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Isolation and Structure of the New Sesquiterpene Lactone 3-oxo-10β-hydroxy-5,7α(H),4,6β(H)-guai-1,11(13)-diene-6,12-olide

The article presents the results of a chemical study of *Tanacetopsis pjataevae*, which is an endemic plant in Kazakhstan. The number of extractive substances was obtained by extraction with chloroform from the air-dry crushed above-ground part of the plant collected in the flowering phase. Isolation of compounds was carried out by column chromatography on a column of silica gel brand KSK at a ratio of sum - carrier = 1:20. A colorless crystalline substance of the composition $C_{15}H_{18}O_4$ with m.p. 189–191°C (recrystallized from diethyl ether) was found when the column was eluted with a mixture of petroleum ether-ethyl acetate (87.5:12.5). The structure of the obtained new compound (3-oxo-10β-hydroxy-5,7α(H),6β(H)-guai-1,11(13)-diene-6,12-olide) was established based on IR, NMR analysis and mass spectra. The spatial structure was determined by the X-ray diffraction method. It was established that the 3-oxo-10β-hydroxy-5,7α(H),6β(H)-guai-1,11(13)-diene-6,12-olide molecule in the crystal is disordered over two conformational states in the 6 :4 ratio. The stability of these conformers was confirmed by semi-empirical quantum-chemical calculations. It was established that the difference in the heat of formation of two conformers was 6.3 kJ/mol for a free molecule.

Keywords: NMR spectroscopy, IR spectroscopy, mass spectrometry, X-ray analysis, *Tanacetopsis pjataevae*, endemic, 3-oxo-10β-hydroxy-5,7α(H),6β(H)-guai-1,11(13)-diene-6,12-olide, sesquiterpene lactones.

Introduction

Natural sesquiterpene γ-lactones (STL) are potentially biologically active substances. The structure of STL includes such pharmacophore groups as α-methylene-γ-lactone ring and α,β-unsaturated enone system. Some STL have an epoxy ring, a hydroxyl group, and chlorine atoms. A study of the chemical composition of endemic plants is being actively carried out to search for new bioactive compounds in Kazakhstan. For the first time, over 30 STL were isolated and identified from endemic plants. A total of 11 of these compounds are new ones, namely raposerine, racerolide, 15-deacetylraposerine, racerin, anolide, achymicrin, gracilin and argracin, 1β-acetoxy-7α,6,11β(H)-eudesm-4(5)-en-6,12-olide, 1β-acetoxy-3β-hydroxy-eudesm-4(5)-en-6,12-olide, and artesin [1, 2].

In continuation of these works, it has been studied the chemical composition of the aboveground part of the *Tanacetopsis pjataevae* (Kovalevsk.) Karmyscheva, which is an endemic species of Kazakhstan, growing in the Karatau mountains [3]. The literature sources [4–8] describe the results of a chemical study of *Tanacetopsis mucronata* Rgl. et Schmalh. growing in Tajikistan. The sesquiterpene lactones, namely deacetyl laurenobiolide, dihydrodeacetyl laurenobiolide, mucrine, tavulin, tanakhine, tamirin, 13α-hydroxymethylene deacetyl laurenbiolide were isolated from Tanacetopsis spiky. Later, the chemical composition of another member of the *Tanacetopsis* genus was investigated. Sesquiterpene lactones 1R,10S,3S,4R-diepoxyguai-5S,6S,7S-11(13)-en-6,12-olide and hanfillin were isolated from the aboveground part of *Tanacetopsis karataviensis* (Kovalevsk.) [9]. The previously known sesquiterpene lactones arglabin and isoepoxyestafiatin were isolated from *Tanacetopsis pjataevae* (Kovalevsk.) Karmyscheva [2].

Experimental

IR spectra were obtained on a spectrometer "Thermo Nicolet Avatar-360" (USA) in potassium bromide tablets in the range from 4000 to 600 cm^{-1}. NMR spectra were recorded on a Bruker DRX-600 spectrometer using standard Bruker software. The Finnigan DMS-8200 high-resolution mass spectrometer with an ionizing voltage of 70 eV (evaporator temperature was 220 °C) was used to record mass spectra, as well as determine the molecular weight and elemental composition. Melting point was determined on an SMF-38 heating table. The reaction progress was monitored by TLC. Sorbfil plates were used for TLC, which were developed by spraying with a 2% aqueous $KMnO_4$ solution. KSK silica gel was used for column chromatography.

