

QUANTUM CHEMICAL ANALYSIS OF THE MOLECULAR STRUCTURE AND VIBRATIONAL SPECTRUM OF ARGLABIN

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Results of a theoretical study of the molecular structure of arglabin are presented. Quantum chemical calculations of the geometry and physicochemical characteristics of arglabin are performed by the semi-empirical PM6 method, the non-empirical Hartree–Fock method, and the hybrid B3LYP DFT method with 6-31G and 6-31G(*d*) basis sets. By the B3LYP/6-31G(*d*) method the vibrational frequencies and intensities of IR absorption bands of arglabin are also calculated and the detailed interpretation of the IR spectrum is given. The theoretical frequencies are well consistent with the experimental data.

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INTRODUCTION

Natural guaianolide arglabin is extracted from an endemic plant growing exclusively in Central Kazakhstan – glacier wormwood (*Artemisia glabella* Kar. et Kir.) [1, 2]. Arglabin belongs to sesquiterpenic γ -lactones of the guaianolide type [1-4] and apart from the γ -lactone ring, its structure contains the epoxy group and the olefinic bond in the ring. The mentioned groups provide the biological activity of the compound, in particular, antitumor, immunomodulatory, and radiation-sensitizing properties. The antitumor drug prepared based on arglabin also has immunomodulatory properties and decreases the risk of metastasis [1-3].

As it has previously been determined by chemical and physical (PMR, IR, X-ray crystallography, and mass spectrometry) methods [1-4], arglabin of the composition $C_{15}H_{18}O_3$ has the configuration $1\beta,10\beta$ -epoxy-5,7 α ,6 β (H)-guaia-3(4),11(13)-dien-6,12-olide.

In this work, a comparative analysis of the results of quantum chemical calculations of the molecular structure, vibrational absorption spectrum, and previously obtained experimental data was performed and also all bands were assigned in the IR spectrum of arglabin. The knowledge of the vibrational motion is essential for the understanding of the mechanism of the biological activity of sesquiterpenic lactones.

CALCULATION METHODS

In the first approximation, calculations of the equilibrium geometry of the molecule were carried out by the semi-empirical PM6 method [5]. For the refinement of the molecular energy the non-empirical Hartree–Fock method with 6-31G

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and 6-31G(*d*) split valence basis sets (single point calculations) was employed (B3LYP/6-31G method using the Gaussian program [6]). The vibrational frequencies and intensities of the IR absorption bands of arglabin were calculated by the density functional method with the Becke 3 Lee Yang Parr correlation functional (DFT/B3LYP) [7] with the 6-31G(*d*) basis set, the accuracy of which surpasses all the known non-empirical methods in the calculation of the vibrational spectra of molecules. In order to achieve the best agreement between the theoretical vibrational frequencies and experimental values a scaling factor of 0.9613 was used (the B3LYP/6-31G(*d*) method) [8].

RESULTS AND DISCUSSION

Fig. 1 shows three-dimensional models of the arglabin molecule constructed based on the quantum chemical and X-ray crystallographic data and also the experimental and theoretical absorption spectra. As seen from Fig. 1*a, b*, the geometric configuration of the arglabin molecule, optimized by the B3LYP/6-31G(*d*) method, completely corresponds to the experimentally found structure of the molecule [4]. The PM6 method yields a similar result. The calculated structural parameters and physicochemical characteristics of the arglabin molecule are listed in Table 1. The semi-empirical and non-empirical methods in general overestimate bond lengths in the molecule (by 0.01-0.06 Å). A deviation of the bond angles from the experimental values varies within 0.1-4.9° (PM6) and 0.1-2.4° (B3LYP/6-31G(*d*)). For the dihedral angles mainly the B3LYP/6-31G(*d*) method yields the values close to the experimental ones (Table 1). As a whole, the B3LYP/6-31G(*d*) and X-ray crystallographic methods yield the consistent results two times more often than PM6 and X-ray crystallography.

Table 1 demonstrates the improvement of the calculation results with an increase in the calculation level. With the use of the obtained data and correcting parameters for calculations in the 6-31G(*d*) basis set we also calculated the formation heat of arglabin under the standard conditions. By means of approximate methods using the enthalpies of combustion and melting the enthalpies of the formation of liquid (-336.7 kJ/mol) and crystalline (-385.2 kJ/mol) arglabin at 298.15 K have previously been estimated [9].

As seen from the data obtained, the quantum chemical values and the formation heats of the authors of [9] are different in the absolute value. This is likely to be explained by that the quantum calculations were performed for the molecule in the gas phase, however, the signs and orders of magnitude of the formation heats are the same. At the same time, the semi-empirical calculations yield a value closer to the data of [9]. A comparison of the Hartree-Fock and B3LYP methods with the identical basis set functions counts in favor of the latter. The density functional method gives the improved values of not only total energy but also dipole moment (Table 1). A considerable dipole moment of the molecule, which indicates a high reactivity of arglabin is common for all methods that we used (numerous reactions of arglabin have been known [1-3]).

