Storage of Gossypol

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IT has long been known that gossypol, the principal pigment of cottonseed, is readily oxidized when heated in the presence of air and that it decomposes rapidly in the presence of most organic solvents. However no systematic investigation appears to have been reported on the storage stability of pure crystalline gossypol. In the course of an extensive investigation on the chemistry and utilization of this pigment it became of considerable importance to determine its stability under various conditions of storage. In view of the various proposed applications of gossypol (1) the following information is being reported as a guide for proper handling and storage of this pigment.

Preparation of Gossypol. Pure gossypol was prepared from cottonseed pigment glands according to the procedure described in a previous publication (2). The procedure involved extraction of the pigment from separated pigment glands with acetone, precipitation of the gossypol from the extract with acetic acid, hydrolysis of the gossypol-acetic complex, and crystallization from diethyl ether and light petroleum naphtha. Analysis of this sample for carbon and hydrogen (Table I), determination of its absorption spectrum in chloroform (Table II), and tests with antimony trichloride (3) indicated that the product was pure gossypol.

TABLE I

Composition of Gossypol Samples Before and After Storage

Sample No.	Temp. of storage	Conditions of storage[a]	Melting point	Carbon[b]	Hydrogen[b]	Gossypol[c]
	°C.		°C.	%	%	%
1[d]	....	Not stored	182-184	69.46	6.08	100
2	3	Screw-capped vial	180-182	69.27	6.30	100
3	3	Sealed vial	179-181	69.24	6.17	97.5
4	3	Under vacuum	180-182	69.16	6.13	97.5
5	3	Under nitrogen	181-183	69.22	6.09	98.0
6	23-28[e]	Sealed vial	179-181	69.22	6.10	97.7
7	23-28	Under vacuum	179-180	68.94	6.05	98.2
8	23-28	Under nitrogen	181-182	69.19	6.13	98.8
9	23-28	Screw-capped vial exposed to light	176-180	67.9	5.86	85.9
10	23-28	Screw-capped vial	179-181	69.01	5.99	100

[a] All samples were protected from light except No. 9.

[b] Calculated theoretical values for gossypol: C, 69.5%; H, 5.79%.

[c] Determined from absorption spectra data after reaction with antimony trichloride, Boatner, Caravella, and Kyame, Ind. Eng. Chem., Anal. Ed., *16*, 566-572 (1944).

[d] Original unstored sample.

[e] The temperature of the room in which these samples were stored varied over this range during the storage period.

Storage and Analysis. The pure gossypol was divided into approximately 100-mg. portions and duplicate samples were stored for 18 months under the conditions shown in Table I. Analytical values for carbon and hydrogen of the original and stored samples of gossypol are recorded in Table I. The antimony trichloride spectrophotometric method (3) for the determination of gossypol was applied to chloroform solutions of all of the gossypol samples. The purities of the samples determined by this method are also recorded in Table I.

The absorption spectra of the various samples of gossypol were determined in cyclohexane solution in the ultraviolet region, 220 to 400 mμ, using a recording spectrophotometer. Specific extinction coefficients at absorption maxima of the original and stored samples are shown in Table II.

TABLE II

Spectral Characteristics of Stored Gossypol Samples in Cyclohexane Solution

Sample No.	Temp. of storage	Conditions of storage[b]	Specific extinction coefficients			
			$E^{1\%}_{1\,\mathrm{cm.}}$ 357-358 mμ	$E^{1\%}_{1\,\mathrm{cm.}}$ 286 mμ	$E^{1\%}_{1\,\mathrm{cm.}}$ 276-277 mμ	$E^{1\%}_{1\,\mathrm{cm.}}$ 236 mμ
	°C.					
1[a]	....	Not stored	376	688	581	....
2	3	Screw-capped vial	381	683	548	1799
3	3	Sealed vial	379	680	544	1939
4	3	Vacuum	374	663	535	1883
5	3	Under nitrogen	380	713	586	1920
6	23-28	Sealed vial	385	689	553	1956
7	23-28	Vacuum	382	683	547	1933
8	23-28	Under nitrogen	391	633	500	1982
9	23-28	Screw-capped vial exposed to light	327	578	480	1530
10	23-28	Screw-capped vial protected from light	390	694	562	1933

[a] Original unstored sample.

[b] All samples were protected from light except No. 9.