Isolation of 3-oxo-10β-hydroxy-5,7α(H),6β(H)-guai-1,11(13)-diene-6,12-olide (**1**). Air-dry crushed raw materials of *Tanacetopsis pjataevae* (0.7 kg, leaves, flower baskets, buds) collected in the flowering phase in the Arpaozen Gorge, Karatau, South Kazakhstan region were extracted with chloroform 3 times. Then the solvent was evaporated. Next, the number of extractives (44 g) was chromatographed on a column of silica gel grade KSK at a ratio of sum – carrier = 1:20. When the column was eluted with a mixture of petroleum ether-ethyl acetate (87.5:12.5), substance **1** was isolated with a yield of 0.200 g (0.029% based on air-dry raw materials). The colorless crystalline substance of the $C_{15}H_{18}O_4$ composition with m.p. 189–191 °C was obtained by recrystallization from diethyl ether.

IR spectrum (KBr, ν, cm^{-1}): 3463 (OH group), 2935, 2872, 1750 (C=O γ-lactone), 1707 (C=O), 1608 (C=C), 1456, 1410, 1371, 1356, 1325, 1261, 1173, 1154, 1081, 1064, 989, 971, 957, 883, 819, 758, 728, 666, 640, 558, 501, 425.

^1H NMR spectrum (600 MHz, $CDCl_3$, δ, ppm, J/Hz): 6.33 (1H, s, H2), 2.57 (1H, d, J=6.0, overlapping with OH-10, H4), 2.69 (1H, d, J=11.0, H5), 3.95 (1H, t, J=10.0, H6), 2.93 (1H, m, H7), 1.75 (1H, m, H8a), 2.23 (1H, dd, J1=7.0, J2=7.0, H8b), 1.99 (2H, m, H9), 5.49 (1H, s, H13a), 6.18 (1H, s, H13b), 1.27 (3H, br.d, J=6.0, CH3-14), 1.54 (3H, s, CH_3-15). 2.57 d (1H, d, J=6.0, overlap with H-4, OH-10).

^{13}C NMR spectrum (150.96 MHz, $CDCl_3$ δ, ppm): 169.12 (s, C1), 129.78 (d, C2), 209.23 (s, C3), 46.52 (d, C4), 55.24 (d, C5), 82.89 (d, C6), 46.42 (d, C7), 21.49 (t, C8), 37.60 (t, C9), 73.42 (s, C10), 139.73 (s, C11), 181.07 (s, C12), 119.90 (t, C13), 27.83 (q, C14), 15.58 (q, C15).

Mass spectrum (70 eV, m/z, Irel. (%)): 262.1 [M]+. Calculated: m/z 262.1200. Found: m/z 262.1196.

Quantum-chemical calculations were carried out using the MOPAC software package version 9.0. Optimization of the molecule geometrical data was carried out by the PM6 method [10].

X-ray analysis of compound **1**. The cell parameters and the intensity of 15346 reflections (3216 independent, R_{int}=0.0491) were measured on a diffractometer “Bruker Kappa APEX2 CCD” (MoK_α, graphite monochromator, ω-scan, $2.667 \leq \theta \leq 27.653$) at 296 K. The crystals are orthorhombic, a=7.7072(3), b=11.8416(5), c=15.2767(6) Å, V=1394.2(1) $Å^3$, Z=4 ($C_{15}H_{18}O_4$), the space group $P2_12_12_1$, d_{calc}=1.250 g/cm^3, μ=0.090 mm^{-1}. The initial array of the measured intensities was processed and absorption was taken into account using the SAINT [11] and SADABS [12] programs (multi-scan, $T_{min.}$ 0.957, $T_{max.}$ 0.981).

The structure was solved via a direct method. The positions of nonhydrogen atoms were refined under anisotropic approximation by full-matrix least-squares method. All hydrogen atoms were put in the geometric positions and refined under isotropic approximation with constant position and heat parameters (*rider* model). The structure was determined and refined using the SHELXS [13] and SHELXL-2018/3 [14] software. A total of 2788 independent reflections with $I \geq 2\sigma(I)$ were used in the calculations and the number of refined parameters was 257.

