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Sesquiterpene coumarins of *Ferula tadshikorum* Pimenov

Komila ESHBAKOVA[1*], Kholida KHASANOVA [1,2*], Kurbonazar JURAEV [1], Junli YANG[3*], Bakhrom KOMILOV[1]

1 Institute of the Chemistry of Plant Substances named after Acad. S.Yu. Yunusov Academy of Sciences of the Republic of Uzbekistan, 100170, Tashkent, 77 M. Ulugbek str.
2 "Tashkent institute of Irrigation and agricultural mechanization engineers" National research university, 39 K. Niyazov Str, Tashkent 100000 Uzbekistan.
3 Lanzhou Technical Institute of Physics and Chemistry, Lanzhou, China.
* Corresponding Author. E-mail: e_komila@yahoo.com (K.E.); Tel. +998-71-120 64 75.
* Corresponding Author. E-mail: kholida_khasanova@yahoo.com (Kh.Kh.); Tel. +998 -71-237 46 68
* Corresponding Author. E-mail: yangjl@licp.cas.cn (Y.J.)

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ABSTRACT: Eight known sesquiterpene coumarins compounds were isolated from the root of *Ferula tadshikorum* Pimenov by column chromatography and semi-preparative HPLC. Their structures were identified by the spectroscopic data and comparison with literatures as, mogoltadone (1), badrakemin (2), colladonin (3), nevskin (4), gummosin (5), samarcandin (6), feshurin (7), samarcandin acetate (8). All compounds were isolated from *F. tadshikorum* for the first time.

KEYWORDS: *Ferula tadshikorum;* sesquiterpene coumarins; samarcandin acetate; mogoltadone; badrakemin.

1. INTRODUCTION

The genus *Ferula* (*Apiaceae*) comprises about 180 species, with most of these growing in Central Asia, the Middle East, and Central Europe. The main phytochemicals present in the genus *Ferula* are as follows: coumarins, sesquiterpenes, monoterpenes, monoterpene coumarins, flavonoids etc [1]. The *Ferula* genus has been reported to be a rich source of biologically active compounds, such as coumarins and sesquiterpens [2-7]. Sesquiterpene derivatives are stored in the roots of these plants, which make the roots a better source for isolating sesquiterpene coumarins in comparison to the aerial parts of such plants [8-10]. Sesquiterpene coumarins isolated mainly from the *Ferula* genus exhibit antiviral, antibacterial, antileishmanial, anti-inflammatory and antitumor activity [11-13]. *Ferula tadshikorum* Pimenov, a medicinal and endemic plant and growing in Afghanistan, Central Asia (Pamir-Alai: mountains of southern Tajikistan and Uzbekistan) [14]. Abu Ali ibn Sina (Avicenna) used it in his medical practice for skin diseases, tuberculosis, joint pain, against parasites, inflammation of the stomach and intestines, as well as for cleansing the body of salt and food debris [15]. The use of *Ferula tadshikorum* in folk medicine has a centuries-old history. Raw materials of *F. tadshikorum* have been used for many years as a pain reliever for joint inflammation and pain. Some sources indicate that when the leaves of the plant are mixed with cucumber, it has a positive effect on malignant tumors and wound diseases [16].

In recent years, due to the production of an oleo-gum-resin (exudate) from *Ferula* species as asafoetida, interest in *F. tadshikorum* has also increased. The oleo-gum-resin is used for needs of the medical industry and as flavoring spice for various foodstuff [17]. *F. tadshikorum* is one of the possible sources of asafoetida resin, which is used for the needs of the medical industry and as a seasoning for various food products [18]. *F. tadshikorum* has a very wide spectrum of pharmacological activity and is widely used in traditional medicine, mainly in Asian countries, and relatively rarely in scientific medicine. The chemical composition of *Ferula tadshikorum* has been studied to a lesser extent and has not yet received practical application. There are data in the literature on the chemical composition and biological activity of essential oils obtained from roots [19]. Previously, some coumarins have been isolated from the roots of the plant [20]. Later, deacetyltadzhikorin also was isolated from the acetone extract of the roots of *F. tadshikorum* [21]. In the present study, we report the

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isolation and the structure elucidation of eight sesquiterpene coumarins from *Ferula tadashikorum* for the first time.

