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NEW GOSSYPOL IMINES

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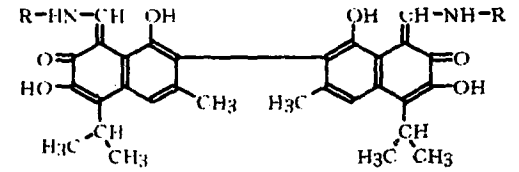
Information is given on new gossypol imines. The use of hydrazines as the imine components produces Schiff bases of gossypol existing in the benzoid form.

It has been shown previously that the form of physiologically active gossypol (GP) imines is determined by the nature of the amine introduced at the aldehyde groups [1], and, at the present time, substances have been found among them that possess interferon-inducing [2], antiherpetic [3], and antioxidant [4] activities.



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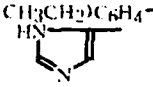
1 $HSO_3CH_2CH_2$ —
2 $C_2H_5CH(OH)$ —
3 $(CH_3)_2C(CH_2OH)$ —
4 $C_2H_5CH(CHOH)$ —
5 $(HOCH_2)_3C$ —
6 $Br(CH_2)_2CH_2$ —
7 N≡C—CH_2—
8 $(CN)C_6H_4$—
9 $(HOOCCH_2NHCO)C_6H_4$—
10 $(HO)[C(CH_3)_3]-C_6H_3$—
11 $(CH_3CH_2)C_6H_4$—



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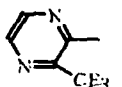

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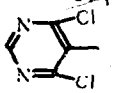

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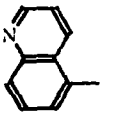

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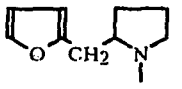

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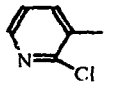

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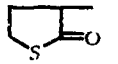

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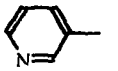

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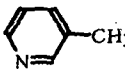

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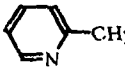

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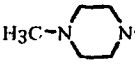

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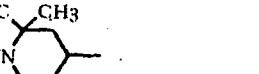

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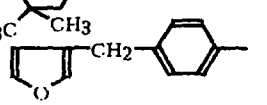

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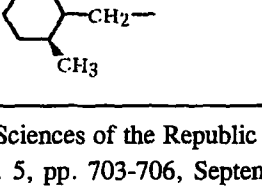

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TABLE 1. Some Physicochemical Characteristics of the New Gossypol Imines

Compound No.	mp, °C	R_f (acetone)	UV spectrum: λ_{max}, nm (log ε) (acetone)	Empirical formula	Yield, %
1	312–314	0.62	370(4.73)	$C_{34}H_{40}N_2O_{12}S_2$	58.6
2	243–245	0.71	435(4.29)	$C_{38}H_{44}N_2O_8$	79.4
3	280–282	0.58	380(4.27)	$C_{38}H_{48}N_2O_8$	45.5
4	255–257	0.89	445(4.45)	$C_{38}H_{48}N_2O_8$	68.3
5	295–297	0.9*	380(3.95); 405(4.30)	$C_{38}H_{48}N_2O_{12}$	32.4
6	183–185	0.9	380(3.95)	$C_{38}H_{44}Br_2N_2O_8$	80.0
7	>360	0.73	455(4.05)	$C_{34}H_{34}N_4O_6$	57.9
8	293–295	0.88	380(4.30)	$C_{44}H_{38}N_4O_6$	87.5
9	>300	0.51	450(4.45)	$C_{42}H_{48}N_4O_{12}$	68.05
10	292–295	0.82	450(4.05)	$C_{52}H_{72}N_2O_8$	62.6
11	235–237	0.73	430(4.45)	$C_{46}H_{48}N_2O_8$	95.9
12	248–250	0.82	430(4.22)	$C_{34}H_{34}N_8O_6$	73.4
13	275–278	0.9 †	445(4.21)	$C_{40}H_{36}F_6N_2O_6$	83.4
14	214–216	0.89	380(4.73)	$C_{38}H_{32}Cl_2N_6O_6$	80.2
15	257–258	0.71	450(4.82)	$C_{48}H_{42}N_4O_6$	89.6
16	265–268	0.71	455(4.43)	$C_{48}H_{56}N_4O_8$	91.3
17	246–248	0.65	460(4.52)	$C_{40}H_{36}Cl_2N_4O_6$	74.3
18	201–203	0.80	430(4.25)	$C_{38}H_{40}N_2O_8S_2$	63.4
19	>300	0.79	440(4.60)	$C_{40}H_{38}N_4O_6$	89.6
20	225–227	0.81	410(4.35)	$C_{42}H_{42}N_4O_6$	96.0
21	245–247	0.85	380(4.40)	$C_{42}H_{42}N_4O_6$	97.4
22	288–290	0.89	440(4.52)	$C_{46}H_{64}N_8O_6$	84.8
23	242–244	0.65	390(4.69)	$C_{48}H_{62}N_4O_6$	59.5
24	170–172	0.73	385(4.05)	$C_{52}H_{60}N_2O_8$	78.6
25	188–190	0.73	395(4.26)	$C_{70}H_{90}N_2O_6$	82.2
26	172–175	0.85	370(4.18)	$C_{44}H_{46}N_4O_6$	68.4
27	256 (decomp.)	0.87	395(4.40)	$C_{44}H_{46}N_4O_8$	52.6
28	250–252	0.85	380(4.60)	$C_{42}H_{32}F_{10}N_4O_6$	91.9