Analysis of the vibrational spectrum of the arglabin molecule. The vibrational spectrum of the arglabin molecule consisting of 36 atoms contains 102 normal vibrations. According to [10], in the experimental IR spectrum of arglabin the absorption bands are observed at 1778 cm⁻¹ and 1666 cm⁻¹, which correspond to the vibrations of C=O and C=C bonds respectively, and at 1156-1062 cm⁻¹ (C-O-C), 3040 cm⁻¹, 1252 cm⁻¹, 931 cm⁻¹ (the epoxide ring). The full IR spectrum of arglabin has not been discussed so far. Fig. 1*c, d* displays the experimental IR absorption spectrum (in the transmission intensity, % – wavenumber, cm⁻¹ coordinates) and the theoretical quantum chemical vibrational spectrum (in the absorption coefficient – wavenumber or frequency coordinates) of arglabin. Table 2 summarizes the theoretically B3LYP calculated forms of stretching vibrations, their frequencies and intensities in comparison with the experimental data.

In the experimental spectrum of arglabin a weak band is observed at 3511 cm⁻¹, which, in our opinion, corresponds to O-H stretching vibrations of adsorbed water, characteristic of liquid water in the range 3480±20 cm⁻¹ [11, 12]. This can be a consequence of the use of not completely dried potassium bromide. It is obvious that in the theoretically calculated spectrum of arglabin this band is absent. It is this fact that made it possible not to assign this band to the first overtone of C=O absorption. Yet another absorption band ν_{exp} 1869 cm⁻¹, which is also absent in the theoretical spectrum, corresponds, in our opinion, to water molecules originating from atmospheric absorption. According to the data of the B3LYP/6-31G(*d*)

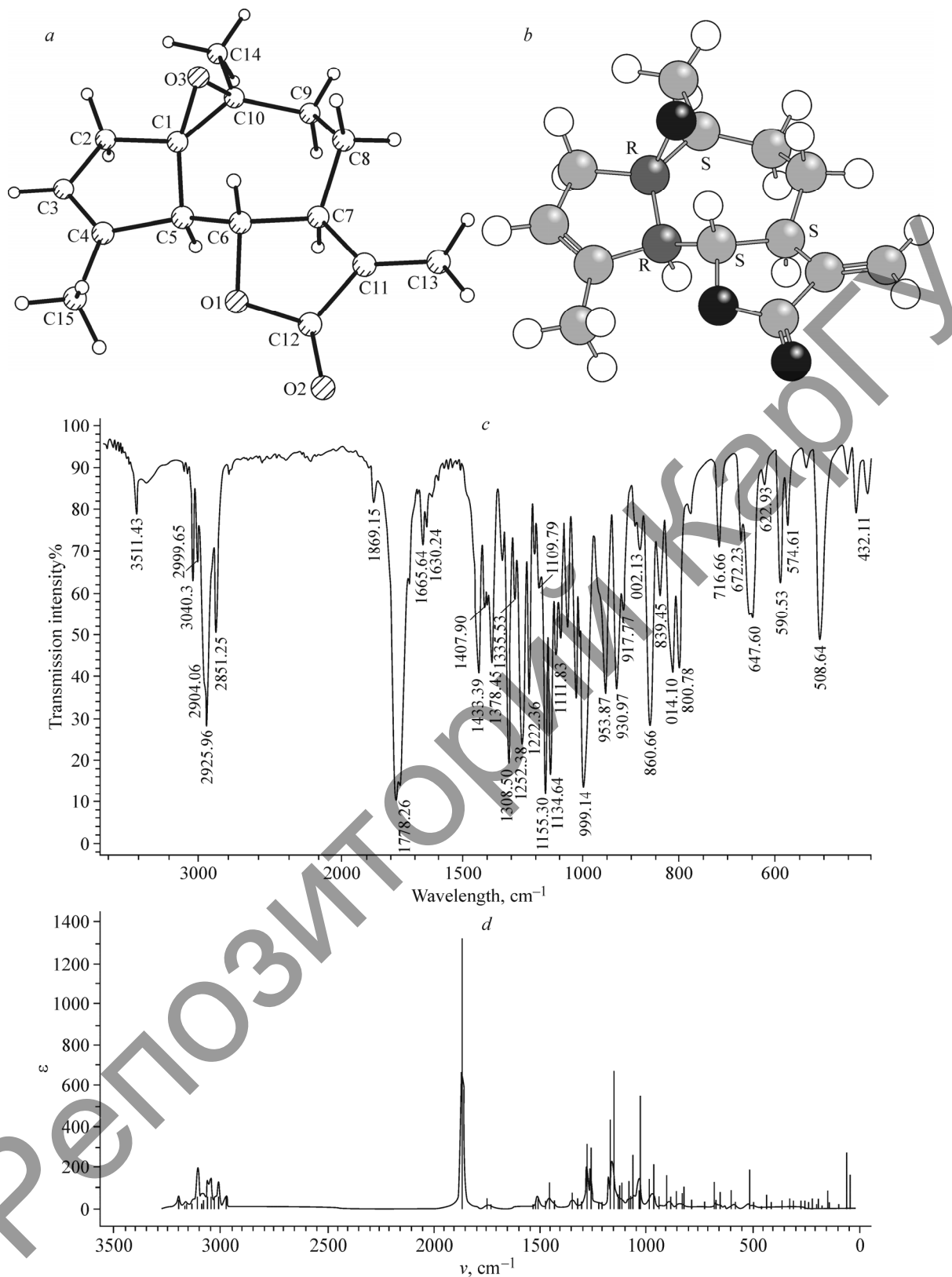


Fig. 1. Molecular structure of arglabin according to the X-ray crystallographic data (a) [4] and B3LYP/6-31G(d) (with the designation of stereochemical centers) (b); experimental IR absorption spectrum [10] (c), and B3LYP/6-31G(d) calculated vibrational spectrum (d) of arglabin.

