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Inclusion Complexes of the Natural Product Gossypol. Crystal Structure of the 2 : 1 Complex of Gossypol with *m*-Xylene

B.T. IBRAGIMOV,* S. A. TALIPOV, T. F. ARIPOV, and A. S. SADYKOV†
Institute of Bioorganic Chemistry of Uz.S.S.R. Academy of Sciences, 700143 Tashkent, M. Gorky Pr. 83, U.S.S.R.

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Abstract. The crystal structure of a 2 : 1 inclusion complex of gossypol with *m*-xylene has been determined by X-ray structure analysis. The crystals of $C_{30}H_{30}O_8 \cdot 0.5C_8H_{10}$ are triclinic, space group $P\bar{1}$, $a = 8.478(1)$, $b = 14.087(2)$, $c = 14.411(2)$ Å, $\alpha = 115{,}39(1)$, $\beta = 75.11(1)$, $\gamma = 86.80(1)°$, $V = 1475.2(4)$ Å^3, $Z = 2$, $D_x = 1.29$ g cm^{-3}, $T = 295$ K, $\mu(\text{Cu } K_\alpha) = 7.01$ cm^{-1}. The structure has been solved by direct methods and refined to the final R value of 0.079 for 3910 observed reflections. The gossypol molecules are linked by intermolecular hydrogen bonds and form bimolecular layers parallel to the '*ab*' plane. Disordered *m*-xylene molecules occupy cavities between these layers. All polar groups of the gossypol molecule are packed in the interior of the bilayer while non-polar groups are directed outwards. An analysis of the crystal packing of other inclusion complexes of gossypol shows that such bilayers are formed in four complexes and three of those structures are generically related to each other.

Key words. crystal structure, X-ray crystallography, gossypol, inclusion complexes

Supplementary Data relating to this material are deposited with the British Library under reference number SUP 82081 (27 pages).

1. Introduction

Gossypol (Figure 1) is a yellow pigment isolated from cotton seeds. Its name is due to Marchlewski [1], its chemical formula was determined by Adams and associates in 1938 [2], and confirmed by total synthesis by Edwards in 1958 [3].

The presence of bulky methyl and hydroxyl groups in positions *ortho* to the C(2)—C(12) bond restricts free rotation around this bond. As a consequence, two atropoisomeric molecules, *R* and *S*, of gossypol exist. Optically active gossypol was first isolated from *Thespesia populnea* [4, 5] and recently it has also been obtained by chromatographic separation of the racemate [6]. Gossypol isolated from the cotton plant is racemic. All attempts to isolate optically active gossypol from this plant have so far failed [7].

The gossypol molecule has three tautomeric forms: aldehyde, lactol and quinoid. The first form is most often observed [2]. The lactol form of gossypol occurs only in some strong polar solvents, being in dynamic equilibrium with the aldehyde form [8].

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* Author for correspondence.
† Deceased.

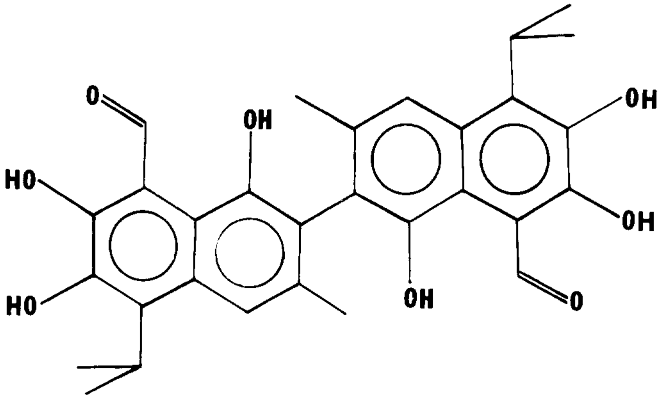

Fig. 1. Chemical formula of gossypol.

Gossypol is an extremely reactive compound. Its hydroxyl groups display acidic properties to a varying degree. The aldehyde carbonyl group may interact with bases, acids, oxygen and many other functional groups, which possibly accounts for its wide range of physiological actions. Gossypol has antitumor [9], antiviral [10] and antifertility [11] properties.

