71, 69, 67, 59, 55. PMR spectrum (δ, ppm, $CDCl_4$): 1.04 (s, 3H, 7-CH_3-syn), 1.09 (d, 3H, 5-CH_3, J = 6.6 Hz), 1.26 (s, 3H, 7-CH_3-anti), 1.56 (dt, 1H, 8-H-anti, ^2J = 12.0 Hz, $^3J_{8\text{-H-anti};1\text{-H}} = {}^3J_{8\text{-H-anti},6\text{-H}}$ = 3.6 Hz), 2.10 (dt, 1H, 6-H, $^3J_{8\text{-H-syn},6\text{-H}}$ = 7.2 Hz, $^3J_{6\text{-H},8\text{-H-anti}} = {}^3J_{6\text{-H},5\text{-H}}$ = 3.6 Hz), 2.22 (m, 1H, 5-H), 2.57 (dd, 1H, 4-H, ^2J = 18.2 Hz, $^3J_{4\text{-H}_e,5\text{-H}_a}$ = 5.4 Hz), 2.70 (dt, 1H, 8-H-syn, ^2J = 12.0 Hz, $^3J_{8\text{-H-syn},1\text{-H}} = {}^3J_{8\text{-H-syn},6\text{-H}}$ = 7.2 Hz), 3.01 (dd, 1H, 4-H , ^2J = 18.2 Hz, $^3J_{4\text{-H}_a,5\text{-H}_a}$ = 9.0 Hz), 3.13 (dt, 1H, 1-H, $^3J_{1\text{-H,NH}} = {}^3J_{1\text{-H},8\text{-H-syn}}$ = 7.2 Hz, $^3J_{1\text{-H},8\text{-H-anti}}$ = 3.6 Hz). According to the literature [7]: mp 88-90°C. PMR spectrum (100 MHz, $CDCl_3$, TMS): 1.09, 1.31 (s, 6H, gem-CH_3), 1.14 (d, (3H, 5-CH_3, J = 7 Hz), 1.58 (dt, 1H, J = 12 Hz, J = 4 Hz, 8-H), 1.99-2.41 (m, 2H, 5-H and 6-H), 2.58 (dd, 1H, J = 18 Hz, J = 5 Hz, 4-H), 2.72 (dt, 1H, J = 12 Hz, J = 7 Hz, 8-H), 3.03 (dd, 1H, J = 18 Hz, J = 9 Hz, 3-H), 3.15 (triplet of broadened doublets, 1H, J = 7 Hz, J = 4 Hz, J = 1 Hz, 1-H).

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REACTIONS AT THE DOUBLE BOND IN THE EPOXY GROUP OF ARGLABIN

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The interaction of arglabin, a sesquiterpene lactone of the guaiane type, with peracetic acid and hydrogen chloride has been investigated. This led to the synthesis of nine compounds the structure of which have been established in the basis of spectral characteristics (IR, PMR, and mass spectra). The structures and absolute configurations of the molecules of 3α,10α-dichloro-1β,4β-dihydroxy- and 10α-chloro-1β-hydroxy-3β,4β-epoxyarglabins have been determined as 3R,10R-dichloro-1R,4R-dihydroxy-5S,6S,7S-trans-trans-guai-11(13)-en-6,12-olide and 10R-chloro-1R-hydroxy-3S,4R-epoxy-5S,6S,7S-trans-trans-guai-11(13)-en-6,12-olide, respectively.

Arglabin (I) is a sesquiterpene lactone of the guaiane type which is characteristic for the epigeal part of Artemisia glabella Kar. et Kir. (~ smooth wormwood) [1, 2]. The presence in the structure of (I) of a exomethylene group conjugated with a γ-lactone

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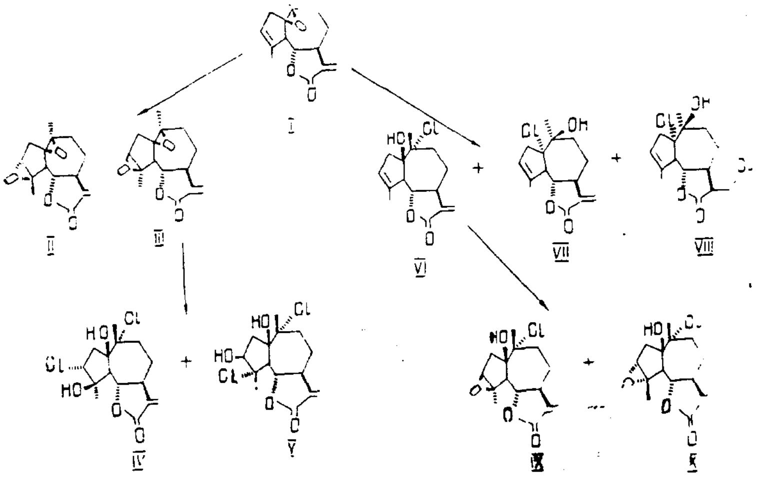
carbonyl and an epoxide ring and also a skeletal C3=C4 double bond determines the possibility of the chemical modification of the molecule of this sesquiterpene lactone.



