10. R. W. Doskotch, E. H. Fairchild, C. T. Huang, J. H. Wilton, M. A. Beno, and G. G. Christoph, J. Org. Chem., 45, 1441 (1980).
11. M. Suchý, L. Dolejs, V. Herout, F. Sorm, G. Snatzke, and J. Himmelreich, Collect. Czech. Chem. Comm., 34, 229 (1969).
12. A. T. McPhail, K. D. Onan, and P. M. Gross, J. Chem. Soc. Perkin Trans. II, 1798 (1975).
13. W. Herz and R. De Groote, Phytochemistry, 16, 1307 (1977).
14. W. Herz and N. Kumar, J. Org. Chem., 45, 489 (1980).
15. A. Quick and D. Roger, J. Chem. Soc. Perkin Trans. II, 465 (1976).
16. W. Herz, S. V. Govindan, and J. F. Blount, J. Org. Chem., 45, 1113 (1980).
17. Z. Samek, M. Holub, U. Rychlewska, H. Grabarczyk, and B. Drozdz, Tetrahedron Lett., 2691 (1979).
18. H. Tada and K. Takeda, J. Chem. Soc., Chem. Commun., 1979 (1971).
19. K. Tori, J. Horibe, K. Kuriyama, H. Tada, and K. Takeda, Chem. Commun., 1393 (1971).
20. H. D. Fisher, N. H. Fisher, R. W. Franek, and E. J. Oliver, Progr. Chem. Org. Nat. Prod., 37, 94 (1979).

PULCHELLIN C AND INUCHINENOLIDE C FROM *Inula caspica*

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The pseudoguaianolide inuchinenolide C and the eudesmanolide pulchellin C have been isolated for the first time from the flower heads and leaves of *Inula caspica* Blume, and their spatial structures have been established by an x-ray structural experiment as 2α,6β-diacetoxy-6α-hydroxy-1α,7α(H),8β,10β(H)-pseudoguai-11(13)-en-8,12-olide and 2α,3β-dihydroxy-5β,7α,8α(H)-eudesma-4(15),11(13)-dien-8,12-olide, respectively.

The isolation from the epigeal part of the Caspian inula, *Inula caspica* Blume of the sesquiterpene lactones britannin, incaspin, and 3β-hydroxy-2α-senecioyloxyisoalantolactone has been reported previously [1, 2].

On the column chromatographic separation of the lactone fractions, after the compounds mentioned had been obtained, after the compounds mentioned had been obtained, two crystalline substances (I) and (II) were isolated.

Substance (I). $C_{19}H_{26}O_7$, mp 156-158°C (ethanol), $[\alpha]_D$ + 95.5° (c 0.0045; chloroform). The IR spectrum of the substance contained signals at (cm^{-1}) 3540 (OH); 1780 (γ-lactone carbonyl); 1760, 1740 (carbonyls of aceto groups); and 1680. The PMR spectrum of the substances showed the following signals (δ, ppm): 0.90 (3 H, s) – characteristic for an angular methyl; 0.98 (3 H, d) – a secondary methy; 2.02 (3 H, s) and 2.10 (3 H, s) – the methyls of acetyl groups; 3.50 (1 H, dd, J_1 = 3 Hz, J_2 = 8 Hz) – a proton at C_7; 4.44 (1 H, ddd, J = 11 Hz) – a lactone proton; 4.88 (1 H, d, J = 3 Hz) – a hemihydroxylic proton; 4.93 (1 H, m) and 5.60 (1 H, dd, J_1 = 9 Hz, J_2 = 11 Hz) – the hemihydroxylic protons H-2 and H-4, respectively; and 5.97 (1 H, d, J = 3 Hz) and 6.20 (1 H, d, J = 3 Hz) – the protons of an exomethylene group conjugated with the carbonyl of a γ-lactone.

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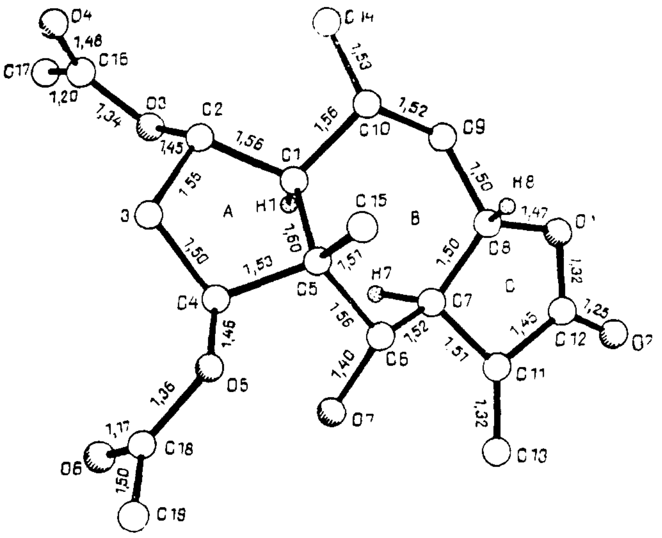
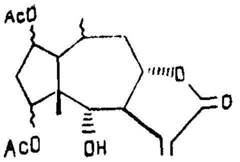


