specific amine or general base catalyzed[10] in which case variation of reaction rate with buffer concentration (at *p*H 7.4) may be expected.

Summary

Hydrolytic stability of three physostigmine analogs at 38° and *p*H 7.4 was investigated by measurement of light absorption of the phenolic hydrolysis product at a wave length of 275 mμ. The two N,N-dialkyl carbamates were stable under these conditions during a four day observation period. The N-methyl carbamate was found to be unstable and to have a half life of 52 minutes and a velocity constant of 0.0133.

CHICAGO, ILLINOIS RECEIVED DECEMBER 12, 1946

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[10] L. P. Hammett, "Physical Organic Chemistry," 1st ed., McGraw-Hill Book Company, Inc., New York, N. Y., 1940, pp. 344–345 and 215–218.

[CONTRIBUTION FROM THE SOUTHERN REGIONAL RESEARCH LABORATORY[1]]

The Pigments of Cottonseed. III.[2] Gossyfulvin, a Native Cottonseed Pigment Related to Gossypol[3]

BY CHARLOTTE H. BOATNER, ROBERT T. O'CONNOR, MAIZIE C. CURET AND CAROLYN S. SAMUELS

An orange colored pigment, gossyfulvin, has previously been detected[4] in cottonseed. Although gossyfulvin has been shown to differ from gossypol in many of its properties it can be readily converted into the latter pigment. Since the work on gossyfulvin was reported, larger quantities of the pigment have been prepared by the procedure outlined in the accompanying diagram and it has therefore been possible to obtain further insight into its structure and its relationship to gossypol.

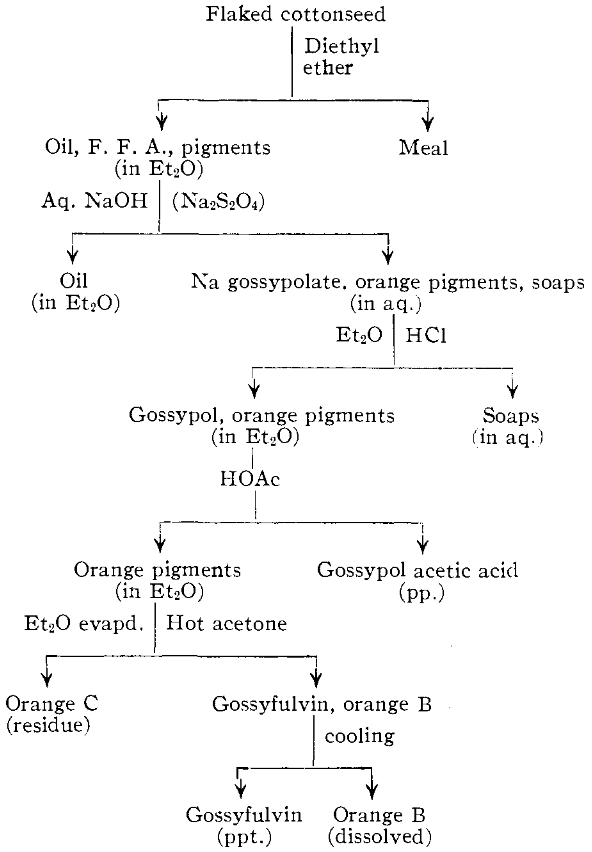
Gossyfulvin forms rather large orange-colored rhombohedra (Fig. 1), changing at 212° to a more deeply colored form which melts with decomposition at 238–239° (cor.). The crystalline form and habit of gossyfulvin differentiate it sharply from gossypol, which latter pigment, upon recrystallization from diethyl ether and petroleum naphtha, forms clusters of dog-toothed prisms (Fig. 2), m. p. 182.5–183.5°.

Gossyfulvin reacts with strong mineral acids when its chloroform solutions are treated with concentrated aqueous solutions of these acids yielding gossypol in amounts equal to as much as 86.8% of the weight of gossyfulvin treated. On the basis of the experimentally determined elementary composition, $C_{34}H_{34}N_2O_8$, the molecular weight of gossyfulvin is 598.

Gossypol obtained after recrystallization from diethyl ether and petroleum naphtha at low temperatures and dried without elevation of temperature yields analytical values which agree with those calculated for $C_{30}H_{32}O_9$.

Comparison of gossyfulvin with such nitrogen derivatives of gossypol as diamino- and dianilinogossypol, reveals several significant differences, *e. g.*, the melting point of gossyfulvin lies between those of the other nitrogen derivatives. The compounds differ with respect to solubility and stability. Diaminogossypol dissolved in diethyl ether or warmed in acetic acid is reported[5] to evolve ammonia and revert to gossypol. Dianilinogossypol, on the other hand, is one of the most stable of the compounds formed from gossypol, and is hydrolyzed to gossypol only upon re-

ISOLATION OF GOSSYFULVIN FROM COTTONSEED



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[1] One of the Laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture. Article not copyrighted.

[2] For previous paper of this series see Boatner, Samuels, Hall and Curet, THIS JOURNAL, **69**, 668–672 (1947).