Scheme of the chemical transformations of arglabin.

In the present paper we discuss the results of the oxidation of (I) and the interaction of the molecule of this guanolide with hydrogen chloride (see Scheme). On the interaction of (I) with peracetic acid in methylene chloride, a mixture of two products was formed, after the separation of which by the method of flash chromatography on a column of silica gel, crystalline substances (II) and (III) were isolated. Compound (II) was a minor component of the reaction product (yield 5%), while the yield of the main compound (III) amounted to 65%. In the course of the reaction no opening of the C1—C2 epoxide ring in the structure of (I) was observed: the IR spectra of (II) and (III) lacked absorption bands characteristic for a hydroxy group. Likewise, no changes were detected in the exomethylene group of the γ-lactone: the PMR spectra of (II) had signals at 5.41 ppm (1H; d; J = 3.5 Hz) and 6.15 ppm (1H; d; J = 3.5 Hz); and the PMR spectrum of (III) signals at 5.43 ppm (1H; d; J = 3 Hz) and 6.16 ppm (1H; d; J = 3 Hz). The PMR spectra of both (II) and (III) (Table 1) contained signals at 3.42 and 3.31 ppm (1 H each), respectively, which are characteristic for the H3 proton at an epoxy group, and the broadened singlet in the 5.53 region that is characteristic for the olefinic proton of arglabin was now absent. Consequently, the two compounds (II) and (III) were isomeric epoxy derivatives of arglabin.

On the interaction of (III) with dry hydrogen chloride in ether—acetone followed by chromatographic purification of the reaction mixture on a column of silica gel, two crystalline substances, (IV) and (V), were obtained. The main reaction product (yield 60%) was (IV), while the yield of (V) was 5% calculated on the initial compound. Judging from their mass spectra, elementary compositions, and IR and PMR spectra, and also from the results of acetylation with acetic anhydride in pyridine, (IV) contained two tertiary hydroxy groups and two chlorine atoms, and (V) a secondary and a tertiary hydroxy group and two chlorine atoms. Consequently, the interaction of (III) with hydrogen chloride was accompanied by the opening of the two epoxy groups in the structure of the initial compound and the formation of isomeric chlorohydrin derivatives.

The structure and absolute configuration of (IV) were determined by the x-ray structural method. The structure of the (IV) molecule is shown in Fig. 1.

The bond lengths (Fig. 1) and valence angles (Table 2) were, in general, the usual ones [3], although, because of the large number of substituents, some bond lengths and valence angles in the basic skeleton differed appreciably from the standard values of the lengths of an ordinary $C(sp^3)—C(sp^3)$ bond (1.54 Å) and the ideal tetrahedral angle (109.5°).

The conformation of the seven-membered ring B was intermediate between twist-chair and chair. The asymmetry parameters $\Delta C_2^9 = 10.7°$, $\Delta C_s^5 = 26.5°$, and the $\Delta C_2/(\Delta C_s + \Delta C_2)$ ratio of 0.29 show that the conformation of the ring is closer to the twist-chair. The

TABLE 1. Details of the PMR Spectra of Arglabin Derivatives

Compound	δ, CDCl$_3$, ppm; multiplicity; SSCC, Hz						
	CH$_3$-10	CH$_3$-4	H-6	H-3	H-13a	H-13b	other protons
Arglabin (I)	1,33 (3H; s)	1,92 (3H; s)	3,97 (1H; tr; 10)	5,53 s (1H; br, s)	5,42 (1H; d; 3)	6,10 (1H; d; 3)	
3α, 4α-Epoxyarglabin (II)	1,27 (3H; s)	1,63 (3H; s)	3,95 (1H; dd; 10, 2)	3,42 (1H; d; 3,5)	5,41 (1H; d; 3,5)	6,15 (1H; d; 3,5)	
3β, 4β-Epoxyarglabin (III)	1,30 (3H; s)	1,68 (3H; s)	4,11 (1H; tr; 10)	3,31 (1H; s)	5,43 (1H; d; 3)	6,16 (1H; d; 3)	
3α, 10α-Dichloro-1β, 4β-dihydroxyarglabin (IV) ((CD$_3$)$_2$CO)	1,61 (3H; s)	1,62 (3H; s)	4,48 (1H; dd; 10)	4,42 (1H; dd; 10,7)	5,52 (1H; d; 3,5)	6,04 (1H; d; 3,0)	
4α, 10α-Dichloro-1β, 3β-dihydroxyarglabin (V)	1,41 (3H; s)	1,57 (3H; s)	4,55 (1H; dd, 10)	4,05 (1H; d; 5,5)	5,54 (1H, d; 3,5)	6,21 (1H; d; 3,5)	H-5 3,39 (1H; d; 10) C$_1$–OH; 3,42 (1H; s) C$_3$—OH; 4,49 (1H; s)
10α-Chloro-1β-hydroxyarglabin (VII)	1,64 (3H; s)	1,92 (3H; br. s)	4,26 (1H; dd; 12; 10)	5,46 (1H; br.. s)	5,49 (1H; d; 3)	6,15 (1H; d, 3)	H-5; 3,51 (1H; d; 10,5)
1α-Chloro-10β-hydroyarglabin (VII)	1,49 (3H; s)	1,92 (3H; br.s)	4,48 (1H; m)	5,47 (1H; s)	5,47 (1H; d; 3)	6,17 (1H; d; 3)	
1α, 13-Dichloro-10β-hydroxyarglabin (VIII)	1,48 (3H; s)	1,88 (3H; br.s)	4,52 (1H; tr, 10)	5,47 (1H; br. s)	3,74 (1H; d; 12; 3,5)	3,94 (1H; dd; 12; 3,5)	
10α-Chloro-1β-hydroxy-3β, 4β-epoxyarglabin (IX)	1,60 (3H; s)	1,66 (3H; s)	4,[illegible]6 (1H; dd; 11; 10)	3,44 (1H; s)	5,41 (1H; d; 3,5)	6,18 (1H; d; 3.5)	C$_1$–OH:3,73 (1H; s) H-5 2,95 (1H; d; 11)
10α-Chloro-1β-hydroxy-3α, 4α-epoxyarglabin (X)	1,37 (3H; s)	1,68 (3H; s)	4,62 (1H; tr. 10)	3,43 (1H; s)	5,51 (1H; d; 3,0)	6,21 (1H; d; 3,0)	C$_1$—OH:4,31 (1H; s) H-5:2,60 (1H; dd; 17)