Fig. 1. Structure of the inuchinelolide C molecule (σ for the bond lengths does not exceed 0.01 Å).

By a comparison of the physicochemical constants and spectral characteristics with information in the literature [3], this compound was identified as the pseudoguaianolide inuchinenolide C, and we are the first to have isolated this compound from Caspian inula.



I

With the aim of establishing the orientation of the methyl group at C10 and of the acetate groups, and the nature of the linkage of rings A and B, and also to refine the spatial structure of (I), we have performed an x-ray structural analysis of it.

The molecule of (I) is shown in Fig. 1. The bond lengths (Fig. 1) and valence angles (Table 1) are close to the usual values within the limits of accuracy [4], with the exception of the length of the C1—C5 bond, 1.60(1) Å, and the valence angles C1C5C4 98.5(6)°, C5C6C7 116.2(6)°, C6C7C8 115.4(6)°, C6C7C11 116.9(6)°, C7C8C9 115.6(7)° and C8C9C10 115.6(7)° (mainly at the positions of linkage of the rings), which, however, are close to the corresponding characteristic values for guaianolides and pseudoguaianolides (see, for example, [2, 5-7]).

The A/B and B/C ring linkages are trans (torsion angles H1C1C5C15 158(1)° and H7C7C8H8 135(1)°). Ring A has a conformation intermediate between envelope and half-chair but closer to the later ($\Delta C_2^2 = 8.5°$, $\Delta C_s^5 = 16.3°$). The C4 and C5 atoms depart from the plane of the other atoms of the ring by 0.209(8) and —0.518(7) Å in the α- and β-directions, respectively. The O3 and O5 atoms of the acetoxy groups have the α- and β-orientations, respectively, with departures from the above-mentioned plane by 1.246(5) and —0.409(5) Å. A comparison of the values of the torsion angles (Table 2) in ring B with the ideal values for various cycloheptane conformations [8] shows that ring B has a conformation intermediate between chair and twist-chair ($\Sigma_2 = 52.2°$, $\Sigma_s = 56.0°$, $\Sigma_2/(\Sigma_s + \Sigma_2) = 0.48$).

It follows from information in the literature that in A/B- and B/C-trans-linked saturated pseudoguaianolides ring B rarely adopts such a conformation, which (with a shift in the direction of the chair conformation) is observed only in graveolide ($\Sigma_2/\Sigma_s + \Sigma_2) = 0.6$ (III) [6]. It can be shown by the use of Freiding molecular models that with the trans-linkage or rings A/B and B/C possible conformations for ring B are 5β,6β,9α-chair (a), 8β,9β,10α,1α-twist-chair (b), and 6β,7β,10α-chair (c) and conformations intermediate between them. However,

TABLE 1. Valence Angles ω (degrees) in the Structure of (I)

Angle	ω	Angle	ω
C8O1C12	108,9 (6)	C6C7C8	115,4 (6)
C2O3C16	118,1 (6)	C6C7C11	116,9 (6)
C4O5C18	116,3 (6)	C8C7C11	102,2 (6)
C2C1C5	103.5 (6)	O1C8C7	106,0 (6)
C2C1C10	111,5 (6)	O1C8C9	106 4 (6)
C5C1C10	115,6 (6)	C7C8C9	115.6 (7)
O3C2C1	104,4 (6)	C8C9C10	115,6 (7)
O3C2C3	111,1 (6)	C1C10C9	112,7 (6)
C1C2C3	106,6 (6)	C1C10C14	110.7 (7)
C2C3C4	104,0 (7)	C9C10C14	106,4 (7)
O5C4C3	109,7 (6)	C7C11C12	105,7 (7)
O5C4C5	108,3 (6)	C7C11C13	131,2 (8)
C3C4C5	106,5 (6)	C12C11C13	123,1 (8)
C1C5C4	98.5 (6)	O1C12O2	121.3 (8)
C1C5C6	113,3 (6)	O1C12C11	111,8 (7)
C1C5C15	113,0 (6)	O2C12C11	126.6 (8)
C4C5C6	111,6 (6)	O3C16O4	121 6 (8)
C4C5C15	112,6 (6)	O3C16C17	111,4 (7)
C6C5C15	107,7 (6)	O4C16C17	126,9 (8)
O7C6C5	112,6 (7)	O5C18O6	123,9 (8)
O7C6C7	104.3 (7)	O5C18C19	109,2 (7)
C5C6C7	116,2 (6)	O6C18C19	126,9 (8)