[3] Presented before the 109th Meeting of the American Chemical Society, Atlantic City, New Jersey, April 8 to 12, 1946.

[4] Boatner, Caravella and Samuels, THIS JOURNAL, **66**, 838 (1944).

[5] Miller and Adams, *ibid.*, 1736–1738 (1937).

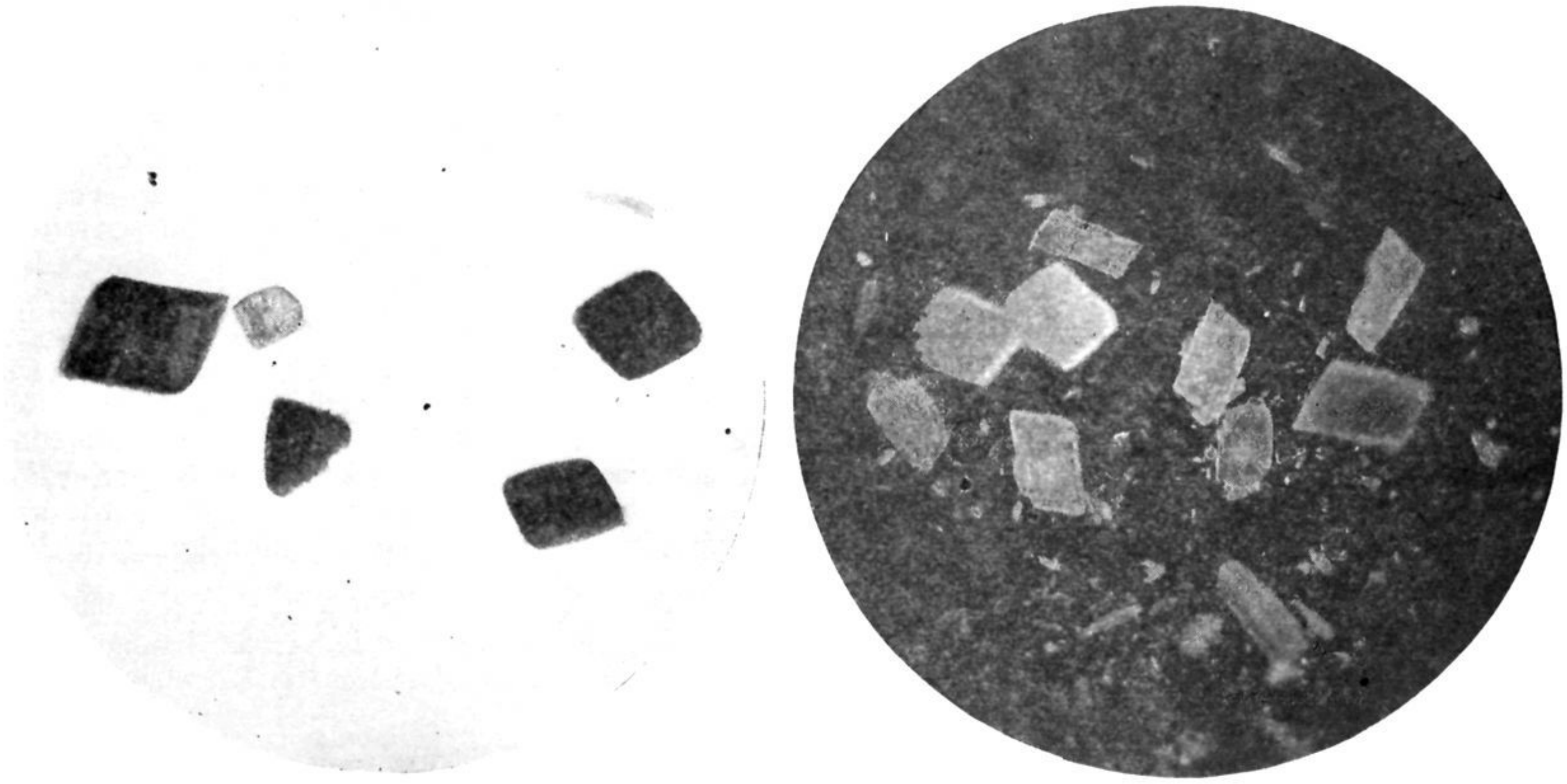

Fig. 1.—Photomicrographs of crystalline gossyfulvin, × 68, (a) in ordinary light, and (b) between crossed nicols, by M. E. Jefferson and F. B. Kreeger.