*Acetone–ethanol (1:9) system.

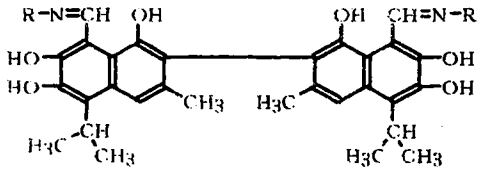
†Acetone–toluene (6:4) system.

In the present paper we give the results of a study of the physicochemical properties and structures of new Schiff bases synthesized by the reaction of GP with aliphatic, aromatic, and heterocyclic amines within the framework of a program of joint investigations with the AO Syntest Ltd.

Compounds (1-25) consisted of brightly colored pulverulent substances with high melting points, the majority of which were sparingly soluble in organic solvents and insoluble in water (Table 1). For this reason it was possible to record the PMR spectra of only some of them.

The PMR spectra of compounds (**1-25**) demonstrated the presence of a doublet of an imine proton broadened to various degrees, which confirmed [5] the existence of these substances in the quinoid form, when doublet splitting is due to a vicinal SSCC in the =CH–NH– fragment.

At the same time, in the case of compounds (**26-28**), when hydrazines had been used as the amine components, the signals of the CH and NH protons in the PMR spectra had the form of narrow singlets, which showed that these compounds existed in the benzoid form with the classical –CH=N– fragment.



R: **26** – $C_6H_5CH_2$–NH–
27 –$(CH_3O)C_6H_4$NH–
28 –C_6F_5NH–

EXPERIMENTAL

The Schiff bases of GP were obtained as in [6]. UV spectra were taken on a SF-26 spectrophotometer at a concentration of 0.002% with a cell thickness of 1 cm.

PMR spectra were recorded on a Varian XL-100 spectrometer with a working frequency of 100 MHz in $CDCl_3$, CD_3OD, or $(CD_3)_2CO$.

TLC was conducted on Silufol UV-254 plates. The nitrogen analyses of the substances corresponded to the calculated figures.

2,2′-(8,8′-Diformyl-1,1′,6,6′,7,7′-hexahydroxy-5,5′-diisopropyl-3,3′-dimethyl)dinaphthalene Bis(2,3,4,5,6-pentafluorophenylhydrazone) (Compound 28). A solution of 0.52 g (0.001 mole) of gossypol in 15 ml of ethyl alcohol was treated with a solution of 0.39 g (0.002 mole) of 2,3,4,5,6-pentafluorophenylhydrazine in 10 ml of ethyl alcohol, and the mixture was heated on the water bath for 3 h. The precipitate that deposited after cooling was filtered off and washed with ethyl alcohol and diethyl ether and was dried. Yield 0.8 g (91.9% of theor.). Mustard-colored powder. PMR spectrum ($CDCl_3$, ppm): 13.20 (1H, s, NH); 10.06 (1H, s, =CH); 9.48 (1H, s, OH); 7.66 (1H, s, H4); 7.50 (1H, s, OH); 4.02 (1H, M, isopropyl CH); 2.08 (3H, s, CH_3); 1.58 (6H, d, J = 6.45 Hz,, 2 × isopropyl CH_3).

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