Chemistry of Natural Compounds, Vol. 30, No. 1, 1994

INVESTIGATION OF THE PRODUCTS OF THE OXIDATION OF GOSSYPOL STRUCTURE OF GOSSINDAN

A. I. Ismailov, Z. Shukurov, S. A. Talipov,
F. G. Kamaev, R. G. Mardanov, and B. T. Ibragimov

UDC 547.554:615.37:578.245

A new compound, which we have called gossindan, has been isolated from the products of the oxidation of gossypol by oxygen in an alkaline medium. The structure of gossindan has been established on the basis of a study of IR, mass, PMR, and ^{13}C NMR spectra and x-ray structural analysis as 6,6'-di-(2,7-dihydroxy-3-isopropyl-5-methylindan-1-one).

As polyphenolic compounds, gossypol and its associated compounds are capable of undergoing various transformations, particularly oxidation. These properties have an adverse effect on the quality of the products obtained on treating cotton seeds. The oxidation of gossypol has been considered in a number of investigations [1-4]; however, no oxidation products have been isolated in the individual form with the exception of gossypolic acid and *o*- and *p*-quinones, and the course of the oxidative decomposition of gossypol has not been established. We have now studied the products of the oxidation of gossypol in alkaline solutions by molecular oxygen.

In the initial stage of oxidation (the first 10-20 h), a relatively stable product, which has been identified as gossypol *o*-quinone, accumulates in the reaction medium. When the oxidation of gossypol is performed in relatively concentrated solutions of alkali (more than 10%), in addition to oxidation conversion into apogossypol takes place. The oxidation products form a complex mixture of compounds of different natures. As a result of the oxidation of gossypol with oxygen in a solution of alkali the concentration of which exceeds 15%, an accumulation of predominantly three to four compounds is observed. The qualitative composition and quantitative ratio of the products formed depend on the conditions and time of performing the oxidation process. Several individual compounds have been isolated by column chromatogrpahy on silica gel from the total products of the oxidation of gossypol in a 20% aqueous solution of alkali.

The present paper gives the results of a study of the structure of one of them, which has been called gossindan.

Gossindan — a colorless crystalline compound with mp 189-191°C, composition $C_{26}H_{30}O_6$ — possesses phenolic properties and gives a bright blue fluorescence in UV light. The IR spectrum shows characteristic absorption bands in the regions of 3510 and 3380 cm^{-1} (OH), and 1680 cm^{-1} (CO). The molecular mass of gossindan is 438, i.e., by analogy with gossypol, its molecule consists of a symmetrical dimer each half of which is 40 units smaller than half a gossypol molecule, which corresponds to a C_{20} fragment.

To determine the structure of gossindan we recorded its ^1H and ^{13}C NMR spectra. The following signals were observed in the PMR spectrum taken in deuteroacetone (ppm): singlets at 8.84 and 7.06, doublet at 5.08 (J = 5.0 Hz), doublet of doublets at 4.70 (J = 5.0 and 7.5 Hz), doublet of doublets at 3.54 (J = 7.5 and 3.1 Hz), and a multiplet at 2.45 (J = 7.0 and 3.1 Hz). The homogeneity of the spectrum indicated a symmetry of the gossindan molecule, the two halves of the gossypol molecule having taken part in chemical transformations to the same degree. On the addition of a small amount of D_2O to the sample, the singlet at 8.84 and the doublet at 4.84 ppm disappeared, with a simultaneous transformation of the doublet of doublets at 4.70 ppm into a doublet with J = 7.5 Hz. This shows the presence in the molecule of phenolic (8.84 ppm) and alcoholic (5.08 ppm) hydroxyls, and the splitting of the signals of the latter shows its retarded proton exchange in the NMR scale, while the magnitude of the splitting (5.0 Hz) indicates the presence of a proton resonating at 4.70 ppm geminal to the hydroxyl.

A. S. Sadykov Institute of Bioorganic Chemistry, Academy of Sciences of the Republic of Uzbekistan, Tashkent, Fax 627071. Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 50-58, January-February, 1994. Original article submitted July 13, 1993.

