X-RAY STRUCTURAL INVESTIGATION OF GOSSYPOL AND ITS DERIVATIVES.

III. STRUCTURE OF THE CRYSTALLINE MODIFICATION OF GOSSYPOL GROWN FROM SOLUTION IN METHYLENE CHLORIDE

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The foundation-laying studies of R. Adams on the structure of gossypol gave information suggesting the possibility of the existence of polymorphic modifications of the compound [1]. To elucidate this question, we have begun the study of the crystallization of gossypol from a number of solvents and have shown that at least seven crystalline forms exist [2]. Single crystals of these forms have been grown with the aim of a further deciphering of their structure. The structure of one of them, obtained by crystallization from ethyl acetate*, has been determined previously [3]. Another crystalline form consists of an adduct of gossypol with acetic acid [4].

TABLE 1. Coordinates of the Atoms in the Crystal Structure of Gossypol Grown from Solution in Methylene Chloride ($\times 10^4$; for hydrogen 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	917 (2)	2642 (2)	−852 (3)	C2	985 (2)	2566 (2)	78 (2)
C3	1046 (2)	3157 (2)	640 (3)	C4	1056 (2)	3803 (2)	259 (3)
C5	1061 (2)	4606 (2)	−1018 (3)	C6	1001 (2)	4673 (2)	−1940 (4)
C7	895 (3)	4083 (2)	−2540 (3)	C8	863 (2)	3407 (2)	−2237 (3)
C9	927 (2)	3304 (2)	−1272 (3)	C10	1012 (2)	3902 (2)	−675 (3)
C11	466 (2)	1537 (2)	551 (3)	C12	1036 (2)	1838 (2)	472 (3)
C13	1655 (2)	1462 (2)	767 (3)	C14	1684 (2)	802 (2)	1116 (4)
C15	1188 (2)	−234 (2)	1585 (3)	C16	606 (3)	−547 (2)	1560 (3)
C17	−32 (2)	−190 (2)	1285 (3)	C18	−89 (2)	512 (2)	1034 (3)
C19	497 (2)	851 (2)	942 (3)	C20	1130 (2)	478 (2)	1223 (3)
C21	1102 (3)	3085 (2)	1654 (3)	C22	773 (3)	2866 (2)	−2941 (3)
C23	1172 (3)	5251 (2)	−399 (3)	C24	584 (4)	5767 (3)	−776 (5)
C25	1861 (4)	5619 (4)	−213 (5)	C26	2282 (3)	1780 (3)	691 (4)
C27	−712 (3)	867 (3)	938 (4)	C28	1875 (3)	−612 (3)	1998 (4)
C29	2069 (3)	−777 (4)	3050 (5)	C30	1901 (3)	−1283 (3)	1488 (5)
O1	839 (2)	2066 (1)	−1421 (2)	O2	687 (2)	2973 (2)	−3774 (2)
O3	8 6 (2)	4236 (2)	−3430 (2)	O4	1058 (2)	5298 (2)	−2311 (2)
O5	− 141 (1)	1883 (1)	273 (2)	O6	−1215 (2)	524 (2)	966 (3)
O7	554 (2)	−562 (2)	1337 (2)	O8	593 (2)	−1231 (1)	1839 (2)
HO1	87	168	−105	HO3	73	379	−384
HO4	92	547	−282	HO5	−19	223	−10
HO7	−91	−27	128	HO8	101	−132	247
H4	106	414	62	H14	216	62	137
H22	73	248	−274	H23	136	518	31
H27	−88	146	71	H28	223	−35	191
$H21_1$	67	271	158	$H21_2$	154	279	202
$H21_3$	111	347	207	$H26_1$	271	150	92
$H2_{2}$	223	193	7	$H26_3$	237	222	102
$H24_1$	14	564	−81	$H24_2$	62	607	−33
$H24_3$	37	597	−153	$H25_1$	218	5 1	−30
$H25_2$	201	598	27	$H25_3$	183	583	−79
$H2_{1}$	244	−102	331	$H2_{2}$	199	−44	347
$H2_{3}$	166	−119	299	H30,	160	−157	141
H[illegible]	185	−125	86	H[illegible]	236	−160	176

*Below, the crystalline forms will be named from the solvent from which they were obtained.

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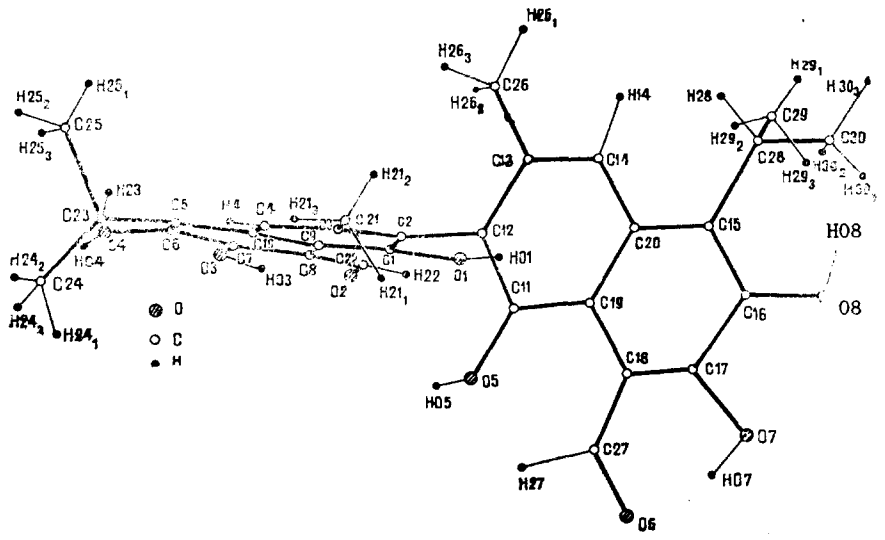

Fig. 1

In the present communication we give the results of the complete decipherment of a new crystalline form obtained by crystallization from methylene chloride. The crystals are monoclinic, a = 21.208(8) Å, b = 19.079(4) Å, c = 15.267(2) Å, β = 113.19(2)°, V = 5678.4(2) Å^3, sp. gr. C2/c, z = 8. The experimental material (2470 reflections) was obtained on a Syntex $P2_1$ diffractometer (Cu K_α radiation, graphite monochromator, $\theta \leq 62°$, $\theta/2\theta$ scanning, $F^2 \geq 2\sigma$). The structure was deciphered by direct methods and was refined by the method of least squares in the anisotropic approximation by the Rentgen-75 program [5] to R = 6.8% taking into account the hydrogen atoms found from difference syntheses. The coordinates of the atoms are given in Table 1.

In the methylene chloride modification of the molecule, the gossypol has the aldehyde form and the crystal lattice contains no solvent. The numbering of the atoms in the molecule is shown in Fig. 1. The dihedral angle between the planes of the naphthalene nuclei amounts to 80.2°. The lengths of the bonds and the magnitudes of the valence angles are the usual ones. The gossypol molecule has two systems of intramolecular H bonds. The O2 carbonyl oxygen forms an H bond with the O3–H hydroxyl group, forming a six-membered ring C7–C8–C22–O2–HO3–O3, and the angle of the H-bond is 141.8°. The corresponding angle for the other half of gossypol has a value of 143°. The formation of a O3...H–O4 H bond closes a five-membered ring but there is no analogous bond in the second naphthalene nucleus. In the crystal structure, the molecules form infinite strips parallel to the c axis through intemolecular H bonds of the O–H...O type.

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