X-RAY STRUCTURAL INVESTIGATION OF GOSSYPOL AND ITS DERIVATIVES.

II. PRELIMINARY X-RAY INVESTIGATION OF SIX CRYSTALLINE FORMS OF GOSSYPOL

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We have previously [1] given the results of an x-ray structural study of gossypol, crystals of which were grown from a mixture of methylene chloride and ethyl acetate. Adams et al. [2] have established that petroleum ether, chloroform, and diethyl ether precipitate dissimilar gossypol crystals. However, they did not carry out a structural identification and limited themselves only to giving the melting points of these three forms and did not attempt to crystallize the substance from other common organic solvents. It is possible that these forms are are polymorphic modifications.

In order to obtain crystals from these solvents and to perform a complete x-ray investigation, we selected six solvents: 1) acetone; 2) benzene; 3) xylene; 4) methylene chloride; 5) chloroform; 6) carbon tetrachloride (Table 1). It was possible to grow single crystals suitable for x-ray structural analysis under specially selected conditions of crystallization. The crystallographic parameters of the single crystals were measured on a precession camera and were refined on a Syntex-$P2_1$ diffractometer. The crystals grown from the six solvents were completely different in their crystal structures. It is characteristic that they all crystallized in the form of diffractionally distinguishible space groups. Apparently, in these groups the unsymmetrical gossypol molecules are packing in the densest possible way [3].

Even in this preliminary stage of the investigation it was possible to establish the presence of solvent molecules in the crystal lattice. For this purpose we calculated the densities of the crystals from the x-ray results on two hypotheses: 1) the solvent is included in the lattice in various ratios of gossypol and solvent molecules $(d_{calc})_1$; and 2) there is no such inclusion $(d_{calc})_2$. A comparison of the calculated densities with those measured by the flotation method permitted the unambiguous determination of the composition of the independent part of the elementary cell; only on crystallation from xylene and methylene chloride did

TABLE 1

Solvent	a, Å	b, Å	c, Å	α, deg	β, deg	γ, deg	V, Å^3
1. Acetone	10,651	11,129	14,891	111.89	75,54	77,99	1494
2. Benzene	11,142	14,883	17,402	80,94	99,70	81,33	2762
3. Xylene	8,477	14,438	14,087	64 57	86,83	104,80	1478
4. Methylene chloride	21,208	19,079	15,267	90,00	113,18	90,00	5678
5. Chloroform	28,651	9,051	26,247	90,00	108,74	90,00	6445
6. Carbon tetrachloride	8,847	13,221	14,304	78 05	91,12	71,64	1547

Solvent	Space group	Z	d_{meas}	$(d_{calc})_1$	$(d_{calc})_2$	Composition
1. Acetone	PI, $P\bar{1}$	2	1,26	1,15	1,28	Gossypol · acetone
2. Benzene	PI, $P\bar{1}$	4	1 32	1,34	1,43	Gossypol · 0.5 C_6H_6
3. Xylene	PI, $\bar{P}\,\bar{1}$	2	1,17	1,16	1,37	Gossypol
4. Methylene chloride	Cc, C2/c	8	1 22	1,21	1,41	Gossypol
5. Chloroform	Cc, C2/c	8	1,30	1,07	1,31	Gossypol · chloroform
6. Carbon tetrachloride	PI, $P\bar{1}$	2	1,43	1.11	1,44	Gossypol · CCl_4.

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it contain pure gossypol, and in the other cases the solvent participated in the structure of the lattice.

Thus, we now have seven different crystalline forms of gossypol. The search for new forms and the interpretation of the structures of the single crystals obtained are continuing.

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THIN-LAYER CHROMATOGRAPHY OF GOSSYPURPURIN ON SILUFOL

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Gossypurpurin is a natural pigment of cotton seeds that is second in importance to gossypol [1]. Accumulating in cotton seeds on storage it adversely affects their quality and, on passing into the oil, because of its intensive coloration, complicates the refining process.

For the qualitative detection of gossypurpurin in samples from the industrial processing of cotton seeds (kernel, meal, oil, flour) we have used the method of thin-layer chromatography on Silufol for the first time. Gossypurpurin was obtained as a model. It was isolated from the products of the chloroform extraction of defatted gossypol-rich flour [2] and the gossypol glands isolated from the same cottonseed flour by the method of wet fractionation [3]. First, a mixture of benzene and hexane (7:3) removed the gossypol from these materials, and then chloroform extracted the gossypurpurin. It was recrystallized from benzene until a positive qualitative reaction with $SbCl_3$ was obtained [4].

Chloroform solutions of gossypurpurin and of gossypol, taken for comparison, were deposited on Silufol plates with dimensions of 5 × 7 cm; the time of chromatography was 5 min. The spots were revealed with a 2% chloroform solution of $SbCl_3$, with which gossypol gave a red and gossypurpurin a blue color. We selected the systems usually used for the chromatography of gossypol and lipids. The R_f values of gossypurpurin and gossypol on TLC in the solvent systems used are given below.

Solvent systems	R_f of gossypurpurin	R_f of gossypol
1. Chloroform [5]	At the start	0.10
2. Heptane–chloroform–acetic acid (80:10:25) [6]	"	0.34
3. Chloroform–acetone–formic acid (95:4:1) [5]	0.12	0.42
4. Chloroform–methanol–water (65:25:4) [7]	0.56	0.74
5. Chloroform–methanol (30.5)	0.58	0.75
6. Chloroform–methanol (20:5) [8]	0.75	0.80
7. Benzene–methanol (19:1) [5]	0.05	0.30
8. Benzene–methanol (20:5)	0.30	0.43
9. Benzene–ethanol (3:1) [8]	0.55	0.57
10. Hexane–diethyl ether–formic acid (70:30:1) [5]	At the start	0.23
11. Hexane–ethyl acetate (3:1) [5]	0.04	0.40
12. Heptane–diethyl ether–methanol–acetic acid (90:20:2:3) [7]	At the start	0.17

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