

ports (2 mm.), II is not converted to I and can be recovered in essentially theoretical yield.

It is of interest to note that Frankel and Cornelius³ isolated a hygroscopic solid, m.p. 63–65° from the reaction of acetyl chloride and ethanolamine which they erroneously identified as I. Their description indicates it may have been the hygroscopic salt (m.p. 65–66°) described in the present communication.

The identity of II was established by elementary analysis, by conversion to I on continued heating, and by preparation of derivatives of both ethanolamine and acetic acid. The previously unreported 3,5-dinitrobenzoate of N-acetyethanolamine was prepared to assist in the identification of I.

EXPERIMENTAL

To a mechanically stirred solution of 61 g. (1.0 mole) of ethanolamine in 150 ml. of absolute methanol was added 51 g. (0.5 mole) of acetic anhydride over a period of 45 min. The temp. was maintained at 15–25° by external cooling. The reaction mixture then was stirred and heated on the steam-bath for one hour or until it reached a temp. of 90–92°. The residue was distilled through an 8-inch Vigreux column and two fractions collected. Fraction (1), boiling at 100–110° (2 mm.), solidified in the receiver, wt. 57.5 g. Fraction (2), boiling at 137–138° (0.5 mm.), remained a colorless, viscous oil, wt. 45.5 g. A small intermediate fraction and the pot residue weighed a total of 8 g.

Fraction (2) was identified as *N*-acetyethanolamine (I), n_D^{25} 1.4701 (lit. value, n_D^{25} 1.4710).⁴

Anal. Calc'd for $C_4H_9NO_2$: N, 13.59. Found: N, 13.38.

On warming at 140–150° with less than the calculated amount of 3,5-dinitrobenzoyl chloride, the 3,5-dinitrobenzoate, m.p. 164–165°, was obtained. It showed no depression in a mixture m.p. determination with a sample prepared from authentic I.

Anal. Calc'd for $C_{11}H_{11}N_2O_7$: C, 44.45; H, 3.73; N, 14.14. Found: C, 44.98; H, 3.88; N, 13.92.

Fraction (1) crystallized with the generation of a large amount of heat. Due to extreme hygroscopicity the melting point was taken after drying under a vacuum on a microscope hot plate,⁵ m.p. 65–66°. Redistillation gave b.p. 103–104° (0.7 mm.). Elementary analysis indicated it was 2-hydroxyethyl ammonium acetate (II).

Anal. Calc'd for $C_4H_9NO_3$: C, 39.66; H, 9.15; N, 11.56. Found: C, 39.42; H, 8.88; N, 11.49.

II yielded a *picrate*,⁶ m.p. 158–160°, and *dibenzoate*,⁷ m.p. 88–89°, neither of which showed depression when mixed with the corresponding derivative of authentic ethanolamine. II also yielded a *p*-bromophenacyl ester,⁸ m.p. 84.5–85.0°, which was not depressed on admixture with the *p*-bromophenacyl ester of authentic acetic acid.

II was heated on a hot plate until bubbling had largely ceased (maximum temperature reached was 210°). The oily product was identified as I.

Anal. Calc'd for $C_4H_9NO_2$: N, 13.59. Found: N, 13.65.

The liquid product yielded a 3,5-dinitrobenzoate, m.p. 164°, which was not depressed in a mixture melting point determination with the corresponding derivative of authentic I.

Acetic acid (0.5 mole) was added to ethanolamine (0.5

mole) in 100 ml. of methanol. The solvent was removed at the water pump and the residue was distilled, b.p. 103–104° (0.6 mm.), to give an essentially quantitative yield of II.

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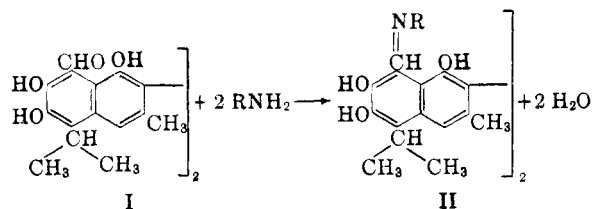
The Structure and Reactions of Gossypol. III. Aliphatic Anil Derivatives of Gossypol²

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Received October 17, 1955

The formation of a derivative of gossypol (I) by its reaction with aniline is a long-known³ and useful process. The resulting dianilnogossypol (II, R = phenyl) is a stable, crystalline product and its formation has provided the means of removal of gossypol from cottonseed products and detoxification of the gossypol in cottonseed meal. Miller and Adams,⁴ prepared some additional aromatic anil derivatives and also isolated a rather unstable diaminogossypol (II, R = H) from the action of liquid ammonia on gossypol. These workers also reported that methylamine, dimethylamine, and piperidine did not form derivatives of gossypol which were sufficiently stable to permit purification.