TABLE 2. Torsion Angles φ (degrees) in the Rings

Molecule I		Molecule II	
angle	φ	angle	φ
Ring A		Ring A	
C1C2C3C4	−8,2 (8)	C1C2C3C4	54,4 (3)
C2C3C4C5	34,9 (8)	C2C3C4C5	−58,7 (3)
C3C4C5C1	−45,0 (9)	C3C4C5C10	60,0 (3)
C4C5C1C2	38,8 (9)	C4C5C10C1	−55,6 (3)
C5C1C2C3	−19,5 (8)	C5C10C1C2	55,8 (3)
		C10C1C2C3	−55,9 (3)
Ring B		Ring B	
C5C6C7C8	53,1 (9)	C5C6C7C8	50,7 (3)
C6C7C8C9	−91,6 (9)	C6C7C8C9	−36,4 (3)
C7C8C9C10	68,1 (9)	C7C8C9C10	35,2 (3)
C8C9C10C1	−53,9 (9)	C8C9C10C5	−45,3 (3)
C9C10C1C5	77.7 (9)	C9C10C5C6	59.8 (3)
C1=C1C5C6	−81,0 (9)	C10C5C6C7	−64,3 (3)
C1C5C6C7	21.1 (7)		
Ring C		Ring C	
C1C8C7C11	22,9 (8)	O1C8C7C11	−31,7 (3)
C8C7C11C12	−20,1 (9)	C8C7C11C12	25,9 (3)
C7C11C12O1	10,2 (8)	C7C11C12O1	−10,2 (3)
C12O1C8C7	−18,1 (9)	C12O1C8C7	27.8 (3)
C11C12O1C8	4,8 (9)	C11C12O1C8	−11,3 (3)

conformation (c) and conformations intermediate between (b) and (c) have not been observed experimentally in crystal structures. Conformation (a) is observed only in (±)-decahydro-4,5-dihydroxy-4a,8-dimethylazuleno[6,5-c]furan-2(3H)-one ($\Sigma_2/\Sigma_s + \Sigma_2$) = 0.80) (IV) [5] and 11,13-dibromopulchellin ($\Sigma_2/\Sigma_s = \Sigma_2$) = 0.90) (V) [9]. Most frequently, ring B has conformation (b). Such a confromation has been observed in ambliolide (VI) [10], (±)-decahydro-4-hydroxy-4a,8-dimethylazuleno[6,5-c]furan-2,5(3H)-dione (VII) [11], bromoisotenulin (VIII) [12], diacetylspathulin (IX) [13], and britannin (X) [2] (($\Sigma_2/\Sigma_s + \Sigma_2$) 0.09, 0.13, 0.07, 0.16, and 0.17, respectively). We may note that small deviations are observed both in the direction of conformation (a) (VI-VIII, X) and also in the direction of (c) in (VIII) (second independent molecule) and (IX). The absence of conformer (c) in the crystal structures is

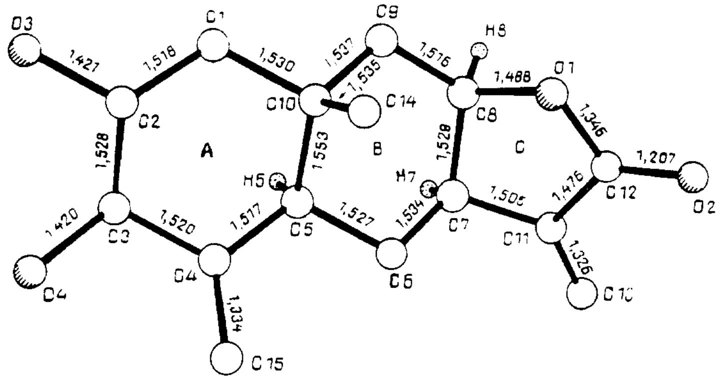


Fig. 2. Structure of the pulchellin C molecules (σ for the bond lengths does not exceed 0.005 Å).

explained, in our view, by the steric repulsion arising between the axially oriented C15 Me group at C5 and the H atom at C8. A comparison of conformations (a) and (b) shows that the former is less favorable, because of this it is rarely realized. Thus, for example, in cycloheptane the chair conformation is less stable than the twist-chair conformation — by 2.80-9.04 kcal/mole according to the results of different authors [14].

