s, CH_3CO), 4.39 (1H, q, J = 10 and 9 Hz, H-6), 5.33 (1H, d, J = 4.5 Hz, H-3), 5.08 (2H, br.s, CH_2-10), 5.51 and 6.22 (1H each, d, J = 3.5 Hz, CH_2-11).

Elution with hexane—ether (1:4) yielded 60 mg (30%) of a colorless crystalline substance $C_{15}H_{19}O_3Cl$, with mp 166-168°C (from diethyl ether), R_f 0.45, which was identified as 4-chloro-3-hydroxyguaia-10(14),11(13)-dien-6,12-olide (VIII), i.e., a part of the initial substance that had not reacted.

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MOLECULAR AND CRYSTAL STRUCTURE OF THE GERMACRANOLIDE ARGOLIDE FROM Artemisia glabella

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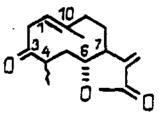
S. V. Lindeman, and Yu. T. Struchkov

UDC 547.314:548.737

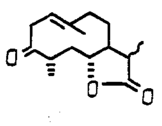
The new germacranolide argolide has been isolated from the epigeal part of Artemisia glabella, and its structure has been shown by its conversion into oxopelenolide B. From the results of an x-ray investigation it is suggested that argolide has the spatial structure of 3-oxo-4α,7α,6β(H)-germacra-1(10),-11(13)-dien-6,12-olide.

Sesquiterpene lactones of the guaiane type — arglabin, glabellin, and matricarin — and of the germacrane type — argolide and oxopelenolide B — have been isolated previously from the epigeal part of Artemisia glabella Kar. et Kir.

The molecule of argolide (I) is close in structure to germacranolides of the ketopelenolide group — ketopelenolides A (II) and B (III) [2] and tansanin [3].



I



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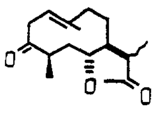

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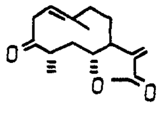

IV

Institute of Organic Synthesis and Coal Chemistry, Kazakh Academy of Sciences, Karaganda. A. N. Nesmeyanov Institute of Organometallic Chemistry, Russian Academy of Sciences, Moscow. Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 653-657, September-October, 1991. Original article submitted December 15, 1990; revision submitted May 15, 1991.

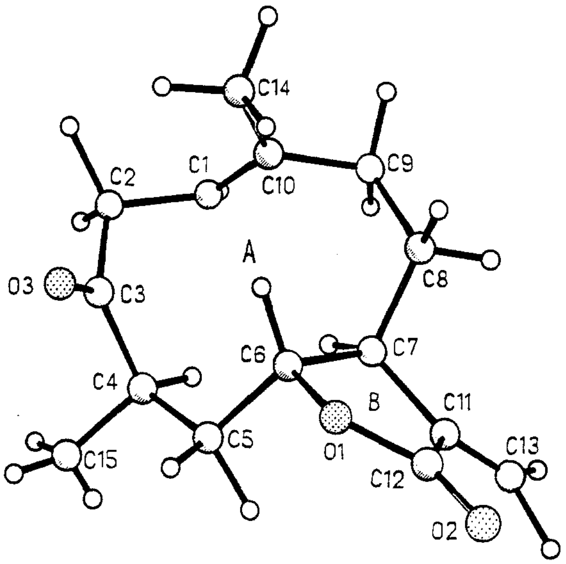

Fig. 1. Structure of the argolide molecule.

TABLE 1. Bond Lengths (Å)

Bond	*d*	Bond	*d*
O1–C6	1,479 (7)	C5–C6	1,536 (9)
O1–C12	1,348 (9)	C6–C7	1,563 (9)
O2–C12	1,198 (9)	C7–C8	1,560 (10)
O3–C3	1,190 (10)	C7–C11	1,510 (10)
C1–C2	1,510 (10)	C8–C9	1,520 (10)
C1–C10	1,320 (10)	C9–C10	1,510 (10)
C2–C3	1,540 (10)	C10–C14	1,510 (10)
C3–C4	1,510 (10)	C11–C12	1,507 (9)
C4–C5	1,546 (9)	C11–C13	1,280 (10)
C4–C15	1,499 (9)		

TABLE 2. Valence Angles ω (degrees)