We have been able to produce stable anils from gossypol and a variety of primary aliphatic amines



by heating equivalent quantities of the reactants in isopropyl alcohol. For example, gossypol and dodecylamine produce didodecylaminogossypol (II, R = $C_{12}H_{25}$) in 95% yield. Crude gossypol acetic acid complex can also be used to produce these anils in good yields. The results of a series of experiments are summarized in Table I. Since gossypol and its derivatives are characterized by high melting points with decomposition, the lower melting points

(1) Preceding paper, Shirley and Dean, *J. Am. Chem. Soc.*, **77**, 6077 (1955).

(2) A report of work conducted under contract with the U. S. Department of Agriculture and authorized by the Research and Marketing Act. The contract is being supervised by the Southern Regional Research Laboratory of the Agricultural Research Service.

(3) Carruth, *J. Am. Chem. Soc.*, **40**, 647 (1918).

(4) Miller and Adams, *J. Am. Chem. Soc.*, **59**, 1736 (1937).

(3) Frankel and Cornelius, *Ber.*, **51**, 1657 (1918).

(4) D'Alerio and Reid, *J. Am. Chem. Soc.*, **59**, 111 (1937).

(5) Kindly performed by Mr. D. G. Grabar.

(6) Klamerth, *Ber.*, **84**, 254 (1951).

(7) Goldberg and Kelly, *J. Chem. Soc.*, 1922 (1948).

(8) Judefind and Reid, *J. Am. Chem. Soc.*, **42**, 1048 (1920).

TABLE I
 ALIPHATIC ANIL DERIVATIVES OF GOSSYPOL

Compound (R in II)	Molecular Formula	M.P., °C.	Yield, %	Recrystal- lization Solvent	Analyses					
					Calc'd		Found		Found	
					C	H	N	C	H	N
CH ₃ CH ₂ —	C ₃₄ H ₄₀ N ₂ O ₆	251-255 (d)	72	Ethyl acetate	71.3	7.04	4.89	71.48	7.08	4.65, 4.71
CH ₃ (CH ₂) ₄ —	C ₄₀ H ₅₂ N ₂ O ₆	218-221 (d)	69	Benzene			4.27			4.41, 4.32
CH ₃ (CH ₂) ₉ —	C ₆₀ H ₇₂ N ₂ O ₆	164.5-165.5	64	Benzene			3.51			3.46, 3.54
CH ₃ (CH ₂) ₁₃ —	C ₈₈ H ₈₈ N ₂ O ₆	126.5-127	75	Isopropyl alcohol			3.08			3.02, 3.07
CH ₃ (CH ₂) ₁₅ —	C ₆₂ H ₉₆ N ₂ O ₆	116-116.5	50	Benzene			2.90			2.71, 2.85
CH ₃ (CH ₂) ₁₇ —	C ₆₆ H ₁₀₄ N ₂ O ₆	112.5-113	60	Ethanol	77.6	10.2	2.75	77.49	10.20	2.95
								77.59	10.40	2.95
C ₆ H ₅ CH ₂ —	C ₄₄ H ₄₄ N ₂ O ₆	241.5 (d)	72	Chloroform and benzene	75.84	6.37	4.02	75.90	6.34	3.83
								75.99	6.40	3.93

(with no decomposition) of the long chain amino-gossypols is a unique feature of these types.

Figure 1 shows the ultraviolet absorption spectra of didodecylaminogossypol and dianilinogossypol. It is noted that the broad band at about 370-410 m μ in the dodecyl derivative is shifted to longer wave lengths in the dianilino compound. This is to be expected in view of the greater conjugation of the latter compound. Dibenzylaminogossypol shows an ultraviolet absorption spectrum nearly identical with the didodecylaminogossypol in the region of the spectrum shown in Figure 1.