The final divergence factors were R_1=0.0408, $_wR_2$=0.1068 (for reflections with $I \geq 2\sigma(I)$), R_1 = 0.0495, $_wR_2$ = 0.1145 (for all reflections), *GooF* = 1.032. Peaks of residual density were Δρ = 0.156 and –0.128 e/$Å^3$. The CIF file containing the complete information on the structure examined was deposited in the Cambridge Center for Crystal Structural Data (CCDC) under number 2006552. The atomic coordinates are shown in Table 1.

Table 1

The coordinates of the atoms in the cell fractions (×10^4) and isotropic thermal parameters ($Å^2$, ×10^3) in the structure 1

Atom	*x*	*y*	*z*	$U_{eq.}$
1	2	3	4	5
O1	2036(2)	–776(1)	–151(1)	53(1)
O2A	260(30)	–2216(13)	–487(9)	86(4)
O2B	–100(40)	–1910(20)	–457(17)	91(6)
O3	4808(4)	2953(2)	–612(2)	113(1)
O4A	4186(16)	2035(8)	2583(6)	79(3)

Continuation of Table 1

1	2	3	4	5
O4B	4680(20)	2013(10)	2656(10)	81(5)
C1	4636(3)	1242(2)	1227(1)	47(1)
C2	4828(3)	2253(2)	863(2)	62(1)
C3	4755(4)	2177(2)	–87(2)	70(1)
C4	4627(4)	949(2)	–334(1)	65(1)
C5	4338(3)	327(2)	542(1)	46(1)
C6	2514(2)	–122(2)	630(1)	43(1)
C7	2233(3)	–948(2)	1382(1)	51(1)
C8A	2266(14)	–292(9)	2274(7)	80(3)
C8B	1867(19)	–541(10)	2289(11)	54(2)
C9A	4134(8)	–17(3)	2539(2)	70(2)
C9B	2465(8)	661(5)	2470(3)	54(2)
C10A	4902(12)	1073(8)	2150(6)	54(2)
C10B	4382(16)	957(12)	2275(8)	50(3)
C11A	610(20)	–1552(14)	988(9)	85(4)
C11B	920(30)	–1660(20)	1126(13)	69(4)
C12A	860(20)	–1507(17)	33(9)	72(4)
C12B	870(30)	–1640(30)	152(13)	64(5)
C13A	–717(14)	–1917(9)	1459(6)	114(4)
C13B	–178(19)	–2477(9)	1407(8)	83(3)
C14A	6907(7)	1086(6)	2354(4)	99(2)
C14B	5673(10)	98(6)	2536(4)	73(2)
C15	6255(6)	571(4)	–800(2)	118(2)

Results and Discussions

A colorless substance **1** of the $C_{15}H_{18}O_4$ composition was obtained from the extract of the aerial part of *Tanacetopsis pjataevae* when the column was eluted with a mixture of petroleum ether-ethyl acetate (87.5:12.5).

The IR spectrum of compound **1** contains absorption bands characteristic of the OH group at 3463 cm^{-1}, the carbonyl of the γ-lactone ring at 1750 cm^{-1}, and the C=O bonds at 1707 cm^{-1}, C=C at 1608 cm^{-1}. In the mass spectrum of **1** there is a peak of the molecular ion m/z 262.1 $[M]^+$, which corresponds to the molecular weight.

In the ^{1}H NMR spectrum of molecule **1**, signals of the protons of the methyl group at the C4 atom are observed as a doublet at 2.57 ppm with SSIC 6.0 Hz, protons of the methyl group at the hydroxyl group as a singlet at 1.54 ppm, proton H5 as a doublet at 2.69 ppm with SSIC 11 Hz. Two symmetrical singlets at 5.49 ppm and 6.18 ppm belong to the protons of the exomethylene group ($C11=C13H_2$). The H7 methine proton appears as a multiplet centered at 2.93 ppm, while the H6 lactone proton appears as a triplet at 3.95 ppm with SSIC 10.0 Hz. The vinyl H2 proton appears as a singlet at 6.33 ppm, the hydroxyl proton appears as a doublet at 2.57 ppm with SSIC 6.0 Hz. The nature of the splitting of the signal of the lactone proton indicates that the lactone ring in compound **1** is located at C6-C7 of the main skeleton, and the spin-spin coupling constant indicates its trans junction.

