tides are concentrated largely in the raffinate fraction and since the addition of phosphatides back to the oil does not produce reverted flavors.

The role of trace metals in flavor reversion is still not clear. The data presented here are brief and inconclusive. However it would not be too surprising to find a relatively high metal content in the raffinate fraction. The raffinate fraction has been shown to be high in phosphorus content, and it is conceivable that the phosphatides could carry metal complexes to the raffinate. During the alkali refining of the raffinate it is possible that some of the phosphatide metal complex is broken down and the phosphatides are removed, leaving detectable amounts of metal in the oil. It is believed that the observed improvement imparted by citric acid and phosphatides upon the raffinate is most easily explained as a complexing of trace metals.

TABLE VIII

Ash, Phosphorus, Iron, and Copper Content of Furfural-Fractionated Soybean Oils

	% Ash	% P	p.p.m. Fe	p.p.m. Cu
Sample 161				
Original crude degummed	.....	.0140	.....	.....
Raffinate crude	.....	.0130	.....	.....
Extract crude	.....	.0007	.....	.....
Original refined	.0002	.0004	.28	.020
Raffinate refined	.0007	.0004	.16	.021
Extract refined	.0005	.0002	.41	.027
Sample 178				
Original crude degummed	.....	.0100	.....	.....
Raffinate crude	.....	.0360	.....	.....
Extract crude	.....	.0006	.....	.....
Original refined	.0003	.....	.17	.005
Raffinate refined	.....	.....	.14	.013
Raffinate refined + 0.02% phosphatides	.0018	.....	.15	.006
Extract refined	.0009	.....	.17	.004
Sample 187				
Original crude degummed	.0340	.0110	1.40	.040
Raffinate crude	.1190	.0340	95.50	.300
Original refined	.0006	.0003	.03	.035
Original refined + 0.02% phosphatides	.0003	.0010	.03	.051
Raffinate refined	.0010	.0002	.02	.077
Raffinate refined + 0.02% phosphatides	.0026	.0011	.02	.070

Summary

Flavor and oxidative stabilities of furfural-fractionated soybean oils have been evaluated. The raffinate fractions did not develop the off-flavors typical of soybean oil as did the extract and original oil samples. The raffinate fractions have a low resistance to oxidation, but the addition of stabilizers improved the oxidative stability. Among the stabilizers tested were phosphatides, α-tocopherol, and citric acid. Citric acid and phosphatides are believed to function in part as metal scavengers.

Acknowledgment

The authors are indebted to the following members of this laboratory: C. R. Scholfield for the preparation of the phosphatides, Joseph Cannon for the tocopherol analysis, J. E. Hawley for the trace metal determinations, members of the Engineering and Development Division for the pilot-plant fractionations, and the 16 members of the taste panel for their continued interest in the evaluation of soybean oil.

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The Tannin and Related Pigments in the Red Skins (Testa) of Peanut Kernels

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THE red skins (testa) represent from 2.0 to 3.5% of peanut kernels and contain tannin and related pigments which will contribute to the presence of undesirable color in the protein preparations made for specialized uses unless the skins are removed completely during initial processing. The purpose of the present communication is to report the results of some investigations on the character of the tannin and related pigments.

Kryz (1) appears to be the first worker to investigate the pigmentation in peanut skins. He extracted a reddish-brown material from the skins with hot water, alcohol, and other solvents, and described its reactions with a number of reagents. Robinson and Robinson (2) reported, on the basis of various qualitative tests, that the peanut testa is rich in leucoanthocyanin which is convertible to cyanidin. More recently Tayeau and coworkers (3, 4, 5) published several papers on the skin pigments, reporting the presence of a tannin, a phlobaphene, a "leuco-anthocyanic chromogen," and a flavanone.