2. RESULTS AND DISCUSSION

Eight known sesquiterpene coumarin compounds have been isolated from the crude root gum of *F. tadshikorum*: mogoltadone (1), badrakemin (2), colladonin (3), nevskin (4), gummosin (5), samarcandin (6) feshurin (7), samarcandin acetate (8). These compounds differ in the presence or absence of a hydroxyl group, the arrangement of double bonds, and the configuration of chiral centers. The ^{13}C NMR spectrum of these compounds revealed 24 carbon signals, 9 of which are typical for the umbelliferon skeleton, and the remaining 15 signals can be attributed to the sesquiterpene fragment. ^{1}H NMR spectra showed resonance corresponding to five hydrogen atoms of coumarin and diastereotopic protons of the methylene group (H-11′), which confirmed the addition of a sesquiterpene residue to the coumarin fragment. Based on chemical transformations, the structures of typical compounds were determined: gummosin, badrakemin, colladonin and samarcandin, as well as coumarins with aliphatic and monocyclic terpenoid residues. Selenium dehydrogenation of gummosin, badrakemin and related compounds containing an oxygen function at C-3 yielded 1,2,5,6-tetramethylnaphthalene. In this transformation, the angular methyl group was eliminated and the tetrasubstituted naphthalene was formed by a tetrapinacol rearrangement, providing chemical evidence for the carbon skeleton of the sesquiterpene moiety and the substituents (-OH, C=O, -OAc) at C-3 of the corresponding coumarins.

This is the first report of these compounds in *F. tadshikorum*.

Compound 1 was obtained as white crystals. It had the molecular formula $C_{24}H_{28}O_4$, mp 131-132°C. The ^{13}C NMR spectrum of the compound refers to sesquiterpene coumarins. In the ^{1}H NMR spectra, the signal from the heme hydroxyl is not observed in position 3'. And in this position in the carbon spectra a signal from the ketone appears (δ_C 214.9 ppm). The signals of the carbon adjacent to it are shifted to a weak field, this confirms that in the third position, in the sesquiterpene part, there is a ketone group. In the proton spectra at δ_H 5.06 ppm one proton singlet and at δ_H 5.05 ppm one proton singlet are very characteristic signals of the protons of the exocyclic group and this prompted that in the 8th position the methyl group was transformed into an exocyclic group. This is confirmed by the signals of the carbon spectra δ_C 115.9 and 149.2 ppm. Thus, based on all the data obtained, the substance was identified as magoltadone [22].

Compound 2 was obtained as a white amorphous powder. It had the molecular formula $C_{24}H_{30}O_4$. The ^{1}H NMR and ^{13}C NMR spectrums of compound shows that this compound also belongs to sesquiterpene coumarins. In the ^{1}H NMR spectrum at 3.46 ppm (1H, m, t. J = 2,5 Hz), the signal of one proton resonates as a multiplet and triplet, characteristic of the geminal proton to the hydroxyl group, which is confirmed by its carbon spectrum δ_C 75.8 ppm and the HSQC experiment. The signal of two protons is also observed as a triplet-triplet (4.51 br.s; 4.91 br.s. 2H), characteristic of the exomethylene group. Accordingly, in the ^{13}C NMR spectrum, two signals are noted at δ 107.65 (C-12′) ppm (carbon of the exomethylene group) and 146.83 (C-8′) (carbon attached to the exomethylene group) [23,24].

Compound 3 were obtained as white crystal, mp 176-177°C, molecular formula $C_{24}H_{30}O_4$, gummosin and badrakemin differ in their configuration at C_9 (the substituent at C_3(OH) in both substances has the axial orientation). In badrakemin, the angular methyl group and the substituent at C_9 (-CH_2OAr) are present in the cis position and in gummosin in the trans position to one another[21]. Compound 3 was isolated from other *Ferula* species such as *F. arrigonii, F. coummunis, F. mogoltavica* [25].

Compound 4 were obtained also as white crystal, molecular formula $C_{24}H_{30}O_4$, mp 160 °C. The ^{13}C NMR spectrum of (**4**) was similar to that of Badrakemin (**2**), the only difference being in the relative configuration of stereocenter at C-3′. A chemical correlation in the HMBC spectrum of 4 was observed between the gem-hydroxyl proton H-3' (3.26 ppm) and the methylene carbon C-2 (δ 27.2), allowing the location of the hydroxyl group to be determined. By NOE experiments; irradiation of H-11' enhanced H-9', H-12' and H-15'. The signal at δH 4.37 (H-11′), 1.75 (H-1′), 1.03 (H-14′) and 0.95 (H-15′), indicating the α-orientation of these protons. In addition, the signal at δ_H 3.26 (H-3′) showed NOE correlations with the signals at δ_H 1.79 (H-9′), 1.57 (H-5′), including the β orientation of 0.80 (H-13′) [10].

Compound 5 were obtained as white crystal, mp 193-194 °C, molecular formula $C_{24}H_{30}O_5$. The ^{13}C NMR spectrum of was similar to that of (**6**), the only difference being in the relative configuration of stereocenter at C-3′. The determination of their relative configuration is justified by NOESY and HMBC