s) singlet; d) doublet; tr) triplet; dd) doublet of doublets; br) broadened.

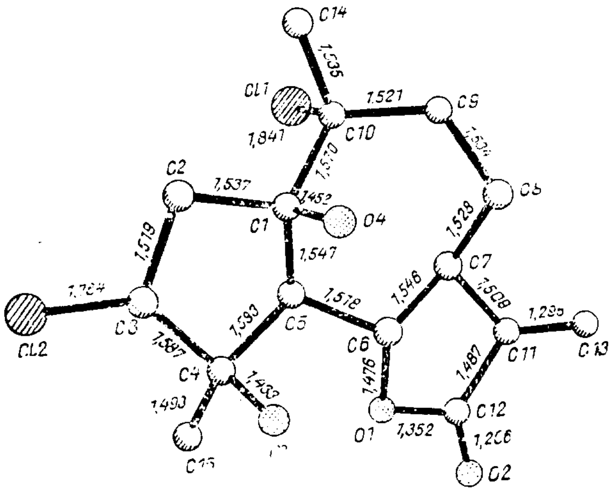


Fig. 1. Structure of the (IV) molecule.

TABLE 2. Valence Angles ω (degrees) of the Molecules of (IV) and (IX), the Probable Errors being 0.3-0.5°

Angle	ω		Angle	ω	
	IV	IX		IV	IX
C6O1C12	109,5	108,2	C4C5C6	113,3	123,9
C3O3C4	—	59,2	O1C6C5	109,4	110,3
O4C1C2	110,5	108,6	O1C6C7	103,0	104,7
O4C1C5	110,9	111,3	C5C6C7	114,0	113,9
O4C1C10	101,8	102,3	C6C7C8	112,2	113,2
C2C1C5	102,8	103,2	C6C7C11	100,3	100,7
C2C1C10	112,7	114,1	C8C7C11	116,2	116,9
C5C1C10	118,2	117,3	C7C8C9	116,6	116,9
C1C2C3	103,6	103,8	C8C9C10	122,4	122,3
Cl2C3C2	110,5	—	Cl1C10C1	106,5	108,2
Cl2C3C4	114,3	—	Cl1C10C9	107,1	107,7
C2C3C4	109,0	110,8	Cl1C10C14	106,6	105,7
O3C3C2	—	112,8	C1C10C9	118,4	115,6
O3C3C4	—	60,1	C1C10C14	110,0	111,5
O3C4C3	106,8	60,7	C9C10C14	107,6	107,8
O3C4C5	105,4	112,3	C7C11C12	106,1	105,6
O3C4C15	111,9	115,4	C7C11C13	130,8	130,7
C3C4C5	101,8	107,2	C12C11C13	123,1	123,7
C3C4C15	116,7	124,5	O1C12O2	121,8	120,2
C5C4C15	113,2	121,6	O1C12C11	108,9	109,7
C1C5C4	103,3	103,6	O2C12C11	129,2	130,1
C1C5C6	113,2	112,6			

