2. T. J. Mabry, K. R. Markham, and M. B. Thomas, The Systematic Identification of Flavonoids, Springer, New York (1970).
3. Rodd's Chemistry of Carbon Compounds (2nd edn.), S. Coffey (ed.), Elsevier, Amsterdam, Vol. IV, Heterocyclic Compounds, Part E (1977), pp. 189, 214, 279.
4. W. Gaffield, Tetrahedron, 26, 4093 (1970).
5. R. Braz Filho, O. R. Gottlieb, and A. P. Mourao, Phytochemistry, 14, 261 (1975).
6. D. A. Murav'eva, in: Pharmacognosy [in Russian], Moscow (1978), p. 463.
7. V. G. Shimanov, in: The Hormonal Activity of Pasture Plants and Their Influence on the Fertility of Karakul Sheep [in Russian], Tashkent (1972), pp. 39, 157.

AN X-RAY STRUCTURAL INVESTIGATION OF GOSSYPOL AND ITS DERIVATIVES.

V. CRYSTAL STRUCTURE OF THE LIGROIN* MODIFICATION OF GOSSYPOL

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Adams [1] obtained tabular crystals with mp 214°C from a solution of gossypol (Gp) in ligroin. Even earlier, Clark had obtained the same crystals from a solution of Gp in diethyl ether at the boundary with water, i.e., from the crust in the hydrolysis of Gp acetate [2]. Single crystals of this modification of solid Gp were obtained for our investigations by the slow evaporation of a solution in a mixture of ether and hexane. All this indicates that the ligroin form is free from solvent and can be used to obtain pure Gp. However, for this purpose the temperature of the solution must not be below 18-20°C. At lower temperatures a solution of Gp in a mixture of ether and hexane gives a precipitate of crystals of a different form – an adduct of Gp with ether, the results of an interpretation of the structure of which has been given in [3]. The density of the crystals of the ligroin form amounts to 1.37 g/cm^3, which is the highest density of the forms known so far. These features of the crystallization of Gp in this modification can be explained by the results of an x-ray structural analysis.

The crystallographic parameters of the crystals investigated were determined on a Syntex-$P2_1$ automatic diffractometer: a = 13.467(1) Å, b = 8.794(1) Å, c = 21.376(3) Å, γ = 97.23(1)°, V = 2511.54 (0.54) Å^3, z = 4, sp. gr. $P2_1/c$. The experimental material was obtained on the same diffractometer by the $\theta/2\theta$-scanning method in CuK_α radiation using a graphite monochromator. The calculations were performed with 2714 reflection having $F^2 \geq 1.96\sigma$. The structure was interpreted by the direct method with the aid of the MULTAN program included in the XTLSM group [4]. Refinement was carried out by the method of least squares, initially in the isotropic approximation (R = 0.119) and then in the anisotropic approximation (R = 0.086). Fourier difference syntheses revealed all the hydrogen atoms. The final value of the R factor was 0.049, and the corresponding coordinates of the atoms in the structure are given in Table 1.

As in the forms studied previously [3, 5, 6], the Gp molecule has the aldehyde tautomeric form. The angle between the planes of the naphthalene nuclei is 87.5°, which is the largest value for the crystalline forms of Gp so far studied. The isopropyl groupings of the two halves are oriented differently with respect to their closest hydroxy groups O4 and O8 (for the numbering of the atoms, see [5]).

In the crystal structure, the molecules are associated into dimers through O5–H (x, y, z)...O_3(–x, –y, –z) and O_3(x, y, z)...O_5–H (–x, –y, –z) hydrogen bonds 2.864(4) Å long. Infinite walls extended along the b direction are formed from the dimers by O1–H (x, y, z)...

*In our investigations, the crystal form of gossypol is indicated by the name of the solvent from which it was obtained.