Gossypol is often used in the form of gossypol-acetic acid as an antifertility agent. X-ray structure analysis has shown that this compound is a stable equimolar crystalline solvate of gossypol with acetic acid [12]. In 1937 Adams and coworkers reported that, depending on the solvents used for crystallization, gossypol forms different polymorphic modifications with melting points of 184°, 199° and 214°C [13]. To solve the problem of the polymorphism of gossypol we have recrystallized racemic gossypol from a large number of organic solvents. Single crystals have been grown from most of the 70 solvents and their unit cell parameters determined [14, 15]. The results of X-ray structure analysis of more than 20 of these crystals have shown that in almost all cases gossypol cocrystallizes with solvent molecules forming an unusually large number of different types of inclusion complexes. The abovementioned crystalline forms of gossypol with melting points of 184 and 199°C have turned out to be complexes of gossypol with ethyl ether [16], and chloroform, respectively, and only the modification with m.p. 214°C appears to be a real polymorph [17]. This paper deals with layer-type inclusion complexes of gossypol and describes their structure, taking as an example the 2 : 1 complex of gossypol with *m*-xylene.

2. Experimental

Single crystals of the gossypol inclusion compound with *m*-xylene were obtained by slow evaporation in a cold room for 1.5 months. A crystal of approximate dimensions 0.2 × 0.4 × 0.6 mm was used for measurements on a Syntex $P2_1$ diffractometer. The lattice parameters were determined by a least-squares fitting of the setting angles of 15 reflections (2θ in the range 25 to 30°).

The crystal data are as follows: $C_{30}H_{30}O_8 \cdot 0.5\, C_8H_{10}$, triclinic, space group $P\bar{1}$, $a = 8.478(1)$, $b = 14.087(2)$, $c = 14.411(2)$ Å, $\alpha = 115{,}39(1)$, $\beta = 75.11(1)$, $\gamma = 86.80(1)°$, $V = 1475.2(4)$ Å^3, $Z = 2$, $D_x = 1.29$ g cm^{-3}, $\mu(\mathrm{Cu}\,K_\alpha) = 7.01$ cm^{-1}, $T = 295$ K.

Intensities of reflections were measured with graphite monochromatized Cu K_α radiation ($\lambda = 1.54178$ Å) to $2\theta = 126°$ using the $\theta/2\theta$ scan technique. No significant intensity variation was observed for 2 standard reflections monitored after each group of 100 reflections. Data were corrected for Lorentz and polarization effects but not for absorption. Out of 4600 measured reflections 3910 had $I > 3\sigma\,(I)$ and were used for further calculations. Initial attempts to determine the structure in space group $P\bar{1}$ failed. The structure was solved using a non-centrosymmetric version of ROENTGEN-75 [18]. The E-synthesis having the best R-factor modulated by the procedure of sequential phase improvement using ROENTGEN-75 produced an electron density map with 66 non-hydrogen atoms. The remaining atoms of the gossypol and *m*-xylene molecules were found in a subsequent F-synthesis. The inversion center was located and structure refinement in a space group $P\bar{1}$ was performed using SHELX-76 [19]. Hydrogen atom positions were determined from the ΔF maps and their positional and isotropic thermal parameters included in the refinement. Unit weights were used throughout the refinement. The solvent molecule, which makes only van der Waals contacts with the gossypol molecules, exhibits high thermal motion and some evidence of disorder contributing to a final R-value of 0.079. Final atomic parameters are given in Table I. The lists of the equations of the least-squares planes through the naphthalene rings of gossypol molecules and deviations of atoms from those planes (Table III), bond lengths and bond angles (Table IV), structure factors, anisotropic thermal parameters of non-hydrogen atoms and parameters of hydrogen atoms have been deposited with the British Library Division, and copies may be ordered quoting Sup. No. 82081.