values of the torsion angles in the ring (Table 3) are also closer to those characteristic for an ideal twist chair than for an ideal chair [4]. The C1, C5, C6, and C7 atoms depart from the plane of the C8, C9, and C10 atoms [plane (1)] by 0.79, 0.22, 0.26, 0.66 Å in the β-, β-, β-, and α-directions, respectively. The C-14 Me group is oriented equatorially relatively to the ring, and the O4 hydroxy group and the Cl1 chlorine atom have the axial orientation. The departures of the C14, O3, and Cl1 atoms from plane (1) amount to 0.49, 2.08, and 1.75 Å in the β-, β-, and α-directions, respectively. The five-membered carbocycle A and the lactone ring C are trans-linked with the seven-membered ring (torsion angles O4C1C5H5 — 167(4)°, and H6C6C7H7 — 165(5)°). The conformation of the five-membered carbocycle is that of a distorted 1β-envelope ($\Delta C_2{}^1 = 7.5°$), the C1 atom departing from the plane of the C2, C3, C4, and C5 atoms (satisfied with an accuracy of +0.04 Å) by 0.65 Å, and the C12, O3, and C15 atoms by 1.47, 1.36, and 1.0 Å in the β-, α-, α-, and β-directions, respectively. The conformation of the lactone ring is 6β,7α-half chair ($C_S{}^{1,2} = 1.2°$). The departure of the C6 and C7 atoms from the plane of the other atoms of the ring amounts to 0.28 and 0.29 Å in the β- and α-directions. The O2 atom of the carbonyl group is actually in this plane.

The absolute configuration of the (IV) molecule was established experimentally from the anomalous scattering effect (see the Experimental section); the (IV) molecule has the

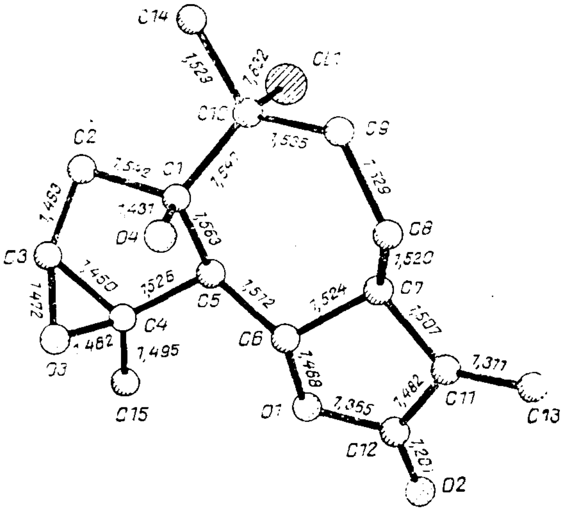


Fig. 2. Structure of the (IX) molecule

TABLE 3. Torsion Angles (°) in the Rings of Compounds (IV) and (IX)

Angle	φ	
	IV	IX
Ring A		
C5C1C2C3	39,9	32
C1C2C3C4	−20,6	−19
C2C3C4C5	−6,1	−1
C3C4C5C1	30,3	21
C4C5C1C2	44,2	−32
Ring B		
C10C1C5C6	68,0	73
C1C5C6C7	−66,2	−66
C5C6C7C8	83,8	81
C6C7C8C9	−79,3	−80
C7C8C9C10	28,9	33
C8C9C10C1	35,0	33
C9C10C1C5	−71,7	−75
Ring C		
C7C6O1C12	27,5	27
C6O1C12C11	−11,8	−10
O1C12C11C7	−11,4	−12
C12C11C7C6	27,8	27
C11C7C6O1	−33,9	−33

following structure: 3R,10R-dichloro-1R,4R-dihydroxy-5S,6S-7S-trans-trans-guai-11(13)-en-6,12-olide.

In the (IV) molecule, the hydroxy groups are linked by a O4—H···O3 hydrogen bond (O···O, 2.80 Å; H···O, 2.13 Å; the angle O—H···O, 131.3°). In the crystal, an intermolecular hydrogen bond is also observed between the O3—H hydroxy group and the O2 atom of the carbonyl group of the molecule with the coordinates 3 − x; −0.5 + y; 0.5 − z (O···O, 2.86 Å; H···O, 2.13 Å; the angle O—H···O, 165.5°). In the crystal, the molecule forms helices around the screw axes of the 2_1 type [0, y, 1/5]. Thus, in the initial compound (III) the epoxy group had the β-orientation relative to C_3—C_4.

Since compound (V) contains a secondary hydroxy group, while the initial (III) is 3β,4β-epoxyarglabin, it is possible to draw the unambiguous conclusion that (V) has the structure of 4α,10α-dichloro-1β,3β-dihydroxy-5,7α(H),6β(H)-guai-11(13)-en-6,12-olide.

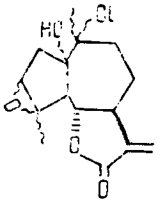
The passage of dry hydrogen chloride through an ethereal solution of arglabin (I) for 30 min led to the formation of three compounds (VI), (VII), and (VIII) in the reaction mixture. The chromatic separation of this mixture on a column of silica gel enabled the three substances to be obtained in crystalline form. The IR spectra of (VI)-(VIII) showed the presence of a hydroxy group in each of these compounds, and high-resolution mass spectrometry showed the presence of a chlorine atom in each of them. Since the multiplicity of the signals of the methyl group at C-4 in the PMR spectra of (VI)-(VIII) had not changed (broadened singlet at 1.88-1.92 ppm), then, consequently, the reaction had taken place with the opening of the epoxy group without affecting the double bond at C3—C4. Only in the third product, in addition to the opening of the epoxy ring and the formation of a