The ^{13}C NMR spectrum of the molecule **1** shows the presence of 5 singlets, 5 doublets, 3 triplets, and 2 quartets. This corresponds to the structural formula of compound **1**.

Based on spectral data, compound **1** was identified as 3-oxo-10β-hydroxy-5,7α(H),6β (H)-guai-1,11(13)-diene-6,12-olide, a new STL of guaiane type (Fig. 1).

An X-ray analysis was performed to finally establish the structure of compound **1**. From the obtained data it follows that there is one molecule **1**, half of whose atoms are statically disordered in two positions, in the independent part of the unitary crystalline cell. The bond lengths (Table 2) and bond angles (Table 3) in compounds **1**

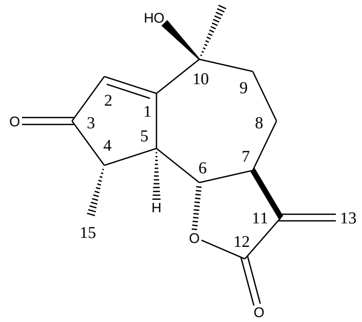


Figure 1. Structural formula of molecule 3-oxo-10β-hydroxy-5,7α(H),6β(H)-guai-1,11(13)-diene-6,12-olide **(1)**

somewhat differ from the usual ones [15]. This is related to the disorder of a number of atoms of structure **1** in the crystalline state.

Table 2

Bond lengths (*d*, Å) in conformers 1a and 1b of the structure 1

Bond	*d*		Bond	*d*	
	1a	**1b**		**1a**	**1b**
O1-C12	1.283(14)	1.44(2)	C4-C15	1.510(3)	1.510(3)
O1-C6	1.470(2)	1.470(2)	C5-C6	1.509(2)	1.509(2)
O2-C12	1.245(11)	1.236(16)	C6-C7	1.523(2)	1.523(2)
O3-C3	1.219(2)	1.219(2)	C7-C8	1.570(8)	1.494(12)
O4-C10	1.429(8)	1.398(12)	C7-C11	1.561(9)	1.372(15)
C1-C2	1.328(2)	1.328(2)	C8-C9	1.531(8)	1.522(9)
C1-C10	1.439(7)	1.648(9)	C9-C10	1.540(6)	1.547(9)
C1-C5	1.523(29)	1.523(29)	C10-14	1.576(8)	1.477(11)
C2-C3	1.455(3)	1.455(3)	C11-12	1.473(10)	1.489(14)
C3-C4	1.506(3)	1.506(3)	C11-13	1.323(10)	1.357(14)
C4-C5	1.544(2)	1.544(2)			

