It has been found that the heat treatment used in the manufacture of raw commercial cashew nutshell liquid does not change the carbon skeleton of the main monophenolic component. The structure of the phenol is established as 3-pentadecadienylphenol which is in agreement with the results obtained by earlier workers using a solvent-extracted shell oil. In the manufacture of Cardanol from the raw commercial shell liquid, almost complete reduction of one of the double bonds in the side chain of the monophenol occurs, but it takes place without alteration in the length, the position, or the configuration of the fifteen-carbon side chain.

CASHEW NUTSHELL LIQUID

Comparison of the Monophenol

Isolated from Commercial Raw Cashew Nutshell Liquid and from Commercial Cardanol

HE oily liquid in the shell of the cashew nut appears to be almost completely phenolic in char-

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acter; its major component is anacardic acid, which is present to the extent of about 90%, and the remainder is mainly cardol (8). Smit (7) working with a solvent extract from the husk of the fruit of *Anacardium occidentale* (cashew tree), showed that anacardic acid was a hydroxybenzoic acid carrying a normal fifteen-carbon side chain containing two double bonds. He believed it to be a homolog of salicylic acid but did not establish the position of the side chain. More recently Backer and Haack (1), working with a solvent-extracted oil from the shell of the cashew nut, showed that anacardic acid is 2-carboxy-3-pentadecadienylphenol, and that cardol is 5-pentadecadienylresorcinol. The positions of the two double bonds in the normal fifteen-carbon side chains have not yet been determined.

Anacardic acid readily loses carbon dioxide on heating (1, 7)to yield a monophenol, which has found considerable industrial application (3). For commercial usage the liquid is obtained from the cashew nutshell by a process that involves heating the shells to a high temperature for several minutes in a vat of previously obtained shell liquid. During this process the shell liquid is held at the high temperature for several hours. Considerable decarboxylation of the anacardic acid takes place, as well as some polymerization of the phenolic bodies to yield a commercial raw cashew nutshell liquid which is mainly monophenolic in character, but contains a small amount (approximately 16%) of anacardic acid (5), cardol, and polymerized material. To obtain the monophenolic portion of the oil, known commercially as Cardanol, the raw cashew nutshell liquid is first treated with small amounts of alkyl sulfates and sulfuric acid, filtered, and then distilled at relatively high temperatures with the aid of steam (3), as Figure 1 shows.

Smit (7) was among the first to investigate the chemical nature of the monophenol resulting from the decarboxylation of anacardic acid obtained from a solvent-extracted oil. Although he did not locate the position of the side chain, he showed that it contained two double bonds in a fifteen-carbon side chain arranged in a normal configuration.

These results were recently confirmed by Backer and Haack (1) who, in addition, located the side chain in the 3-position and named the monophenol "anacardol". Harvey and Caplan (3), investigating the same problem, except that they worked with Cardanol, concluded that its main constituent was a mono-

phenol substituted in the 3-position with a normal fourteen-carbon side chain containing one double bond.

In comparing the results of Harvey and Caplan with those of Smit and of Backer and Haack with reference to the length and degree of unsaturation of the monophenol side chain, it seemed probable that the disagreements might be due to the difference in the method of isolation of Cardanol and Anacardol. With this in mind it seemed advisable to determine whether structural changes, outside of decarboxylation, occur during the commercial preparation of raw cashew nutshell oil and Cardanol.

The purpose of this communication is to report that the monophenol obtained by direct vacuum distillation of the commercial raw cashew nutshell liquid is identical with that isolated by Backer and Haack from solvent-extracted oil. In other words, the heat treatment during the preparation of the commercial raw cashew nutshell liquid apparently does not lead to any serious structural change in the side chain of the phenol.

It has likewise been found, as previously reported by Harvey and Caplan, that the side chain of Cardanol has approximately one double bond. However, the side chain contains fifteen carbon atoms instead of fourteen as they reported (3). Thus in the commercial preparation of Cardanol from commercial cashew nutshell liquid, almost complete reduction of one of the double bonds in the side chain occurs.

