X-RAY STRUCTURAL INVESTIGATION OF GOSSYPOL AND ITS DERIVATIVES.

VI. THE STRUCTURE OF THE ADDUCT OF GOSSYPOL WITH CARBON TETRACHLORIDE

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In previous papers [1-5] we have given the crystallographic characteristics of single crystals for nine crystalline forms of gossypol (Gp) and the results of the interpretation of four of them. In four cases out of the nine, the crystal lattice was constructed without the participation of solvent molecules, and in the other cases the crystalline forms of Gp were solvated. The product of the crystallization of Gp from carbon tetrachloride is also a solvated crystal. The interpretation of the structure of this crystalline form of Gp, together with the other forms, is necessary in order to determine the reason for the diversity of the crystalline modifications of Gp.

TABLE 1. Coordinates of the Atoms in the Crystal Structure of the Adduct of Gp with CCl_4 ($\times 10^4$; for the H atoms, $\times 10^3$; the standard deviations are given in parentheses)

Atom	x a	y b	z c	Atom	x a	y b	z c
C1	1292 (7)	2778 (5)	6727 (5)	C2	680 (8)	1887 (4)	7332 (6)
C3	−912 (8)	1727 (5)	8017 (6)	C4	−1867 (8)	2466 (6)	7974 (6)
C5	−2347 (8)	4161 (5)	7376 (6)	C6	−1738 (9)	5034 (6)	6849 (6)
C7	−58 (9)	5295 (5)	6244 (6)	C8	996 (8)	4574 (5)	6189 (5)
C9	375 (8)	3601 (5)	6736 (6)	C10	−1266 (9)	3413 (5)	7345 (6)
C11	1908 (8)	532 (5)	6549 (6)	C12	1841 (9)	1136 (5)	7258 (6)
C13	2795 (9)	961 (6)	7945 (7)	C14	3886 (9)	264 (6)	7814 (7)
C15	5052 (9)	−1063 (5)	6979 (6)	C16	5088 (9)	−1636 (5)	6258 (7)
C17	4121 (9)	−1485 (5)	5557 (7)	C18	3025 (8)	−820 (5)	5643 (6)
C19	2910 (8)	−214 (5)	6411 (6)	C20	3947 (9)	−338 (5)	7055 (7)
C21	−1532 (11)	746 (6)	8742 (9)	C22	2656 (10)	4905 (5)	5606 (6)
C23	−4109 (10)	3952 (6)	8032 (7)	C24	−5242 (12)	4263 (9)	7380 (9)
C25	−4538 (12)	4430 (9)	8997 (9)	C26	2757 (12)	1576 (6)	8773 (7)
C27	1951 (10)	−821 (6)	4983 (7)	C28	6076 (9)	−1257 (6)	7745 (7)
C29	7825 (11)	−1303 (8)	7135 (9)	C30	5391 (13)	−2075 (9)	8687 (8)
O1	2853 (6)	2981 (3)	6055 (4)	O2	3113 (8)	5780 (4)	5200 (5)
O3	384 (7)	6213 (3)	5784 (4)	O4	−2654 (7)	5816 (4)	6815 (5)
O5	934 (6)	700 (3)	5893 (4)	O6	2089 (7)	−1361 (4)	4356 (5)
O7	4335 (6)	−2080 (3)	4872 (4)	O8	6042 (6)	−2389 (4)	6160 (5)
HO1	336	224	623	HO3	134	678	515
HO4	−195	640	633	HO5	9	124	617
HO7	340	−210	473	HO8	532	−311	648
H4	−298	233	848	H14	463	33	828
H22	356	422	546	H23	−442	309	837
H27	100	−46	523	H28	596	−58	816
$H21_1$	−274	78	916	$H21_2$	−112	36	904
$H21_3$	−171	23	833	$H26_1$	313	234	834
$H26_2$	329	130	935	$H26_3$	168	132	928
$H24_1$	−648	398	794	$H24_2$	−495	356	700
$H24_3$	−519	498	688	$H25_1$	−584	417	951
$H25_2$	−408	406	959	$H25_3$	−414	520	870
$H29_1$	793	−205	716	$H29_2$	889	−100	741
$H29_3$	808	−51	652	$H30_1$	610	−244	932
$H30_2$	427	−179	892	$H30_3$	482	−272	855
C31	618 (9)	6714 (6)	8083 (7)	Cl_1	−1118 (3)	6312 (2)	8782 (3)
Cl_2	962 (3)	7935 (2)	8592 (3)	Cl_3	2196 (4)	6170 (3)	8244 (3)
Cl_4	371 (5)	6345 (3)	10364 (3)				

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Single crystals of Gp were grown from carbon tetrachloride solution by the slow evaporation of the solvent. The crystallographic parameters of the single crystals measured and refined on a Syntex-P2 diffractometer were as follows: a = 8.847(2) Å, b = 14.304(6) Å, c = 13.221(5) Å, α = 78.6(3)°, β = 71.65(3)°, γ = 91.12(3)°, V = 1547.09(0.89) Å^3, z = 2, sp. gr. PT.

The set of experimental intensities was obtained on the diffractometer mentioned ($\theta/2\theta$ scanning, CuK_α radiation, graphite monochromator). In the calculations 2559 reflections with $F^2 > 2\sigma$ were used.

A model of the structure was found with the aid of the MULTAN-78 program [6] and was subsequently refined by the programs of the Rentgen-75 group [7]. Course of refinement: two stages of Fourier F synthesis refined by the method of least squares (MLS) in the isotropic (R = 0.132) and the anisotropic (R + 0.109) approximations. The coordinates of the hydrogen atoms were found from Fourier difference syntheses. The coordinates of the atoms of the structure, referred to a single molecule and corresponding to a value of the R factor of 0.088, are given in Table 1 (for the numbering of the atoms, see [3]).

The crystal structure included CCl_4 in a ratio Gp:CCl_4 = 1:1. The tautomeric form of the Gp molecule in the crystals grown from solution in carbon tetrachloride is the aldehyde form. The dihedral angle between the naphthalene nuclei of the molecule amounts to 82.1°. The isopropyl groupings of the two halves of the molecule are oriented similarly with respect to their closest-hydroxy grops, O4 or O8.

In the ab plane of the crystal structure, the Gp molecules are packed in the same way as in the corresponding plane of the adduct of Gp with diethyl ether [4]. This agrees with the closeness of the parameters a and b of the elementary cells of the two Gp adducts. A layer of CCl_4 molecules is located between infinite parallel walls consisting of bilayers of Gp molecules.

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