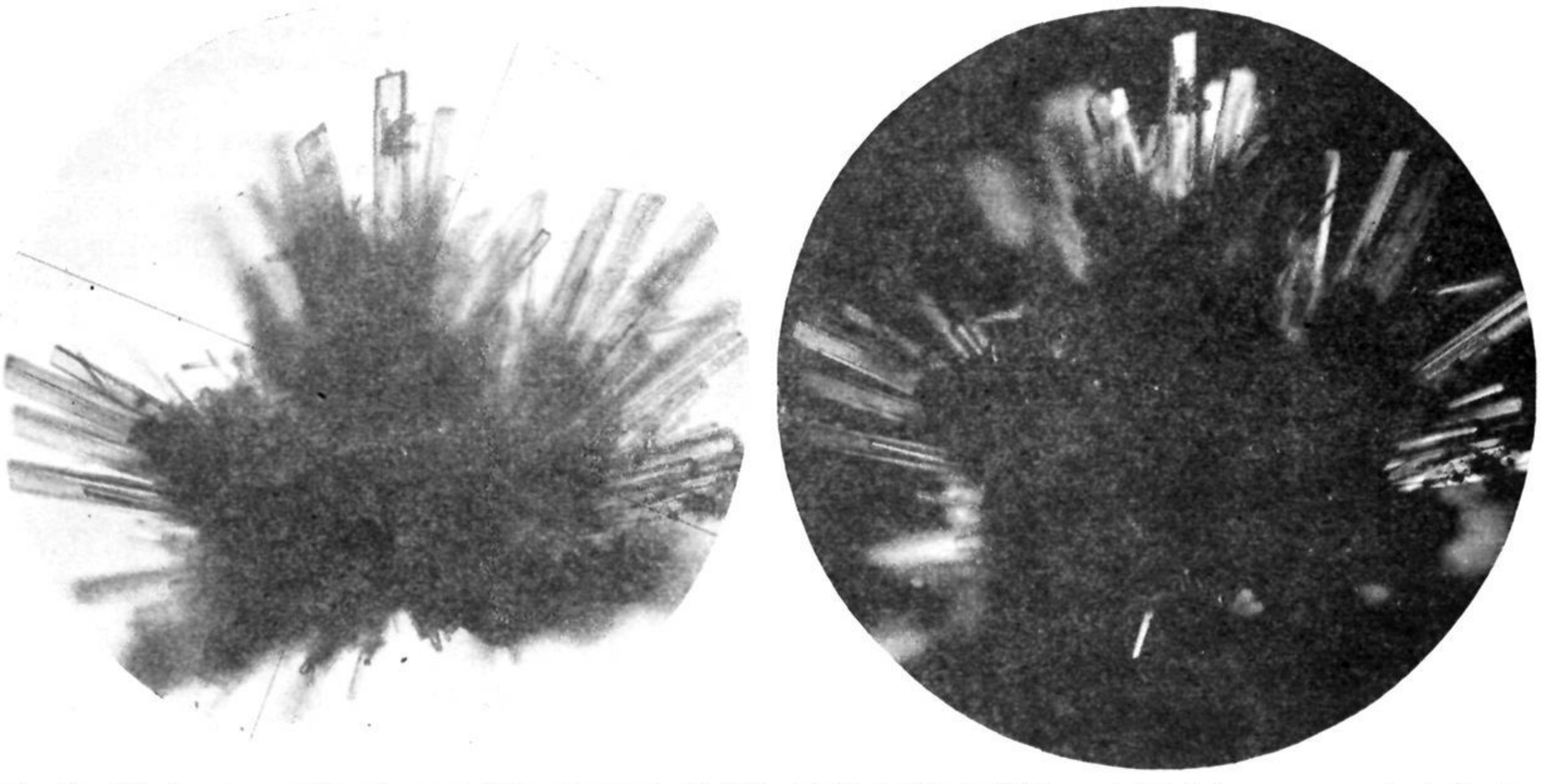

Fig. 2.—Photomicrographs of crystalline gossypol, × 123, (a) in ordinary light, and (b) between crossed nicols, by M. E. Jefferson and F. B. Kreeger.

action in concentrated sulfuric acid,[6] alcoholic potassium hydroxide[7] or hot acetic anhydride.[8] Gossyfulvin is very unstable in solution, and in the absence of strong mineral acids it decomposes without loss of nitrogen. The absorption spectrum (Fig. 3) of gossyfulvin is identical, within the limits of experimental error, with that of dianilinogossypol (Fig. 4). From the latter observation it may be concluded that the basic structures of gossyfulvin and dianilinogossypol are identical.

The tautomeric structures which have been proposed for dianilinogossypol[9] closely resemble those proposed for gossypol,[10] differing only in the substitution of two anilino groups for the two doubly-bound oxygen atoms of the carbonyl groups of gossypol. In view of the observation

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(6) Clark, *J. Biol. Chem.*, **76**, 229–235 (1928).

(7) Carruth, THIS JOURNAL, **40**, 647–663 (1918).

(8) Murty, Murty and Seshadri, *Proc. Indian Acad. Sci.*, **16A**, 54–61 (1942).

(9) Adams, Price and Dial, THIS JOURNAL, **60**, 1258–1260 (1938).

(10) Adams, Morris, Geissman, Butterbaugh and Kirkpatrick *ibid.*, **60**, 2193–2204 (1938).