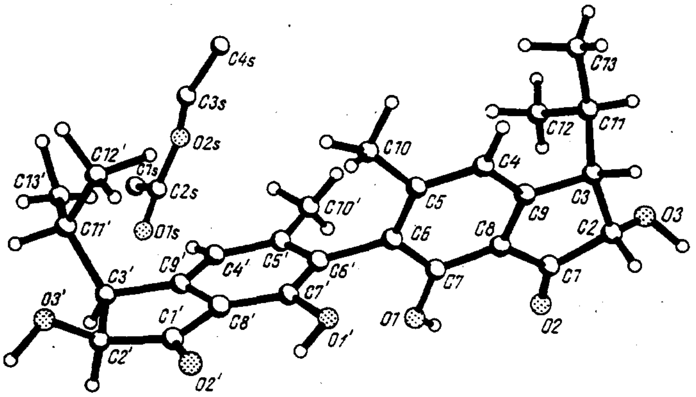
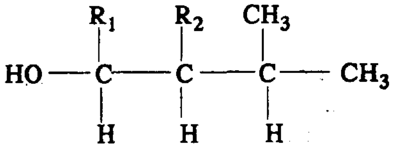


Fig. 1. Conformation of the gossindan molecule.

The presence of two types of hydroxyl was confirmed by the formation of tetraacetate and dimethoxy derivatives of gossindan. Double resonance experiments with irradiation by a strong secondary high-frequency field of the signals at 5.08, 4.70, 3.54, and 2.45 ppm revealed the following sequence of atoms in the molecule:



$$\mathrm{HO-\overset{\overset{R_1}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{R_2}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{C}}-CH_3}$$

The presence of SSCCs not averaged by free rotation in the spectrum of the aliphatic protons showed that this chain of atoms participated in the formation of some cyclic structure. The ^{13}C NMR spectrum of gossindan had a signal at 190.8 ppm, which is characteristic for a carbonyl carbon conjugated with a double bond or an aromatic system. Irradiation by a weak high-frequency field of the singlet of an aromatic methyl group at 2.10 ppm led to an increase in the intensity of the signal of the H4 aromatic proton (7.06 ppm) by 28% through suppression of long-range spin-spin coupling and the nuclear Overhauser effect. On the basis of the totality of the PMR parameters and structural considerations it is possible to propose for gossindan the structure of shown in Fig. 1.

The proposed structure is in harmony with the ^{13}C NMR spectrum, which contains the signals of seven sp^2- and six sp^3-hybridized carbon atoms (see the Experimental part). The assignment of the signals was made from the multiplicities in the off-resonance spectrum, by comparison with the spectra of model compounds, and by the additive scheme of calculating shifts [5]. The molecular mass of the gossindan ion (438) corresponds to the proposed structure.

The SSCC between the H3 and H11 protons was 3. 1 Hz, which caused some doubts, since usually in such cases, because of free rotation around the C–C bond, this constant has an averaged value of 6.0-6.5 Hz. It was established from the x-ray results that the dihedral angle between the H3 and H11 protons amounted to 61.9%, which, according to Karplus's curve [6] corresponds to a constant of 3.1 Hz. The spatial structure of the gossindan molecule in the crystal apparently coincides with the conformation of this molecule in solution.

According to the results of the x-ray structural investigation, the gossindan molecule consists of two symmetrical halves joined by an ordinary C6–C6′ bond (Fig. 1). Each half is represented by an indan nucleus to which four substituents are attached: hydroxy groups to the C2 and C7 atoms, an isopropyl group to the C3 carbon atom, and a methyl group to the C5 atom. Gossypol therefore has the full chemical formula of 6,6′-di-(2,7-dihydroxy-3-isopropyl-5-methylindan-1-one).