TABLE 4. Coordinates of the Nonhydrogen Atoms (×10⁴) of Compounds (IV) and (IX)

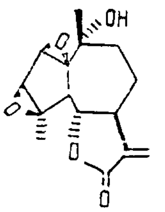
Atom	Compound IV			Compound IX		
	x	y	z	x	y	z
Cl1	8712 (2)	3861 (1)	2874 (1)	—0683 (1)	5245 (1)	3128 (1)
Cl2	12213 (3)	2742 (2)	1616 (1)	—	—	—
O1	12755 (5)	7186 (3)	2200 (2)	2242 (5)	1402 (3)	5288 (2)
O2	12595 (6)	9282 (3)	3402 (2)	2323 (4)	3317 (3)	4884 (1)
O3	15253 (4)	4793 (3)	2790 (2)	5218 (5)	6644 (3)	4525 (2)
O4	13989 (4)	3449 (3)	2941 (2)	4878 (3)	5705 (2)	3205 (1)
C1	12283 (6)	3612 (4)	2595 (2)	2984 (5)	5856 (3)	3466 (2)
C2	12060 (7)	2617 (4)	3018 (2)	2697 (7)	7211 (4)	3672 (2)
C3	13182 (6)	3146 (5)	2430 (2)	3393 (8)	7277 (4)	4422 (2)
C4	13460 (7)	4628 (5)	2546 (2)	3495 (6)	6070 (4)	4744 (2)
C5	12224 (7)	4888 (4)	3195 (2)	2693 (5)	5168 (3)	4189 (2)
C6	12828 (7)	6019 (4)	2626 (2)	3548 (5)	3858 (3)	4183 (2)
C7	11573 (6)	6337 (4)	4237 (2)	2592 (5)	3021 (3)	3663 (2)
C8	11968 (8)	5521 (5)	4874 (2)	3266 (7)	3181 (4)	2899 (2)
C9	11225 (7)	4159 (5)	4871 (2)	2391 (6)	4225 (4)	2475 (2)
C10	10431 (6)	2413 (4)	4206 (2)	1772 (5)	5433 (4)	2824 (2)
C11	11017 (7)	7748 (5)	4310 (2)	3005 (6)	1802 (4)	4015 (2)
C12	12445 (7)	8205 (5)	5612 (3)	3199 (6)	2082 (4)	4785 (2)
C13	11869 (8)	8482 (5)	4849 (3)	3204 (8)	0712 (4)	3741 (3)
C14	10828 (7)	1985 (5)	4397 (3)	1700 (7)	6411 (4)	2241 (2)
C15	13057 (8)	5478 (5)	1947 (2)	3243 (9)	5829 (5)	5525 (2)

chlorohydrin derivative, had a chlorine atom also being added at the C11—C13 bond of the α-methylene-γ-lactone. The PMR spectrum of (VIII) showed an upfield shift of the signals of the H-13 protons (see Table 1).

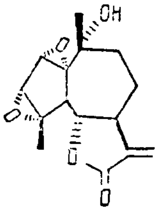
The epoxidation of (VI) with peracetic acid in chloroform led to a reaction product the chromatographic separation of which on a column of silica gel yielded two colorless crystalline substances: (IX) and (X).



X



XI



XII

The structure and absolute configuration of (IX) were determined by the x-ray structural method.

Figure 2 shows the spatial structure and bond lengths of the (IX) molecule. The probable errors of the bond lengths are in the range of 0.004-0.006 Å. The valence angles of the molecule are given in Table 2, and some torsion angles in Table 3. Among the guaianolides investigated by the XSA method, chrysartemin B (XI) is closest to (IX) with respect to the stereochemistry of the linkage of the rings and their positions [6].

A comparison of the bond lengths and valence angles of the seven-membered and lactone rings of compounds (IX) and (XI) showed their respective agreement with one another within the limits of error. We may note, incidentally, that all the bond lengths of the (IX) molecule fall into the interval of expected values. However, the conformations of the seven-membered rings of guanolides (IX) and (XI) are apparently different. Thus, in the (IX) the seven-membered ring has the advantageous form of a slightly distorted twist-chair (TW) with the following torsion angles (in degrees, starting with the C5—C6, C7—C8, etc. bonds): —66/—54, 81/72, —80/—88, 33/39, 33/39, —75/—88, and 73/72, where under the fraction sign are given the calculated values of the torsion angles of the TW conformation of cycloheptane. In the (XI) molecule, judging only from the figure, the form of this ring is closest to the chair form in which the C7C8C9C10 torsional angle is almost zero. The difference in the conformations of the seven-membered rings is apparently due to the structures of the five-membered rings of guanolides (IX) and (XI) — in the (IX) molecule this ring is present in the form of a E^1 envelope (see [7]) with a departure by 0.525 Å of the C1 atom from the plane of the other atoms, while in the (XI) molecule, this ring is appreciably flattened because of the presence of the two epoxy groups. It is interesting to note that in the isomeric chrysartemin A (XII) [8], which has the cis-linkage of the five-membered and the seven-membered ring, the latter has the TW conformation, as in the (IX) molecule, but the C_2 axis of symmetry of the ring passes through the C8 atom, while in (IX) the axis passes through the C9 atom. The lactone rings of the (IX) and (XI) molecules have the same twist conformation $^6T_7$ [7]. In compound (IX) a O—H···O3 intramolecular hydrogen bond is observed which is characterized by the parameters: O—H 0.86, H···O 2.03, O···O 2.691 Å; the angle O—H···O 133°.

