

CRYSTALLINE STRUCTURE OF THE ADDITION COMPOUND
OF COSTUNOLIDE WITH SILVER NITRATE

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Costunolide (I), a native sesquiterpenic lactone, was isolated by Indian workers from a Himalayan plant, *Saussurea lappa* Clarke (1), and later in our laboratories from a Central-Asian plant, *Artemisia balchanorum* H. Krasch. (2). We succeeded in solving the structure and the absolute configuration of the mentioned lactone (3). In a subsequent paper (4) we discussed the geometry of the double bonds in its molecule and we assigned a trans configuration to both trisubstituted double bonds. However, we were unable to establish mutual relationships between the steric arrangement of these bonds and the fusion points of the lactone ring.

In order to ascertain the conformation of costunolide (I) and to obtain further information concerning its molecular geometry we carried out an X-ray crystallographic study of the addition compound of costunolide with silver nitrate (II; $C_{15}H_{20}O_2 \cdot 2 AgNO_3$; M.W. 572.1), prepared according to a known method (5). The following crystallographic data were obtained: orthorhombic, space group $P 2_1 2_1 2_1$, $Z = 4$, $a = 7.489$, $b = 11.400$, $c = 21.415$ (Å).

Using Mo K_{α} radiation 2550 reflections were estimated on a Hilger and Watts 4-circle diffractometer. The positions of the silver atoms were determined from the three-dimensional Patterson function.

The positions of the lighter atoms were determined from Fourier syntheses. The found coordinates of atoms are given in Tab. 1.

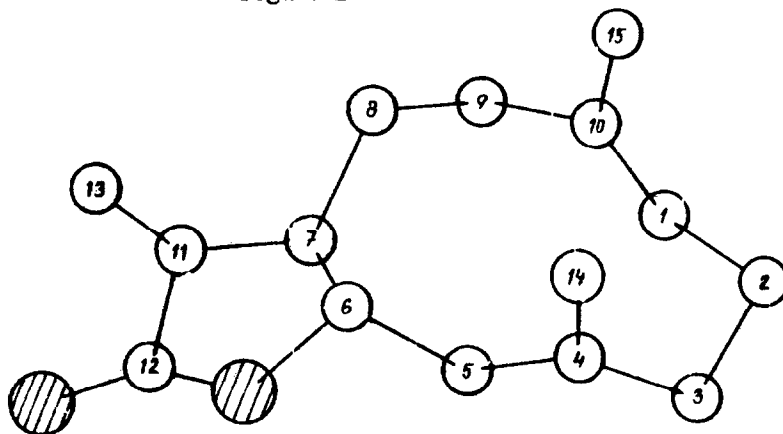
Table 1⁺

Coordinates of atoms of the addition compound
of costunolide with silver nitrate

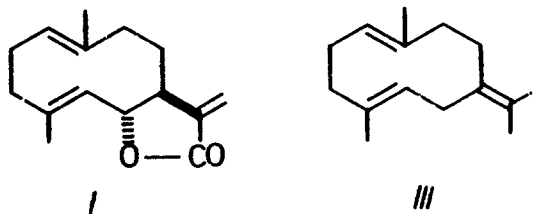
C ₍₁₎	0.23	0.88	0.62	Ag	0.11	0.20	0.20
C ₍₂₎	11	78	58	Ag	06	56	07
C ₍₃₎	03	84	52	N	11	21	33
C ₍₄₎	06	44	96	N	14	87	36
C ₍₅₎	04	05	53	O	03	13	30
C ₍₆₎	01	66	94	O	20	28	30
C ₍₇₎	15	22	60	O	04	19	39
C ₍₈₎	18	16	67	O	03	38	13
C ₍₉₎	22	94	18	O	25	93	38
C ₍₁₀₎	17	94	66	O	18	77	31
C ₍₁₁₎	11	34	60				
C ₍₁₂₎	-0.01	35	53				
C ₍₁₃₎	12	43	63				
C ₍₁₄₎	25	43	93				
C ₍₁₅₎	03	92	70				
O	06	75	98				
O	05	94	99				

⁺ The positions of atoms are given before refinement by means of the LS-method.

Figure 1



The schematic figure 1 (looking along the diagonal in the XZ plane) shows the shape of the molecule. A similar arrangement between the silver ions and the double bonds in the neighbouring molecules as in our preparation also occurs in the addition compound of germacatriene with silver nitrate (6). The ions of silver in compound II are coordinated to the $C_{(1)}-C_{(10)}$, $C_{(4)}-C_{(5)}$ and $C_{(11)}-C_{(13)}$ double bonds. The Ag - C distances range from 2.4 to 2.8 Å, on an average 2.56 Å.



X-ray analysis of compound II corroborated the correctness of the structure of costunolide (I) proposed earlier (3) and elucidated the geometry of trisubstituted double bonds in the molecule of costunolide

in agreement with the configuration proposed by us earlier (4), as well as their position with respect to the lactone ring. The conformation of the molecule of costunolide is characterised by trans fusion of the γ -lactone and the ten-membered rings, by an almost true trans position of protons at C₍₅₎ and C₍₆₎, and by a trans configuration of the double bonds substituted with methyls which are oriented in the same plane of the costunolide molecule. The arrangement of the double bonds and the whole conformation of ten-membered ring in costunolide are analogous to that in the molecule of germacatriene (III) (6).

REFERENCES

1. A.S. Rao, G.R. Kelkar and S.C. Bhattacharyya, Chem. Ind. (London), 1958, 1359.
2. V. Herout and F. Šorm, Chem. Ind. (London), 1959, 1067.
3. V. Herout, M. Suchý and F. Šorm, Coll. Czechoslov. Chem. Commun., 26, 2612 (1961).
4. M. Suchý, V. Herout and F. Šorm, Coll. Czechoslov. Chem. Commun., 31, 2899 (1966).
5. R.P. Hildebrand and M.D. Sutherland, Austr. J. Chem., 14, 272 (1961).
6. F.H. Allen and D. Rogers, Chem. Commun., 1967, 588.