Angle	ω	Angle	ω
C6O1C12	111,7 (5)	C6C7C11	103 0 (5)
C2C1C10	125,5 (7)	C8C7C11	110,7 (6)
C1C2C3	104,8 (6)	C7C8C9	116 4 (6)
O3C3C2	120,8 (7)	C8C9C10	114,3 (7)
O3C3C4	121,7 (7)	C1C10C9	119,9 (7)
C2C3C4	117,3 (7)	C1C10C14	122,0 (7)
C3C4C5	110,1 (6)	C9C10C14	117,9 (7)
C3C4C15	109,0 (6)	C7C11C12	105,5 (6)
C5C4C15	111,0 (6)	C7C11C13	131,8 (7)
C4C5C6	113,8 (6)	C12C11C13	122,6 (7)
O1C6C5	105,8 (5)	O1C12O2	123,0 (7)
O1C6C7	103,2 (5)	O1C12C11	109,4 (6)
C5C6C7	115,3 (5)	O2C12C11	127,6 (7)
C6C7C8	112,5 (6)		

The catalytic hydrogenation of argolide over $Pd/CaCO_3$ in ethyl acetate led to 11,13-dihydroargolide. The same compound was isolated in a yield of 0.0007% on the chromatographic separation of an extract of the plant under study. The natural and synthetic specimens of dihydroargolide were identical according to TLC and PMR spectroscopy.

The identity of dihdyroargolide and ketopelenolide B (III), which had been isolated previously from Artemisia absinthium [2], was shown by their physicochemical constants and spectral characteristics. Consequently, argolide can be represented as 11,13-dehydroketopelenolide B or the epimer of tansanin at C_4–Me.

In order to establish the spatial structure of argolide (I) and, in particular, the conformation of the 10-membered ring A and also to answer the question of the stereoisomerism of this lactone in relation to the ketopelenolides, an x-ray structural investigation of (I) has been carried out.

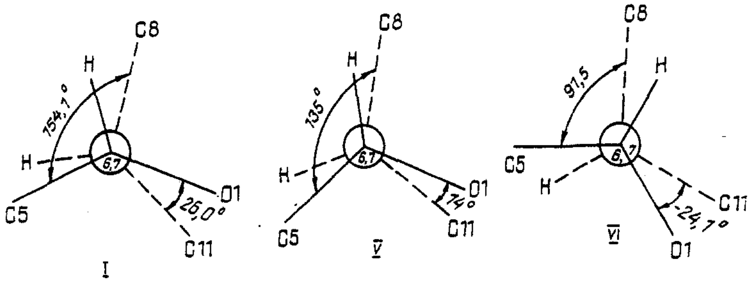

Fig. 2. Newman projections along the C6—C7 bond in the molecules of (I), (V), and (VI).

TABLE 3. Principal Torsional Angles φ (degrees)

Angle	φ	Angle	φ
C10C1C2C3	—76,5(10)	C9C10C1C2	164,6(12)
C1C2C3C4	—58,5(9)	C11C7C6O1	26,0(6)
C2C3C4C5	129,8(10)	C7C6O1C12	—19,9(8)
C3C4C5C6	—53,5(8)	C6O1C12C11	5,2(7)
C4C5C6C7	—80 3(8)	O1C12C11C7	12,5(6)
C5C6C7C8	151 4(10)	C12C11C7C6	—23,5(8)
C6C7C8C9	—82,7(9)	C5C6C7C11	—89,3(7)
C7C8C9C10	54,1(8)	O1C6C7C8	—93,3(8)
C8C9C10C1	—98,3(10)		

The general shape of the molecule is shown in Fig. 1. The bond lengths (Table 1) and valence angles (Table 2) are the usual ones, within the limits of error [4]. As follows from the values of the torsional angles C2C1C10C9 (164.6°) and C3C4C5C6 (—53.5°), (I) belongs to the class of E,Z-germacranolides (helioangolides). A comparison of the intracyclic torsional angles in ring A (Table 3) with the corresponding angles in the eupaformonin (V) molecule, showed that in the C7...C10...C3 section their difference does not exceed ±7°. However, the presence in (V) of a double bond at C4=C5 leads to a considerable difference in the torsional angles (Δφ) in the C3...C7 section of ring A: $\Delta\varphi_{3,4}=38°$, $\Delta\varphi_{4,5}=58°$, $\Delta\varphi_{5,6}=44°$, $\Delta\varphi_{6,7}=16°$. Nevertheless, ring A of the (I) molecule qualitatively retains the same conformation as that in (V) — boat-chair of the ${}_{1}D^{14}$, ${}_{15}D_{5}$.