3. Results and Discussion

3.1. MOLECULAR STRUCTURE

The host and guest molecules and atom numbering scheme are shown in Figure 2. Gossypol has an aldehyde form in the crystal structure of the gossypol : *m*-xylene complex as it does in all the previously identified structures [12, 14–17]. The dihedral angle between two naphthyl groups is equal to 90.8°. The previous IR-spectral analysis revealed the presence of intramolecular hydrogen bonds in the gossypol molecule [22]. The formation of hydrogen bonds O—H···O=C results in the closing of the six-membered rings C(7)—C(8)—C(22)—O(2)—H(30)—O(3) and C(17)—C(18)—C(27)—O(6)—H(70)—O(7). Bonds O(4)—H(40)···O(3) and O(8)—H(80)···O(7) close five-membered rings C(6)—C(7)—O(3)—H(40)—O(4) and C(16)—C(17)—O(7)—H(80)—O(8), respectively. The H-bond parameters are listed in Table II.

Both naphthyl groups are planar. The maximum atomic deviation from the least-squares planes through the naphthyl groups AB and CD are 0.024 and 0.039 Å, respectively (Table III). The crystal field has had less effect on the molecular conformation in this structure than in crystals of gossypol grown from

Table I. Fractional atomic coordinates and equivalent isotropic thermal parameters with e.s.d.'s in parentheses

$$U_{\mathrm{eq}} = \frac{1}{3}\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

Atom	x/a	y/b	z/c	U_{eq}
C(1)	0.6587(8)	0.6551(4)	0.6556(4)	0.036(2)
C(2)	0.5916(7)	0.7595(4)	0.7332(4)	0.036(3)
C(3)	0.4275(7)	0.7837(4)	0.8022(5)	0.042(3)
C(4)	0.3373(7)	0.7033(4)	0.7900(5)	0.041(3)
C(5)	0.3041(7)	0.5132(4)	0.7024(5)	0.042(3)
C(6)	0.3740(7)	0.4110(4)	0.6238(5)	0.043(3)
C(7)	0.5374(7)	0.3844(4)	0.5524(4)	0.038(3)
C(8)	0.6392(7)	0.4591(4)	0.5602(4)	0.034(2)
C(9)	0.5695(7)	0.5694(4)	0.6417(4)	0.033(3)
C(10)	0.4033(7)	0.5954(4)	0.7111(4)	0.035(2)
C(11)	0.6925(7)	0.8957(4)	0.6776(4)	0.035(2)
C(12)	0.6949(7)	0.8445(4)	0.7413(4)	0.035(3)
C(13)	0.7949(7)	0.8719(4)	0.8096(5)	0.039(3)
C(14)	0.8880(7)	0.9493(4)	0.8122(5)	0.042(3)
C(15)	0.9873(7)	1.0857(5)	0.7552(5)	0.042(3)
C(16)	0.9823(8)	1.1330(5)	0.6908(5)	0.049(3)
C(17)	0.8790(8)	1.1107(5)	0.6248(5)	0.048(3)
C(18)	0.7773(8)	1.0355(5)	0.6183(5)	0.041(3)
C(19)	0.7837(7)	0.9780(4)	0.6804(4)	0.036(2)
C(20)	0.8858(7)	1.0043(4)	0.7491(5)	0.037(3)
C(21)	0.3486(9)	0.8972(5)	0.8896(6)	0.070(4)
C(22)	0.8073(8)	0.4191(6)	0.4919(6)	0.058(3)
C(23)	0.1289(8)	0.5364(6)	0.7812(5)	0.054(3)
C(24)	−0.0024(8)	0.5077(6)	0.7240(7)	0.079(4)
C(25)	0.1290(10)	0.4858(6)	0.8561(6)	0.075(4)
C(26)	0.8020(9)	0.8180(5)	0.8797(5)	0.112(3)
C(27)	0.6687(9)	1.0259(5)	0.5534(6)	0.074(4)
C(28)	1.0908(8)	1.1204(5)	0.8315(5)	0.055(3)
C(29)	1.2757(9)	1.1005(7)	0.7726(7)	0.089(4)
C(30)	1.0251(10)	1.2364(6)	0.9192(6)	0.081(4)
O(1)	0.8155(4)	0.6301(2)	0.5858(3)	0.049(2)
O(2)	0.8630(5)	0.3233(3)	0.4233(4)	0.064(2)
O(3)	0.5889(5)	0.2808(2)	0.4784(3)	0.048(2)
O(4)	0.2874(5)	0.3292(3)	0.6130(3)	0.063(2)
O(5)	0.5997(5)	0.8673(3)	0.6091(3)	0.048(2)
O(6)	0.6684(7)	1.0769(4)	0.5025(4)	0.080(3)
O(7)	0.8846(6)	1.1685(3)	0.5705(4)	0.066(3)
O(8)	1.0778(6)	1.2087(3)	0.6914(4)	0.074(3)
C(1X)	0.5189(12)	1.3886(10)	0.9672(11)	0.121(9)
C(2X)	0.4663(12)	1.4670(10)	1.0698(11)	0.124(9)
C(3X)	0.5542(13)	1.4177(10)	0.8987(10)	0.123(9)
C(4X)	0.5377(15)	1.2799(11)	0.9391(12)	0.110(12)
C(5X)	0.6124(16)	1.3486(12)	0.7894(13)	0.138(12)