The C4–C9 aromatic ring is practically planar — the observed deviations of the carbon atoms from the mean square plane of this ring do not exceed 0. 04 Å. The conformation of the C1–C2–C3–C9–C8 five-membered ring is half-chair, and the C2 and C3 atoms deviate from the mean square plane of the other four atoms by 0.21 and −0.16 Å, respectively. The structure of the pentacycle of the upper half of the molecule is different: its conformation is that of an envelope in which the C3 atom deviates by 0.21 Å.

The bisectrices of the C11–C3–H3 and O3–C2–H3 angles are approximately in the mean square plane of the pentacycle. The C11 and O3 atoms are therefore in positions intermediate between equatorial and axial. The arrangement of these atoms (substituents) relative to the C2–C3 bond is closer to the eclipsed than to the gauche conformation, since the torsional

TABLE 1. Bond Lengths (Å) in the Gossindan Molecule

C6—C7	1.409(9)	C6—C5	1.406(7)
C6—C6′	1.487(9)	C5—C4	1.40(1)
C5—C10	1.49(1)	C4—C9	1.376(9)
C3—C2	1.549(9)	C3—C9	1.52(1)
C3—C11	1.55(1)	C2—C1	1.520(9)
C2—O3	1.414(9)	C1—C8	1.45(1)
C1—O2	1.224(7)	C8—C7	1.391(9)
C8—C9	1.383(7)	C11—C12	1.53(1)
C11—C13	1.51(1)	O1—C7	1.350(6)
C7′—C6′	1.400(9)	C7′—C8′	1.375(9)
C7′—O1′	1.362(6)	C6′—C5′	1.397(7)
C5′—C4′	1.39(1)	C5′—C10′	1.502(9)
C4′—C9′	1.378(9)	C3′—C2′	1.553(8)
C3′—C9′	1.51(1)	C3′—C11′	1.54(1)
C2′—C1′	1.506(9)	C2′—O3′	1.418(8)
C1′—C8′	1.464(9)	C1′—O2′	1.222(7)
C8′—C9′	1.373(7)	C11′—C12′	1.51(1)
C11′—C13′	1.50(1)	O1s—C2s	1.27(4)
O2s—C2s	1.31(2)	O2s—C3s	1.38(2)
C1s—C2s	1.45(3)	C3s—C4s	1.60(4)

angles O3–C2–C3–C11 and O3′–C2′–C3′–C11′ are 23.7 and 11.7°, respectively. In the two halves the isopropyl groups are oriented identically: the H atoms at the C11 and C11′ atoms are directed within the molecule.

Because of these fairly voluminous substituents in the C5 (C5′) and C7 (C7′) positions, the gossindan molecule cannot assume a planar conformation (the dihedral angle between the aromatic rings is 69. 7°), but, at the same time, free rotation around the ordinary bond is impossible. This leads to the existence of two atropostereoisomers that are mirror-wise identical with one another. However, this is not the only source of chirality of the gossindan molecule. In each half of the molecule there are two asymmetric carbon atoms: C2 (C2′) and C3 (C3′). The configurations of the neighboring asymmetric atoms, C2 and C3, are the same (R or S). The C2′ and C3′ atoms also have the same configuration. Consequently, the molecule possesses a second-order axis of symmetry which runs perpendicular to the middle of the C6–C6′ bond.

The O1–H···O2 (O1′–H′···O2′) intramolecular bonds form six-membered rings consisting of the atoms O2–C1–C8–C7–O1–H (O2′–C1′–C8′–C7′–O1′–H′), The lengths and angles of these bonds amount to 2. 91 Å and 138°, (2.84 Å and 128°), respectively.

EXPERIMENTAL

For chromatography we used type KSK silica gel and Silpearl, with elution of the substance from the column by means of chloroform–methanol in ratios of 9. 5:0.5 (system 1) and 9.25:0.75 (system 2). The revealing agent was a 1% alcoholic solution of $FeCl_3$.

UV spectra were taken on SF-26 and Hitachi spectrometers. IR spectra were recorded on a UR-20 double-beam spectrophotometer in the interval of 3700–750 cm^{-1} in tablets with KBr. PMR and ^{13}C NMR spectra were taken in deuteroacetone solution on XL-100 and XL-200 instruments (Varian, USA) with TMS as internal standard, and mass spectra on a MAT-311 instrument.