Thus, compound (IX) has the structure of 10α-chloro-1β-hydroxy-3β,4β-epoxy-5α,6β,7α(H)-guai-11(13)-en-6,12-olide.

EXPERIMENTAL

The individuality of the substances isolated and synthesized was checked by TLC on Silufol plates with the vapors of concentrated H_2SO_4 as the revealing agent. Specific optical rotations were determined on a Polamat instrument. Melting points were determined on a Boëtius instrument. IR spectra were taken on UR-20 spectrophotometer, and PMR spectra on a Bruker WP-200 SY instrument (200.13 MHz) (δ scale; internal standards $CHCl_3$, the signal of which was taken as 7.24 ppm, and $(CH_3)_2CO$, the signal of which was taken as 2.04 ppm). High-resolution mass spectra were obtained on a Finnigan MAT 8200 instrument. The results of the elementary analyses of the compounds obtained corresponded to the calculated figures.

Air-dry type KSK silica gel with a grain size of 0.07-0.16 mm was used for chromatography at a ratio of the total material to support of 1:20, the eluent being petroleum ether with increasing concentrations of diethyl ether (from 0 to 100%). The size of the fractions collected was 20 ml.

The isolation and identification of the sesquiterpene lactone arglabin (I) from Artemisia glabella Kar. et Kir. (~ smooth wormwood) was carried out by a procedure described previously [1, 2]. Arglabin is a colorless crystalline substance with the composition $C_{15}H_{18}O_3$, mp 100-102°C (from hexane), $[\alpha]_D^{20}$ +45.6° (c 0.3; chloroform).

Epoxidation of Arglabin (I). At room temperature, 2.0 g of (I) was dissolved in 40 ml of methylene chloride, 2.0 g of sodium bicarbonate ($NaHCO_3$) was added and then, with stirring, 65 ml of a chloroform solution of peracetic acid (35 mg of the peracid in 1 ml of solution), in small portions. After 72 h, TLC showed two spots with R_f 0.75 and 0.50 (diethyl ether). The reaction mixture was transferred to a separatory funnel containing a 20% solution of sodium bicarbonate and, after vigorous shaking several times, the ethylene chloride layer was separated off, treated with a saturated solution of sodium chloride, and dried over magnesium sulfate, and the solvent was evaporated off in a rotary evaporator. The residue (1.8 g) was chromatographed on a column of silica gel.

When the column was eluted with petroleum ether—diethyl ether (1:1), fractions 15-19 yielded a colorless crystalline substance (II) with the composition $C_{15}H_{18}O_4$, mp 171-173°C [methylene chloride—diethyl ether (1:1)], $[\alpha]_D^{22}$ +94.0° (c 1.7; chloroform). TLC showed a single spot with R_f 0.75. Yield 0.104 g. IR spectrum, cm^{-1}: 1760 (C=O of a lactone, 1670 (C=C). Mass spectrum (m/z; intensity, %): M^+ 262 (16.43); 219(8.2), 201(3.42), 177(5.47), 150(13.7), 139(34.24), 123(34.24), 111(45.2), 95(41.1), 79(13.7), 67(16.43), 55(23.28), 43(100).

Fractions 27-49 (diethyl ether) yielded a colorless crystalline substance (III) with the composition $C_{15}H_{18}O_4$, mp 149-151°C [methylene chloride—ether (1:1)], $[\alpha]_D^{18}$ +58.9° (c 2.07; chloroform). TLC showed a single spot with R_f 0.5. Yield 1.42 g. IR spectrum, cm^{-1}: 1780 (carbonyl of a γ-lactone), 1670 (C=C). Mass spectrum (m/z; intensity, %): M^+ 262 (16.4), 219(8.21), 201(3.42), 191(6.84), 163(6.84), 150(13.7), 145(5.47), 139(34.24), 131(5.47), 123(34.24), 111(45.2), 105(8.2), 95(41.09), 91(12.32), 79(13.7), 67(16.43), 55(23.28), 43(100).

Interaction of the Epoxyarglabin (III) with Hydrogen Chloride. At room temperature, 1.32 g of (III) was dissolved in 15 ml of acetone, and 85 ml of ether was added. With vigorous stirring, dry hydrogen chloride was passed through the reaction mixture for 20 min (pH 3-4). Then stirring was continued for another 1 h. On TLC, two spots were observed with R_f 0.75 and 0.31 (diethyl ether). The reaction mixture was treated twice with a saturated solution of sodium bicarbonate and sodium chloride. The ethereal layer was dried with magnesium sulfate and the solvent was evaporated off. The residue, amounting to 1.3 g, was chromatographed on a column of silica gel.