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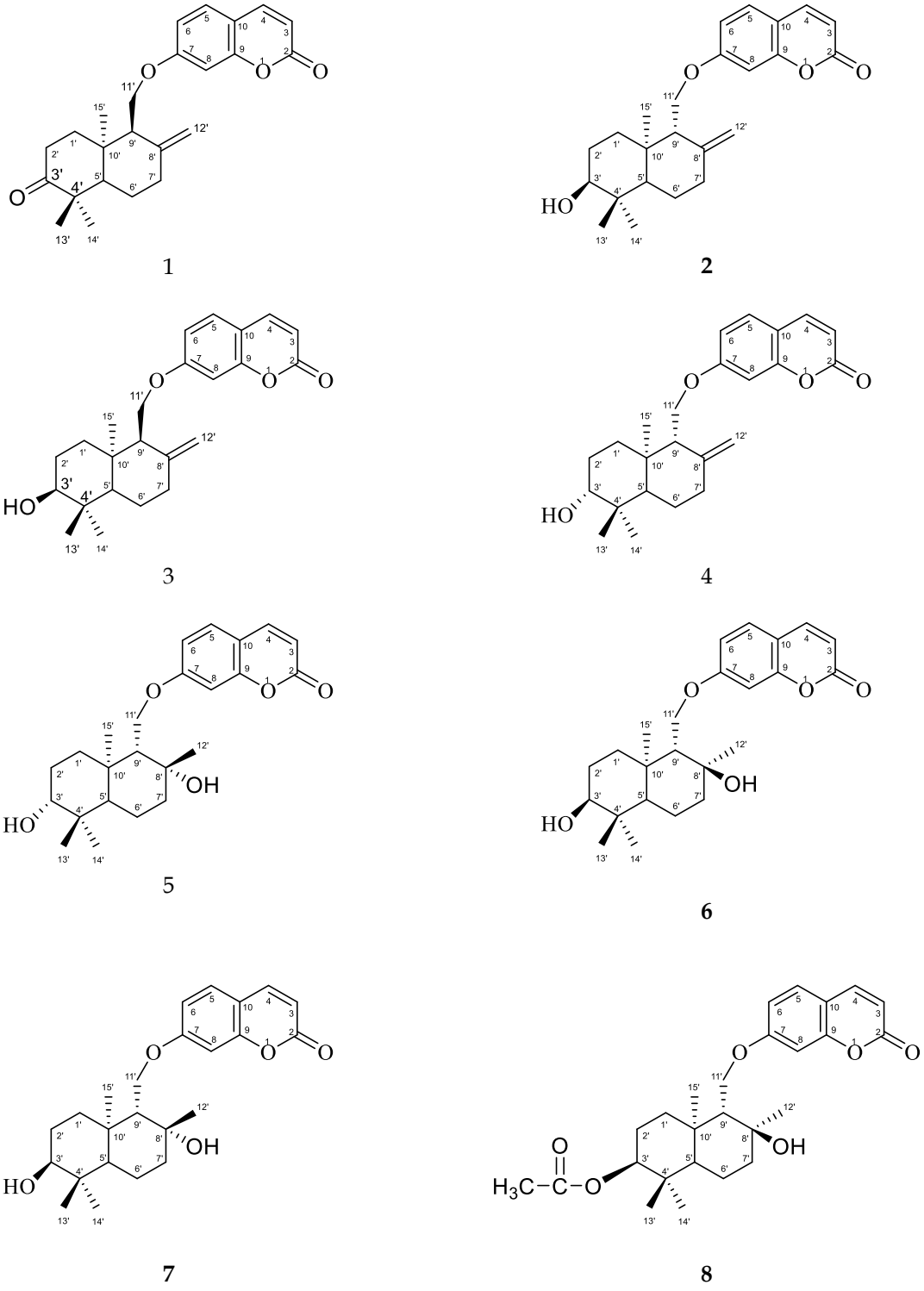

Figure 1. Chemical structures of sesquiterpene coumarins isolated from ***Ferula tadshikorum***

correlation. Gummosin was isolated from other *F. assafoetida F. gummosa F. kokanica F. linczevskii F. lipskyi F. schtschurowski ana F. vicaria* [25].

Compound 6 were obtained as white crystal, mp 176-177 °C, molecular formula $C_{24}H_{32}O_5$. The structure of compound (6) was established from analysis of the ^1H and ^{13}C NMR spectra. Secondary and tertiary alcoholic carbon resonances at δ_C 76.51 and 71.78 ppm attributed to C-3′ and C-8′. The NOESY experiment assigned the relative configuration of the stereogenic centres at C-3′, C-4′, C-5′, C-8′, C-9′ and C-10′

and exhibited correlations. Cross-peaks of Me-13′ /OH-3′ and Me-15′ /Me-12′ confirmed that the Me-13′ and OH-3′ were located on the same face of the two fused six-membered ring also Me-15′ and 12′. Compound 6 was isolated from other *Ferula* species such as *Ferula badrakema*, *Ferula microloba* and *Ferula sinacia* [25].

Compound 7 were obtained as white crystal, mp 212-214 °C, molecular formula $C_{24}H_{32}O_5$. The ^{13}C NMR spectrum of (7) was similar to that of (6), the only difference being in the relative configuration of stereocenter at C-8′. The determination of their relative configuration is justified by NOESY and HMBC correlation. There have been reports on the isolation of this compound from other *Ferula families*, e.g. *Ferula persika, Ferula nevskia* and *Ferula iliensis* [25,26].