TABLE 1. Structural Parameters from the Data of Quantum Chemical Calculations and X-ray Crystallography [6], Energy of the Ground State (E), Formation Heat ($\Delta_f H$), and Dipole Moment (μ) of the Arglabine Molecule

Bond	Bond length R , Å			Angle	Bond angle α , deg		
	Calculation		Experiment [4]		Calculation		Experiment [4]
	PM6	B3LYP/6-31G(d)			PM6	B3LYP/6-31G(d)	
C ¹ –C ²	1.53	1.54	1.53	C ¹ C ² C ³	103.7	102.7	102.5
C ¹ –C ¹⁰	1.52	1.48	1.46	C ¹ C ⁵ C ⁴	102.9	102.6	101.7
C ¹ –O ³	1.47	1.45	1.46	C ¹ C ⁵ C ⁶	109.2	111.7	114.1
C ² –C ³	1.51	1.50	1.49	C ¹ O ³ C ¹⁰	62.2	61.6	60.2
C ³ –C ⁴	1.35	1.34	1.32	C ² C ³ C ⁴	112.4	113.6	113.0
C ⁴ –C ⁵	1.53	1.53	1.52	C ³ C ⁴ C ⁵	111.2	110.4	110.6
C ⁴ –C ¹⁵	1.48	1.50	1.50	C ³ C ⁴ C ¹⁵	127.8	125.5	126.0
C ⁵ –C ⁶	1.52	1.53	1.51	C ⁴ C ⁵ C ⁶	117.5	118.0	119.1
C ⁶ –C ⁷	1.56	1.54	1.52	C ⁵ C ⁴ C ¹⁵	121.0	123.9	123.3
C ⁶ –O ¹	1.47	1.46	1.47	C ⁵ C ⁶ C ⁷	111.6	114.3	114.5
C ⁷ –C ⁸	1.53	1.53	1.50	C ⁶ C ⁷ C ⁸	111.5	116.0	115.7
C ⁷ –C ¹¹	1.51	1.51	1.51	C ⁶ C ⁷ C ¹¹	102.5	100.6	100.7
C ⁸ –C ⁹	1.54	1.54	1.53	C ⁶ O ¹ C ¹²	109.7	110.1	109.7
C ⁹ –C ¹⁰	1.52	1.53	1.51	C ⁷ C ⁶ O ¹	104.3	103.8	104.2
C ¹⁰ –C ¹⁴	1.51	1.52	1.52	C ⁷ C ⁸ C ⁹	111.5	113.9	113.5
C ¹¹ –C ¹²	1.50	1.50	1.48	C ⁸ C ⁹ C ¹⁰	114.7	116.9	117.8
C ¹¹ –C ¹³	1.33	1.33	1.31	C ⁹ C ¹⁰ C ¹	122.3	123.7	125.4
C ¹² –O ¹	1.40	1.37	1.36	C ⁹ C ¹⁰ C ¹⁴	114.3	112.5	112.3
C ¹² –O ²	1.20	1.21	1.19	C ¹⁰ C ¹ C ⁵	124.4	126.7	128.6
				Dihedral angle, deg			
C ² C ³ C ⁴ C ⁵	–2.9	–1.9	0.0	H ⁶ C ⁶ C ⁷ H ⁷	–163.4	–167.4	–167.8 (–162.5)*
O ³ C ¹ C ⁵ H ⁵	–131.6	–135.5	–143.8 (–138.6)*	C ⁸ C ⁹ C ¹⁰ C ¹	–56.0	–51.9	–44.9 (–54.1)*
C ⁵ C ¹ C ¹⁰ C ⁹	–1.8	–0.8	–1.3 (–0.4)*	C ¹⁰ C ¹ C ⁵ C ⁶	58.7	53.5	45.3 (50.3)*
Physicochemical characteristics							
Parameter	PM6	HF/6-31G	HF/6-31G(d)	B3LYP/6-31G	B3LYP/6-31G(d)		
E , au	–	–802.665187	–803.021981	–807.812170	–808.056592		
$\Delta_f H$, kJ/mol	–360.057	–	–226.363	–	–		
μ , D	5.999	6.511	5.789	5.566	5.056		

* Data are given for two crystallographically independent molecules.

method, C–H stretching vibrations in the CH₃, CH₂, and CH groups of arglabine are observed in the range 3123–2854 cm^{–1}. Very low-intensity vibrational mode 102 belongs to vibrations of the C¹³–H bond with a frequency of 3123 cm^{–1} (Table 2).

Asymmetrical C–H vibrations of methyl and methylene groups lie in the higher frequency region than symmetrical ones. Absorption observed in the experimental spectrum in the range 3040–2850 cm^{–1} gives a composite band with a maximum at 2926 cm^{–1} which corresponds to C–H stretching vibrations of methyl and methylene groups. The medium intensity peak with ν_{exp} 3040 cm^{–1} is assigned to C–H stretching vibrations of the methyl group (mode 99 with ν_{calc} 3038 cm^{–1} belongs to C–H asymmetrical vibrations of the C¹⁴H₃ group at the epoxide ring). The mentioned vibrations mix with the vibrations of methylene and methine groups.