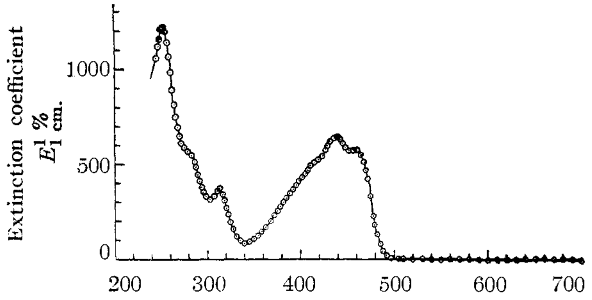

Fig. 3.—Absorption spectrum of gossyfulvin in chloroform.

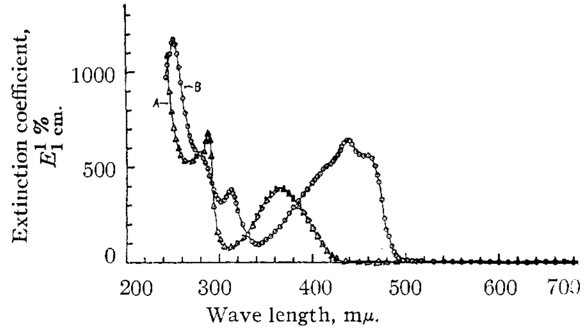

Fig. 4.—Absorption spectra of (A) gossypol and (B) dianilinogossypol in chloroform.

that the absorption spectrum and, therefore, by inference, the structure of gossyfulvin is identical with that of dianilinogossypol, but very different from that of gossypol, it seems evident that the changes occurring during the formation of both gossyfulvin and dianilinogossypol from gossypol must involve more than the simple substitution of nitrogen-containing groups for the oxygen atoms of the carbonyl groups of gossypol.

The observation that the specific extinction coefficients of gossyfulvin and dianilinogossypol are identical indicates that the presence of two phenyl groups in dianilinogossypol produces *enhancement* of its molecular absorption over that of gossyfulvin.

The absorption spectra of the antimony trichloride reaction products (Fig. 5) of gossypol, dianilinogossypol, and gossyfulvin exhibit the same interrelation as those of the pure pigments. Gossypol and dianilinogossypol form stable reaction products with antimony trichloride, but their absorption spectra are very different. The antimony trichloride reaction product formed by gossyfulvin is very unstable; its absorption spectrum is similar in shape but less intense than that of the dianilinogossypol reaction product.

Further evidence of the complexity of the interrelation of gossypol, gossyfulvin, and dianilinogossypol is observed on comparison of the oximes formed by these compounds (Table I). All three compounds form dioximes of identical elemental composition but they differ in melting points, and a mixture of any pair of oximes melts over a wide range. The isomerism of these dioximes can therefore be related to their origins from closely related compounds. The formation of isomeric carbonyl derivatives requires that the nitrogen-containing groups of gossyfulvin and dianilinogossypol be removed during reaction. The existence of three isomeric dioximes suggests that the carbonyl groups of gossypol are more labile than has heretofore been presumed.

Acetylation of gossyfulvin gave a yellow solid, m. p. 185–185.25°. The color, melting point, and acetyl content, 34.6%, of this compound suggested that it might be identical with one of the compounds reported to be formed in small proportion upon acetylation of gossypol,[11] and as the sole product of acetylation of dianilinogossypol.[9,12]

TABLE I

COMPOSITION AND MELTING POINTS OF OXIMES FORMED FROM GOSSYPOL, GOSSYFULVIN AND DIANILINOGOSSYPOL

Compound	M. p., °C.	Formula	Elementary composition %, Found[a] C	H	N
Dioxime of gossypol	312	$C_{30}H_{32}O_8N_2$	65.70	5.72	5.04
Dioxime formed by gossyfulvin	204.5	$C_{30}H_{32}O_8N_2$	65.35	6.02	5.00
Dioxime formed by dianilinogossypol	221–221.5	$C_{30}H_{32}O_8N_2$	65.25	6.03	5.33

[a] Composition calculated for gossypol dioxime, $C_{30}H_{32}O_8N_2$: C, 65.66; H, 5.83; N, 5.12.

Acetylation of gossypol has been variously reported to yield a colorless tetra- or pentaacetate,[7] a colorless hexaacetate,[6] and a mixture of a colorless and a yellow hexaacetate.[11] The elementary composition of the colorless acetate prepared during the present investigation agreed with the values calculated for tetraacetoxygossypol, and determination of its acetyl content by the method of Elek and Harte[13] for O-acyl compounds also yielded values consistent with the formula of a tetraacetate. Attempts to obtain the yellow acetylated gossypol derivative, m. p. 185°, reported by Miller, Butterbaugh and Adams[11] in sufficiently pure condition for reliable analytical values were no more successful than those of the aforementioned investigators. The colorless acetate was found to be very stable and retreatment with the acetylating agent provided no evidence of its convertibility to the more highly acetylated yellow form.