Compound 8 molecular formula $C_{26}H_{34}O_6$, mp 152-153 °C. ^1H NMR and ^{13}C NMR spectra dates from 8-compound very character to acylation sesquiterpene coumarins [27]. Indeed, in the spectra of the polar region of the compound, a characteristic signal from the methyl group of acetate is observed at δH 2.01 ppm. Also in the ^{13}C NMR spectra are present two signals δ_C 21.7 (CH_3-OAc) and 172.1 (C=O, -OAc) ppm corresponding to the acetate group. In the HMBC spectra, a correlation is observed with the proton in position 3' of the ketone carbon. It turns out that the acetyl group is in position 3'. In the carbon spectra of the compound, there is a signal δ_C 101.6 ppm, which indicates the presence of a quaternary hydroxyl group in the methyl group, the same as in compounds 5-7. Thus, based on all the data obtained, the substance was identified as samarcandine acetate [28].

3. CONCLUSION

In this study, eight known sesquiterpene coumarin compounds were successfully isolated from the crude root gum of Ferula tadshikorum. These compounds—mogoltadone (1), badrakemin (2), colladonin (3), nevskin (4), gummosin (5), samarcandin (6), feshurin (7), and samarcandin acetate (8)—were characterized by differences in hydroxyl groups, double bond arrangements, and chiral center configurations. Structural elucidation was achieved through ^1H and ^{13}C NMR spectra, supported by chemical transformations.

This research represents the first report of these specific compounds being isolated from F. tadshikorum, contributing valuable knowledge to the chemical diversity of the Ferula genus. Further studies on their bioactivities and potential applications could provide insights into their medicinal value.

4. MATERIALS AND METHODS

4.1. Chemicals and reagents

Column chromatographic separation was performed on Sephadex LH-20 gel (Amersham Pharmacia Biotech, Stockholm, Sweden), ODS-A (50 μm) (manufactured by YMC CO. Ltd., Japan), silica gel (CC 100-200 mesh) (Qingdao Haiyang Chemical Factory, China) and MCI CHP 20/120 (Mitsubishi Chemical Corporation, Japan).

In TLC monitoring of fractions and compounds, visualization was performed by heating silica gel plates, sprayed with H_2SO_4 (5%) in EtOH with heating 105 °C.

The organic solvents including chloroform, methanol anhydrous, acetone, hexane, ethyl acetate, petroleum ether (60-90 °C) and ethanol were purchased from Tianjin Hongyan Chemical Reagent Factory, China. The HPLC grade solvents such as acetonitrile (ACN), methanol (MeOH) and formic acid were purchased from Merck K.GaA., Darmstadt, Germany.

IR spectra were recorded on an FT-IR/NIR Spectrum 3 spectrometer (Perkin Elmer, Switzerland) using an NTR system. ^1H and ^{13}C NMR spectra were recorded on a JNM-ECZ600R spectrometer (JEOL, Japan) at an operating frequency of 600 MHz for ^1H in DMSO-d_6+CCl_4 solutions. TMS (0 ppm) was used as an internal standard in ^1H NMR spectra. In the ^{13}C NMR spectra, the chemical shift of the solvent (DMSO-d_6, 39.52 ppm relative to TMS) was used as an internal standard.

4.2. Plant materials

The roots of *Ferula tadshikorum* Pimenov (Apiaceae) were collected in June 2021 from Kashkadarya region, southwestern spurs of the Gissar Range, river basin. Tarkapchigay, env. Buztepa village, rocky and gravelly slope, Republic of Uzbekistan (2.06.2021, 69.838889 41.555556 h=1500 Isolation processes). The investigated plants were identified by Prof. Alim Magnurovich Nigmatullayev Institute of the Chemistry of Plant Substances, Academy of Sciences of the Republic of Uzbekistan. The voucher specimen (FT2135) has

been deposited in Institute of the Chemistry of Plant Substances, Academy of Sciences of the Republic of Uzbekistan