TABLE 2. Experimental and Theoretical (B3LYP/6-31G(*d*) method) Frequencies (ν) and Intensities (I) of Stretching, Moderate- and Low-Frequency Vibrations in the Arglabin Molecule

Type of vibrations	Frequency (ν), cm^{-1}		I , km/mol	Type of vibrations	Frequency (ν), cm^{-1}		I , km/mol
	Calc.	Exp. [10]			Calc.	Exp. [10]	
1	2	3	4	5	6	7	8
$\nu(\text{O-H})^*$	–	3511	–	$\nu_s(\text{C}^{14}\text{H}_3)$, $\nu_{as}(\text{C}^9\text{H}_2)$,	2935		23
$\nu_{as}(\text{C}^{13}\text{H}_2)$ (102)**	3130	3040	3	$\nu_{as}(\text{C}^8\text{H}_2)$ (91)			
$\nu(\text{C}^3\text{-H})$ (101)	3076		23	$\nu_{as}(\text{C}^8\text{H}_2)$, $\nu_{as}(\text{C}^9\text{H}_2)$ –	2932		19
$\nu_s(\text{C}^{13}\text{H}_2)$ (100)	3048		6	in phase opposition (90)			
$\nu_{as}(\text{C}^{14}\text{H}_3)$ (99)	3038		17	$\nu_s(\text{C}^{15}\text{H}_3)$ (89)	2931	2926	27
$\nu_{as}(\text{C}^{15}\text{H}_3)$ (98)	3011		19	$\nu_{as}(\text{C}^8\text{H}_2)$, $\nu_s(\text{C}^9\text{H}_2)$ –			22
$\nu_{as}(\text{C}^{14}\text{H}_2)$ (97)	2989	3000	25	in phase opposition,	2911		
$\nu_{as}(\text{C}^{15}\text{H}_3)$ (96)	2988		22	$\nu_s(\text{C}^{14}\text{H}_3)$			
$\nu_{as}(\text{C}^8\text{H}_2)$ (95)	2985		17	(88)			
$\nu(\text{C}^6\text{-H})$, $\nu_{as}(\text{C}^8\text{H}_2)$,	2971		10	$\nu_{as}(\text{C}^2\text{H}_2)$ (87)	2895		36
$\nu(\text{C}^{5,7}\text{-H})$ (94)		2964	14	$\nu(\text{C}^5\text{-H}$ и $\text{C}^7\text{-H})$ (86)	2864		28
$\nu_{as}(\text{C}^2\text{H}_2)$ (93)	2965		14	(85)	2854	2852	7
$\nu_{as}(\text{C}^9\text{H}_2)$, $\nu_{as}(\text{C}^8\text{H}_2)$ (92)	2948		39	$\nu(\text{C}^{12}=\text{O}^2)$ (84)	1795	1778	352
				$\nu(\text{C}^{11}=\text{C}^{13})$ (83)	1679	1666	12
				$\nu(\text{C}^3=\text{C}^4)$ (82)	1666	1630	1
Moderate frequencies							
$\nu(\text{C}^1\text{-C}^{10})$, $\delta(\text{C}^1\text{O}^3\text{C}^{10})$,	1474		3	$\nu(\text{C}^7\text{-C}^8)$, $\text{O}^1\text{-C}^{12}$,	1095		5
$\delta(\text{C}^{14}\text{H}_3)$, $\delta(\text{C}^9\text{H}_2)$ (81)			5	$\text{C}^{11}\text{-C}^{12}$, $\tau(\text{C}^2\text{H}_2)$,		1092	
$\delta(\text{C}^{14}\text{H}_3)$, $\delta(\text{C}^9\text{H}_2)$,	1465			$\delta(\text{lactone ring})$,			
$\delta(\text{C}^2\text{H}_2)$ (80)				$\rho(\text{C}^{13}\text{H}_2, \text{C}^{14}\text{H}_3)$ (52)			
$\delta(\text{C}^{15}\text{H}_3)$, $\delta(\text{C}^2\text{H}_2)$ (79)	1457		13	$\nu(\text{C-C}, \text{O}^1\text{-C}^{12})$,	1081		18
$\delta(\text{C}^8\text{H}_2, \text{C}^9\text{H}_2, \text{C}^2\text{H}_2)$ (78)	1456	1433	4	$\delta(\text{C}^{11}\text{C}^{13}\text{H}_2)$, $\delta(\text{C}^5\text{H}, \text{C}^7\text{H})$,			
$\delta(\text{C}^8\text{H}_2)$, $\delta(\text{C}^9\text{H}_2)$,	1452		7	skeleton rocking (51)	1074		19
$\delta(\text{C}^{14}\text{H}_3)$ (77)				$\nu(\text{C-C}, \text{C}^6\text{-O}^1, \text{O}^1\text{-C}^{12})$,			
$\delta(\text{C}^{15}\text{H}_3)$, $\delta(\text{C}^2\text{H}_2)$ (76)	1449		7	$\tau(\text{C}^2\text{H}_2)$, $\rho(\text{C}^{13}\text{H}_2, \text{C}^{14}\text{H}_3)$		1063	
$\delta(\text{C}^2\text{H}_2)$, $\delta(\text{C}^{15}\text{H}_3)$,	1447		0,4	(50)	1046		21
$\delta(\text{C}^{14}\text{H}_3)$ (75)				$\nu(\text{C-C}, \text{C}^1\text{-O}^3)$, $\delta(\text{C}^7\text{H})$,			
$\nu(\text{C}^1\text{-C}^{10})$, $\delta(\text{C}^2\text{H}_2)$,	1415		8	skeleton rocking,	1036		7
$\delta(\text{C}^1\text{O}^3\text{C}^{10})$, $\delta(\text{C}^8\text{H}_2)$,				stronger – 7-memb. ring,			
$\delta(\text{C}^9\text{H}_2)$, $\delta(\text{C}^{14}\text{H}_3)$ (74)		1408		rocking C^{14}H_3 , C^{15}H_3 (49)			
$\nu(\text{C}^{11}\text{-C}^{13})$, $\delta(\text{C}^{13}\text{H}_2)$ (73)	1401		24	$\nu(\text{C}^1\text{-C}^2, \text{C}^1\text{-O}^3, \text{C}^5\text{-C}^6)$,			
$\delta(\text{C}^{15}\text{H}_3)$ (72)	1394		2	$\rho(\text{C}^{14}\text{H}_3, \text{C}^{15}\text{H}_3)$,		1027	
$\delta(\text{C}^{14}\text{H}_3)$ (71)	1386		6	skeleton rocking (48)			
$\nu(\text{C-C})$, $w(\text{C}^8\text{H}_2)$, (70)	1374	1379	9	$\nu(\text{C}^2\text{-C}^3, \text{O}^1\text{-C}^{12}, \text{C}^6\text{-O}^1)$,	1021		39
$\delta(\text{CH})$ (69)	1365		0,4	$\text{C}^4\text{-C}^{15}$, $\rho(\text{C}^{15}\text{H}_3)$, $\delta(\text{C}^3\text{H})$,			
$\nu(\text{C-C})$, $\tau(\text{C}^8\text{H}_2)$,	1353		2	rocking C^{14}H_3 (47)			
$w(\text{C}^9\text{H}_2)$, $\delta(\text{CH})$ (68)		1336		$\nu(\text{C-C}, \text{C}^6\text{-O}^1)$, $\rho(\text{C}^{14}\text{H}_3)$,	1015		2
				C^{15}H_3 , $\delta(\text{C}^3\text{H}, \text{C}^7\text{H})$ (46)			
				$\nu(\text{C-C}, \text{C}^1\text{-O}^3, \text{C}^6\text{-O}^1)$,	1003		12