Experimental

Preliminary Investigations. Two and one-half kilograms of peanut skins were extracted for 48 hours at room temperature with 25 liters of ethanol containing 1% of hydrochloric acid. The dark red extract was filtered, the filtrate was concentrated under reduced pressure to approximately 2 liters, and the concentrate was diluted with 2 volumes of water. The resulting precipitate was removed by centrifugation, dissolved in ethanol, and the solution diluted with 3 volumes of diethyl ether. The precipitate was removed by filtration, washed thoroughly with ether, and dried *in vacuo*. The dark, reddish-brown product weighed 89 g.

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When a portion of this product was refluxed with 10% alcoholic hydrochloric acid, a dark water-insoluble phlobaphene was obtained. Upon methylation of the phlobaphene, followed by hot alkaline permanganate oxidation, crystalline veratric acid (3,4-dimethoxybenzoic acid) was isolated. The recrystallized acid melted at 180.5°-181.5°C. (cor.). An authentic sample of veratric acid melted at 181.5°-182.5°C.(cor.). The mixed melting point was 181.5°-182.5°C. (cor.). X-ray diffraction patterns of the two samples showed them to be the same chemical substance.

Preparation of Skins. The skins used for the isolation work reported below were removed without heating from fresh U. S. No. 1 Spanish peanut kernels by means of a blanching machine. Kernel fragments were separated by screening, air separating, and hand-picking. The skins were ground to pass a 20-mesh sieve.

Extraction of "Total Pigment" and Isolation of Tannin. The lipids were extracted from 100 g. of the skins with diethyl ether at room temperature and the skins were air dried. The lipid-free skins were extracted with redistilled 95% ethanol in a Soxhlet extractor for 3 to 4 hours. The dark red "total pigment" extract was filtered, concentrated to dryness under reduced pressure at low temperature, and dried in a vacuum desiccator over concentrated sulfuric acid. This "total pigment" was dissolved in 400 to 500 ml. water, centrifuged, the supernatants filtered, the insoluble residue washed several times with small portions of water, and the washings filtered and combined with the original filtrate. [The water-insoluble residue, phlobaphene (A), which remained weighed 0.75 g. after drying in a vacuum desiccator. It was saved for further work described later.] The combined aqueous solution was saturated with sodium chloride and the tannin which flocculated was removed by centrifugation. The tannin was washed several times with saturated sodium chloride solution, then dried in a vacuum desiccator over concentrated sulfuric acid. The dried product was dissolved in a total of 400 ml. of anhydrous acetone, the solution was filtered, and approximately 2,600 ml. of anhydrous ether were added to the filtered solution to precipitate the tannin. The tannin was separated by filtration, washed thoroughly with ether, and dried in a vacuum desiccator over phosphorus pentoxide. It was redissolved in acetone, again precipitated with ether, separated by filtration, washed with ether, and dried as before. The amorphous, light-brown colored tannin weighed 7.11 g., which represents 7.11% of the weight of the skins.

Analysis and Properties of the Tannin. Analysis of the tannin, after drying *in vacuo* at 105°, gave values of 61.19% carbon, 4.33% hydrogen, no methoxyl. (A second preparation isolated by the same procedure contained 61.20% carbon, 4.38% hydrogen, no methoxyl.) The molecular weight, using the Menzies and Wright ebullioscopic method (6), was found to be 2,031 in absolute ethanol and 1,489 in acetone.

The tannin, which had a characteristic odor and bitter taste, was soluble in water, alcohol, acetone, and pyridine, but insoluble in solvents such as ether, petroleum ether, benzene, etc. It had no definite melting point but darkened slightly at about 200°C. and became quite dark at 230 to 240°C. The reddish color of the aqueous solution of the tannin became more intense upon the addition of alkali. An aqueous solution of the tannin gave a precipitate with gelatin, a green color with ferric alum or ferric chloride, a dark brown precipitate with potassium dichromate, and a light brown precipitate with bromine water. Stiasny's formaldehyde test gave complete precipitation of the tannin, but his lead acetate-acetic acid test gave no precipitate. When boiled with 10% aqueous hydrochloric acid, the tannin gave a red, water-insoluble phlobaphene. These tests indicate that the tannin is a catechol tannin or "phlobatannin."