The crude gum obtained from the roots of *F. tadshikorum* was air-dried and then extracted with ethanol (95% v/v) at 75°C for 5 h under reflux. The ratio of ethanol to crude gum was 35:1 (w/w) and the solvent was used in two cycles. Ethanol insoluble materials were separated and oven dried at 80 °C. The resulting white powder was mixed with five-fold (w/w) of distilled water and was stirred for 30 min at 45 °C, followed by 2 h at room temperature. Water insoluble materials were separated using filtration (cloth filter) by centrifugation at 25 min. In order to purify gum, the supernatant was mixed with three volumes of ethanol letting to precipitate overnight at 4 °C. Then, the resulting precipitate was air dried and mixed with five volumes of acetone liquid, pressed three times and dried at 50 °C overnight. The purification step was performed for one more time after resolubilizing gum powder in ultra-pure water. The final purified gum powder was milled and kept for structural analysis. The gum powder (100 gr) eluted with petroleum ether–ethyl acetate (50:1 to 0:1, v/v), was fractionated into ten fractions (Ft 1~10) by chromatography on a silica gel column (200–300 mesh, 10 × 100 cm). Subfraction Ft-3 was separated with Sephadex LH-20 eluting with CH_2Cl_2–MeOH (100:1-0:1, v/v) to give 5 fractions (A1~A5). The fraction A3 (159 mg) was separated by semi-preparative HPLC [with 10% aqueous acetonitrile (ACN) as mobile phase, at a flow rate 3.0 mL/min] to afford compounds 1 (7.0 mg), 2 (8.0 mg), 3 (7.0 mg), and 4 (21.0 mg). Subfraction Ft 7 was (177 mg) isolated by Sephadex LH-20 (CH_3CI-MeOH, 100:1-0:1, v/v) colunm and purified by HPLC (MeCN-H_2O, 70:30, v/v, 30 min) to obtain compounds 5 (16 mg), 6 (15 mg), 7 (4 mg), and 8 (18 mg).

4.3. Spectroscopic data of 1-8

4.3.1. Mogoltadone (1): $C_{24}H_{28}O_4$, white crystal, mp 131-132°C, ^{1}H NMR (600 MHz, $CDCl_3$, δ, ppm, *J*/Hz): 6.26 (1H, d, *J* = 9.3, H-3), 7.63 (1H, d, *J* = 9.4, H-4), 7.36 (1H, t, *J* = 7.9 Hz, H-5), 5.06 (1H, d, *J* = 8.7 Hz, H-6), 6.76 (1H, dd, *J* = 8.6: 2.4, H-8), 1.86 (1H, m H-1′$_{axi}$). 1.64 (1H, d, *J* = 13.0 Hz, H-1′$_{eq}$), 2.49 (1H, d, *J* = 13.1 Hz, H-2′axi), 2.34 (1H, m, H-2′eq), 1.74 (1H, s, H-5′), 2.86 (1H, dt, *J* = 14.4, 5.0 Hz, H-6′axi), 1.40 (1H, m, H-6′eq), 2.49 (1H, d, *J* = 13.1 Hz, H-7′axi), 2.34 (1H, m, H-7′eq), 2.47 (1H, s, H-9′), 4.20 (1H, d, *J* = 7.7, H-11′axi), 4.06 (1H, dd, J = 9.4, 5.5, H-11′eq), 5.06 (1H, s, H-12′a), 5.05 (1H, s, H-12′b), 1.42 (3H, s H-13′), 1.23 (3H, s, H-14′), 1.50 (3H, s, H-15′). ^{13}C NMR (150 MHz, $CDCl_3$, δ, ppm): 160.8 (C-2), 113.5 (C-3), 143.41 (C-4), 128.96 (C-5), 113.08 (C-6), 161.39 (C-7), 101.74 (C-8), 153.69 (C-9), 113.8 (C-10), 37.4 (C-1′), 42.0 (C-2′), 214.9 (C-3′), 49.1 (C-4′), 50.9 (C-5′), 35.1 (C-6′), 42.0 (C-7′), 149.2 (C-8′), 55.7 (C-9′), 38.2 (C-10′), 68.0 (C-11′), 115.9 (C-12′), 24.3 (C-13′), 26.2 (C-14′), 24.8 (C-15′).

4.3.2. Badrakemin (2): $C_{24}H_{30}O_4$, mp 200°C, ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm, *J*/Hz): 6.24 (1H, d, *J* = 9.3, H-3), 7.62 (1H, d, *J* = 9.3, H-4), 7.34 (1H, m, H-5), 6.84 (1H, dd, *J* = 7.3; 2.5 Hz H-6), 6.82 (1H, s, H-8), 1.51 (1H, dt, *J* = 12.7:3.4 Hz, H-1′$_{axi}$). 1.86 (1H, td, *J* = 12.7; 2.9 Hz, H-1′$_{eq}$), 1.66 (1H, m, H-2′$_{axi}$), 1.97 (1H, tt, *J* = 14.2; 2.9 Hz. H-2′$_{eq}$), 3.46 (1H, m, t. *J* = 2,5 Hz, H-3′), 1.66 (1H, m, H-5′), 1,43 (1H, dd, *J* = 13.2: 3.9 Hz, H-6′$_{axi}$), 1.68 (1H, m, H-6′$_{eq}$), 2.14 (1H, td, *J* = 13.2; 4.9 Hz, H-7′$_{axi}$), 2.46 (1H, ddd *J* = 13.2; 3.9; 2.4 Hz, H-7′$_{eq}$), 2.33 (1H, m, H-9′), 4.18 (1H, dd, *J* = 9.8; 7.8 Hz, H-11′$_{axi}$), 4.24 (1H, dd, *J* = 9.8; 3.9 Hz, H-11′$_{eq}$), 4.51 (1H, br s, H-12$_{axi}$), 4.91 (1H, br s, H-12′$_{eq}$), 0.87 (3H, s H-13′), 0.88 (3H, s, H-14′), 0.86 (3H, s, H-15′) ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 161.4 (C-2), 113.1 (C-3), 143.6 (C-4), 128.8 (C-5), 113.4 (C-6), 162.5 (C-7), 101.5 (C-8), 156.1 (C-9), 112.6 (C-10), 32.0 (C-1′), 25.9 (C-2′), 75.8 (C-3′), 37.9 (C-4′), 48.3 (C-5′), 23.6 (C-6′), 37.7 (C-7′), 146.8 (C-8′), 54. 9 (C-9′), 39.0 (C-10′), 65.9 (C-11′), 107.6 (C-12′), 28.0 (C-13′), 22.5 (C-14′), 15.4 (C-15′).

