forms predominantly tertiary alcohols with the trans orientation of the vicinal OH and CH_3 groups.

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X-RAY STRUCTURAL INVESTIGATION OF SESQUITERPENE ESTERS FROM PLANTS OF THE GENUS Ferula.

III. CRYSTAL AND MOLECULAR STRUCTURE OF THE GERMACRANE ESTER CHIMGANIDIN

M. K. Makhmudov, B. Tashkhodzhaev,
A. I. Saidkhodzhaev, M. R. Yagudaev,
and V. M. Maikov

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An x-ray structural investigation of the germacrane ester chimganidin (diffractometer Cu K_α radiation, 1028 reflections, direct method, R factor 0.114) has been carried out. The stereochemistry of chimganidin has been established; it is 6α-hydroxy-8β-vanilloyloxygermacra-1(10),4(5)-diene. The double bonds in the macro cycle have the trans configuration.

Chimganidin — a germacrane ester with the composition $C_{23}H_{32}O_5$, was isolated from the plants *Ferula pallida* Korov. and *Ferula tschimganica* Lypsky [1, 2]. Structure (Ia) with a germacrane macrocycle was proposed for chimganidin on the basis of IR, mass, and PMR spectrosocpy and some chemical transformations [3]. However, an unambiguous determination of the structure and stereochemistry of chimganidin by spectroscopic methods especially PMR, proved to be difficult because of the presence of a labile ten-membered macrocyclic unit; moreover, the Cope chemical transformation performed did not permit the positions of the double bonds in the germacrane ring to be fixed definitively as 1(10),4(5) or 1(10),-5(6) [3].

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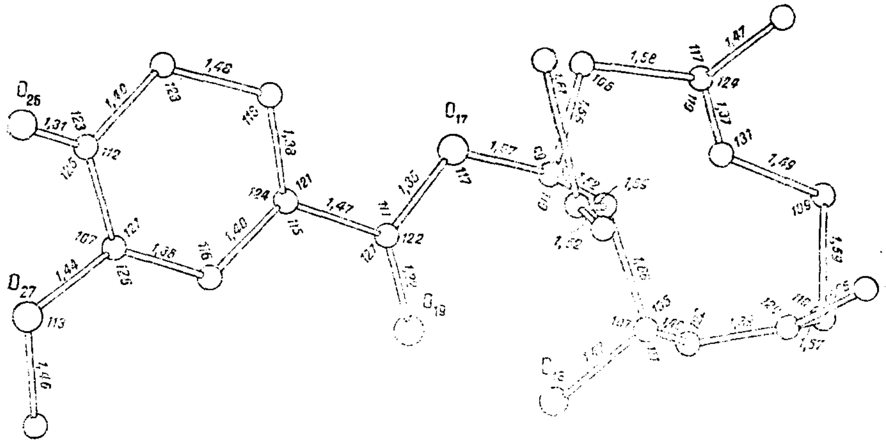
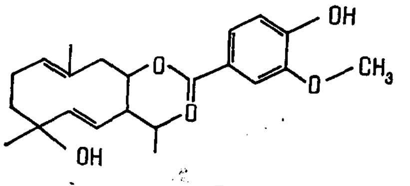


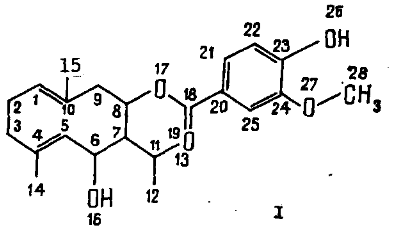
Fig. 1. Geometry of the chimganidin molecule:

C (3)–C (4)–C (14)	115	C (7) –C (8) –C(9)	117
C (5)–C (4)–C (14)	123	C (7) –C (11)–C(12)	113
C (6)–C (7)–C (8)	114	C (7) –C (11)–C(13)	107
C (6)–C (7)–C (11)	110	C (12)–C (11)–C(13)	110
C (8)–C (7)–C (11)	117		

In order to confirm the proposed structure definitively and to establish the stereochemistry of chimganidin, we have carried out an x-ray structural investigation. The unambiguous determination of the structure of chimganidin also enables the structure of the related ester ferolin and the natural diol from which it is derived — angrendiol to be established.