Oxidation of Gossypol by Oxygen in Alkaline Solution. Oxygen was passed through a solution of 100 g of gossypol in 3.6 liters of 20% aqueous NaOH for 600 h. The precipitate that had deposited was filtered off and suspended in water, and the suspension was acidified with 10% H_2SO_4. The new precipitate that deposited was separated off, washed to neutrality, and dried in the air. This gave 22.4 g of an amorphous cream-colored powder.

Separation of the Oxidation Products. A solution of 20 g of the powder obtained in 300 ml of acetone was filtered and was mixed with 180 g of type KSK silica gel powder and transferred to a porcelain dish for the complete elimination of the acetone. A slurry of 800 g of silica gel in petroleum ether was transferred to a 6 × 55 cm column and the adsorbent was compacted by the passage of petroleum ether. Then the prepared silica gel with the total substances absorbed was added to the column, which was eluted with system 2, the eluate being collected in 200-ml fractions. Separation was monitored by chromato-

TABLE 2. Valence Angles (°) in the Gossindan Molecule

C6—C7—C8	119.3 (5)	C6—C7—O1	118.4 (6)
C8—C7—O1	122.3 (6)	C7—C6—C5	118.1 (6)
C7—C6—C6′	120.8 (5)	C5—C6—C6′	121.0 (6)
C6—C5—C4	121.2 (6)	C6—C5—C10	121.3 (6)
C4—C5—C10	117.5 (5)	C5—C4—C9	119.7 (5)
C2—C3—C9	102.8 (5)	C2—C3—C11	114.0 (5)
C9—C3—C11	111.4 (6)	C3—C2—C1	104.5 (5)
C3—C2—O3	113.9 (5)	C1—C2—O3	112.8 (4)
C2—C1—C8	107.2 (5)	C2—C1—O2	126.8 (7)
C8—C1—O2	126.0 (6)	C7—C8—C1	127.7 (5)
C7—C8—C9	121.9 (6)	C1—C8—C9	110.3 (6)
C4—C9—C3	129.8 (5)	C4—C9—C8	119.4 (6)
C3—C9—C8	110.7 (5)	C3—C11—C12	112.7 (6)
C3—C11—C13	112.4 (6)	C12—C11—C13	110.1 (7)
C6′—C7′—C8′	120.0 (5)	C6′—C7′—O1′	119.3 (6)
C8′—C7′—O1′	120.7 (6)	C6—C6′—C7′	120.7 (5)
C6—C6′—C5′	121.6 (5)	C7′—C6′—C5′	117.5 (6)
C6′—C5′—C4′	121.1 (6)	C6′—C5′—C10′	120.7 (6)
C4′—C5′—C10′	118.2 (5)	C5′—C4′—C9′	120.4 (5)
C2′—C3′—C9′	103.3 (5)	C2′—C3′—C11′	112.9 (5)
C9′—C3′—C11′	113.5 (6)	C3′—C2′—C1′	105.8 (5)
C3′—C2′—O3′	114.8 (5)	C1′—C2′—O3′	110.7 (4)
C2′—C1′—C8′	107.3 (4)	C2′—C1′—O2′	126.3 (6)
C8′—C1′—O2′	126.4 (6)	C7′—C8′—C1′	126.7 (5)
C7′—C8′—C9′	122.6 (6)	C1′—C8′—C9′	110.5 (6)
C4′—C9′—C3′	130.5 (5)	C4′—C9′—C8′	118.1 (6)
C3′—C9′—C8′	111.4 (5)	C3′—C11′—C12′	112.4 (7)
C3′—C11′—C13′	112.3 (7)	C12′—C11′—C13′	110.8 (8)
C2s—O2s—C3s	127.9 (12)	O1s—C2s—O2s	133.8 (19)
O1s—C2s—C1s	122.6 (22)	O2s—C2s—C1s	102.4 (16)
O2s—C3s—C4s	100.7 (17)		

graphy on Silufol UV-254 plates in system 1. The fractions contained two substances, one of which (the main one) was revealed in UV light as a bright blue spot with R_f 0.55.