4.3.3. Colladonin (3): $C_{24}H_{30}O_4$, mp 160°C, ^{1}H NMR (600 MHz, $CDCl_3$, δ, ppm, *J*/Hz): 6.24 (1H, d, *J* = 9.3, H-3), 7.63 (1H, d, *J* = 9.3, H-4), 7.35 (1H, m, H-5), 6.83 (1H, dd, *J* = 7.3:2.5 Hz, H-6), 6.82 (1H, s, H-8), 2.10 (1H, dt *J* = 12.7:3.4 Hz, H-1′$_{axi}$). 2.45 (1H, td, *J* = 12.7; 2.9 Hz, H-1′$_{eq}$), 1.64 (1H, m, H-2′axi), 1.73 (1H, tt, *J* = 14.2; 2.9 Hz. H-2′eq), 3.30 (1H, m, brt *J* = 2,5 Hz, H-3′), 1.58 (1H, m, H-5′), 1.44 (1H, dd, *J* = 13.2: 3.9 Hz, H-6′$_{axi}$), 1.77, (1H, m, H-6′$_{eq}$), 1.81 (1H, td, *J* = 13.2; 4.9 Hz, H-7′$_{axi}$), 1.45 (1H, ddd *J* = 13.2; 3.9; 2.4 Hz, H-7′$_{eq}$), 2.21 (1H, m, H-9′), 4.19 (1H, dd, *J* = 9.8; 7.8 Hz, H-11′$_{axi}$), 4.03 (1H, dd, *J* = 9.8; 3.9 Hz, H-11′$_{eq}$), 4.92 (1H, br s, H-12′$_{axi}$), 4.54 (1H, br s, H-12′$_{eq}$), 0.85 (3H, s H-13′), 1.03 (3H, s, H-14′), 0.82 (3H, s, H-15′). ^{13}C NMR (150 MHz, $CDCl_3$, δ, ppm): 161.3 (C-2), 113.1 (C-3), 143.5 (C-4), 128.8 (C-5), 113.1 (C-6), 162.3 (C-7), 101.5 (C-8), 156.0 (C-9), 112.6 (C-10), 37.5 (C-1′), 27.8 (C-2′), 78.1 (C-3′), 39.3 (C-4′), 54.4 (C-5′), 23.6 (C-6′), 37.3 (C-7′), 146.4 (C-8′), 54. 9 (C-9′), 38.9 (C-10′), 65.8 (C-11′), 107.9 (C-12′), 28.4 (C-13′), 15.6 (C-14′), 15.5 (C-15′).

4.3.4. Nevskin (4): $C_{24}H_{32}O_5$, mp 193-194 °C, ^{1}H NMR (600 MHz, $CDCl_3$, δ, ppm, *J*/Hz): 6.25 (1H, d, *J* = 9.3, H-3), 7.62 (1H, d, *J* = 9.5, H-4), 7.36 (1H, d, *J* = 8.6, H-5), 6.85 (1H, dd, *J* = 8.6; 9.5 H-6), 6.91 (1H, s, H-8), 1.75 (1H, d, *J* = 4.2, H-1′axi). 1.32 (1H, d, *J* = 3.7, H-1′$_{eq}$), 1.68 (1H, d, *J* = 4.1, H-2′$_{axi}$), 2.00 (1H, m. H-2′$_{eq}$), 3.26 (1H, dd, *J* = 11.6; 4.6 Hz, H-3′), 1.57 (1H, d, *J* = 1.8 Hz, H-5′), 1.72 (1H, dd, *J* = 2.6; Hz, H-6′$_{axi}$), 1.37, (1H, d, *J* = 3.3 Hz, H-

