3. R. W. Evans, M. Kates, and G. W. Wood, Chem. Phys. Lipids, 31, 331 (1982).
4. N. Sato and M. Furuya, Plant Cell Physiol., 24, 1113 (1983).
5. V. M. Dembitskii, Khim. Prir. Soedin., 511 (1981).
6. V. M. Dembitskii, Khim. Prir. Soedin., 513 (1981).

PRODUCTS OF TRANSFORMATION OF GOSSYPOL IN METHANOL

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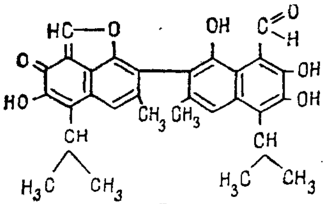
The instability of gossypol in alcoholic solutions has been reported in the literature [1], but there have been practically no investigation to determine the causes of such instability.

We have studied the products of the transformation of gossypol in methanol. With the aid of TLC on Silufol in the benzene—methanol (20:5) system it was found that, on the storage of room temperature of a methanolic solution of pure gossypol [(I), R_f 0.55], substances (II) (R_f 0.37) and (III) (R_f 0.31) giving qualitative reactions for aldehyde groups appeared in addition, and with time the quantitative ratio of all three components (I, II, and III) changed. The spot of (I) gradually diminished, changing into (II) and (III) and finally it was mainly (III) that remained in solution with a very small amount of (II).

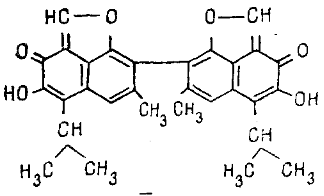
A comparison of the behavior (I) in a number of other organic substances showed such transformations only in low-molecular-weight alcohols (methanol, ethanol, and propanol), while they did not take place in acetone, diethyl ether, benzene and chloroform. At the same time, with an increase in the molecular weight of the alcohol the rate of the transformations of gossypol fell. Thus, while (I) in methanol was converted completely into (II) and (III) in a week, in ethanol after the same time a certain amount of gossypol remained and the amount of substance (II) was greater than that of (III); in propanol, only (I) and (II) remained.

In the UV spectra of the products of the transformatin of (I) in methanol a shift of the absorption band of the binaphthyl ring in the direction of shorter wavelengths from 236 to 223 nm and the appearance of three maxima at 249, 261, and 270 nm, absent from the spectrum of gossypol and characteristic for anhydrogossypol [2], were observed. Simultaneously a rise in intensity of the absorption at 261 nm with a fall in that at 376 nm was seen, which was due to a decrease in the amount of aldehyde groups from 96.3 to 10.6% [3].

By preparative TLC it was possible to separate the methanolic products of the transformation of (I) but not to chromatographic purity. According to their UV spectra, the amount of aldehyde groups in (II) was 41.0%, and in (III) 2.2%, which correspond to the hypothesis of a possible dehydration of gossypol [4] with the formation of its anhydro derivatives: with the participation of one aldehyde group for substance (II) and of two aldehyde groups for (III).



II



III

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The molecule of an anhydrogossypol contains a readily cleaved oxygen-containing ring. For this reason it proved impossible to obtain substances (II) and (III) in sufficiently pure state on PTLC, since transformations of (III) into (II) and into (I) took place. The formation of anhydro derivatives of gossypol was also confirmed by the IR and mass spectra of the methanolic products. In their IR spectra, in comparison with the spectra of gossypol, a fall in the intensity of the absorption of phenolic OH groups (3520 cm^{-1}) was observed [5].

In the mass spectrum of the products of the transformation of (I) in methanol, the peaks of molecular ions for (II) (M^+ 500) and (III) (M^+ 482) and the absence of ions with m/z 518, which are characteristic for gossypol, were detected.

In an investigation of the bound lipids extracted from cottonseed kernels by chloroform—methanol (2:1), in addition to gossypol, two other pigments, G-2 and G-3 that were difficult to identify were found [6].

A comparison of the chromatographic mobilities and UV spectra of these pigments with those of (II) and (III) gave grounds for assuming the G-2 and G-3 were anhydro derivatives of gossypol, since they were extracted with a mixture of chloroform and methanol.

Thus, the use of methanol and of methanol-containing solvents in the study of lipids and pigments of the cotton plant leads to the formation of mono- and dianhydrogossypols which are not natural derivatives of it.

LITERATURE CITED

1. A. A. Nomeir and M. B. Abou-Donia, J. Am. Oil Chem. Soc., 59, 546 (1982).
2. A. L. Markman and V. P. Rzhekhin, Gossypol and Its Derivatives [in Russian], Pishchevaya Prom-St', Moscow (1965), p. 37.
3. I. P. Nazarova, G. A. Nezhinskaya, A. I. Glushenkova, and A. U. Umarov, Khim. Prir. Soedin., 608 (1979).
4. A. A. Bell, R. D. Stipanovic, C. L. Howell, and A. I. Fryxell, Phytochemistry, 14, 225 (1975).
5. T. A. Danilova and A. N. Mironova, Trudy VNIIZha, Proc. All-Union Scientific-Research Institute of Fats, 23, 202 (1963).
6. S. D. Gusakova, S. G. Yunusova, T. V. Chernenko, I. P. Nazarova, and A. I. Glushenkova, Khim. Prir. Soedin., 677 (1986).