The fractions were combined, concentrated, and mixed with 40 g of Silpearl silica gel, and the solvent was eliminated with stirring. A column with dimensions of 4 × 105 cm was prepared from silica gel of the same brand, and the silica gel with the two substances adsorbed on it was added to the column, which was then washed with system 2, giving a number of fractions.

Isolation of Gossindan. The fractions containing a substance with R_f 0.55 were combined (about 3 liters) and concentrated under vacuum at 35-40°C to a volume of 500 ml, and this solution was left for 2 h. The crystals that deposited were filtered off and dried under vacuum. Yield 3.2 g. mp 189-191°C. Readily soluble in alcohols and acetone. Insoluble in water. Gave a violet coloration with $FeCl_3$ solution. IR spectrum (ν_{max}^{KBr}, cm^{-1}): 3510-3389, 2960, 2910, 2880, 1680, 1630, 1660, 1430, 1390, 1320. UV spectrum ($\lambda_{max}^{C_2H_5OH}$, nm): 224 (lgε 4.46), 265 (lgε 4.00), 322 (lgε 3.80).

TABLE 3. Coordinates (× 10^4; for the H atoms, × 10^3) and Temperature Factors (Å^2 × 10^3) of the Gossindan Atoms

Atom	*x*	*y*	*z*	*U**
C1	2645 (7)	7102 (3)	10999 (4)	50 (3)
C2	3048 (7)	6908 (3)	12056 (4)	50 (3)
C3	4267 (7)	6379 (3)	12218 (4)	52 (3)
C4	6225 (7)	6229 (3)	11286 (4)	53 (3)
C5	6459 (7)	6323 (3)	10407 (4)	50 (3)
C6	5421 (7)	6700 (3)	9666 (4)	43 (2)
C7	4144 (6)	6987 (3)	9836 (4)	43 (2)
C8	3918 (6)	6873 (3)	10706 (4)	41 (2)
C9	4910 (7)	6482 (3)	11412 (4)	44 (2)
C10	7854 (8)	6009 (3)	10288 (5)	71 (3)
C11	3513 (9)	5738 (3)	12143 (6)	71 (4)
C12	2240 (9)	5606 (4)	11125 (7)	90 (4)
C13	4766 (10)	5238 (4)	12438 (7)	98 (5)
O1	3173 (5)	7364 (2)	9140 (3)	60 (2)
O2	1490 (5)	7408 (2)	10494 (3)	63 (2)
O3	1669 (5)	6750 (2)	12254 (3)	65 (2)
C1′	8595 (7)	7325 (3)	7624 (4)	48 (2)
C2′	8334 (7)	7220 (3)	6564 (4)	47 (2)
C3′	6891 (7)	6773 (3)	6166 (4)	50 (2)
C4′	4824 (7)	6511 (3)	6986 (4)	46 (2)
C5′	4551 (6)	6490 (3)	7858 (4)	45 (2)
C6′	5613 (6)	6767 (3)	8710 (4)	42 (2)
C7′	6945 (7)	7073 (3)	8650 (4)	48 (2)
C8′	7206 (6)	7070 (3)	7786 (4)	42 (2)
C9′	6208 (6)	6773 (3)	6962 (4)	42 (2)
C10′	3099 (7)	6150 (3)	7865 (5)	63 (3)
C11′	7383 (10)	6134 (4)	5940 (6)	80 (4)
C12′	8401 (10)	5793 (4)	6859 (8)	99 (5)
C13′	5963 (14)	5760 (5)	5332 (9)	165 (8)
O1′	7983 (5)	7365 (2)	9456 (3)	65 (2)
O2′	9744 (5)	7584 (2)	8233 (3)	66 (2)
O3′	9771 (5)	7012 (2)	6473 (3)	64 (2)
O1s	712 (37)	5940 (13)	4462 (24)	260 (17)
O2s	0	5000	5000	127 (3)
C1s	−1557 (28)	5316 (12)	3573 (16)	174 (10)
C2s	−172 (26)	5480 (8)	4437 (14)	123 (7)
C3s	−1007 (26)	4500 (9)	4841 (17)	142 (9)
C4s	−114 (48)	4121 (16)	5824 (24)	219 (16)
H1O	254 (7)	746 (3)	921 (4)	