6′$_{eq}$), 1.95(1H, dt, *J* = 12.6; 3.1 Hz, H-7′axi), 1.54 (1H, d, *J* = 4.0, H-7′eq), 1.74 (1H, s, H-9′), 4.37 (1H, dd, *J* = 9.9; 4.8 Hz, H-11′$_{axi}$), 4.19 (1H, dd, *J* = 9.9; 5.5 Hz, H-11′$_{eq}$), 1.25 (1H, s, H-12′), 0.80 (3H, s H-13′), 1.03 (3H, s, H-14′), 0.95 (3H, s, H-15′). ^{13}C NMR spectrum (150 MHz, $CDCl_3$, δ, ppm): 161.8 (C-2), 113.4 (C-3), 143.4 (C-4), 128.8 (C-5), 113.2 (C-6), 161.8 (C-7), 101.8 (C-8), 156.0 (C-9), 112.8 (C-10), 38.2 (C-1′), 27.2 (C-2′), 78.5 (C-3′), 39.0 (C-4′), 54.9 (C-5′), 20.1 (C-6′), 44.2(C-7′), 72.6 (C-8′), 59.4 (C-9′), 29.8 (C-10′), 66.7 (C-11′), 24.9 (C-12′), 15.6 (C-13′), 28.3 (C-14′), 16.2 (C-15′).

4.3.5. Gummosin (5): $C_{24}H_{30}O_4$, white crystal, mp 176-177 °C, ^{1}H NMR (600 MHz, $CDCl_3$, δ, ppm, *J*/Hz): 6.25 (1H, d, *J* = 9.5, H-3), 7.89 (1H, d, *J* = 9.5, H-4), 7.52 (1H, t, *J* = 8.6 Hz, H-5), 6.97 (1H, d, *J* = 2.3 Hz, H-6), 6.92 (1H, dd, *J* = 8.6: 2.4, H-8), 2.11 (1H, d, *J* = 3.5 Hz, H-1′$_{axi}$). 2.07 (1H, m, H-1′$_{eq}$), 2.05 (1H, d, *J* = 3.6 Hz, H-2′axi), 2.01 (1H, m, H-2′eq), 3.42 (1H, s, H-3′), 1.83 (1H, dd *J* = 12.9; 3.1 Hz, H-5′), 1.63 (1H, ddd, *J* = 13.5, 5.5, 2.8 Hz H-6′axi), 1.40 (1H, m, H-6′eq), 2.31 (1H, d, *J* = 12.6 Hz, H-7′axi), 2.13 (1H, m, H-7′eq), 2.10 (1H, s, H-9′), 4.13 (1H, m, H-11′axi), 4.44 (1H, m, H-11′eq), 4.82 (1H, t, *J* = 2.1 Hz, H-12′a), 4.71 (1H, s, H-12′b), 0.98 (3H, s H-13′), 0.86 (3H, s, H-14′), 1.03 (3H, s, H-15′). ^{13}C NMR (150 MHz, $CDCl_3$, δ, ppm): 163.4 (C-2), 113.1 (C-3), 145.8 (C-4), 130.2 (C-5), 114.5 (C-6), 164.1 (C-7), 102.4 (C-8), 157.1 (C-9), 113.8 (C-10), 30.5 (C-1′), 26.7 (C-2′), 77.0 (C-3′), 38.7 (C-4′), 42.0 (C-5′), 24.2 (C-6′), 33.4 (C-7′), 148.7 (C-8′), 58.7 (C-9′), 38.6 (C-10′), 69.1 (C-11′), 111.3 (C-12′), 29.1 (C-13′), 23.0 (C-14′), 22.6 (C-15′).

4.3.6. Samarcandin (6): $C_{24}H_{32}O_5$, mp 176-177 °C, ^{1}H NMR (600 MHz, $CDCl_3$, δ, ppm, *J*/Hz): 6.21 (1H, d, *J* = 9.3, H-3), 7.63 (1H, d, *J* = 9.5, H-4), 7.34 (1H, d, *J* = 8.4, H-5), 6.83 (1H, dd (*J* = 8.6; 9.5) H-6), 6.87 (1H, s, H-8′), 1.44 (1H, d *J* = 13.0, H-1′$_{axi}$). 1.69 (1H, d *J* = 3.7, H-1′$_{eq}$), 1.59 (1H, d, *J* = 4.1, H-2′$_{axi}$), 1.93 (1H, m. H-2′$_{eq}$), 3.42 (1H, s, H-3′), 1.52 (1H, d, *J* = 12.2 Hz, H-5′), 1.34 (1H, d, *J* = 13.00; Hz, H-6′$_{axi}$), 1.69 (1H, dt, *J* = 13.0; 2.5 Hz, H-6′eq), 1.58 (1H, m, H-7′$_{axi}$), 1.95 (1H, m, H-7′$_{eq}$), 1.86 (1H, t, *J* = 4.79, H-9′), 4.17 (1H, dd, *J* = 9.75; 5.55 Hz, H-11′$_{axi}$), 4.37 (1H, d, *J* = 4.37, H-11′$_{eq}$), 1.22 (1H, s, H-12′), 0.97 (3H, s H-13′), 0.84 (3H, s, H-14′), 0.94 (3H, s, H-15′). ^{13}C NMR (150 MHz, $CDCl_3$, δ, ppm): 161.3 (C-2), 113.3 (C-3), 143.5 (C-4), 128.8 (C-5), 113.1 (C-6), 161.9 (C-7), 101.7 (C-8), 155.9 (C-9), 112.6 (C-10), 32.9 (C-1′), 25.2 (C-2′), 76.1 (C-3′), 38.0 (C-4′), 48.5 (C-5′), 20.0 (C-6′), 44.2 (C-7′), 71.7 (C-8′), 59.4 (C-9′), 37.5 (C-10′), 66.7 (C-11′), 24.7 (C-12′), 22.2 (C-13′), 28.5 (C-14′), 16.1 (C-15′).