For the trans-trans-linked pseudoguaianolide under consideration, the difference in the energies of the conformers must be even greater, since in conformer (a) the conformation relative to the C5—C6, C6—C7, and C7—C8 bonds is eclipsed, and only relative to the C1—C5 bond is it staggered. In conformation (b), conversely, the eclipsed conformation is observed only relative to the C1—C5 bond. We may note that the presence of different substituents at the C6 and C9 atoms in (VI-X) does not in fact affect the conformation of ring B (the difference in the corresponding intracyclic torsion angles does not exceed 10°).

The conformation of the lactine ring C in (I) is intermediate between 7α,8β-half-chair and 7α-envelope (ΔC_s^7 = 5.7° and ΔC_2^{12} = 4.3°). The departures of the C7 and C13 atoms in the α- and β-directions from the plane passing through the other atoms of the ring and the O2 atom (satisfied to within ±0.02 Å) amount to 0.36(1) Å and —0.23(1) Å, respectively. In the crystal, through O7—H...O2 (1 − x, —0.5 + y, 0.5 − z) hydrogen bonds (distances O...O 2.92 Å, H...O 2.23 Å, the angle O—H...O 144.9°), the molecule of (I) forms helical chains along axes of the 2_1(1/2, y, 1/4) type.

Substance (II). $C_{15}H_{20}O_4$, M^+ 264, mp 200-203°C, $[\alpha]_D$ + 92.8° (c 0, 0045; chloroform). In the IR spectrum of the substance absorption bands were observed at (cm^{-1}) 3600, 3490 (—OH); 1760 (γ-lactone CO); and 1660 (double bond). The PMR spectrum exhibited signals at (δ, ppm): 0.83 (3 H, s) — angular methyl; 2.24 (1 H, dd, J_1 = 1.5 Hz, J_2 = 15 Hz) — the proton at C_5; 2.73 (2 H, br.s) — the protons of two hydroxy groups; 2.94 (1 H, q; J_1 = J_2 = 6 Hz) — the proton at C_7; 3.54 (1 H, m) and 3.83 (1 H, d, J = 9 Hz) — the hemihydroxylic protons H-2 and H-3; 4.56 (1 H, m) — the lactone proton; 4.72 (1 H, s) and 5.23 (1 H, s) — the protons of an exomethylene group; and 5.62 (1 H, d, J = 1 Hz) and 6.15 (1 H, d, J = 1 Hz) — the protons of the exomethylene group of the lactone ring.

On acetylation with acetic anhydride in pyridine, the diacetate $C_{19}H_{26}O_8$, with mp 192-194°C (ethanol), was formed. In the IR spectrum of the diacetate the absorption bands characteristic for hydroxy groups were absent.

On the basis of the physicochemical constants obtained and its spectral characteristics and a comparison of them with the literature [15], the second substance was identified as the sesquiterpene lactone pulchellin C; this is the first time it has been isolated from Caspian inula.

A study of the stereochemistry of the (II) molecule was carried out by the method of x-ray structural investigation. The general form of the (II) molecule is shown in Fig. 2. The bond lengths (Fig. 2) and valence angles (Table 3) are close to the usual values [4] within

TABLE 3. Valence Angles ω (degrees) in the Structure of (II)

Angle	ω	Angle	ω
C8O1C12	108,8 (2)	C8C7C11	100,5 (3)
C2C1C10	115,0 (2)	O1C8C7	103,9 (2)
O3C2C1	110,7 (2)	O1C8C9	110,9 (2)
O3C2C3	105,7 (2)	C7C8C9	117,0 (3)
C1C2C3	109,6 (2)	C8C9C10	117,4 (3)
O4C3C2	111,7 (2)	C1C10C5	107,1 (2)
O4C3C4	111,1 (2)	C1C10C9	107,6 (2)
C2C3C4	110,1 (2)	C1C10C14	110,8 (2)
C3C4C5	112,4 (2)	C5C10C9	108,1 (2)
C3C4C15	123,0 (3)	C5C10C14	112,0 (2)
C5C4C15	124,6 (3)	C9C10C14	111,0 (2)
C4C5C6	115,4 (2)	C7C11C12	106,7 (3)
C4C5C10	110,2 (2)	C7C11C13	128,9 (3)
C6C5C10	110,7 (2)	C12C11C13	124,3 (3)
C5C6C7	110,5 (2)	O1C12O2	122,5 (3)
C6C7C8	112,9 (3)	O1C12C11	109,5 (2)
C6C7C11	110,6 (2)	O2C12C11	128,1 (3)