Ia



I

The x-ray structural analysis enabled the structure of chimganidin to be refined to (I) in which one of the double bonds in the germacrane ring is present in the 4(5) position, and not the 5(6) position as was assumed previously [3], and the hydroxy group is located at C(6) and not at C(4). Figure 1 shows the chimganidin molecule in a projection on the (011) plane. It can be seen that the hydroxy and isopropyl groups in positions 6 and 7 have the α orientation. The ethylenic fragment of the germacrane ring has the trans form with a torsional angle about the double bond of 168°, this deviation of the torsional angle from the ideal 180° being explained by shortened contacts in the macrocycle (C(1)—C(5) 3.01 Å; C(7)—C(10) 3.13 Å). The planar sections of the (I) molecule — the ester group and the substituted benzene ring — are practically coplanar, the dihedral angle between them amounting to 7°. These planar fragments are twisted relative to the mean square plane of the macrocycle by 47°, which leads to the formation of a O(16)—H···O(19) intramolecular H-bond 2.71 Å long. The hydroxy groups participate not only in intramolecular but also in intermolecular O(26)—H···O(16) hydrogen bonds 2.62 Å long, leading to the formation of chains of molecules linked by screw axes in the c direction. On comparing the torsional angles of the macrocycles of chimganidin and of the hydroxy derivative of (—)-isobicyclogermacranol [4] (Table 1), it can be seen that their values in the 8—9—10—1—2—3—4—5 section are symbatic, although in the latter compound a cyclopropane ring is linked with the germacrane ring in the 6,7 position.

Figure 1 gives the values of the bond lengths and valence angles (mean deviation not greater than 0.06 Å and 4°, respectively). An anomalous increase in the length of the bonds in the germacrane ring is observed (for example, the double bonds reach 1.39 Å and the ordinary C(6)—C(7) bond 1.66 Å) or an anomalous decrease in the length of a bond (C(5)—C(6) to 1.49 Å) as compared with the standard values [5]. This variation in the lengths of the bonds found is explained by experimental errors (the limited set of structural amplitudes and the relatively high value of the R factor).

TABLE 1. Torsional Angles of the Germacrane Ring (degrees)

Angle	(−)-Isobicyclogermacranol	Chimganidin
10—1—2—3	94,8	110.6
1—2—3—4	−60,7	—46.2
2—3—4—5	89,2	86,1
3—4—5—6	3.2	−168,2
4—5—6—7	—113,1	96.5
5—6—7—8	3.3	40.8
6—7—8—9	90,5	—130.2
7—8—9—10	—70,5	65,8
8—9—10—1	90.1	60,0
9—10—1—2	—163,4	−167.0
2—1—10—15	9,5	5,0

TABLE 2. Coordinates ($\times 10^4$) of the Atoms of the Chimganidin Molecule

Atom	x/a	y/b	z/c
C (1)	5916 (8)	5682 (11)	—842 (8)
C (2)	6228 (10)	5869 (18)	—1621 (6)
C (3)	5865 (10)	4460 (17)	—2091 (8)
C (4)	4782 (9)	4112 (16)	—1899 (6)
C (5)	4563 (8)	3148 (15)	—1313 (5)
C (6)	3565 (9)	3018 (13)	—1013 (6)
C (7)	3538 (6)	4214 (12)	— 302 (5)
C (8)	4452 (7)	4207 (14)	155 (6)
C (9)	4910 (8)	5778 (14)	332 (7)
C (10)	5248 (7)	6469 (12)	—433 (6)
C (11)	2547 (8)	4039 (16)	125 (6)
C (12)	1688 (7)	3969 (16)	—390 (7)
C (13)	2418 (9)	5532 (13)	635 (7)
C (14)	4029 (9)	5181 (15)	—2271 (8)
C (15)	4738 (10)	7832 (13)	—701 (8)
O (16)	3386 (7)	1493 (8)	—713 (5)
O (17)	4235 (5)	3669 (9)	963 (4)
C (18)	4118 (7)	2161 (11)	1074 (7)
O (19)	4305 (5)	1214 (8)	602 (4)
C (20)	3829 (8)	1859 (13)	1839 (6)
C (21)	3580 (11)	3035 (13)	2304 (7)
C (22)	3209 (11)	2638 (17)	3044 (11)
C (23)	3061 (8)	1140 (13)	3278 (8)
C (24)	3392 (10)	13 (12)	2709 (9)
C (25)	3740 (7)	315 (12)	2026 (6)
O (26)	2737 (6)	784 (10)	3931 (4)
O (27)	3303 (6)	—1473 (9)	3036 (4)
C (28)	3622 (11)	—2705 (11)	2555 (7)