TABLE 2. (Cont.)

1	2	3	4	5	6	7	8
$\nu(\text{C}-\text{C}), w(\text{C}^8\text{H}_2),$ $\delta(\text{CH})$ (67)	1329		2	$\rho(\text{C}^{14}\text{H}_3), \rho(\text{C}^2\text{H}_2),$ $\tau(\text{C}^8\text{H}_2),$ $\delta(\text{C}^3\text{H}, \text{C}^7\text{H}),$			
$\nu(\text{C}-\text{C}), \nu(\text{O}^1-\text{C}^6,$ $\text{O}^1-\text{C}^{12}), \tau(\text{C}^8\text{H}_2), \delta(\text{CH}),$ skeleton rocking (66)	1302	1309	13	skeleton rocking (45) $(\text{C}^6-\text{O}^1, \text{O}^1-\text{C}^{12}, \text{C}-\text{C}),$ $\rho(\text{C}^{14}\text{H}_3), \rho(\text{C}^9\text{H}_2),$ $\delta(\text{C}^3\text{H}),$	994	999	81
$\nu(\text{C}-\text{C}), w(\text{C}^8\text{H}_2), \tau(\text{C}^9\text{H}_2),$ $\delta(\text{CH}),$ skeleton rocking (65)	1296		14	skeleton rocking (44) $\nu(\text{C}-\text{C}), \rho(\text{C}^{15}\text{H}_3), \rho(\text{C}^2\text{H}_2,$ $\text{C}^{13}\text{H}_2), \delta(\text{C}^3\text{H}, \text{C}^5\text{H})$ (43)	962		2
$\nu(\text{C}-\text{C}), w(\text{C}^2\text{H}_2),$ $\tau(\text{C}^8\text{H}_2, \text{C}^9\text{H}_2), \delta(\text{CH}),$ skeleton rocking, stronger – 5-memb. (64) carbocycle (63)	1287 1274		1 9	$\nu(\text{C}-\text{C}, \text{C}^6-\text{O}^1), \rho(\text{C}^{15}\text{H}_3),$ $\rho(\text{C}^2\text{H}_2, \text{C}^9\text{H}_2, \text{C}^{13}\text{H}_2),$ $\delta(\text{C}^5\text{H}, \text{C}^7\text{H}),$ rocking $\text{C}^{14}\text{H}_3, \text{C}^{15}\text{H}_3$ (42)	950	954	12
$\nu(\text{C}-\text{C}), w(\text{C}^2\text{H}_2), \tau(\text{C}^8\text{H}_2,$ $\text{C}^9\text{H}_2), \delta(\text{C}^5\text{H}, \text{C}^6\text{H}),$ skeleton rocking (62)	1256	1252	4	$\nu(\text{C}-\text{C}, \text{C}^6-\text{O}^1), \rho(\text{C}^{15}\text{H}_3),$ $w(\text{C}^2\text{H}_2), \delta(\text{C}^3\text{H}),$ skeleton rocking (41) $w(\text{C}^{13}\text{H}_2)$ (40)	944		19
$\nu(\text{C}-\text{C}, \text{C}^{12}-\text{O}^1), \delta(\text{CH}),$ $\tau(\text{C}^8\text{H}_2, \text{C}^9\text{H}_2), \rho(\text{C}^{13}\text{H}_2),$ skeleton rocking (61)	1233		54	$\nu(\text{O}^3-\text{C}^{10}, \text{C}-\text{C}), \rho(\text{C}^{14}\text{H}_3),$ $\tau(\text{C}^8\text{H}_2), \rho(\text{C}^{13}\text{H}_2), \delta(\text{C}^5\text{H},$ $\text{C}^7\text{H})$ (39)	930 903	931	29 7