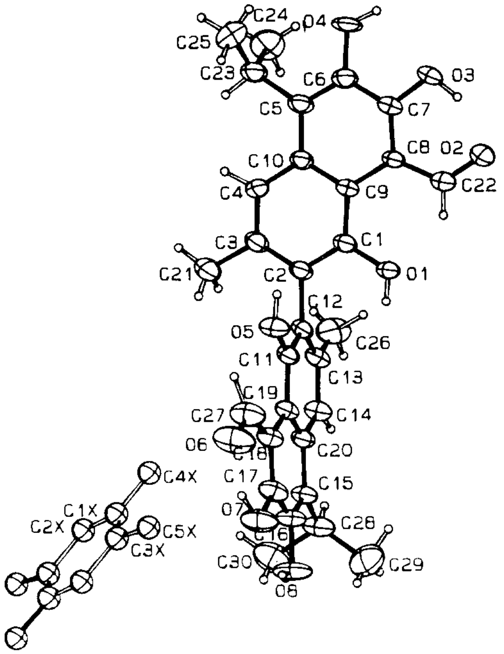

Fig. 2. The atom numbering scheme of the gossypol and *m*-xylene molecules [ORTEP(20)] (the guest molecule, *m*-xylene, appears as a superposition of the two equally probable, centrosymmetrically related orientations).

Table II. Geometry of hydrogen bonds

D—H···A	D···A (Å)	D—H (Å)	H···A (Å)	D—H···A (°)
(a) *Intramolecular hydrogen bonds*				
O(3)—H(30)···O(2)	2.450(7)	0.91(5)	1.63(6)	148(4)
O(7)—H(70)···O(6)	2.468(7)	1.04(6)	1.53(6)	147(4)
*O(4)—H(40)···O(3)	2.623(6)	0.91(5)	2.20(5)	108(4)
*O(8)—H(80)···O(7)	2.600(6)	0.89(5)	1.96(5)	127(6)
(b) *Intermolecular hydrogen bonds*				
O(5)—H(50)···O(3^{i})	2.767(6)	0.87(5)	2.11(5)	132(4)
O(1)—H(10)···O(2^{ii})	2.822(7)	0.80(6)	2.27(5)	127(5)
*O(4)—H(40)···O(5^{i})	3.058(6)	0.91(5)	2.20(7)	158(5)
*O(8)—H(80)···O(4^{iii})	2.875(6)	0.89(5)	2.62(7)	98(5)

Symmetry codes: (i) $1-x$, $1-y$, $1-z$; (ii) $2-x$, $1-y$, $1-z$; (iii) $1+x$, $1+y$, z.
* Three centre H-bonds.

ligroin where the maximum atomic deviation from the respective least-squares plane of the CD ring amounts to 0.144 Å [17].

The C(2)—C(12) bond distance of 1.504(8) Å connecting naphthyl groups is comparable to the value observed in other gossypol crystal forms and with the theoretical value for an aryl C_{sp^2}—C_{sp^2} bond [23]. The interatomic distances in the naphthyl nuclei vary from 1.363 to 1.458 Å, the endocyclic valence angles from 117° to 123° (Table IV). All this correlates generally with the values found in chiral [24, 25] and racemic [26] 1,1′-binaphthyls. Substituent effects cause a minor redistribution of bond distances when compared to unsubstituted naphthalene [27]. In napthalene, bonds C(1)—C(2), C(3)—C(4), C(5)—C(6) and C(7)—C(8) have an average length of 1.36 Å, while the C(8)—C(9) and C(5)—C(10) bonds have an average value of 1.42 Å. The same trend is seen in the naphthyl groups of gossypol where the corresponding average geometries are 1.38 and 1.45 Å.