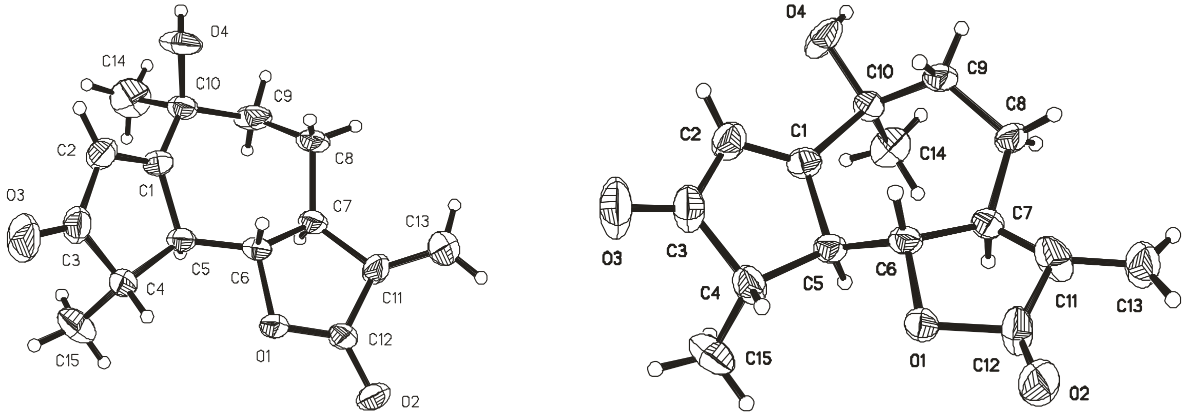
Table 3

Valent angles (ω, deg.) in conformers 1a and 1b of the structure 1

Angle	ω		Angle	ω	
	1a	**1b**		**1a**	**1b**
C12-O1-C6	110.8(4)	105.7(6)	C6-C7-C11	96.7(4)	106.5(6)
C2-C1-C5	111.7(1)	111.7(1)	C6-C7-C8	109.5(3)	121.2(4)
C2-C1-C10	121.3(3)	127.2(4)	C11-C7-C8	125.0(6)	108.8(7)
C10-C1-C5	126.6(3)	120.2(4)	C9-C8-C7	110.4(5)	114.4(7)
C1-C2-C3	110.9(2)	110.9(2)	C8-C9-C10	115.9(5)	117.7(6)
O3-C3-C2	127.4(2)	127.4(2)	O4-C10-C1	106.8(5)	101.6(7)
O3-C3-C4	124.4(2)	124.4(2)	O4-C10-C9	110.0(5)	106.3(8)
C2-C3-C4	108.2(2)	108.2(2)	C1-C10-C9	116.1(5)	110.3(6)
C3-C4-C5	104.7(1)	104.7(1)	O4-C10-C14	106.3(6)	113.0(9)
C3-C4-C15	110.5(2)	110.5(2)	C1-C10-C14	109.3(4)	108.9(6)
C15-C4-C5	112.8(2)	112.8(2)	C9-C10-C14	108.0(5)	115.8(6)
C6-C5-C1	109.2(1)	109.2(1)	C13-C11-C12	130.7(9)	107.9(14)
C6-C5-C4	112.4(1)	112.4(1)	C13-C11-C7	124.0(8)	143.9(11)
C1-C5-C4	103.6(1)	103.6(1)	C12-C11-C7	105.1(7)	107.3(11)
O1-C6-C5	110.3(1)	110.3(1)	O2-C12-O1	125.3(11)	108.8(17)
O1-C6-C7	103.8(1)	103.8(1)	O2-C12-C11	123.9(13)	139.9(18)
C5-C6-C7	115.2(1)	115.2(1)	O1-C12-C11	109.5(8)	108.2(12)

It should be noted that in some STL crystalline structures, disordering of atoms is observed. Usually, some substituents are disordered in the main framework. For example, the phenyl group is disordered in eupatocunin-*o*-bromobenzoate [16], and the isobutyl group is disordered in 8α-isobutyryloxy-9-oxo-germacr-4E,1(10) Z-dien-6β,12-olide [17].

In compounds **1**, an unusual disorder of a part of the atoms of the main framework was observed. An analysis of the data showed that the positions of the atoms in the crystal structure **1** corresponded to two conformers **1a** and **1b** (Fig. 2).



1a **1b**

Figure 2. Conformers **1a** and **1b** of disordered molecule 3-oxo-10β-hydroxy-5,7α(H),6β (H)-guai-1,11(13)-diene-6,12-olide **(1)** (thermal vibration ellipsoids are shown with a probability of 30%)

The conformation of the five-membered carbocycle (A) in both conformers is a strongly flattened, distorted 4α-envelope ((ΔCs^4=2.0º). The seven-membered cycle (B) in conformer **1a** accepts the intermediate conformation between the 7α,1,10β- chair (ΔCs^7=17.1°) и 5,6α,7,8β- twist-chair (ΔC_2^{10}=13.7°), in the conformer, **1b** accepts the intermediate conformation between 7.8α,1β-chair ((ΔCs^1=18.5°) and 1.10α, 5,6β-twist-chair (ΔC_2^8=19.7°). The conformation of lactone cycle in both conformers is a distorted 6β,7α-half-chair (($\Delta C_2^{6,7}$=4.8° and 2.4° for **1a** and **1b**, respectively). Intracyclic torsion angles are illustrated in Table 4.