No anomalies were observed in the values of the valence angles. On the whole, the bond lengths and valence angles in (I) coincide within the 3σ limits with those observed in other germacrane esters [6, 7].

EXPERIMENTAL

Colorless crystals of chimganidin in the form of elongated prisms were grown from a mixture of ether and hexane and were first studied by the photographic method. The space group and parameters of the elementary cell were determined from precision x-ray patterns. Then these parameters were refined on a Sintex $P2_1$ diffractometer using Cu K_α radiation: a = 13.891(3), b = 8.775(2), c = 18.139(4) Å, d_{calc} = 1.219(4) g/cm^3; space group $P2_12_12_1$; z = 4. The intensities of 1028 independent reflections with $I \geqslant 2\sigma$ were measured on the same diffractometer. The structure was determined by the direct method using the Roentgen-75 program [8] in the automatic regime. From the best variant of the signs an E-series was constructed from which 26 out of the 28 nonhydrogen atoms were found (R factor 0.32). In the subsequent ρ(x, y, z) syntheses all the nonhydrogen atoms were revealed (R = 0.23). The structure was refined by the method of least squares in the anisotropic approximation to R = 0.114. The coordinates of the atoms are given in Table 2.

SUMMARY

By x-ray structural analysis, the structure of chimganidin has been refined and its stereochemistry has been established unambiguously; it is 6α-hydroxy-8β-vanilloyloxygermacra-1(10),4(5)-diene.

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PHYTOECDYSTEROIDS OF PLANTS OF THE GENUS Silene.

XI. 2-DEOXY-α-ECDYSONE 3-ACETATE FROM Silene scabrifolia

Z. Saatov, M. B. Gorovich,
and N. K. Abubakirov

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From the epigeal organs of Silene scabrifolia Kom. has been isolated the new phytoecdysteroid 2-deoxy-α-ecdysone 3-acetate (II) (0.0011%), $C_{29}H_{46}O_6$, mp 216-218°, $[\alpha]_D^{20}$ +131.9° (methanol). The enzymatic hydrolysis of (II) led to 2-deoxy-α-ecdysone (I). The acetylation of 2-deoxy-α-ecdysone (I) yielded (II) and the 22-monoacetate (III) and 3,22-diacetate (IV) of 2-deoxy-α-ecdysone, which have been described previously. Details of the IR, UV, CD, mass, and NMR spectra are given for (I) and of the IR, mass, and NMR spectra for (III).

We are continuing a study of the ecdysteroids of Silene scabrifolia Kom. (family Caryophyllaceae) [1]. Additional chromatography which isolated 2-deoxy-α-ecdysone and ecdysterone 22-O-benzoate produced mother liquors which contained a new ecdysteroid (II) with the composition $C_{29}H_{46}O_6$.

The α,β-unsaturated keto grouping that is characteristic for ecdysteroids was shown in the UV spectrum of compound (II) by a maximum at 245 nm (log ε 4.00) and in the UV spectrum by a band at 1665 cm^{-1}. In addition, absorption in the IR spectrum at 1735 and 1250 cm^{-1} and the presence in the PMR spectrum of a three-proton singlet at 1.85 ppm showed that ecdysteroid (II) contained one acetyl group.

The enzymatic hydrolysis of compound (II) performed with the combined enzymes isolated from bakers' yeast [2] led to 2-deoxy-α-ecdysone [1]. The peak of an ion with m/z 374 (cleavage of the C-20—C-22 bond), its derivatives with m/z 356 and 341, and also a fragment with m/z 326 (cleavage of the C-17—C-20 bond) observed in the mass spectrum of the acetate (II) made it possible to assume that the acetyl group was located in the steroid nucleus [3, 4].

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