The germacranolide skeleton is linked to the γ-lactone ring (B) in the trans-manner, although the torsional angle H6C6C7H7 = —84.7(8)° is less than 90°. This is a consequence of the fact that the torsional angle C5C6C7C8 is considerably greater than 120° [in (I) and (V) it is 151.4 [sic, but see Fig. 2] and 135°, respectively], while in the majority of A/B-trans-linked germacranolides this angle is less than 120° — for example, in hanphyllin (VI) it is 91.5° [6, 7]. As can be seen from Fig. 2, which shows Newman projections along the C6—C7 bond for the molecules of (I), (V), and (VI), at a value of the torsional angle C5C6-C7C8 of 120° the conformation along the C6—C7 bond of the (I) and (IV) molecules is (—)-anticlinal, while in (VI) it is (+)-anticlinal.

Also interesting is the fact that the conformation along the C6—C7 bond observed in (I) and (V) leads to a change in the sign of the torsional angle O1C6C7C11 in lactone ring B. Thus, while in the majority of sesquiterpene lactones the conformation of the γ-lactone ring is that of a 7α-envelope or a 6β,7α-half-chair, in (I) and (V) the conformation of this ring is inverted: It is intermediate between a 7β-envelope and a 6α,7β-half-chair in (I) ($\Delta C_s{}^7$ = 5.5° and $\Delta C_2{}^{12}$ = 5°) and is a 6α,7β-half-chair in (V) ($\Delta C_2{}^{12}$ = 1.4°). At the same time, the increase in the torsional angle O1C6C7C11 from 14° in (I) to 26° in (V) leads to an increase in the degree of flatness of the lactone ring ($\Sigma\varphi_i$ = 48 and 87.1°, respectively).

EXPERIMENTAL

PMR spectra were recorded on a Bruker AC-200 instrument (200.13 MHz) for solutions in $CDCl_3$ (δ scale, 0 — TMS). High-resolution mass spectra were obtained on a Finnigan MAT 8200 instrument. IR spectra were recorded on a UR-20 instrument. Specific rotations were determined on an SM-2 instrument for solutions in $CHCl_3$. Melting points were determined on a Boetius instrument.

TABLE 4. Coordinates of the Nonhydrogen Atoms ($\times 10^4$) and Temperature Factors (Å^2)

Atom	*x*	y	*z*	B_{iso}^{eq}
O1	11644(7)	6250	7148(4)	4,1(1)
O2	12892(8)	7752(6)	8289(5)	6,8(2)
O3	9401(9)	3788(6)	4455(5)	5,8(2)
C1	5158(12)	3905(8)	6437(8)	4,7(2)
C2	5706(12)	3429(7)	5078(8)	5,1(2)
C3	7601(14)	4162(7)	4604(7)	4,3(2)
C4	7127(12)	5383(6)	4442(6)	4,0(2)
C5	9012(11)	6061(6)	5199(6)	3,6(2)
C6	9475(10)	5736(6)	6705(7)	3,6(2)
C7	7843(10)	6219(7)	7729(6)	3,4(2)
C8	7613(13)	5459(7)	8991(7)	4,9(2)
C9	5973(13)	4508(8)	8804(7)	5,2(2)
C10	6362(12)	3769(8)	7606(8)	4,8(2)
C11	8931(10)	7297(7)	8152(6)	3,6(2)
C12	11371(12)	7163(7)	7904(8)	4,8(2)
C13	8148(12)	8174(8)	8662(8)	5,6(3)
C14	8276(14)	2953(8)	7758(8)	6,3(3)
C15	6924(15)	5661(7)	2951(7)	6,7(3)

The isolation of argolide (I) was described in [1]. Argolide (I) is a colorless crystalline substance with mp 133-135°C (from methylene chloride–diethyl ether, $[\alpha]_D^{23}$ +203.8° (c 0.52; chloroform); empirical formula $C_{15}H_{20}O_3$ (high-resolution mass spectrometry).

Hydrogenation of Argolide (I). A solution of 0.1 g of argolide in 10 ml of ethyl acetate was stirred in a flask containing the catalyst 5% Pd/$CaCO_3$ and hydrogen was passed through. After 5 h, TLC showed two spots: R_{f_1} 0.5 and R_{f_2} 0.45 (ether). The reaction mixture was filtered, the solvent was distilled off under vacuum, and the residue was chromatographed on a column of type KSK silica gel at a ratio of material to sorbent of 1:20.