TABLE 4. Coordinates (×10⁴) and Thermal Parameters B_{iso}^{eq} (Å²) of the Nonhydrogen Atoms of the Structure of (I)

Atom	x	y	z	B_{iso}^{eq}
O1	945 (8)	786 (8)	2669 (2)	6,5 (2)
O2	2745 (10)	1021 (8)	3230 (2)	7.6 (2)
O3	1961 (7)	2531 (6)	691 (1)	4.8 (2)
O4	593 (10)	2244 (10)	76 (2)	8.3 (2)
O5	4760 (7)	−2560 (6)	944 (2)	5,9 (2)
O6	7410 (8)	−1461 (8)	735 (2)	8.7 (2)
O7	5600 (8)	−628 (11)	1760 (2)	10,3 (3)
C1	1689 (10)	798 (9)	1289 (2)	3,8 (2)
C2	1507 (12)	852 (10)	802 (2)	5,0 (2)
C3	2930 (14)	−367 (10)	625 (2)	5.8 (3)
C4	4025 (12)	−853 (9)	1003 (2)	5,1 (3)
C5	2709 (10)	−897 (9)	1374 (2)	3,9 (2)
C6	3737 (11)	−939 (10)	1803 (3)	5,2 (3)
C7	3107 (11)	286 (9)	2133 (2)	4,2 (2)
C8	1122 (11)	258 (11)	2229 (2)	4,8 (2)
C9	−26 (11)	1410 (11)	1973 (3)	5.6 (3)
C10	−192 (11)	997 (9)	1509 (2)	4,6 (2)
C11	3938 (12)	138 (10)	2565 (2)	5,2 (3)
C12	2534 (13)	632 (10)	2856 (2)	5,5 (3)
C13	5569 (14)	−341 (12)	2686 (3)	6,8 (3)
C14	−1271 (13)	2394 (14)	1308 (3)	7,9 (4)
C15	1456 (11)	−2360 (9)	1369 (2)	4,4 (2)
C16	1455 (11)	3081 (11)	314 (2)	5,3 (3)
C17	2021 (12)	4806 (10)	249 (3)	5,6 (3)
C18	6480 (11)	−2601 (13)	792 (2)	5.7 (3)
C19	6969 (12)	−4373 (11)	724 (3)	6,3 (3)

the limits of accuracy, with the exception of the angles C7C8C9, 117.0(3)°; C8C9C10, 117.4(3)°; and C8C7C11, 100.5(3)°, which are highly distorted relative to ideal tetrahedral value of 109.5°. The distortion of these valence angles is apparently a consequence of the cis-linkage of the six-membered ring B and the five-membered lactone ring C, since analogous distortion is also observed in other 7,8-cis-eudesmanolids (see, for example, [2, 16, 17]).

The linkage of rings A/B is trans- and of rings B/C cis- (torsion angles: C14C10C5H5, 173(2)°; and H7C7C7H8, 26(3)°). The conformation of the six-membered ring A is an almost symmetrical chair (ΔC_s^2 = 3.2°). The values of the torsion angles in this ring (Table 2) are close to the ideal values (56° in cyclohexane), and the sum of the intracyclic torsion angles (Σφ) is 340.4°. A similar conformation of ring A is observed in other A/B-trans-linked eudesmanolides: 3β-hydroxy-2α-senecioyloxyisoalantolactone (XI) [2], subcordatolide C (XII)

TABLE 5. Coordinates ($\times 10^4$) and Thermal Parameters B_{iso}^{eq} ($\mathring{A}^2$) of the Nonhydrogen Atoms of the Structure of (II)