When the column was eluted with petroleum ether—diethyl ether (1:1), fractions 10-29 gave a colorless crystalline substance (IV) with the composition $C_{15}H_{20}O_4Cl_2$, mp 190-191°C (acetone), $[\alpha]_D^{20}$ −90.1° (c 0.34; acetone). TLC showed a single spot with R_f 0.75. Yield 0.980 g. IR spectrum, cm^{-1}: 3465 (OH), 1750 (carbonyl of a γlactone) 1670 (C=C). Mass spectrum (m/z, intensity, %: 316 ($M^+ - H_2O$; 6.16), 298 (M^+ − HCl), 281 (M^+ − HCl − HO), 263 (M^+ − HCl − HCl), 245 (M^+ − HCl − HCl − H_2O), 227(21.23), 199(12.32), 171(10), 157 (45.20), 131(53.42), 95(32.87), 91(19.17), 69(17.8), 43(100).

Fractions 34-48 (petroleum ether—diethyl ether in (1:1) and (1:2)) yielded a colorless crystalline substance (V) with the composition $C_{15}H_{20}O_4Cl_2$, mp 176-178°C (diethyl ether—methylene chloride (1:1), $[\alpha]_D^{24}$ +23.25° (c 0.43; chloroform). GLC showed a single spot with R_f 0.31. Yield 0.090 g. IR spectrum, cm^{-1}: 3680 (OH), 1770 (carbonyl of a γ-lactone), 1670 (C=C). Mass spectrum (m/z; intensity, %): 316(3.97), 301(2.19), 281(31.50), 263 (14.38), 245(30.82), 227(15.06), 201(10), 189(10.95), 167(19.17), 149(10.95), 125(10), 109(16.43), 95(13.7), 83(15.06), 55(13.7), 43(100).

Interaction of Arglabin (I) with Hydrogen Chloride. At room temperature, 1.1 g of arglabin was dissolved in 100 ml of diethyl ether, and a current of hydrogen chloride was passed through the solution for 30 min. The reaction mixture was left in the refrigerator for 3 days. TLC showed three spots with R_{f1} 0.9; R_{f2} 0.8; and R_{f3} 0.4 (diethyl ether). The reaction mixture was treated with a saturated solution of sodium bicarbonate and sodium chloride. The ethereal layer was dried over anhydrous magnesium sulfate and was evaporated. The residue (1.15 g) was chromatographed on a column of silica gel.

Fractions 12-25 [petroleum ether—diethyl ether (2:1)] yielded a colorless crystalline substance (VI) with the composition $C_{15}H_{19}O_3Cl$, mp 137-138°C [diethyl ether—chloroform (2:1)], $[\alpha]_D^{21}$ +26.6° (c 0.3; chloroform). TLC showed a single spot with R_f 0.9. Yield 0.75 g. IR spectrum, cm^{-1}: 3620 (—OH), 1765 (carbonyl of a γ-lactone), 1660 (C=C). Mass spectrum (m/z; intensity, %): M^+ 282(41.09), 264 ($M^+ - H_2O$, 56.16), 246 ($M^+ - H_2O$ − HCl), 236(10.95), 228(50.68), 213(28.76), 203(23.28), 188(23.28), 157(61.64), 150(16.43), 133 (21.91), 126(45.20), 107(90.4), 96(100), 91(34.24), 79(36.98), 67(31.50), 53(50.68), 43 (64.39).

When the column was eluted with petroleum ether—diethyl ether (2:1) and (1:1) fractions 28-45 yielded a colorless crystalline substance (VII) with the composition $C_{15}H_{19}O_3Cl$, mp 110.5-111.5°C [diethyl ether—chloroform (2:1)], $[\alpha]_D^{22}$ +140° (c 0.56; chloroform). TLC showed a single spot with R_f 0.8. Yield 0.120 g. IR spectrum, cm^{-1}: 3620 (—OH), 1770 (carbonyl of a γ-lactone), 1665 (C=C). Mass spectrum (m/z; intensity, %): M^+ 282(0.54), 264(3.56), 246(1.37), 229(100), 211(4.8), 203(2.7), 193(2.5), 183(8.21), 169(2.5), 157 (17.80), 149(4.10), 127(6.84), 119(6.84), 107(10), 91(9.85), 79(13.7), 67(5.48), 55(10.95), 43(54.79).

When the column was washed with ether, fractions 51-64 yielded a colorless crystalline substance (VIII) with the composition $C_{15}H_{20}O_3Cl_2$, mp 153-154°C (diethyl ether—chloroform), $[\alpha]_D^{21}$ +133.3° (c 0.33; chloroform). TLC showed a single spot with R_f 0.4. Yield 0.11 g. IR spectrum, cm^{-1}: 3620 (—OH), 1770 (carbonyl of a γ-lactone), 1665 (C=C). Mass spectrum (m/z; intensity, %): M^+ 318(0.5), 300 ($M^+ - H_2O$), 282 (M^+ − HCl), 265(100), 229(15.75), 224(6.84), 203(3.42), 175(3.42), 157(26.02), 145(4.10), 133(6.16), 115(6.16), 91(10), 79 (13.7), 71(13.7), 67(4.79), 55(10), 47(3.42), 43(56.16).