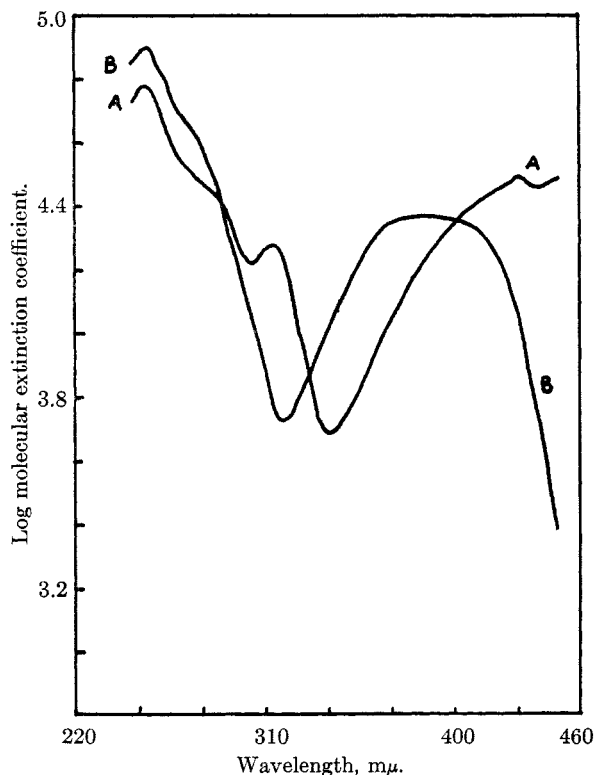


FIG. 1.—ULTRAVIOLET ABSORPTION SPECTRA IN CHLOROFORM. A, Dianilinogossypol; B, Didodecylaminogossypol.

Acknowledgment. The authors wish to acknowledge the help and advice of Doctors F. H. Thurber and A. M. Altshul of the Southern Regional Research Laboratory.

 EXPERIMENTAL⁵

Didodecylaminogossypol. A solution of 0.52 g. (0.001 mole) of pure gossypol⁶ in 45 ml. of isopropyl alcohol was heated to boiling and a solution of 0.37 g. (0.002 mole) of pure dodecylamine in 10 ml. of isopropyl alcohol was added. The mixture was boiled for one minute and allowed to stand at 5° overnight. The precipitated yellow crystalline solid was filtered off and dried to yield 0.81 g. of yellow, crystalline product corresponding to a 95% yield. The product melted at 170-171° and this melting range was not altered by additional crystallization.

Anal. Calc'd for C₆₄H₈₀N₂O₆: C, 76.0; H, 9.40; N, 3.29. Found: C, 76.0 and 75.9; H, 9.42 and 9.46; N, 3.21 and 3.26.

Crude gossypol acetic acid complex can also be used to form didodecylaminogossypol in fair yield. One gram (0.00173 mole) of the chocolate-brown complex⁶ in 70 ml. of isopropyl alcohol and 0.64 g. (0.00346 mole) of amine treated as before gave 0.84 g. (58%) of didodecylaminogossypol, m.p. 170-171°. One recrystallization from isopropyl alcohol was necessary to reach this melting point.

The compounds listed in Table I were prepared in general accordance with the above procedure except that recrystallization solvents varied as shown in the table.

(5) Microanalyses by Galbraith Microanalytical Laboratories of Knoxville, Tennessee.

(6) Supplied by Dr. F. H. Thurber.

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 Some New 2- and 3-Substituted
 Dibenzarsenolic Acids¹

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Received October 19, 1955

Recently, the preparation of several amino derivatives of dibenzarsenolic acid (arsafluorinic acid, 9-arsafluorenic acid) have been described.^{2,3} Thus,

(1) Abstracted from the theses presented by Albert A. Carr and Thomas R. Hauser in partial fulfillment of the requirements for the Master of Science degree at Xavier University.

(2) Fietelson and Petrow, *J. Chem. Soc.*, 2279 (1951).

(3) Garascia and Mattei, *J. Am. Chem. Soc.*, 75, 4589 (1953).