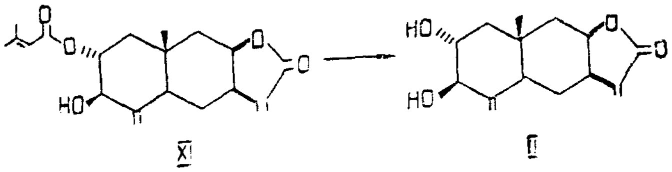
Atom	x	y	z	B_{iso}^{eq}
O1	5004 (2)	1604	7098 (2)	3,68 (6)
O2	6705 (2)	3198 (3)	8554 (2)	4,39 (7)
O3	−704 (2)	925 (3)	742 (2)	4,36 (7)
O4	−996 (2)	4421 (3)	1029 (2)	3,54 (6)
C1	1171 (3)	782 (4)	2979 (3)	2,97 (9)
C2	420 (3)	1848 (4)	1686 (3)	2,97 (9)
C3	−320 (3)	3355 (4)	2197 (3)	2,50 (8)
C4	758 (3)	4318 (4)	3335 (3)	2,43 (9)
C5	1444 (3)	3236 (4)	4635 (3)	2,35 (8)
C6	2428 (3)	4170 (4)	5906 (3)	2,76 (9)
C7	2826 (3)	3025 (5)	7244 (3)	3,59 (9)
C8	3413 (3)	1307 (5)	6925 (3)	3,63 (9)
C9	2732 (3)	526 (4)	5465 (3)	3,30 (9)
C10	2268 (3)	1724 (4)	4167 (8)	2,71 (9)
C11	4134 (3)	3768 (4)	8331 (3)	3,8 (1)
C12	5433 (3)	2870 (4)	8046 (3)	3,4 (1)
C13	4177 (4)	4828 (7)	9374 (4)	6,9 (1)
C14	3597 (3)	2298 (4)	3626 (3)	3,5 (1)
C15	1102 (3)	5925 (4)	3175 (3)	3,6 (1)

[17], the diacetate of 13β-p-bromophenylthio-11α,13-dihydropulchellin C (XIII) [18], and erivanin (XIV) [19], which also have a C14–C15 exocyclic double bond. We may note that Σφ ranges from 324° in (XI) to 358° in (XIII) and does not correlate with the presence of substituents at C1, C2, and C3. The hydroxy groups in (II) at C2 and C3 have the equatorial orientation and depart from the plane of the C2, C3, C5, and C10 atoms (satisfied to within ±0.007 Å) by 0.783(2) and −0.630(2) Å in the α- and β-directions, respectively.

The conformation of ring B is a highly distorted chair (Table 2). Out of all the possible symmetry elements in it, practically only the plane passing through the C5 and C8 atoms is actually satisfied (ΔC_s^5 = 4.1°). The greatest deviation from the ideal value of 56° is experienced by the C6C7C8C9 and C7C8C9C10 torsion angles, amounting the −36.4 and 35.2°, respectively. Such a pronounced distortion of ring B is possibly a consequence of the axial orientation of the O1 atom and the 1,3-interactions so arising, especially the C14 Me group at C10 and O1 atom. A similar distortion of ring B is also observed in the molecules of (XI)-(XIII), the difference between the corresponding intracyclic torsion angles not exceeding 6°. We may note that with the 7,8-cis linkage of rings B and C the existence of ring B in the twist conformation is theoretically possible [20]. However, our conformational calculations by the method of molecular mechanics for model (skeletal) analogues of (II) – 14β,4β, 11β(H), 5α,7α,8α(H)-eudesm-8,12-olide and 14β,4β(H),5α,7α,8α,11α(H)-eudesm-8,12-olide – show [20] that the distorted chair conformation observed for ring B is nevertheless more favorable than the twist conformation by 3.0-6.0 kcal/mole.

The conformation of the lactine ring C is an almost ideal 7α,8α-half-chair ($\Delta C_2^{1 2}$ = 1.6°). The C7 and C8 atoms depart from the mean plane of the other atoms of the ring and O2 (satisfied to within ±0.003 Å) by 0.247(3) and −0.282(3) Å in the α- and β-directions, respectively. The C12 atom also departs in the β-direction by −0.203(4) Å. In the crystal, the molecules of (II) are joined by the hydrogen bonds O3–H...O4 (−x, −0.5 + y, −z) (distances: O...O 2.86 Å. H...O 2.18 Å; the angle O–H...O 169.3°) into helical chains along axes of the 2_1 type (0, y, 0); these chains are "cross-linked" into layers parallel to (1, 0, $\bar{1}$) by O4–H... O2 (−1 + x, y, −1 + z) H-bonds (distances O...O 2.95 Å, H...O 2.19 Å; angle O–H...O 153.0°).

On the basis of biogenetic considerations it may be assumed that pulchellin C is possibly formed from 3β-hydroxy-2α-senecioyloxyisoalantolactone by the enzymatic hydrolysis of this compound in the vegetable organism. The interaction of 3β-hydroxy-2α-senecioyloxyisoalantolactone (XI) with 4% KOH gave a derivative which, in elementary composition, melting point, and spectral characteristics, proved to be identical with pulchellin C (II).