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TABLE 1. Coordinates of the Atoms in the Crystal Structure of the Ligroin Modification of Gossypol (× 10^4; for H atoms, 10^3; standard deviations are given in parentheses)

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
C1	2146 (3)	860 (5)	175 (2)	C2	2665 (3)	2227 (5)	356 (2)
C3	2455 (3)	3596 (5)	63 (2)	C4	1756 (3)	3514 (5)	−405 (2)
C5	489 (3)	2079 (5)	−1104 (2)	C6	−35 (3)	714 (5)	−1263 (2)
C7	132 (3)	−669 (5)	−965 (2)	C8	845 (3)	−696 (5)	−495 (2)
C9	1407 (3)	736 (5)	−302 (2)	C10	1218 (3)	2106 (5)	−606 (2)
C11	3340 (3)	2365 (5)	1452 (2)	C12	3496 (3)	2215 (5)	819 (2)
C13	4465 (3)	2023 (5)	606 (2)	C14	5209 (3)	1890 (5)	1027 (2)
C15	5828 (3)	1646 (5)	2122 (2)	C16	5587 (4)	1560 (6)	2727 (2)
C17	4669 (3)	1980 (6)	2962 (2)	C18	3945 (3)	2442 (5)	2569 (2)
C19	4103 (3)	2290 (5)	1909 (2)	C20	5057 (3)	1959 (3)	1684 (2)
C21	3016 (4)	5115 (6)	259 (3)	C22	952 (4)	−2195 (6)	−239 (2)
C23	328 (4)	3524 (5)	−1468 (2)	C24	−718 (4)	3949 (6)	−1390 (3)
C25	610 (5)	3389 (7)	−2167 (3)	C26	4666 (4)	1919 (6)	−86 (2)
C27	3182 (4)	3236 (6)	2845 (2)	C28	6894 (3)	1436 (6)	1944 (2)
C29	7451 (4)	2796 (6)	1624 (3)	C30	6986 (4)	−54 (6)	1612 (3)
O1	2360 (3)	−474 (3)	445 (1)	O2	469 (3)	−3396 (3)	−433 (2)
O3	−421 (2)	−1939 (3)	−1176 (1)	O4	−736 (2)	618 (3)	−1731 (1)
O5	2403 (2)	2530 (4)	1679 (1)	O6	3115 (3)	3371 (4)	3431 (1)
O7	4609 (3)	2012 (4)	3590 (1)	O8	6252 (3)	1127 (4)	3165 (1)
HO1	260	−23	82	HO3	−17	−267	−94
H 34	−98	−25	−252	HO5	206	255	137
HO7	401	257	367	HO8	599	105	359
H4	163	450	−63	H14	588	167	88
H22	141	−234	19	H23	79	432	−133
H27	262	361	252	H28	741	128	245
$H21_1$	277	543	71	$H21_2$	358	513	47
$H21_3$	292	576	1	$H26_1$	527	190	14
$H26_1$	414	106	−29	$H26_3$	451	290	−28
$H24_1$	−80	414	−95	$H24_2$	−118	314	−151
$H24_3$	−80	470	156	$H25_1$	61	443	−241
$H25_2$	−4	275	236	$H25_3$	119	327	−217
$H29_1$	718	284	109	$H29_2$	813	277	157
$H29_3$	732	366	175	$H30_1$	672	−4	114
$H30_3$	680	−72	188	$H30_2$	769	−25	152

O6 (x, y, $-\frac{1}{2}$, $\frac{1}{2}$, −z) and O6 (x, y, z)...O1 (x, $\frac{1}{2}$ + y, $\frac{1}{2}$ − z) hydrogen bonds 2.847(4) Å long. The walls, with a thickness of two molecules, are constructed in such a way that the hydrophilic parts of the Gp molecule are turned inward and the hydrophobic parts outward, forming special hydrophobic zones. The hydrophobic zones or "channels" have a zig-zag course in the *ac* plane.

LITERATURE CITED

1. K. N. Campbell, R. S. Morris, and R. Adams, J. Am. Chem. Soc., 59, 1723 (1937).
2. E. P. Clark, J. Biol. Chem., 75, 725 (1927).
3. B. T. Ibragimov, S. A. Talipov, T. F. Aripov, B. N. Dadaboev, and A. S. Sadykov, Khim. Prir. Soedin., 837 (1985).
4. V. K. Pecharskii, P. Yu. Zavalii, L. G. Aksel'rud, Yu. N. Grin', and E. I. Gladyshevskii, Vestn. L'vov. Univ., Ser. Khim., No. 25, 9 (1984).
5. S. A. Talipov, B. T. Ibragimov, G. B. Nazarov, T. F. Aripov, and A. S. Sadykov, Khim. Prir. Soedin., 835 (1985).
6. B. T. Ibragimov, S. A. Talipov, G. B. Nazarov, T. F. Aripov, Z. Shukurov, and A. I. Ismailov, Khim. Prir. Soedin., 664 (1981).