3.2. CRYSTAL STRUCTURE

In the crystal structure, centrosymmetrically related gossypol molecules I(x, y, z) and II$(1-x, 1-y, 1-z)$ form dimers via H-bonds O(5)—H(50)···O(3) of length 2.767(6) Å (Figure 3, Table II). The same dimer is further linked by a weaker H-bond O(4)—H(40)···O(5) of length 3.058(6) Å. By means of the H-bond O(1)—H(10)···O(2) 2.822(7) Å a gossypol molecule I(x, y, z) is linked to a molecule III $(2-x, 1-y, 1-z)$ forming centrosymmetric dimers of another type. These interactions taken together result in the formation of a continuous column of molecules extending parallel to the *a* direction. The functional groups on the AB naphthyl ring and the hydroxyl group O(5)—H are involved in these bonds. The hydroxyl group O(8)—H forms intermolecular H-bonds between translationally related molecules I(x, y, z) and IV$(x+1, y+1, z)$. The hydrogen atom of the O(8)—H hydroxyl group is simultaneously involved in intramolecular and intermolecular H-bonds. Though the O(8)—H···O(4) contact distance of 2.875(6) Å is typical for an H-bond the relative arrangement of the molecules produces an H···O(4) distance equal to 2.62 Å and an O···H—O angle of 98° suggesting a weak H-bond. So there are two three-center or bifurcated hydrogen bonds formed by O(4)—H and O(8)—H. These three-center bonds involve two acceptors, O(3) and O(5) in the former and O(7), O(4) in the latter. Commonly the major component has an O—H···O angle close to 180° and the H···O distance is

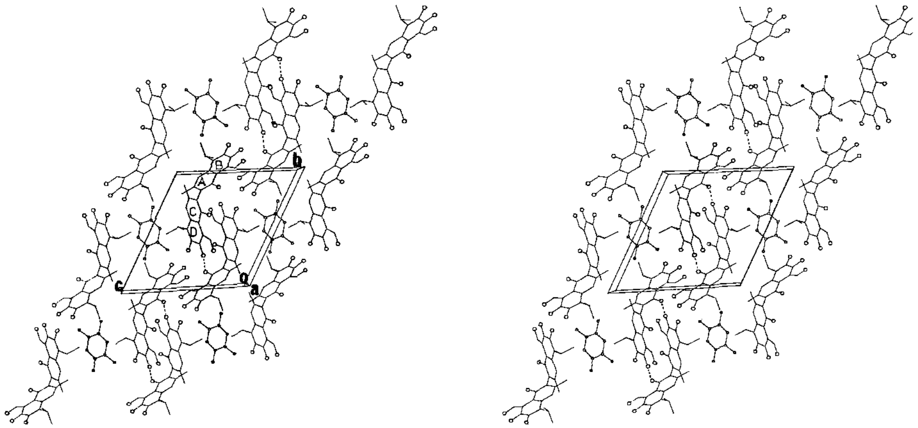

Fig. 3. The crystal packing viewed along *a* drawn using PLUTO [21]. The oxygen atoms are marked with circles, hydrogen atoms are omitted for clarity.

shorter than for the minor component, which generally has a smaller O—H···O angle. Such asymmetry of components is also found in this present case. Two other groups potentially capable of forming H-bonds, C(27)=O(6) and O(7)—H fail to do so. The relative positions of C(27)=O(6) of molecule I(x, y, z) and O(3)—H of molecule V$(x, y + 1, z)$ suggest a tendency toward formation of an H-bond. However, steric factors limit the contact between O(6) and O(3) to 3.10 Å.

