2 for others and $U_{eq}$ is the equivalent isotropic thermal parameter of the corresponding C, N, or O atom.

The structure of **2** was solved utilizing the isostructural nature of crystals of **1** and **2**, i.e., all non-hydrogen coordinates of atoms in **1** were refined by isotropic and anisotropic LSM using the dataset of reflections from the crystal of **2**. H atoms were situated geometrically using a rider method. The XSA data for **1** and **2** were deposited in the Cambridge Crystallographic Data Centre (CCDC 252386).


## ACKNOWLEDGMENT

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