Epoxidation of the Chlorohydrin Derivative of Arglabin (VI). With stirring, a chloroform solution of peracetic acid at a molar ratio of 1:2 was added to a solution of 0.230 g of arglabin chlorohydrin (VI) in chloroform, and the mixture was left at room temperature for 72 h.

It was then treated successively with a saturated solution of sodium bicarbonate and sodium chloride and was dried over magnesium sulfate, and the solvent was evaporated off. The residue (0.22 g), showing on TLC two spots with R_{f1} 0.8 and R_{f2} 0.5 (diethyl ether), was chromatographed on a column of silica gel.

Fractions 7-19 (petroleum ether—diethyl ether (2:1) and (1:1)) yielded a colorless crystalline substance (IX) with the composition $C_{15}H_{19}O_4Cl$, mp 109.5-110.5°C (ether), $[\alpha]_D^{21}$ +27.2° (c 0.43; chloroform). TLC showed a single spot with R_f 0.8. Yield 0.095 g. IR spectrum, cm^{-1}: 3460 (—OH), 1770 (carbonyl of a γ-lactone), 1670 (C=C). Mass spectrum (m/z; intensity, %): M^+ 298(17.8), 263 (M^+ – Cl), 252(13), 245(23.97), 217(10.95), 191(7.53), 175(13.7), 147(13.7), 123(18.5), 111(26.02), 95(45.9), 69(26), 53(46.6), 43(100).

Elution of the column with petroleum ether—diethyl ether (1:1 and 1:2) yielded a colorless crystalline substance (X) with the composition $C_{15}H_{19}O_4Cl$, mp 125-126°C (diethyl ether—methylene chloride), $[\alpha]_D^{21}$ +81.8° (c 0.43; chloroform). TLC showed a single spot with R_f 0.5. Yield 0.105 g. IR spectrum, cm^{-1}: 3370-3340 (—OH), 1770 (carbonyl of a γ-lactone), 1675 (C=C). Mass spectrum (m/z; intensity, %): M^+ 298(3.42), 283(4.79), 263(13.7), 262 (12.32), 245(15.06), 227(4.8), 201(6.85), 175(8.21), 167(15.06), 151(10.95), 139(21.23), 123(24.65), 111(26.02), 95(30.13), 79(16.06), 53(24.65), 43(100).

X-Ray Structural Investigation of 3α,10α-Dichloro-1β,10β-Dihydroxyarglabin (IV). The cell parameters and the intensities of 2016 reflections were measured on a Hilger—Watts four-circle diffractometer (λ MoK_α, graphite monochromator, θ/2θ scanning 2θ ≤ 56°). The crystals of (IV) were rhombic, a = 7.4838(4), b = 10.4918(6), c = 19.342(1) Å, V = 1518.7(2) $Å^3$, M = 335.2, d_{calc} = 1.465 g/cm^3, Z = 4 ($C_{15}H_{20}O_4Cl_2$), sp. gr. $P2_12_12_1$. The calculations made use of 1414 reflections with I ≥ 2σ. The structure was interpreted by the direct method. Refinement was carried out by block-diagonal MLS in the anisotropic approximation for the nonhydrogen atoms. The H atoms were revealed in a difference synthesis and were refined in the isotropic approximation. The absolute configuration was determined by means of Hamilton's test on the basis of the anomalous scattering by the Cl and O atoms. The final divergence factors were R = 0.0513 and R_w = 0.0376 for the direct structure and R = 0.0524 and R_w = 0.0379 for the inverted structure. The probability of the correct determination of the absolute configuration is 99.5%. All the calculations were performed on an Eclipse S/200 computer by the INEXTL programs [5]. The coordinates of the nonhydrogen atoms are given in Table 4.

X-Ray Investigation of 10α-Chloro-1β-hydroxy-3β,4β-epoxyarglabin (IX). The cell parameters and the intensities of 1921 reflections were measured on a Syntex $P2_1$ four-circle diffractometer (λ MoK_α, graphite monochromator, θ/2θ scanning, 2θ ≤ 56°C). The crystals of (IX) were rhombic, a = 7.043(1), b = 10.921(1), c = 18.755(2) Å, V = 1442.6(1) $Å^3$, M = 298.8, d_{calc} = 1.380 g/cm^3. Z = 4 ($C_{15}H_{18}O_4Cl$), sp. gr. $P2_12_12_1$. The calculations made use of 1587 reflections with I ≥ 2σ. The structure was interpreted by the direct method using the SHELX-86 program. Refinement was carried out by block-diagonal MLS using the SHELX-76 program in the anisotropic approximation for the nonhydrogen atoms. The H atoms were revealed in a difference synthesis and were refined in the isotropic approximation. The final divergence factors were R = 0.0505 and R_w = 0.0515. The coordinates of the nonhydrogen atoms are given in Table 4.

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