A yellow compound, m. p. 185°, formed by acetylation of dianilinogossypol was reported by Adams, Price and Dial[9] to be hexaacetoxydianilinogossypol, and by Murty and Seshadri[12] to be a nitrogen-free hexaacetoxygossypol, identical with the compound formed in small amounts by the direct acetylation of gossypol. During the present investigation, neither of the previously reported derivatives was obtained by acetylation of

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[11] Miller, Butterbaugh and Adams, THIS JOURNAL, **59**, 1729–1731 (1937).

[12] Murty and Seshadri, *Proc. Indian Acad. Sci.*, **16A**, 141–145 (1942).

[13] Elek and Harte, *Ind. Eng. Chem., Anal. Ed.*, **8**, 267–269 (1936).

dianilinogossypol, but mixtures were obtained whose content of acetyl indicated the introduction of only four acetyl groups.

Experimental

Isolation and Purification of Gossypol and Gossyfulvin.—Gossyfulvin was isolated from an ethereal extract of cottonseed after removal of gossypol according to the following procedure. The ethereal extract obtained from 110 lb. of decorticated and flaked cottonseed was extracted in 1-liter portions with 500 ml. of 0.5 *N* sodium hydroxide containing 10 g. sodium dithionite (sodium hydrosulfite: $Na_2S_2O_4$). The ethereal layer was washed with 250 ml. water, and the washings added to the alkaline extract. The combined alkaline extract and washings were then washed with 250 ml. of diethyl ether. Concentrated hydrochloric acid was added slowly with stirring to the alkaline extract until the solution attained a *p*H of 7 to 7.5, and a yellow ethereal layer separated from the aqueous extract. To the separated ethereal layer there was added 25 ml. of glacial acetic acid, after which the solution was heated on a steam-bath for about one-half hour, until the ether no longer evolved rapidly. Upon cooling, a copious precipitate of gossypolacetic acid formed. The precipitate was washed several times by decantation with large volumes of petroleum naphtha until the washings became lightly colored after which it was transferred to a Buchner funnel, and dried by aspiration; total yield of crude gossypolacetic acid, 142 g.

The crude gossypolacetic acid was hydrolyzed to free gossypol by heating its aqueous suspension on a steam-bath for two hours.[8] When the gossypol thus obtained was digested with toluene at room temperature, colored impurities were removed leaving yellow microcrystals, m. p. 181-181.5° (cor.).

Anal. Calcd. for $C_{30}H_{30}O_8$: C, 69.5; H, 5.79. Found: C, 68.46; H, 5.88.

After three successive recrystallizations at 3.3° (38°F.). from mixtures of diethyl ether and petroleum naphtha, large clusters of dog-toothed prisms were obtained which were dried for twenty-four hours in a vacuum desiccator over Drierite, m. p. 182.5-183.5° (cor.).

Anal. Calcd. for $C_{30}H_{32}O_9$: C, 67.16; H, 5.97. Found: C, 66.72; H, 6.21.

Gossyfulvin was obtained from the combined filtrates and washings of crude gossypolacetic acid. When these had been allowed to evaporate in an uncovered beaker for a period of one week, a precipitate formed in the dark colored, gummy liquid. This precipitate was transferred to a Buchner funnel and washed with large volumes of Skellysolve F. The brilliant orange precipitate residue was washed exhaustively with diethyl ether (in the presence of water) in order to remove remaining traces of gossypol. Yield of crude orange precipitate, 21.4 g.: m. p. 214.5-215.5° (cor.).

Five grams of the crude precipitate was suspended in 200 ml. of hot acetone, and the hot acetone solution was filtered through a pre-heated Buchner funnel. The precipitate which formed in the acetone filtrate upon cooling was removed by filtration. The precipitate which consisted of stout dark orange needles lost its original luster upon exposure to air. It was recrystallized three times at 3.3° (38°F.) from a mixture of chloroform and ether. The gossyfulvin obtained in this manner melted at 212° (cor.), changing during fusion to a more deeply colored compound, m. p. 238-239° (cor.) with decomposition. Solubility: very soluble in 2,4-dioxane; soluble in chloroform, aniline, carbon disulfide, hot acetone: very slightly soluble in ethanol, cold acetone, diethyl ether; insoluble in aqueous sodium hydroxide and saturated aqueous sodium bisulfite.

Anal. Calcd. for $C_{34}H_{34}N_2O_8$: C, 68.23; H, 5.69; N, 4.68. Found: C, 68.90; H, 5.62; N, 4.61.

Conversion of Gossyfulvin to Gossypol.—The amount of gossypol formed from weighed amounts of gossyfulvin in chloroform solution was determined by the gossypol–antimony trichloride spectrophotometric method.[14] The maximum yield of gossypol was 86.8% based on the weight of gossyfulvin used. Other yields of gossypol obtained from several independently purified preparations of gossyfulvin were 82.6, 86.8, 86.0, 81.7 and 86.0%. Treatment with concentrated aqueous solution of hydrochloric, sulfuric, phosphoric or trichloroacetic acid was found to be equally effective in converting gossyfulvin to gossypol. Gossyfulvin was unaffected by treatment with dry hydrogen chloride, or glacial or aqueous acetic acid.

