STATE OF IMINO COMPOUNDS OF GOSSYPOL IN SOLUTIONS

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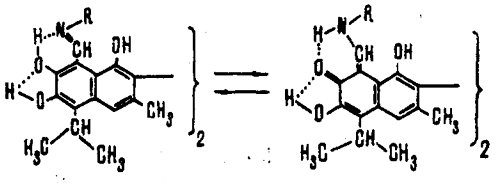
It is known that the existence of a tautomeric amide–imidol equilibrium is characteristic for the Schiff's base of 2-hydroxy-1-naphthaldehydes [1, 2]. The existence of phenol-imine (I) and keto-amine (II) forms, together with tautomeric [3] and atropoisomeric [4] forms, which are known for gossypol – a natural aldehydo naphthol – itself, can also be assumed for imino compounds of gossypol.

The present paper gives the results of a study by the PMR method of the structure of a series of imino compounds of gossypol obtained by condensing it with the corresponding amines:



I

II

where 1—CH_2CH_2OH; 2—CH_2CH_2Cl; 3—CH_2CONH_2; 4—C_6H_5; 5—C_6H_4COOH; 6—C_6H_4OH; 7—$C_6H_4NO_2$; 8—$C_6H_4SO_3Na$.

All the compounds are sparingly soluble in organic solvents, for which reason their spectra were recorded in dimethyl sulfoxide. The substances studied can be separated into two groups: with an aliphatic (substances 1, 2, and 3) and with an aromatic (substances 4, 5, 6, 7, and 8) amine component.

In the PMR spectra of solutions of the substances of the first group in DMSO and dioxane (Table 1) a broadened signal of an NH group is observed in a 13.00-13.25 ppm region and the doublet of a =CH–N in the 9.40-9.80 ppm region, its spin–spin coupling constant varying between 7 and 12 Hz according to the composition of the amine component. As a result of experiments on deuterium exchange, the transformation of the CH doublet into a singlet and the disappearance of the signal of the proton in the 13.00-13.40 ppm region was observed. The action of a strong high-frequency field on the signal of the NH proton also converted the CH signals into singlets.

TABLE 1

Solvent	δ, ppm			
	=CH–N–	J, Hz	NH–	–CH=N–
Dioxane	9,58—9,70	12	13,25	—
DMSO	9,65—9,73	10	13,17	—
DMSO+D_2O	9,68	—	—	—
DMSO	9,66—9,78	7	13,15	—
DMSO+D_2O	9,70	—	—	—
DMSO	9,47—9,68	10	13,00	
Dioxane	—	—	—	10,20
$CDCl_3$	—	—	—	10,17
DMSO	—	—	—	10,28
DMSO				10,40
DMSO				10,25
DMSO+D_2O	—	—	—	10,25
DMSO	—	—	—	10,00
DMSO	—	—	—	10,30
DMSO+D_2O	—	—	—	10,30

In the spectra of solutions of the second group in DMSO (see Table 1), a singlet of an HC–N group is observed in the 10.00-10.40 ppm region. In the case of these derivatives, the addition of D_2O leaves the signal of the proton of the azomethine group unchanged.

On the basis of the results obtained it may be concluded that for alkylamines of gossypol in the solvents studied the predominant form is the keto-amine form (II), and for alkylimines (2.02 ppm) and arylimines (2.28 ppm) of gossypol in pyridine shows a greater degree of coplanarity of the molecules of the latter.

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