The melting points of all the samples, both original and stored, were determined using a capillary tube and are recorded in Table I.

Discussion

As may be seen in Table I, the carbon and hydrogen values of all the stored samples except No. 9 agree with those for the original sample and with those calculated for pure gossypol. Sample No. 9 was stored at room temperature (23-28°C.) in a screw-capped vial exposed to light.

The antimony trichloride tests show, within the limits of experimental error, that all of the stored samples were stable except No. 9. The amount of unaltered gossypol remaining in this sample after storage for 18 months was only 85.9%.

The absorption spectrum of pure gossypol in cyclohexane solution has previously been shown (4, 5) to exhibit maxima in the ultraviolet region at 357, 286, 276, and 236 mμ. Samples of gossypol after removal from storage and solution in cyclohexane showed the same characteristic absorption as a similar solution of the original gossypol. As may be seen in Table II, the specific extinction coefficients at 357 mμ agree, within the limits of error of the method, in all cases except No. 9. The extinction coefficient for this sample which was exposed to light during storage for 18 months is appreciably lower than that of the other samples.

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There is considerable variation in the extinction coefficients at the other maxima, which has also been found to be true in the case of duplicate samples of freshly recrystallized pure gossypol; therefore the extinction coefficients at these maxima should not be used as criteria of purity of gossypol.

The melting points of some of the stored samples (Table I) were slightly lower than that of the original sample prior to storage, but these differences are not believed to be significant because pure gossypol undergoes decomposition in the region of its melting point and sharp melting points are extremely difficult to obtain.

The foregoing results indicate that pure gossypol may be stored over a temperature range of 3 to 28° C. without appreciable deterioration for at least 18 months if it is protected from light. These observations apply only for pure gossypol because the presence of impurities tends to accelerate the rate of decomposition during storage.

Summary

Pure gossypol was stored for 18 months at temperatures of 3° and 23-28°C. in the presence or absence of light and air. On the basis of combustion data, absorption spectra, antimony trichloride tests, and melting points of the original and stored samples it can be concluded that gossypol can be stored without deterioration for at least 18 months at temperatures from 3° to 23-28°C. in the absence of light, irrespective of the presence or absence of air.

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Report of the Refining Committee, 1950-51

DURING the past year the work of the Refining Committee has been carried out by two small subcommittees which were appointed by the chairman shortly after the Atlanta meeting.

The first, under the chairmanship of T. C. Smith, undertook the study of existing cup refining methods for crude soybean oil with particular reference to the following points:

a) The general technique involved, particularly with reference to the presence of free lye in degummed oils of both the solvent extracted and expeller type.
b) The number of remelts required to make sure that as complete a recovery of oil as possible be made from the soapstock.
c) The amount and strength of lye to be employed.

Mr. Smith's committee did collaborative work on 12 samples of degummed oil, six solvent extracted and six expeller. A report was presented at the meeting held on April 30, and a number of suggestions for strengthening the method were put forward.

Particularly notable among these was the observation that close temperature control of the refining bath is essential and that the oil be chilled in a refrigerator for at least 12 hours at 10°C. ±2°. They also recommended the use of at least this temperature for chilling the foots after remelting. The method of coagulating sloppy or soft foots remaining after the pour-off recommended by Mr. Henry was also found very useful. No recommendation for changes in lye strength and percentage was made.

The Refining Committee voted to accept the report of the subcommittee but, before making any recommendations to the Uniform Methods Committee, the committee as a whole will study the procedure recommended by the subcommittee, and accumulate further data. It is planned to review these data at the fall meeting with the hope that recommendations can be made at that time to the Uniform Methods Committee.

The second subcommittee, under the chairmanship of Mr. Holman, investigated a method for the refining of solvent extracted cottonseed oil. This committee was somewhat hampered by difficulty in obtaining samples. However two oils were investigated, one a straight solvent extracted crude and the other a mixture of 75% prepressed and 25% extracted oil. Mr. Holman's laboratory investigated the regular and slow breaking methods on the first oil, and the regular and expeller methods on the second. Indications were that the best losses and good colors were obtained by the regular method.

The two samples were then refined collaboratively by the committee members with the regular method, with good results. Mr. Holman presented a progress report at the meeting on April 30, and the committee requested his committee to continue their work during the coming season and to make every effort to obtain a larger number of samples.

E. M. JAMES, chairman