In the crystal, the ratio of conformers 1a and **1b** is 60:40, and the conformations of the seven-membered cycle in them are significantly distorted relative to the ideal chair and the twist chair. To optimize the geometry of conformers **1a** and **1b**, a quantum chemical calculation was performed using the MOPAC program in the PM6 [10] parameterization. As follows from the obtained calculations, the five-membered carbocycle is slightly flattened in comparison with the X-ray diffraction data and takes in **1a** and **1b** the conformation intermediate between the 4α-envelope and 4α,5β- half-chair (ΔCs^4=2.0°, $\Delta C_2^{4,5}$=1.7°) for **1a** and (ΔCs^4=1.9°, $\Delta C_2^{4,5}$=0.5° for **1b**. The seven-cycle conformation in **1a** and **1b** undergoes the greatest changes. In conformer **1a**, it changes from that observed in the crystal to the intermediate between the 7α,1,10β-chair (ΔCs^7=19.8°) and 8.9α,6,7β-twist-chair (ΔC_2^8=8.8°). In conformer **1b**, the conformation of cycle B is generally preserved, leaning toward a highly distorted 1,10α, 5,6β-twist-chair (ΔC_2^8=8.8°). The lactone cycle is also somewhat flattened, but remains in the conformation of the somewhat distorted 6β,7α-half-chair (3.8º for **1a** and 3.1º for **1b**).

Table 4

Intracyclic torsion angles (τ, degr.) in n conformers 1a and 1b

Angle	τ			
	1a (X-ray)	**1a** (PM6)	**1b** (X-ray)	**1b** (PM6)
1	2	3	4	5
Cycle A				
C5-C1-C2-C3	–2.0(3)	–1.8	–2.0(3)	–1.7
C1-C2-C3-C4	–4.5(3)	–4.0	–4.5(3)	–2.4
C2-C3-C4-C5	8.7(3)	7.7	8.7(3)	5.2
C3-C4-C5-C1	–9.3(2)	–8.5	–9.3(2)	–5.9
C2-C1-C5-C4	7.3(2)	6.7	7.3(2)	5.0
Cycle B				
C10-C1-C5-C6	74.6(5)	47.6	57.6(6)	52.1
C1-C5-C6-C7	–77.8(2)	–90.1	–77.8(2)	–72.5
C5-C6-C7-C8	72.7(5)	84.2	84.4(7)	95.9
C6-C7-C8-C	–77.7(7)	–67.8	–22.2(13)	–43.9
C7-C8-C9-C10	85.4(8)	79.6	–53.5(13)	–36.5
C8-C9-C10-C1	–46.5(9)	–75.5	82.2(11)	83.3
C5-C1-C10-C9	–25.4(9)	20.5	–64.6(10)	–68.0

Continuation of Table 4

1	2	3	4	5
Cycle C				
O1-C6-C7-C11	–35.7(6)	–28.4	–30.1(12)	–20.0
C12-O1-C6-C7	30.6(8)	22.4	24.3(11)	15.7
C6-O1-C12-C11	–8.9(13)	–6.9	–11.0(20)	–4.7
C7-C11-C12-O1	–15.7(15)	–11.9	–8.0(30)	–8.7
C6-C7-C11-C12	31.4(10)	24.3	23.0(20)	17.4

It should be noted that for a free molecule, the heat of formation of conformer **1a** is lower than that of **1b** (ΔH_f = 6.3 kJ/mol. Such a conformation of cycle B (ΔC_2^1=7.8°), as in **1a**, was observed in the structure of hypochaerin [18], which was the only studied by the X-ray diffraction method with the sp^2-hybridized C(1) atom of the seven-membered ring, being consistent with the theory of the implementation of the most stable conformer in the crystal [19].

Conclusions

As a result of the *Tanacetopsis pjataevae* chemical study, an endemic plant of Kazakhstan, a colorless crystalline substance of the $C_{15}H_{18}O_4$ composition with m.p. 189–191°C was isolated. The structure of the obtained new compound according to IR, NMR and mass spectra was determined as 3-oxo-10β-hydroxy-5,7α(H),6β(H)-guai-1,11(13)-diene-6,12-olide. From the data of X-ray diffraction analysis, it was established that the molecule of 3-oxo-10β-hydroxy-5,7α(H),6β(H)-guai-1(2),11(13)-diene-6,12-olide in the crystal was disordered in two conformational states in a ratio of 6:4. Quantum-chemical semi-empirical calculations established that for a free molecule the difference in the heats of formation of conformers was 6.3 kJ/mol.