TABLE 3. (Continued)

H30	149 (7)	709 (3)	1264 (5)
H10′	894 (7)	763 (3)	937 (4)
H30′	1018 (6)	730 (2)	612 (4)
H4	694 (6)	598 (2)	1179 (4)
H3	509 (6)	647 (2)	1297 (4)
H2	369 (6)	726 (2)	1243 (4)
H11	305 (7)	571 (3)	1267 (4)
H10a	822 (8)	566 (3)	1079 (5)
H10b	879 (8)	616 (3)	1031 (5)
H10c	759 (8)	584 (3)	969 (5)
H12a	162 (7)	522 (3)	1104 (4)
H12b	135 (7)	588 (3)	1089 (4)
H12c	271 (8)	553 (3)	1063 (5)
H13a	533 (7)	517 (3)	1187 (4)
H13b	580 (8)	534 (3)	1300 (5)
H13c	422 (8)	489 (3)	1255 (5)
H4′	401 (6)	636 (2)	640 (3)
H3′	612 (6)	696 (3)	-559 (4)
H2′	799 (7)	758 (3)	624 (4)
H11′	807 (7)	623 (3)	550 (4)
H10d	270 (7)	586 (3)	724 (4)
H10e	333 (7)	588 (3)	842 (4)
H10f	258 (8)	635 (3)	792 (5)
H12d	777 (8)	567 (3)	736 (4)
H12e	908 (8)	540 (3)	676 (5)
H12f	916 (8)	606 (3)	735 (5)
H13d	614 (9)	523 (4)	528 (6)
H13e	520 (8)	577 (3)	544 (5)
H13f	595 (10)	562 (4)	486 (6)

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

PMR spectrum 8.84 (1H, s, OH-7), 7.06 (1H, s, H-4), 5.08 (1H, d, J = 5.0 Hz, OH-2), 4.70 (1H, dd, J = 7.4 and 5.0 Hz, H-2), 3.54 (1H, dd, J = 7.4 and 3.1 Hz, H-3), 2.45 (1H, m, H-11), 2.10 (3H, s, CH_3-5), 1.14 (3H, d, J = 7.0 Hz, CH_3-12), 0.50 (3H, d, J = 7.0 Hz, CH_3-13).

^{13}C NMR: 190.8 (s, C-1), 154.4 (s, C-7), 152.0 (s, C-9), 148.3 (s, C-5), 122.0 (s, C-6), 120.5 (d, C-4), 119.7 (s, C-8), 77.2 (d, C-2), 50.8 (d, C-3), 29.1 (d, C-11), 21.7-21.0 (q, CH_3-12 and 13), 18.6 (q, CH_3-5).

Mass spectrum: 438 (M^+ 56); 423 (17); 405 (48); 395 (100); 377 (33); 349 (23).

Methylation of Gossindan. Gossindan (1 g) was methylated with diazomethane (from 20 g of nitrosomethylurea) in absolute ether. The residue after elimination of the solvent and the excess of diazomethane was dissolved in 200 ml of dry acetone. When the solution was cooled, small colorless crystals deposited, which were filtered off on a Schott funnel. Yield 0.61 g. mp 208-210°C. The substance was readily soluble in alcohol and sparingly soluble in acetone. It gave no coloration with $FeCl_3$. IR spectrum (ν_{max}^{KBr}, cm^{-1}): 3490, 2960, 2910, 2880, 1680, 1460, 1430, 1390, 1320. Mass spectrum: (m/z, %): 466 (M^+ 18), 435 (18), 423 (22), 405 (9), 343 (100), 327 (29), 311 (21).