The conversion of gossyfulvin to gossypol was also demonstrated by precipitation of dianilinogossypol from chloroform solutions of gossyfulvin which had first been treated with concentrated hydrochloric acid, then with aniline, and heated.

Absorption Spectra of Gossypol, Gossyfulvin and Dianilinogossypol.—The absorption spectra of chloroform solutions of weighed amounts of gossypol, gossyfulvin and dianilinogossypol[15] were determined with a Beckmann quartz spectrophotometer. The concentrations of the solutions were adjusted so that the optical densities always lay within the most sensitive range of the spectrophotometer, *i.e.*, between 0.1 and 1.0. The values of $E^{1\%}_{1\text{ cm.}}$ for gossypol, gossyfulvin and dianilinogossypol at critical points throughout the wave length region from 240 to 700 mμ are reproduced in Tables II and III and the complete spectra in Figs. 3 and 4.

TABLE II

SPECIFIC EXTINCTION COEFFICIENTS ($E^{1\%}_{1\text{ cm.}}$) OF GOSSYPOL IN CHLOROFORM AT POINTS OF CHARACTERISTIC ABSORPTION

Wave length, millimicrons	Description	$E^{1\%}_{1\text{ cm.}}$
263–264	Minimum	488
278–280	Maximum	530
282	Minimum	521
288–289	Maximum	610
309–310	Minimum	72.7
362–366	Maximum	352

TABLE III

SPECIFIC EXTINCTION COEFFICIENTS ($E^{1\%}_{1\text{ cm.}}$) OF GOSSYFULVIN AND DIANILINOGOSSYPOL IN CHLOROFORM AT POINTS OF CHARACTERISTIC ABSORPTION

Wave length, millimicrons	Description	$E^{1\%}_{1\text{ cm.}}$ Gossyfulvin	$E^{1\%}_{1\text{ cm.}}$ Dianilinogossypol
251–252	Maximum	1215.6	1168.6
302–303	Minimum	311.7	314.4
312–313	Maximum	370.9	372.8
341	Minimum	87.79	94.0
439–440	Maximum	649.4	
437–439	Maximum		634.4
456–462	Shoulder	571.5	555.3–555.9

Antimony Trichloride Reaction Products of Gossyfulvin and Dianilinogossypol.—The antimony trichloride reaction was carried out with chloroform solutions of gossyfulvin and dianilinogossypol according to the procedure described for the antimony trichloride-spectrophotometric method for the determination of gossypol in cottonseed.[14] The absorption spectra of the reaction mixtures were determined in a Coleman monochromator spectrophotometer equipped with absorption cells having

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[14] Boatner, Caravella and Kyame, THIS JOURNAL, 566–572 (1944).

[15] The elementary composition of dianilinogossypol, prepared by the method of Clark,[8] corresponded closely with the theoretical values.

an optical depth of 1.27 cm. The absorption spectrum of the yellow gossyfulvin–antimony trichloride reaction product is stable for a maximum of one hour. It exhibits a single absorption band at 460 mμ, $E^{1\%}_{1\text{ cm.}}$ 522 (Fig. 5).

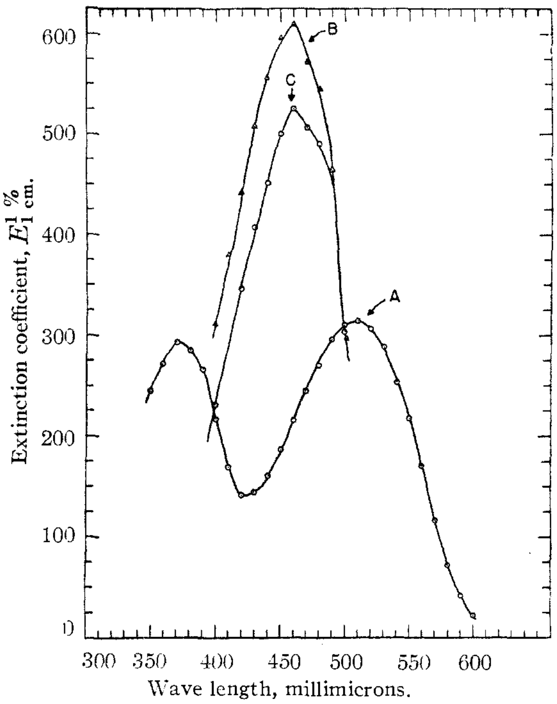

Fig. 5.—Absorption spectra of antimony trichloride reaction products of (A) gossypol, (B) dianilinogossypol and (C) gossyfulvin.

The absorption in the region of the visible spectrum of the dianilinogossypol–antimony trichloride reaction product is very stable, but the curve (Fig. 5) is of a shape similar to that of the gossyfulvin–antimony trichloride reaction product with a single absorption maximum at 460 mμ, $E^{1\%}_{1\text{ cm.}}$ 608.