X-RAY DIFFRACTION DATA

(VS = very strong; S = strong; M = medium; and F = faint)

Veratric acid standard	Veratric acid from peanut skin phlobaphene
Spacing	Spacing
10.78 F	10.57 F
8.04 M	7.95 MS
7.32 S	7.32 MS
6.57 M	6.57 M
5.86 S	5.78 MS
5.21 MS	5.20 M
4.69 F	.....
4.26 F	.....
3.93 F	4.00 F
3.69 S	3.69 MS
3.48 F	3.49 F
3.33 VS	3.33 VS
3.05 F	.....
2.86 F	.....
2.74 MF	2.74 F
2.68 MF	2.66 F
2.57 MF	2.57 F
2.40 F	.....
2.33 F	.....
2.27 F	2.26 F
2.04 F	2.04 F
1.67 F	.....

On acetylation at room temperature with acetic anhydride in pyridine, a cream colored product was obtained. This product was purified by dissolving in boiling 95% ethanol from which it precipitated on cooling. After the repeating of this purification several times the product, though not crystalline, decomposed rather sharply at 242° to 245°C. (cor.). It contained 39.36% acetyl.

Purification of Phlobaphene. The 0.75 g. of water-insoluble phlobaphene (A) from the "total pigment" extract was dissolved in 15 to 20 ml. of anhydrous acetone, filtered, and precipitated by diluting to 200 ml. with absolute ether. The product was separated by centrifugation and washed with ether. The phlobaphene was then redissolved in 5 ml. of acetone and precipitated with an excess of ether. After removal by centrifugation the precipitate was washed with ether and dried *in vacuo* over concentrated sulfuric acid. The amorphous phlobaphene weighed 0.225 g. and was darker brown in color than the tannin.

Analysis and Properties of the Phlobaphene. After drying *in vacuo* at 105° the phlobaphene gave values of 63.48% carbon, 5.83% hydrogen, 2.10% methoxyl. Its ash content was 0.99%.

The purified phlobaphene was water-insoluble, but like the tannin it was soluble in alcohol and acetone. The phlobaphene (and the tannin) in alcohol solution gave a dark gray-black color with ferric chloride, which changed to purple upon addition of sodium bicarbonate.

Isolation of "Leuco-Anthocyanic Chromogen." One hundred grams of lipid-free skins were covered with 1 liter of 1% hydrochloric acid and stirred frequently during a 48-hour contact period. The skins were pressed to remove as much liquid as possible, and the total extract was centrifuged to remove suspended matter. The centrifugate was filtered, saturated with sodium chloride, transferred to a separatory funnel, and extracted twice with 250-ml. portions of amyl alcohol. To the combined amyl alcohol layers in a separatory funnel was added 1½ volumes (750 ml.) of benzene and 1/10 volume (50 ml.) of 1% hydrochloric acid. After shaking and allowing to separate, the lower acid layer was removed. The extraction was repeated with four additional 50-ml. portions of 1% hydrochloric acid. The combined acid layers were saturated with sodium chloride and extracted with 50-, 30-, and 20-ml. portions of amyl alcohol. The combined amyl alcohol layers were washed with four 35-ml. portions of saturated sodium chloride. The upper amyl alcohol layers were dried over anhydrous sodium sulfate, filtered, and the chromogen was precipitated by diluting to approximately 1 liter with benzene. The orange product was removed by filtration, washed with benzene, air-dried, then dried thoroughly in a vacuum desiccator. The dried product was dissolved in a total of 10-12 ml. of anhydrous acetone, the solution filtered, and the pigment precipitated by diluting to 200 ml. with absolute ether. It was removed by filtration, washed thoroughly with ether, and dried. The product was purified two additional times in the same manner. (The ether supernatants gave no yellow flavonic color when treated with dilute sodium hydroxide solution.) The final product was an orange-tan amorphous powder which, after drying in a vacuum desiccator over sulfuric acid, weighed 0.735 g.