A similar relationship appears to govern interactions between hydroxyl O(7) and carbonyl O(2) where the observed distance between O(7) and O(2) is 3.67 Å. Although all possible H bonds are usually formed in the process of crystallization, gossypol illustrates that in small molecules that are highly substituted with hydrogen bond forming groups, diversity of interaction and competition for H-bonds can limit the number that can be incorporated into a single crystal form. Taken together all of the hydrogen bonds link the gossypol molecules in infinite bilayers extending parallel to the *ab* plane. All polar groups are on the interior of the bilayers. The outer surface of the bilayer is covered by the hydrophobic side of the molecules. Cavities on the surface of the bilayer are formed by gossypol molecules A, B, C and D related by the following symmetry operations: (x, y, z); $(x + 1, y, z)$; $(x, y + 1, z)$; $(x + 1, y + 1, z)$. When two adjacent bilayers come together solvent is included in these cavities.

3.3. HOST–GUEST INTERACTION

Since there is no way for a guest molecule located in a cavity of the host structure to leave the crystal, because the cage is closed on each side by host molecules, the inclusion complex of gossypol with *m*-xylene can be regarded as a clathrate. The fact that this inclusion complex is stable under normal conditions and decomposes close to the crystal melting point speaks in favour of this classification. On the other hand, if we notice that the guest molecules fill cavities formed between bimolecular layers of the host we will see a close relation between this structure and layer-type inclusion compounds. The guest molecules located in cavities exhibit high thermal motion and disorder. They occupy two equivalent positions around the center of symmetry. Due to such a dislocation it is possible to construct a centrosymmetrical crystal, with non-centrosymmetrical molecules being located in a particular position.

In the inclusion compound of gossypol with CCl_4, where the guest : host molecular ratio is changed to 1 : 1, orientational disorder of guest molecules is not necessary to form a centrosymmetrical crystal. In this case two molecules of CCl_4 fill the space in a cage formed by the host structure. A large number of other solvents form inclusion compounds that are isostructural with gossypol : *m*-xylene. Single crystals were grown for inclusion compounds of gossypol with the two remaining xylene isomers, ethylbenzene, *p*-chlorotoluene and paraldehyde and their crystal data are given in Table V.

4. Concluding Remarks

In the inclusion compound of gossypol with *m*-xylene and isostructural compounds, a bimolecular layer of the host is built of two molecular layers, each of them comprising molecules of the same chirality. Guest molecules are located between

Table V. Crystal data for inclusion compounds isostructural with gossypol: *m*-xylene

Guest	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	V	d(g cm^{-3})	host : guest
1. CCl_4	8.847(2)	14.304(6)	14.395(5)	102.54(3)	69.53(3)	91.12(3)	1547	1.66	1 : 1
2. *o*-xylene	8.505(5)	14.072(9)	14.409(4)	115.51(4)	74.24(4)	86.63(5)	1477	1.28	2 : 1
3. *p*-xylene	8.406(4)	14.213(9)	14.079(8)	115.82(4)	75.24(4)	87.80(4)	1475	1.28	2 : 1
4. ethylbenzene	8.451(1)	14.195(3)	14.398(3)	114.89(2)	77.45(4)	87.79(1)	1470	1.29	2 : 1
5. *p*-chlorotoluene	8.575(1)	14.060(3)	14.269(4)	115.48(2)	72.89(1)	86.78(2)	1476	1.31	2 : 1
6. paraldehyde	8.97(2)	14.69(2)	12.95(1)	101.2(1)	89.5(1)	88.9(1)	1674	1.29	1 : 1

translationally related bilayers. The cages are formed between monolayers of different chirality and guest molecules are located in achiral cavities. In the inclusion compound of gossypol with ethyl ether, which crystallizes in space group $P2_1/b$ [16], adjacent bimolecular layers are related by the two-fold screw axis. Cages are formed between monolayers of the same chirality and hence are chiral. Desolvation of this inclusion compound is very unusual. The ether molecules located in channels of whatever (but the same) chirality leave the crystal first and an inclusion compound with a host : guest ratio of 2 : 1 is formed. The space group is changed to $P2_1$. The 2 : 1 inclusion compound of gossypol with ethyl ether exhibits the bilayer structure as well. The remaining guest molecules occupying channels of the other chirality are released when the temperature is increased to 140–142°C. The channel inclusion compound of gossypol with ethyl ether resembles channel structures of deoxycholic acid. In the latter case, however, the intermediate and unsolvated structures are not known [28].

In summary, let us notice that employing the above described bimolecular layers Nature is able to construct four different structures, three of them being generically related to each other.

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