Acetylation of Gossindan Methyl Ether. A solution of 0.1 g of the substance in 2 ml of absolutely dry pyridine was cooled, and 1 ml of acetyl chloride was added. After an hour, the reaction mixture was poured into cold water. The precipitate that deposited was separated off, dried, and recrystallized from a mixture of diethyl ether and petroleum ether. This gave 0.04 g of rhombic crystals with mp 203-204°C. The substance was readily soluble in acetone, alcohols, and ether. IR spectrum (ν_{max}^{KBr}, cm^{-1}): 2980, 1720, 1600, 1570, 1470, 1440, 1396, 1380, 1290-1295, 1240, 1220, 1110, 970. The analyses of all the compounds corresponded to the calculated figures.

X-Ray Structural Investigation. Single crystals with the composition gossindan:ethyl acetate = 2:1 were grown from a solution of gossindan in ethyl acetate. The crystallographic parameters of a single crystal were determined and refined from 15 reflections on a Syntex-$P2_1$ automatic four-circle diffractometer.

$a = 8{,}960(1)$ Å
$b = 21{,}937(3)$ Å
$c = 14{,}712(2)$ Å
$\beta = 111{,}98(2)°$
$V = 2681{,}5(1{,}4)$ Å^3
$Z = 4$
$D_x = 1{,}19$ g/cm^3
space gr. $P2_1/c$.

A group of integral intensities (3658 reflections) was obtained by $\theta/2\theta$ scanning with a graphite monochromator using CuK_α radiation. After taking the Lorentz and polarization factors into account and eliminating weak reflections with $F < 4\sigma$, the working group consisted of 2767 reflections. The structure was interpreted by the direct method with the aid of the SHELXS-86 program package realized on an IBM-386 computer [14].

The structure was refined with the aid of the SHELX-76 program package [15] on an IBM-386 computer. The atoms of the solvent and the hydrogen atoms of the gossindan molecule were located with the aid of difference Fourier syntheses. The divergence factor after the final stage of refinement of the positional and anisotropic temperature factors was R = 0.086. The coordinates of the atoms are given in Table 3.

REFERENCES

1. R. Adam, T. A. Geissman, and J. D. Edwards, Chem. Rev., **60**, 555 (1960).
2. A. A. Nomeir and M. B. Abou-Donia, J. Am. Oil Chem. Soc., **62**, No. 2, 87 (1965).
3. E. W. Scheiffele and D. A. Shirley, J. Org. Chem., **29**, 3617 (1964).
4. R. H. Haas and D. A. Shirley, J. Org. Chem., **30**, No. 12, 4111 (1965).
5. G. Levy and G. L. Nelson, Carbon-13 Nuclear Magnetic Resonance for Chemists, Wiley, New York (1972).
6. J. W. Emsley, J. Feeney, and L. H. Sutcliffe, High Resolution NMR Spectroscopy, Pergamon, Oxford (1965-1966).
7. B. T. Ibragimov, S. A. Talipov, and M. Gdaniec, J. Inclusion Phen. Molec. Recognition, **8**, 409 (1990).
8. M. Gdaniec, B. T. Ibragimov, and B. N. Dadabaev, Acta Cryst., **8**, 431 (1990).
9. M. Gdaniec, B. T. Ibragimov, and B. N. Dadabaev, Acta Cryst., **C46**, 810 (1990).
10. P. Maslak, P. E. Fanwich, and R. D. Guthrie, J. Org. Chem. **49**, 655 (1984).
11. M. Shoja, Acta Crystallogr., **C44**, 1496 (1988).
12. S. N. Bertz, G. Rihs, and R. B. Woodward, Tetrahedron, **38**, 63 (1982),
13. L. Pauling, The Nature of the Chemical Bond, 3rd ed., Cornel University Press, New York (1960).
14. G. M. Sheldrick, SHELX-76. Program for the Solution of Crystal Structures, University of Göttingen, FRG (1986).
15. G. M. Sheldrick, SHELX-76 Program for Crystal Structure Determination, University of Cambridge, England (1976).