$\nu(\text{C}^{12}-\text{O}^1), \nu(\text{C}^{11}-\text{C}^{12}),$ $w(\text{C}^2\text{H}_2, \text{C}^8\text{H}_2), \tau(\text{C}^9\text{H}_2),$ $\delta(\text{CH}),$ skeleton rocking (59)	1230 1214	1222	58 54	$\nu(\text{C}^1-\text{O}^3, \text{O}^3-\text{C}^{10}, \text{C}^4-\text{C}^5,$ $\text{C}^6-\text{C}^7), \rho(\text{C}^{14}\text{H}_3), \tau(\text{C}^8\text{H}_2),$ $\rho(\text{C}^2\text{H}_2, \text{C}^9\text{H}_2, \text{C}^{13}\text{H}_2),$ $\delta(\text{C}^5\text{H}, \text{C}^7\text{H})$ (38)	872		3
$\nu(\text{C}-\text{C}), \tau(\text{C}^2\text{H}_2), \tau(\text{C}^8\text{H}_2,$ $\text{C}^9\text{H}_2), \rho(\text{C}^{13}\text{H}_2), \delta(\text{C}^5\text{H},$ $\text{C}^7\text{H}),$ skeleton rocking (58)	1183		6	$\nu(\text{C}^1-\text{O}^3, \text{O}^3-\text{C}^{10}, \text{C}^4-\text{C}^5,$ $\text{C}^6-\text{C}^7), \rho(\text{C}^{14}\text{H}_3), \tau(\text{C}^8\text{H}_2),$ $\rho(\text{C}^2\text{H}_2, \text{C}^9\text{H}_2, \text{C}^{13}\text{H}_2),$ $\delta(\text{C}^5\text{H}, \text{C}^7\text{H}),$ skeleton rocking (37)	867	861	20
$\nu(\text{C}^{10}-\text{C}^{14}), \tau(\text{C}^2\text{H}_2, \text{C}^8\text{H}_2),$ $w(\text{C}^9\text{H}_2), \tau(\text{epoxide ring}),$ $\delta(\text{C}^3\text{H}, \text{C}^5\text{H}, \text{C}^7\text{H})$ (57)	1165		3	$\nu(\text{C}-\text{C}), \rho(\text{CH}_2)$ (36) $\nu(\text{C}-\text{C}), \rho(\text{CH}_2), \tau(\text{C}^2\text{H}_2)$ (35)	852 825	840 814	7 11
$\tau(\text{C}^2\text{H}_2, \text{C}^8\text{H}_2, \text{C}^9\text{H}_2),$ $\rho(\text{C}^{13}\text{H}_2), \delta(\text{C}^9\text{H}, \text{C}^7\text{H})$ (56)	1161		1	$\nu(\text{C}-\text{C}), \rho(\text{CH}_2),$ rocking CH_3 (34) $\tau(\text{C}^{13}\text{H}_2),$	805	801	9 12
$\nu(\text{C}^4-\text{C}^{15}, \text{C}^5-\text{C}^6),$ $\delta(5\text{-memb. ring}), \tau(\text{C}^2\text{H}_2,$ $\text{C}^8\text{H}_2), \rho(\text{C}^3\text{H}_2, \text{C}^{13}\text{H}_2),$ $\delta(\text{C}^3\text{H}, \text{C}^5\text{H}, \text{C}^6\text{H})$ (55)	1158	1155	5	skeleton rocking (33) $\nu(\text{C}-\text{C}), \rho(\text{CH}_2),$ rocking CH_3 (32)	796 791		3
$\nu(\text{C}-\text{C}, \text{O}^1-\text{C}^{12}), \delta(\text{CH}),$ skeleton rocking (54)	1129		72	$\nu(\text{C}-\text{C}), \rho(\text{CH}_2), \delta(\text{CO}^1\text{C}),$ $\delta(\text{C}^3\text{H}),$ breathing vibrations of the rings, rocking CH_3 (31)	762		4
$\nu(\text{C}-\text{C}, \text{O}^1-\text{C}^{12}), \tau(\text{C}^2\text{H}_2),$ $\delta(\text{C}^{11}\text{C}^{13}\text{H}), \delta(\text{CH})$ (53)	1109	1112	111	$\nu(\text{C}-\text{C}), \tau(\text{CH}_2), \delta(\text{CO}^1\text{C}),$ $\delta(\text{C}^6\text{H}, \text{C}^7\text{H})$ (30)	698	717	3

TABLE 2. (Concl.)