Analysis and Properties of the "Chromogen." Analysis of the "chromogen" gave values of 61.87% carbon, 4.37% hydrogen, 0.00% chlorine, and 0.69% methoxyl, after drying *in vacuo* at 105°. The molecular weight, ebullioscopic method (absolute ethanol), was 1696.

The isolated "chromogen" was soluble in alcohol and acetone but practically insoluble in water, ethyl acetate, and organic solvents such as ether and benzene. Like the tannin and phlobaphene, an alcoholic solution of the chromogen gave a dark, gray-black color with alcoholic ferric chloride, which changed to purple upon the addition of sodium bicarbonate.

Conversion of Tannin to Water-Soluble Red Pigment. Although the tannin was converted to a water-insoluble "phlobaphene" by refluxing with 10% aqueous hydrochloric acid, if alcoholic hydrochloric acid was employed a water-soluble red pigment was produced. The procedure used for its preparation was as follows: 2.5 g. of tannin was dissolved in 100 ml. of redistilled 95% alcohol and 25 ml. of concentrated hydrochloric acid was added. The solution was refluxed for 20 minutes, cooled, filtered; and the filtrate was concentrated almost to dryness under reduced pressure. The product was then dried in a vacuum desiccator over phosphorus pentoxide and sodium hydroxide pellets, a water aspirator being used to remove hydrochloric acid vapors. The dried product was dissolved in anhydrous acetone, centrifuged to remove insoluble material, and precipitated with a large excess of absolute ether. The product

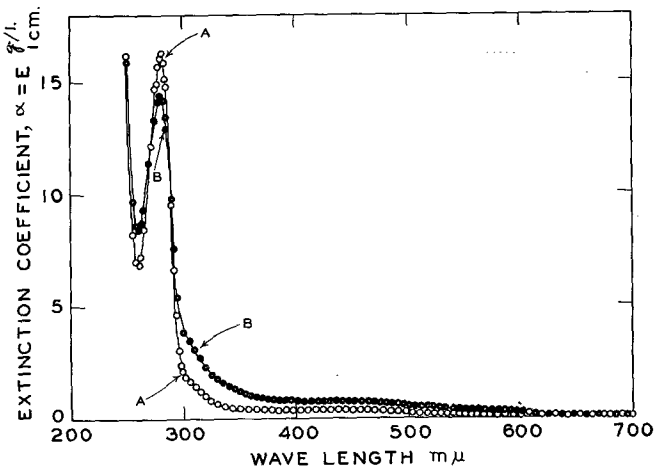

FIG. 1. Visible and ultraviolet absorption spectra of the tannin (curve A) and phlobaphene (curve B) in ethyl alcohol.

was separated by filtration, washed thoroughly with ether, and dried. The purification was repeated in the same manner, and the dark brownish-red product was dried in a vacuum desiccator over phosphorus pentoxide. It weighed 0.75 g.

Analysis and Properties of the Water-Soluble Red Pigment. After drying *in vacuo* at 105°, the pigment was found to contain 62.18% carbon, 4.61% hydrogen, 2.46% chlorine, 2.60% methoxyl.

The pigment was completely water-soluble, giving a deep red solution, and was also soluble in alcohol, acetone, and amyl alcohol. It was insoluble in solvents such as chloroform and diethyl ether. Its aqueous solution gave a deep purplish color with ferric chloride, a blue color with sodium hydroxide or carbonate which turned red upon acidification, and a blue lead salt precipitate with neutral lead acetate. An alcoholic solution of pigment gave similar tests. It had no characteristic melting point but darkened above 230°C. Attempts to prepare a picrate derivative were unsuccessful.