XI

II

EXPERIMENTAL

The individuality of the substances isolated was checked by TLC on Silufol plates in the hexane—ethyl acetate (1:1) system. The spots were revealed with iodine vapor and with 0.5% $KMnO_4$ in 0.5% H_2SO_4. The substances were dried in a vacuum pistol with P_2O_5 over alcohol for 6 h. The optical rotation were measured on SM-2 circular polarimeter in a tube 0.5 dm long with a volume of 10 ml. IR spectra were taken on a UR-20 spectrophotometer; PMR on a Bruker HX-90E instrument (in $CDCl_3$ and C_5D_5N, with TMS as internal standard, δ scale); and mass spectra on a Finnigan MAT 8200 mass spectrometer. The elementary analyses of the compounds obtained corresponded to the calculated values.

Isolation of the Lactones. Leaves and flower heads of Caspian inula gathered in the flowering phase (2.4 kg) were exhaustively extracted with chloroform. The solvent was evaporated off in a rotary evaporator. The yield of total extracted substances amounted to 157.0 g. This total was treated with 60% ethanol. The resulting precipitate was separated off, and the lactones were extracted from the aqueous ethanolic solution with chloroform (3 × 500 ml). After the chloroform had been distilled off, a cream-colored viscous mass (67.5 g) was obtained.

This cream-colored mass (40 g) was chromatographed on a column containing 846 g of type KSK silica gel. Elution of the column with benzene (1 liter) yielded 0.1107 g of the pseudoguaianolide incaspin [1]. From 2 liters of benzene—ether (1:1) fractions, 0.3144 g of the pseudoguaianolide britannin was isolated. From 1 liter of ethereal fractions, 0.0728 g of 3β-hydroxy-2α-senecioyloxyisoalantolactone [2] was obtained.

On chromatographic reseparation of the combined lactone mother liquors after the isolation of the above-mentioned lactones, with elution of the column by benzene—ether (4:1), a crystalline mass was isolated. After three recrystallizations from ethanol 1.0667 g (0.04% calculated on the air-dry raw material) of the colorless crystalline substance (I) was isolated with m/z 246 ($M^+ - 2\ CH_3COOH$).

On further elution of the column with ether—ethyl acetate (1:1), a crystalline mass was isolated the recrystallization of which from ethanol yielded 0.1721 g of the colorless crystalline substance (II) (0.007%, calculated on the dry material).

Acetylation of (II). A solution of 0.1 g of pulchellin C (II) in 1.6 ml of pyridine was treated with 1 ml of acetic anhydride, and the mixture was heated in the water bath at 60°C for 1 h. After cooling, it was diluted with a five-fold amount of water and the reaction product was extracted with chloroform. The chloroform extract was washed with 3% HCl solution and then with water to neutrality, the chloroform was distilled off, and a liquid product was obtained which crystallized on being washed with ether. The crystalline mass was recrystallized on being washed with ether. The crystalline mass was recrystallized from ethanol, giving a colorless crystalline substance with the composition $C_{19}H_{26}O_8$, mp 192-194°C (ethanol). On TLC it gave a single spot with R_f 0.90. The yield of the substance was 47%.

Hydrolysis of 3β-Hydroxy-2α-senecioyloxyisoalantolactone (XI). With stirring, 3 ml of 4% KOH was added to a solution of 39 mg of (XI) in 2 ml of C_2H_5OH, and the mixture was left at room temperature for 1 h. Then it was acidified with 10% H_2SO_4 to pH 1 and was extracted with ethyl acetate four times, and the extract was washed with 5% Na_2CO_3 and with distilled water to neutrality. It was dried over $MgSO_4$ for 30 min and was filtered. The filtrate was evaporated in a rotary evaporator. On TLC, the R_f values of the reaction product and of pulchellin C coincided. The yield of product was 0.06%.

X-Ray Structural Experiment. The parameters of the cells and the intensities of the reflections of crystals of (I) and (II) were measured on a Hilger-Watts automatic four-circle diffractometer at room temperature (λMoK_α, graphite monochromator, θ/2θ scanning, $2\theta \leq 60°$). The crystals of (I) were rhombic, $a = 7.3718(6)$, $b = 8.1462(5)$, $c = 31.845(2)$ Å, $V = 1912.4(2)$, Å^3, $M = 366.4$, $d_{calc} = 1.272$ g/cm^3, $Z = 4$ ($C_{19}H_{26}O_7$), sp.gr. $P2_12_12_1$. The crystals of (II) were monoclonic $a = 9.4280(5)$, $b = 7.9337(4)$, $c = 9.5338(8)$ Å, $\beta = 104.087(5)°$, $V = 691.67(7)$ Å^3, $M = 264.3$, $d_{calc} = 1.269$ g/cm^3, $Z = 2$ ($C_{15}H_{20}O_4$), sp.gr. $P2_1$.