1	2	3	4	5	6	7	8
Low frequencies							
$\nu_{as}(\text{O}^3\text{C}_2)$, $\nu(\text{C}^9-\text{C}^{10})$, $\nu(\text{C}^4-\text{C}^{15})$, $\delta(\text{C}^1\text{C}^2\text{C}^3)$,	660	672	12	rocking of the whole skeleton, $\rho(\text{C}^8\text{H}_2)$, rocking C^{15}H_3 (15)	309		0.2
$\delta(\text{C}^2\text{C}^3\text{C}^4)$, $\delta(\text{C}^3\text{C}^4\text{C}^5)$,				rocking of the whole skeleton, $\rho(\text{C}^{11}\text{C}^{13}\text{H}_2)$ (14)	301		2
$\rho(\text{C}^8\text{H}_2)$ (29) $\tau(\text{C}^{13}\text{H}_2)$, $\rho(\text{C}^8\text{H}_2)$,	652	648	4	skeleton rocking (13)	275		0.1
$\nu(\text{C}^4-\text{C}^{15})$, $\delta(\text{O}^1\text{C}^{12}\text{C}^{11})$, $\delta(\text{C}^1\text{C}^2\text{C}^3)$ (28)				(12)	264		2
$\nu(\text{C}^6-\text{C}^7)$, $\delta(\text{O}^1\text{C}^{12}\text{C}^{11})$, $\delta(\text{C}^6\text{O}^1\text{C}^{12})$, $\delta(\text{C}^2\text{C}^3\text{C}^4)$, $\delta(\text{C}^{12}\text{C}^{11}\text{C}^{13})$ (27)	630	623	7	skeleton rocking, $\rho(\text{C}^2\text{H}_2)$, $\rho(\text{C}^{11}\text{C}^{13}\text{H}_2)$, $\tau(\text{C}^{15}\text{H}_3)$ (11)			
$\tau(\text{C}^{13}\text{H}_2)$, $\rho(\text{C}^8\text{H}_2)$, $\tau(\text{lactone ring})$ (26)	606	591	2	skeleton rocking, stronger – 7-memb. ring, $\rho(\text{C}^2\text{H}_2)$, $\rho(\text{C}^{14}\text{H}_2)$, $\rho(\text{C}^{11}\text{C}^{13}\text{H}_2)$, rocking C^{15}H_3 (10)	235		1
$\tau(\text{C}^{13}\text{H}_2)$, rocking C^{15}H_3 , $\rho(\text{C}^8\text{H}_2)$, $\rho(\text{C}^2\text{H}_2)$ (25)	578	575	8	skeleton rocking, $\tau(\text{C}^{14}\text{H}_3)$,	214		1.5
$\rho(\text{C}^8\text{H}_2)$, $\delta(\text{C}^8\text{C}^9\text{C}^{10})$, rocking C^{14}H_3 (24)	562		3	$\tau(\text{C}^{15}\text{H}_3)$ (9) (8)	194		1
$\delta(\text{C}^1\text{C}^{10}\text{C}^9)$, $\delta(\text{O}^3\text{C}^{10}\text{C}^9)$, $\delta(\text{C}^6\text{C}^7\text{C}^{11})$, skeleton rocking (23)	514		1	skeleton rocking, stronger – 7-memb. and lactone rings, $\rho(\text{C}^9\text{H}_2)$, $\rho(\text{C}^{14}\text{H}_3)$ (7)	190		1
$\delta(\text{C}^3\text{C}^4\text{C}^{15}\text{H}_3)$, $\delta(\text{C}^5\text{C}^4\text{C}^{15}\text{H}_3)$, $\delta(\text{C}^2\text{C}^1\text{O}^3)$, $\delta(\text{O}^1\text{C}^{12}\text{O}^2)$, $\delta(\text{C}^7\text{C}^{11}\text{C}^{12})$ (22)	496	509	14	skeleton rocking, $\tau(\text{C}^{14}\text{H}_3)$, $\rho(\text{C}^{15}\text{H}_3)$ (6)	173		0.2
rocking of the whole skeleton, $\rho(\text{C}^2\text{H}_2)$, $\rho(\text{C}^9\text{H}_2)$, rocking C^{15}H_3 (21)	482		2	rocking of the whole skeleton, $\delta(5\text{-memb. ring})$ (5)	148		2
skeleton rocking, $\rho(\text{C}^2\text{H}_2)$ rocking C^{15}H_3 (20)	441	432	1	rocking of the whole skeleton, rocking (C^{14}H_3), (C^{15}H_3) (4)	136		1
rocking of the whole skeleton, stronger – 7-memb. ring, rocking C^{14}H_3 (19)	416		4	skeleton rocking (breathing vibration) (3)	98		0.3
skeleton rocking, $\rho(\text{C}^2\text{H}_2)$ rocking C^{15}H_3 , $\rho(\text{C}^8\text{H}_2)$ (18)	402		2	rocking of the whole skeleton, rocking ($\text{C}^{11}\text{C}^{13}\text{H}_2$) (2)	63		3
skeleton rocking, $\rho(\text{C}^2\text{H}_2)$ rocking C^{15}H_3 (17)	348		2	rocking of the whole skeleton (1)	45		1
skeleton rocking, $\rho(\text{C}^8\text{H}_2)$ $\rho(\text{C}^9\text{H}_2)$, breathing vibration of the 7-memb. ring (16)	313		2				

* ν is the stretching vibration, ν_{as} is asymmetrical stretching, ν_s is symmetrical stretching, $\nu(\text{C}-\text{C})$ are stretching vibrations of the carbon skeleton; bending vibrations: δ is a change in the bond angle; ρ is rocking; w is wagging; τ is twisting; $\delta(\text{ring})$ is the vibration of the ring.