When the column was eluted with petroleum ether–diethyl ether (1:1), colorless crystals were isolated, and after two recrystallizations from ethanol a substance was obtained with the composition $C_{15}H_{22}O_3$, mp 170.5-172°C, $[\alpha]_D^{22}$ + 45.0° (c 0.43; chloroform). IR spectrum (cm^{-1}): 1765 (carbonyl of a γ-lactone, 1710 (C=O), 1675 (C=C). Mass spectrum [m/z, intensity (%)]: M^+ 250(28.76), 235(10), 208(12.85), 193(55.71), 177(15.71), 159(5.71), 149(14.28), 135(8.57), 123(47.14), 119(28.57), 108(100), 88(82.85), 95(62.85), 81(58.57), 71(35.71), 68(75.71), 55(55.71). PMR spectrum ($CDCl_3$), 200 MHz, 0 – TMS): br.s 1.59 ppm (methyl at a double bond, Me-10), d 1.05 ppm (secondary methyl group, Me-4), d 3.03 ppm (2H; J = 8.5 Hz) (the H-2 protons), dd 3.54 ppm (1H; J_1 = 12 Hz, J_2 = 2 Hz) (the lactone protone H-6), d 1.15 ppm (a secondary methyl, Me-11), t 5.47 ppm (1H; J_1 = 10 Hz, J_2 = 8 Hz) (the H-1 olefinic proton).

X-Ray Structural Experiment. The cell parameters and the intensities of 1148 reflections were measured on a Hilger–Watts automatic four-circle diffractometer (λMoK_α, graphite monochromator, θ/2θ scanning, $2\theta < 60°$). The crystals were monoclinic, a = 5.9904(4), b = 12.124(1), c = 9.815(1) Å, β = 93.920(6)°, M = 248.3, d_{calc} = 1.160 g/cm^3, z = 2 ($C_{15}H_{20}O_3$), sp. gr. $P2_1$.

In the calculations we used 914 reflections with $I > 3\sigma$. The structure was interpreted by the direct method and was refined by the block-diagonal MLS in the anisotropic approximation for the nonhydrogen atoms. All the H atoms were revealed in a difference synthesis but were not refined. The final divergence factors were R = 0.062 and R_w = 0.046. The coordinates of the nonhydrogen atoms are given in Table 4. All the calculations were performed on an Eclipse S/200 computer by the INEXTL programs [8].

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TRANSFORMATIONS OF TERPENOIDS ON SYNTHETIC ZEOLITES

I. REACTIONS OF LABDANE ALCOHOLS ON ZEOLITE HY

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The transformations on zeolite HY of epimanool and of 13-hydroxylabd-8(17),14-dien-6-one and its $\Delta^{7,8}$ isomer have been studied.

Catalysts based on synthetic zeolites are widely used in various petrochemical processes (cracking, hydrocracking, etc.) [1]. Recently, interest in synthetic zeolites as catalysts of fine organic reactions – the isomerization of organic compounds and substitution reactions in them – has intensified [2, 3].

Extremely interesting in view of the promising nature of zeolites as ecologically pure catalysts is an attempt to use zeolites for transformations of terpene compounds with the aim of obtaining new substances. There is little information in the literature on the use of solid catalysts in the chemistry of natural compounds. We must mention studies on the cyclization and isomerization of monoterpenes on solid acids [3], on zeolites [4], and on sorbents impregnated with chromic acid [5-7]. Zeolites of various brands have been used for hydration of sesquiterpenes [8, 9].

A large number of studies have been devoted to the chemistry of the labdane diterpenoids [10-12], which is explained by the wide distribution and availability of these compounds; although they form a raw material for obtaining valuable industrial products, we have found no reports of reactions of diterpenoids on zeolites. A large amount of experimental material has accumulated that is devoted to the study of the transformations of bicyclic diterpenoids in acid media over a very wide range of acidities (from weak acid media to "superacids") [13, 14]. In view of this, the task of a systematic study of the reactions of diterpenoids on zeolites in comparison with their transformations taking place in a liquid-phase acid medium is extremely urgent.

The present work was devoted to a study of the transformations of diterpenes of the labdane type – epimanool (I) and 13-hydroxylabda-8(17),14-dien-6-one (below, 6-oxolarixol) (II) and its $\Delta^{7,8}$ isomer (13-hydroxylabda-7,14-dien-6-one) – on zeolite HY.

Epimanool (I), isolated from the oleoresin of the Siberian larch, was deposited on the zeolite in solution in diethyl ether (DE), and the mixture was kept at 40°C for 4.5 h (see the Experimental part). The reaction products consisted of a difficultly separable multicomponent mixture of hydrocarbons (five components, according to GLC) from which it was possible by chromatography on silica gel with silver nitrate to isolate only two individual compounds, (IV) and (V). According to GLC and IR and PMR spectroscopy, compound (IV) was identical with pimara-8,9-diene, and hydrocarbon (V) with isopimara-8,9-diene.*

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*Specimens of pimara-8,9-diene and isopimara-8,9-diene were kindly supplied by P. F. Vlad.

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