4.3.7. Feshurin (7): $C_{24}H_{32}O_5$, mp 212-214 °C, ^{1}H NMR (600 MHz, $CDCl_3$, δ, ppm, *J*/Hz): 6.24 (1H, d, *J* = 9.5, H-3), 7.63 (1H, d, *J* = 9.4, H-4), 7.36 (1H, d, *J* = 8.2, H-5), 6.83 (1H, d (1H, *J* = 8.4) H-6), 6.85 (1H, s, H-8), 1.55 (1H, m, H-1′$_{axi}$), 1.41 (1H, d, *J* = 12.0, H-1′$_{eq}$), 1.99 (1H, d, *J* = 2.4 Hz, H-6′$_{axi}$), 1.45 (1H, m, H-6′$_{eq}$), 1.81 (1H, d, *J* = 2.5 Hz, H-7′$_{axi}$), 1.55 (1H, br s, H-7′$_{eq}$), 1.52 (1H, m, H-9′), 4.35 (1H, d, *J* = 9.6 Hz, H-11′$_{axi}$), 4.18 (1H, dd, *J* = 9.6; 3.0 Hz, H-11′$_{eq}$), 1.24 (1H, s, H-12′), 0.96 (3H, s H-13′), 0.87 (3H, s, H-14′), 1.08 (3H, s, H-15′). ^{13}C NMR (150 MHz, $CDCl_3$, δ, ppm): 161.9 (C-2), 113.3 (C-3), 143.4 (C-4), 128.8 (C-5), 113.1 (C-6), 161.3 (C-7), 101.7 (C-8), 156.0 (C-9), 112.7 (C-10), 37.7 (C-1′), 27.8 (C-2′), 75.7 (C-3′), 42.6 (C-4′), 54.4 (C-5′), 18.0 (C-6′), 48.6 (C-7′), 72.7 (C-8′), 57.5 (C-9′), 38.0 (C-10′), 66.5 (C-11′), 32.5 (C-12′), 18.0 (C-13′), 22.2 (C-14′), 16.4 (C-15′).

4.3.8. Samarcandin acetate (8): $C_{26}H_{34}O_6$, mp 152-153 °C, ^{1}H NMR spectrum (600 MHz, $CDCl_3$, δ, ppm, *J*/Hz): 6.26 (1H, d, *J* = 9.5, H-3), 7.63 (1H, d, *J* = 9.5, H-4), 7.34 (1H, d, *J* = 8.6, H-5), 6.87 (1H, dd (*J* = 8.6; 9.5) H-6), 6.92 (1H, s, H-8), 1.52 (1H, m, H-1′), 1.67 (1H, d, *J* = 3.4, H-2′$_{axi}$), 1.88 (1H, s, H-2′$_{eq}$), 4.65 (1H, d *J* = 3.3 Hz, H-3′), 1.52 (1H, d, *J* =1.6 Hz, H-5′), 1.65 (1H, m, H-6′$_{axi}$), 1.35 (1H, dt, *J* = 9.7 Hz, H-6′$_{eq}$), 1.98 (1H, m, H-7′$_{axi}$), 1.95 (1H, s, H-7′$_{eq}$), 1.88 (1H, s, H-9′), 4.37 (1H, dd, *J* = 8.4; 3.7 Hz, H-11′axi), 4.20 (1H, dd, *J* = 9.8; 5.3 Hz, H-11′eq), 1.26 (1H, s, H-12′), 0.89 (3H, s H-13′), 0.91 (3H, s, H-14′), 0.97 (3H, s, H-15′). ^{13}C NMR (150 MHz, $CDCl_3$, δ, ppm): 161.2 (C-2), 113.1 (C-3), 143.0 (C-4), 128.7 (C-5), 113.2 (C-6), 161.7 (C-7), 101.6 (C-8), 155.9 (C-9), 112.7 (C-10), 33.5 (C-1′), 22.6 (C-2′), 77.5 (C-3′), 37.7 (C-4′), 49.6 (C-5′), 19.7 (C-6′), 43.9 (C-7′), 72.6 (C-8′), 59.2 (C-9′), 37.7 (C-10′), 66.7 (C-11′), 24.8 (C-12′), 28.0 (C-13′), 22.6 (C-14′), 15.9 (C-15′).

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