The structures were interpreted by the direct method and were defined by the block-diagonal method of least squares in the anisotropic approximation for the nonhydrogen atoms. The positions of the H atoms in (I) were calculated (apart from the H-(07), H-14.1, H-15.1, H-17.1, H-19.1 atoms, which were revealed in a difference synthesis). The H atoms in (II) were revealed in a different synthesis and were included in the refinement with a fixed B_{iso} = 3.0 Å^2. The coordinates of the H atoms were not refined, but their contribution to the value of F_{calc} was taken into account with B_{iso} = 4.0 Å^2. The final divergence factors were R = 0.044 and R_w = 0.034 for 1225 independent reflections with $I \geq 3\sigma$ in the structure of (II) and R = 0.078 and R_w = 0.076 for 1153 independent reflections with $I \geq 2\sigma$ in the structure of (I).

All the calculations were performed on an Eclipse S/200 computer by the INEXTL program [21]. The coordinates and thermal parameters of the nonhydrogen atoms in the structures of (I) and (II) are given in Tables 4 and 5, respectively. Although the absolute configurations of the asymmetric centers in the molecules of (I) and (II) were not established objectively in this investigation, the correct (with respect to chirality) system of coordinates deduced on the basis of the known R-configuration of the C7 atoms in (I) and (II) [3, 9] is used throughout the paper.

LITERATURE CITED

1. S. M. Adekenov, M. A. Abdykalykov, A. D. Kagarlitskii, A. N. Kupriyanov, and K. M. Turdybekov, Khim. Prir. Soedin., No. 6, 797 (1984).
2. S. M. Adekenov, M. A. Abdykalykov, K. M. Turdybekov, A. D. Kagarlitskii, and Yu. V. Gatilov, Izv. Akad. Nauk KazSSR, Ser. Khim., 74 (1986).
3. K. Ito and T. Iida, Phytochemistry, 20, No. 2, 271 (1981).
4. F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, and R. Taylor, J. Chem. Soc. Perkin Trans. II, S1 (1987).
5. J. P. De Clercq, G. Germain, M. Van Meerssche, P. Kok, P. De Clercq, and M. Vandewalle, Acta Crystallogr., B36, 190 (1980).
6. G. Appendino, M. Calleri, G. Chiari, P. Gariboldi, and F. Merichini, Gazz. Chim. Ital., 116, 637 (1986).
7. B. Tashkhodzhaev and Z. Karimov, Khim. Prir. Soedin., 291 (1986).
8. J. B. Hendrickson, J. Am. Soc., 89, 7036 (1967).
9. T. Sekita, S. Inayama, and Y. Iitaka, Acta Crystallogr., B27, 877 (1971).
10. W. Herz and J. F. Mount, J. Org. Chem., 47, 1594 (1982).
11. J. P. De Clercq, G. Germain, M. Van Meerssche, P. Kok, and M. Vandewalle, Acta Crystallogr., B36, 739 (1980).
12. M. Ul-Haque and D. Rogers, J. Chem. Soc., Perkin Trans. II, 223 (1974).
13. S. Inayama and T. Ohkura, Chem. Pharm. Bull, 25, 1928 (1977).
14. U. Burkert and N. L. Allinger, Molecular Mechanisms, ACS Monograph No. 177, American Chemical Society, Washington, DC (1982).
15. H. Yosioka, T. J. Mabry, N. Dennis, and W. Herz, J. Org. Chem., 35, No. 3, 627 (1970).
16. G. Appendino, M. Calleri, G. Chiari, and D. Viterbo, J. Chem. Soc., Perkin Trans. II, 903 (1984).
17. A. G. Ober and F. R. Fronczek, J. Nat. Prod., 47, 920 (1984).
18. M. Currie and G. A. Sim, J. Chem. Soc., Perkin Trans. II, 400 (1973).
19. U. Rychlewska, M. Holub, E. Bloszyk, and B. Drozdz, Coll. Czech. Chem. Common., 47, 88 (1982).
20. K. M. Turdybekov, S. V. Lindeman, T. V. Timofeeva, and Yu. T. Struchkov, Khim. Prir. Soedin., 193 (1990).
21. R. G. Gerr, A. I. Yanovskii, and Yu. T. Struchkov, Kristallografiya, 28, 1029 (1983).