** Corresponding mode.

The highest intensity band in the experimental IR spectrum ($\nu_{\text{exp}} 1778 \text{ cm}^{-1}$) is due to stretching vibrations of the polar C=O bond. The calculated value $\nu_{\text{calc}} (\text{C}^{12}=\text{O}^2)$ is 1795 cm^{-1} . The mentioned frequencies are much higher than the respective value for ketones (1715 cm^{-1}), which is supported by the well-known fact of an increase in the vibrational frequency of the carbonyl group. This increase is induced by an electron acceptor such as the oxygen atom conjugated with this group. The bond order does not change, which is indicated by the length of the $\text{C}^{12}=\text{O}^2$ band (Table 1). The stretching modes of C=C double bonds ($\text{C}^3=\text{C}^4$ and $\text{C}^{11}=\text{C}^{13}$) form a rather weak band with $\nu_{\text{exp}} 1630 \text{ cm}^{-1}$ and 1666 cm^{-1} . For these bonds the frequency correlates with their length: $R (\text{C}^3=\text{C}^4) 1.339 \text{ \AA}$ and $R (\text{C}^{11}=\text{C}^{13}) 1.333 \text{ \AA}$; frequencies have the values of 1666 cm^{-1} and 1679 cm^{-1} (calculation) respectively. For C–H bonds the correlation between the length and the frequency is also: thus, the $\text{C}^3\text{--H}$ bond has a length of 1.087 \AA and a frequency of 3076 cm^{-1} (calculation), $\text{C}^5\text{--H}$ and $\text{C}^7\text{--H}$ with lengths of 1.1037 \AA and 1.1044 \AA and frequencies of 2864 cm^{-1} and 2854 cm^{-1} (calculation) respectively.

Skeletal and bending vibrations of atoms in molecules are known to be assigned to the fingerprint region (below 1500 cm^{-1}). Stretching vibrations of C–C bonds, changes in COC bond angles, scissoring vibrations of methylene groups, symmetrical and asymmetrical bending vibrations of methyl groups, bending (rocking) vibrations of the rings are observed in the range $1500\text{--}600 \text{ cm}^{-1}$. The C–O stretching vibrations are observed near $\nu_{\text{calc}} 1300 \text{ cm}^{-1}$ and 1214 cm^{-1} , in the range $1130\text{--}940 \text{ cm}^{-1}$ (lactone ring) (modes 53, 54) and in the range $1050\text{--}860 \text{ cm}^{-1}$ (epoxide ring) (modes 37–39). Motions of atoms in molecules are mixed and delocalized (this is especially noticeable in the low-frequency region), which complicates the accurate description of these motions by one term. Asymmetrical bending vibrations of CH_3 group are observed together with scissoring vibrations of CH_2 groups in the form of rather weak bands in the range $1475\text{--}1415 \text{ cm}^{-1}$ of the theoretical spectrum and in the range $1435\text{--}1405 \text{ cm}^{-1}$ of the experimental spectrum of arglabin. Symmetrical bending vibration of CH_3 (umbrella) is manifested by C^{14}H_3 and C^{15}H_3 groups in the calculated spectrum at 1386 cm^{-1} and 1394 cm^{-1} (modes 71, 72 respectively). Near $\nu_{\text{rock}} 1407 \text{ cm}^{-1}$ (mode 73) the scissoring vibration of the C^2H_2 group is mixed with the C=C stretching vibration. Wagging ($1374\text{--}1164 \text{ cm}^{-1}$) and twisting ($1353\text{--}1073 \text{ cm}^{-1}$) vibrations of methylene groups and also rocking vibrations of CH_2 ($1233\text{--}1073 \text{ cm}^{-1}$) and CH_3 ($1095\text{--}860 \text{ cm}^{-1}$) groups are mixed with the skeletal vibrations $\nu(\text{C}\text{--C})$. Near 800 cm^{-1} there are breathing [13] vibrations of the rings which correspond to the symmetrical expansion compression of the rings.

The application of quantum chemical research methods provides the prediction of the frequencies and types of normal vibrations along with the intensities of IR bands for the low-frequency region of the spectrum. In the experimental spectrum of arglabin there is an absorption region within $660\text{--}430 \text{ cm}^{-1}$, then the bands below 400 cm^{-1} we predicted based on the calculations. The analysis of vibrations shows that in this region the stretching vibrations of $\text{O}^3\text{--C}$, C–C bonds (modes 29, 28, 27), rocking vibrations of CH_2 and other groups are still active; changes in the bond angles between the carbon–carbon bonds (mode 22) and the rocking of the whole skeleton of the molecule occur. In the latter case, one or two rings out of three experience a stronger motion. In their interaction the vibrations of the adjacent groups give mixed vibrations.

CONCLUSIONS

Thus, the quantum chemical B3LYP calculations of the IR spectrum of arglabin enabled the assignment of bands in the experimental spectrum and also the identification of the types of normal vibrations, showed the correspondence of the calculated structural parameters and vibrational frequencies to the experimental data. The results obtained confirm the reliability of the method in the prediction of the equilibrium geometry and the vibrational spectrum of molecules of sesquiterpenic lactones of the guaianolide type.

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