Spectrophotometric Investigations of the Various Preparations. The visible and ultraviolet absorption spectra of the tannin and the phlobaphene in ethyl alcohol solution are given in Figure 1. The two curves are quite similar. The tannin showed a single maximum at 281 mμ. with an extinction coefficient, $E^{g./l.}_{1cm.}$, of 16.19. The phlobaphene exhibits extinction coefficients of 14.36 at 280 mμ., 0.79 at 420 mμ. (inflection), and 0.375 at 530 mμ. (inflection).

The absorption spectrum of the "chromogen" in ethyl alcohol solution is shown in Figure 2. The positions of maxima are at 280, 456, and 550 (inflection) mμ., with extinction coefficients of 17.37, 1.84, and 0.75, respectively.

In Figure 3 are shown the ethyl alcohol and amyl alcohol absorption spectra of the water-soluble red pigment obtained by refluxing the tannin with alcoholic hydrochloric acid. In ethyl alcohol solution it exhibited maxima at 282 and 548 mμ., with extinction coefficients of 25.35 and 17.38, respectively. In amyl alcohol solution the positions of maxima were at 281-82 and 554-56 mμ., with extinction coefficients of 23.51 and 22.56, respectively. The amyl alcohol caused a slight solvent shift of the maximum from 548 to 554-56 mμ. This pigment appeared to be more

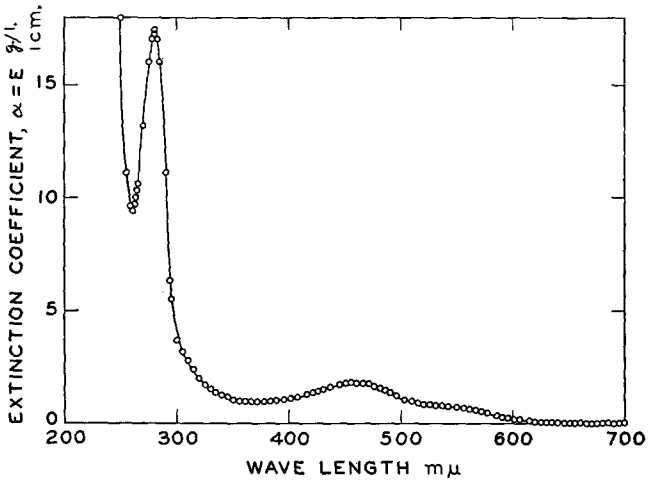

FIG. 2. Visible and ultraviolet absorption spectra of the "chromogen" in ethyl alcohol.

stable if 1% alcoholic hydrochloric acid (v/v) was employed as solvent. The over-all curve in this solvent was quite similar to the ethyl alcohol curve, but the extinction coefficient at 546-48 mμ. increased from 17.38 to 22.29 because of the increased acidity.

The red product obtained by refluxing the "chromogen" with alcoholic hydrochloric acid gave spectrophotometric curves which were similar to those obtained for the water-soluble red pigment derived from the tannin. In 1% alcoholic hydrochloric acid (v/v) the positions of maxima were at 281-83 and 550 mμ., with extinction coefficients of 27.17 and 21.10, respectively. In amyl alcohol solution the positions of maxima were at 280-81 and 552-54 mμ., with extinction coefficients of 25.83 and 19.1, respectively.

To investigate the possibility that the "chromogen" is converted to cyanidin chloride by boiling with 10% hydrochloric acid, a 0.2-g. portion of "chromogen" was refluxed for 5 minutes with 15 ml. of the acid. After extracting with amyl alcohol, diluting the extract with benzene, and transferring to 1% hydrochloric acid, the entire process was repeated, using a small volume of 0.5% hydrochloric acid. After having transferred to amyl alcohol and washed with water, the purplish-red solution showed maxima at 280, 454-55, and 558-60 mμ. with optical densities (log I_o/I) of 3.25, 0.561, and 0.725, respectively.