Preparation of Oximes.—To a solution of 2 g. gossypol-acetic acid in 25 ml. of 95% ethanol and 25 ml. of pyridine[16,17,18] were added 2 g. hydroxylamine hydrochloride, and the reaction mixture was maintained at 3.3° (38°F.) for twenty-four hours. Upon pouring the solution into cold, water, a pale cream-colored precipitate formed; weight 2.5 g. Recrystallization from benzene and methanol yielded 0.73 g. cream-colored solid, m. p. greater than 310°.

Anal. Calcd. for $C_{30}H_{32}O_8N_2$: C, 65.66; H, 5.84; N, 5.12. Found: C, 65.70; H, 5.72; N, 5.04.

To a suspension of 0.1 g. gossyfulvin in 10 ml. of ethanol and 30 drops of pyridine heated to boiling on a steam-bath, there was added a solution of 0.1 g. of hydroxylamine hydrochloride in 5 ml. of ethanol and 10 drops of pyridine, after which the mixture was heated for twenty-five minutes. Upon addition of 5 ml. of ethanol and 60 drops of pyridine, followed by heating for an additional hour, all suspended and unreacted gossyfulvin remaining after the first reaction period had disappeared, and a clear solution resulted. The solution was allowed to stand at room temperature overnight, and then poured into water. The emulsion which formed was converted to a suspension of a cream-colored precipitate by the dropwise addition of concentrated hydrochloric acid and stirring until no further odor of pyridine could be detected. Recrystallization of the precipitate from benzene and methanol yielded a cream-colored solid, m. p. 204.5° dec. (cor.).

Anal. Calcd. for $C_{30}H_{32}O_8N_2$: C, 65.66; H, 5.84; N, 5.12. Found: C, 65.35; H, 6.02; N, 5.00.

A suspension of 0.1 g. of dianilinogossypol and 0.1 g. of hydroxylamine hydrochloride in 5 ml. of ethanol and 5 ml. of pyridine heated on a steam-bath for one hour yielded a pale yellow solution which formed a pale yellow precipitate upon addition of water. In order to separate the oxime from unreacted dianilinogossypol, the precipitate was digested in ethanol and the supernatant poured into water; weight of precipitate, 0.055 g.; m. p. 221–221.5°. (cor.).

Anal. Calcd. for $C_{30}H_{32}O_8N_2$: C, 65.66; H, 5.84; N, 5.12. Found: C, 65.25; H, 6.03; N, 5.33.

Acetylation of Gossypol.—The addition of 15 ml. of acetic anhydride to a dark red solution of 0.5 g. of gossypol in 10 ml. of pyridine produced an immediate reduction of the color of the solution. The orange-colored solution was heated on a steam-bath for four hours and allowed to stand at room temperature overnight, after which it was poured over ice. The oily product changed to a pale cream-colored solid upon stirring; weight 0.69 g. The crude product dissolved completely in 25 ml. of hot methanol and within a few seconds separated as a nearly colorless solid which did not redissolve when the methanol suspension was heated to boiling. Recrystallization of the methanol-insoluble solid from hot benzene and petroleum naphtha (Skellysolve F) yielded a colorless solid; m. p. 276–279°.

Anal. Calcd. for gossypol tetraacetate, $C_{38}H_{38}O_{12}$: C, 66.48; H, 5.54; acetyl, 25.07. Found: C, 66.41; H, 5.76; acetyl, 25.0.

The same yield of tetraacetoxygossypol, admixed with a small quantity of a yellow compound, was obtained when fused sodium acetate was present and the reaction product was the same regardless of whether the reaction mixture was heated on a steam-bath for three or fifteen minutes. The product was recovered unchanged after retreatment with acetic anhydride and sodium acetate or pyridine and after heating for periods as long as seventeen hours.

Acetylation of Gossyfulvin.—Addition of 5 ml. of acetic anhydride to a suspension of 0.1 g. of gossyfulvin in 10 ml. of pyridine produced a pale yellow solution. The solution was heated on a steam-bath for one hour and then poured over crushed ice. A brilliant yellow solid separated immediately; m. p. 178–185°, weight 0.13 g. When the crude precipitate was dissolved in a small volume of diethyl ether and four times the volume of petroleum naphtha (Skellysolve F) was added, a flocculent precipitate separated from the yellow supernatant; weight, 0.02 g., m. p. 185–185.25°.

Anal. Found: acetyl, 34.6.

The absorption spectrum of a chloroform solution of acetylated gossyfulvin determined by means of a Coleman monochromator spectrophotometer equipped with absorption cells having an optical depth of 1.27 cm. exhibited two maxima: $E^{1\%}_{1\text{ cm.}}$ at 440 mμ, 64.6; $E^{1\%}_{1\text{ cm.}}$ at 460 mμ, 59.1.

Acknowledgment.—The authors wish to thank Catherine M. Hall and Leah E. Castillon for assistance in the preparation of the manuscript, C. M. Hoffpauir and L. E. Brown for the microanalyses, and Mildred Murray for the spectrophotometric data.