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Жаңа сесквитерпендік лактон 3-оксо-10β-гидрокси-5,7α(Н),4,6β(Н)-гвай-1,11(13)-диен-6,12-олидтың оқшаулануы және құрылымы

Мақалада Қазақстанның эндемикалық Пятаева танацетопсисі (*Tanacetopsis Pyataeva*) өсімдігінің химиялық зерттеу нәтижелері келтірілген. Экстрактивті заттардың қосындысы гүлдену кезеңінде жиналған өсімдіктің ауада құрғақ ұсақталған жерүсті бөлігінен хлороформмен экстракцияланды. Қосылыстардың индивидуалды түрде бөлінуі КСК маркалы силикагель бағанасында қосындыны – тасымалдаушы = 1:20 қатынасында хроматография әдісімен жүргізілді. Бағананы петролейн эфир-этилацетат (87.5:12.5) қоспасымен элюирлегенде құрамы $C_{15}H_{18}O_4$ болатын, балқу температурасы 189-191°С құрайтын түссіз кристалды зат (диэтилді эфирімен қайта кристаллдандыру) бөлініп алынды. Бөлініп алынған жаңа қосылыстың құрылысы (3-оксо-10β-гидрокси-5,7α(Н),6β(Н)-гвай-1,11(13)-диен-6,12-олид) ИҚ-, ЯМР- және масс-спектрлердің талдау негізінде дәлелденген. Кеңістіктік құрылымы рентген құрылымдық әдіспен анықталған. Кристаллдағы 3-оксо-10β-гидрокси-5,7α(Н),6β(Н)-гвай-1,11(13)-диен-6,12-олид молекуласы 6:4 қатынасында екі конформациялық күйге бөлінгені анықталды. Бұл конформерлердің тұрақтылығы квантты-химиялық жартылай эмпирикалық есептеулермен расталады. Еркін молекула үшін екі конформердің пайда болу жылуының айырмашылығы 6.3 кДж/моль болатындығы белгілі болды.

Кілт сөздер: ЯМР спектроскопиясы, ИҚ спектроскопиясы, масс-спектрометрия, рентгендік дифракциялық талдау, Пятаева танацетопсисі, эндемикалық, 3-оксо-10β-гидрокси-5,7α(Н),6β(Н)-гвай-1,11(13) -диен-6,12-олид, сесквитерпенді лактондар.

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Выделение и структура нового сесквитерпенового лактона 3-оксо-10β-гидрокси-5,7α(Н),4,6β(Н)-гвай-1,11(13)-диен-6,12-олида

В статье приведены результаты химического исследования танацетопсиса Пятаева (*Tanacetopsis Pjataevae*), эндемичного растения Казахстана. Сумма экстрактивных веществ получена экстракцией хлороформом из воздушно-сухой измельченной надземной части растения, собранного в фазу цветения. Выделение соединений проведено методом колоночной хромотографии на колонке с силикагелем марки КСК при соотношении сумма–носитель = 1:20. При элюировании колонки смесью петролейный эфир–этилацетат (87,5:12,5) выделено бесцветное кристаллическое вещество состава $C_{15}H_{18}O_4$ с т. пл. 189–191 °С (перекристаллизация из диэтилового эфира). Строение полученного нового соединения (3-оксо-10β-гидрокси-5,7α(Н),6β(Н)-гвай-1,11(13)-диен-6,12-олида) установлено на основании анализа ИК-, ЯМР- и масс-спектров. Пространственная структура определена рентгеноструктурным методом. Установлено, что молекула 3-оксо-10β-гидрокси-5,7α(Н),6β(Н)-гвай-1,11(13)-диен-6,12-олида в кристалле разупорядочена по двум конформационным состояниям в соотношении 6:4. Устойчивость этих конформеров подтверждена квантово-химическими полуэмпирическими расчетами. Отмечено, что для свободной молекулы разница теплот образования двух конформеров составляет 6,3 кДж/моль.

Ключевые слова: ЯМР-спектроскопия, ИК-спектрпоскопия, масс-спектрометрия, рентгеноструктурный анализ, танацетопсис Пятаева, эндемик, 3-оксо-10β-гидрокси-5,7α(Н),6β(Н)-гвай-1,11(13)-диен-6,12-олид, сесквитерпеновые лактоны.

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