Discussion

The phlobaphene which was isolated in the course of the preliminary investigations yielded veratric acid after methylation and subsequent oxidation with hot alkaline permanganate. The isolation of this acid established that the catechol grouping was present in the phlobaphene. Since phlobaphenes are known to be derived from the corresponding tannins which contain the same phenolic nucleus, the peanut skin tannin belongs to the group of catechol tannins. This fact was further supported by the results of classification tests applied to the isolated tannin.

The purified tannin represented about 7% of the weight of the skins, which is in agreement with the analytical value reported by Pickett (7). Masquelier (5) found 15% tannin in the lipid-free skins used in his work. This higher tannin content is probably due to differences in variety and environment under which the peanuts were produced.

Although Masquelier (5) reports no elementary analysis of the tannin, the structural formula which he postulates ($C_{30}H_{26}O_{16}$, empirical) requires a molecular weight of 642.51, with 56.08% carbon and 4.08% hydrogen, while the tannin isolated in the present investigation analyzed 61.19% carbon and 4.33% hydrogen, with a molecular weight of 1489-2031. (A second preparation isolated by the same procedure gave almost identical carbon and hydrogen values, namely 61.20 and 4.38%.) Russell and Todd (8) have synthesized bis (5,7,3',4'-tetrahydroxy) flavpinacol which is quite similar to the natural phlobatannins which give phloroglucinol and protocatechuic acid upon alkaline cleavage. This flavpinacol ($C_{30}H_{26}O_{12}$) has a molecular weight of 578.51 and requires 62.28% carbon and 4.53% hydrogen. These values are in fair agreement with those obtained on the isolated tannin. The Menzies and Wright ebullioscopic method was used for molecular weight determinations on the tannin since it was not soluble in cryoscopic solvents such as camphor. Only approximate values could be obtained due to the exceedingly small elevation readings. However this fact alone indicates that the tannin is a rather high molecular weight substance. Perhaps several of Russell's flavpinacol units constitute the tannin.

The spectrophotometric curves of the tannin (and the phlobaphene) are quite similar to those published for other catechol tannins and their phlobaphenes (9), whose predominating maximum is in the ultraviolet region at about 280-290 mμ.

It is probable that a considerable portion of the red color of peanut skins is due to phlobaphenes originating from the catechol tannin present. Less than 1% of phlobaphene (prior to purification) was isolated from the skins of U. S. No. 1 Spanish peanut kernels. Undoubtedly the amount of water-insoluble phlobaphene will vary for different samples of skins, increasing in amount when the skins are heated or receive other drastic treatment which converts the tannin to phlobaphene. The isolated phlobaphene had properties similar to those of the tannin. It was however water-insoluble and had a higher carbon, hydrogen, and methoxyl content. It also contained about 1% ash while the tannin was ash-free.

Analysis of the "chromogen" isolated in the present work gave carbon, hydrogen, and methoxyl values in fair agreement with those obtained for the tannin, and its molecular weight was of the same magnitude. The close similarity of the spectrophotometric curve of the "chromogen" in ethanol to those of the phlobaphene and the tannin indicates a close relationship of the three pigments. These findings do not support the formula ($C_{15}H_{14}O_8$) postulated by Tayeau and Masquelier (3).

Qualitative tests of Robinson and Robinson (10) indicated that the "chromogen" was converted to a pigment related to cyanidin chloride by refluxing with 10% aqueous hydrochloric acid. A spectrophotometric curve of an amyl alcohol solution of the pigment prepared in this way from the chromogen showed maxima at 280, 454-55, and 558-60 mμ. Thimann and Edmondson (11) recently published a visible region curve for a purified amyl alcohol extract of cyanidin chloride which shows a maximum at about 550 mμ. (estimated from the curve) with a shoulder at about 430-50 mμ. The absorption spectrum of an amyl alcohol solution of the red product obtained from the "chromogen" by refluxing with alcoholic