Summary

The molecular formula, $C_{34}H_{34}N_2O_8$, has been proposed for gossyfulvin on the basis of its elementary composition, and the yields of gossypol obtained from it upon acid hydrolysis.

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(16) Bryant and Smith, This Journal, **57**, 57–61 (1935).

(17) Bachmann and Boatner, *ibid.*, **58**, 2097–2101 (1936).

(18) Bachmann and Barton, *J. Org. Chem.*, **3**, 300–311 (1938).

The exact correspondence of the absorption spectra of gossyfulvin and dianilinogossypol, and their dissimilarity with that of gossypol have been assumed as evidence that gossyfulvin and dianilinogossypol possess identical basic structures and that both are different from the preponderant tautomeric form of gossypol.

The isomerism of the three oximes formed from gossypol, dianilinogossypol, and gossyfulvin has been presented as evidence for the lability of the carbonyl groups of gossypol.

Evidence has been presented indicating that the acetyl derivative formed in preponderant amounts upon acetylation of gossypol is tetraacetoxygossypol, and that formed from gossyfulvin is a hexaacetyl derivative.

NEW ORLEANS, LOUISIANA

RECEIVED SEPTEMBER 26, 1946

[CONTRIBUTION FROM THE RESEARCH LABORATORY, STANDARD OIL COMPANY (INDIANA)]

Vapor Pressures and Saturated Liquid and Vapor Densities of Cyclopentane, Methylcyclopentane, Ethylcyclopentane and Methylcyclohexane

BY WEBSTER B. KAY[1]

Studies on the physical properties of petroleum hydrocarbons in the gasoline boiling range[1a] have been continued with the determination of the vapor pressure and saturated liquid and vapor densities of cyclopentane, methylcyclopentane, ethylcyclopentane and methylcyclohexane. The measurements here presented cover the temperature range from the standard boiling point to the critical point and were made with particular care on samples of exceptional purity.

Description of Materials

The hydrocarbons were samples of API–NBS hydrocarbons which were made available by the American Petroleum Institute and the National Bureau of Standards through the API Research Project 44. The samples were purified at the National Bureau of Standards by the API Research Project 6 on the "Analysis, purification and properties of hydrocarbons" under the supervision of Frederick D. Rossini from material supplied by the following laboratories: cyclopentane and ethylcyclopentane, by the API Research Project 45 on the "Synthesis and properties of hydrocarbons of low molecular weight" at the Ohio State University, under the supervision of Cecil E. Boord; methylcyclopentane, by the Houdry Process Corporation of Pennsylvania, Marcus Hook, Pennsylvania, through the courtesy of E. A. Smith, and methylcyclohexane by the API Project 45 and the Barrett Division of the Allied Chemical and Dye Corporation.

The impurities in the samples were stated to be as follows: cyclopentane 0.02 ± 0.01 mole per cent.; ethylcyclopentane 0.22 ± 0.10 mole per cent.; methylcylclopentane 0.16 ± 0.06 mole per cent. and methylcyclohexane 0.10 ± 0.08 mole per cent.

The samples were received from the National Bureau of Standards in sealed glass ampules and were used without further purification.

Apparatus and Procedure

The static method of measurement was employed. The apparatus was basically the same as described in an earlier paper.[2] However, for the purpose of increasing the accuracy of the measurements a number of changes were made which included the reconstruction of the high temperature bath and thermocouple, replacement of the electromagnet by a permanent magnet in the stirring device, use of precision bore tubing for the experimental tubes and the replacement of the spring dial gage by a dead weight piston gage for the pressure measurements.

High Temperature Bath.—The experimental tube (H) (Fig. 1) containing the sample under investigation was surrounded by a jacket (G) and held at a constant temperature by the condensing vapors of a series of pure organic liquids which were heated in a side arm boiler (E) by means of an electric heater (B). To prevent excessive heat loss the jacket was constructed with a double wall with the inner walls silvered and the inner space evacuated. Two narrow unsilvered strips, diametrically opposite each other, were left to serve as a window for observing the tube. The upper part of the jacket was connected through a side arm to a manometer and a simple pressure regulating assembly (DD), manually operated, for regulating the pressure on the boiling liquid in E. By the use of highly purified compounds and by close regulation of the pressure any temperature within a range of 30 to 40°, constant to within 0.01°, was obtained with a single compound. The compounds used and their working temperature range were as follows: carbon tetrachloride, 55–75°; chlorobenzene 75–131°; bromobenzene, 131–155°; aniline, 155–183°; naphthalene, 183–218°; diphenyl ether, 218–256°; α-bromonaphthalene, 256–280°; benzophenone, 280–305°.

The Thermocouple.—The temperature to which the experimental tube was heated was

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[1] Present address: Department of Chemical Engineering, Ohio State University.

[1a] W. B. Kay, THIS JOURNAL, **68**, 1336 (1946).

[2] W. B. Kay, *Ind. Eng. Chem.*, **28**, 1014 (1936).