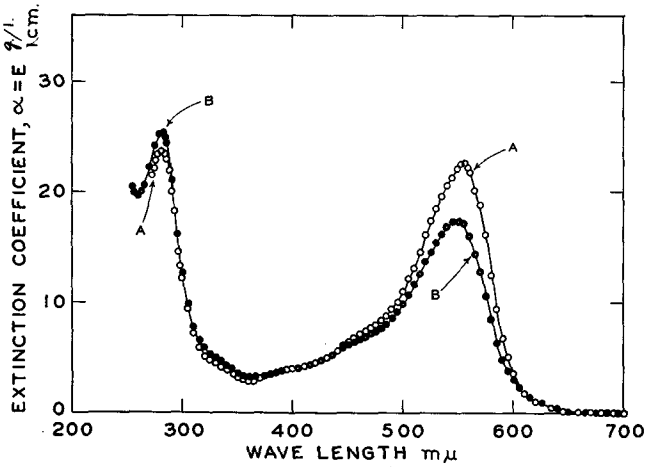

FIG. 3. Visible and ultraviolet absorption spectra of the water-soluble red pigment obtained from the tannin. Curve A—in n-amyl alcohol; curve B—in ethyl alcohol.

hydrochloric acid showed maxima at 280-81 and 552-54 mμ., with extinction coefficients of 25.83 and 19.1, respectively.

The water-soluble red pigment obtained from the tannin by refluxing with alcoholic hydrochloric acid gave qualitative tests indicative of an oxonium type structure. The visible portion of its spectrophotometric curve in amyl alcohol was similar to that reported for cyanidin chloride (11), but the elementary analyses, solubility, and other properties were quite dissimilar. Other points of variance were the failure of the pigment to give a picrate derivative and the relatively low extinction coefficients at positions of maxima in the absorption spectra.

All attempts to isolate a crystalline flavanone from peanut skins as described by Masquelier and Blanquet (4) were unsuccessful. The traces of oily product obtained gave qualitative tests characteristic of flavonic-type pigments.

Summary

The red skins of peanut kernels contain a catechol-type tannin. The purified tannin represented about 7% of the weight of the skins. Much smaller quantities of phlobaphene and so-called "leuco-anthocyanic chromogen" were isolated from the skins. Some evidence of the presence of traces of a flavonic-type pigment was obtained.

Spectrophotometric investigations of the isolated tannin, phlobaphene, and "leuco-anthocyanic chromogen" indicated a close relationship of the three pigments.

The tannin gave a water-soluble red pigment when refluxed with alcoholic hydrochloric acid. This pigment exhibited certain properties which are indicative of an oxonium-type structure.

The elementary analyses and certain properties of the isolated tannin and related pigments were considerably different from those reported by previous investigators. The amorphous nature of these substances makes chemical investigation difficult.

Acknowledgment

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Adaptation of the Volumetric-Evolution Method for Carbonates in Soaps to Synthetic Detergents[1]

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THE advent of synthetic detergents and their phenomenal growth in diversity, complexity, and volume during the last two decades have produced many problems for the chemist. In the analytical field one of these problems has been the determination of carbonates, especially bicarbonates, in the presence of synthetic detergents. It is possible to isolate carbonates by utilizing an alcohol separation to remove the synthetic detergent. This technique fails when applied to bicarbonates since they tend to decompose in hot alcoholic solutions.

[1] Presented at the fall meeting of the American Oil Chemists' Society, Oct. 31-Nov. 2, 1949, Chicago, Ill.

Methods

There are a number of reliable and comparatively simple methods for determining carbonates in soaps and soap-carbonate mixes, most of which are based on the evolution of CO_2. None of these methods succeed when applied to synthetic detergent-carbonate mixes because of the interference of foam and emulsions or the decomposition of bicarbonate. One of these is the Hitchcock-Divine Method (Oil and Soap *15*, 8-10, January, 1938) which has been adopted as A.O.C.S. official method DA 19b-42. In this method the CO_2, liberated in a closed, partially evacuated system, is absorbed in an alkaline solution. The excess absorbent is titrated along with a blank, and