MONOPHENOL FROM COMMERCIAL RAW LIQUID

The series of reactions used to establish the identity of the monophenol obtainable from commercial raw cashew nutshell liquid are shown in Figure 1. The phenol (I) was obtained from the commercial liquid by direct vacuum distillation after decarboxylation for a period of 2 hours at 130-200° C, under vacuum. About 50% of the liquid distilled over as a light yellow oil and left a black elastic solid in the flask. After two fractionations of the light yellow oil in vacuo, a clear colorless oil was obtained that analyzed correctly for C21H32O. Quantitative hydrogenation, with palladium oxide catalyst, resulted in the absorption of two moles of hydrogen; the presence of two double bonds in the side chain was thereby confirmed. The white crystalline tetrahydrophenol (II) obtained melted at 51.0-51.5° C. and analyzed correctly for C₂₁H₃₅O. (Backer and Haack (1) report a melting point of 51.5-52.5° C. for tetrahydroanacardol.] To establish the length of the side chain, the tetrahydrophenol (II) was oxidized with potassium permanganate in wet acetone to yield an aliphatic carboxylic acid melting at $61-2^{\circ}$ C. The identity of this acid with palmitic acid (melting at $61.5-62.5^{\circ}$ C.) was proved by mixed melting point. Mixtures of the acid with stearic and myristic acids gave depressions of the melting point of $5-11^{\circ}$ C. The isolation of palmitic acid thereby established the side chain as a normal configuration of fifteen carbon atoms, since Furukawa (2) showed previously that a fifteen-carbon side chain yields palmitic acid under these conditions of oxidation. The methyl ether of the tetrahydrophenol (III) analyzed correctly for C₂₂H₃₈O (tetrahydroanacardol methyl ether).

To locate the position of the side chain of the monophenol, the methyl ether of the unsaturated phenol (IV) was prepared by methylating the decarboxylated cashew nutshell liquid just prior to distillation. A pure sample of the ether which analyzed correctly for $C_{12}H_{24}O$ was obtained. On oxidation with alkaline potassium permanganate, a white solid (melting point 105-106° C.) resulted; by mixed melting point it was found to be identical with *m*-methoxybenzoic acid (melting point 106-107° C.). The position of the pentadecadienyl side chain was thereby established as meta to the phenolic hydroxyl group. Quantita-

tive hydrogenation of the methyl ether (IV) resulted in the absorption of two moles of hydrogen, to yield 3-pentadecylanisole (melting point 29-30° C., 1) which proved to be identical with tetrahydroanacardol methyl ether (III), obtained previously by methylation of tetrahydroanacardol (II).

MONOPHENOL FROM CARDANOL

Upon direct vacuum distillation of commercial Cardanol it was found that about 70% by weight came over as a yellow oil which darkened on standing. The residue in the flask set to a black viscous semi-liquid. After two fractionations of the yellow oil in vacuo, a clear light yellow monophenol (VI) was obtained. Catalytic quantitative hydrogenation of this oil resulted in absorption of 1.15 molar equivalents of hydrogen, calculated on the basis of the molecular weight of anacardol. The hydrogenation experiment was repeated with several samples of distilled phenol. Although fresh catalyst was added in several of the experiments after the absorption of hydrogen had ceased, in no case were more than 1.15 moles of hydrogen absorbed; this was the hydrogen absorption obtained with the sample of phenol purified for analysis. The purified sample of phenol upon analysis gave carbon and hydrogen values that were in accordance with the quantitative hydrogenation data. That is, they agreed with values calculated for a phenol having a fifteen-carbon side chain containing an average of 1.15 double bonds.

The hydrogenated phenol was found to be identical with the tetrahydroanacardol (II) prepared from raw cashew nutshell liquid as previously described. This was established by carbon and hydrogen analysis, mixed melting point, and the fact that oxidation with potassium permanganate in wet acetone yielded palmitic acid as in the case of tetrahydroanacardol.

EXPERIMENTAL

The raw commercial cashew nutshell liquid and the commercial Cardanol used in this investigation were provided by the Irvington Varnish and Insulator Company. Melting and boiling points were obtained with a thermometer calibrated against a Bureau of Standards thermometer, and are otherwise uncorrected. Solubility data are based on the solubility of one drop of material in ten drops of solvent.

Figure 1. Flow Sheet



3-PENTADECADIENTLPHENOL (I). About 750 grams of raw commercial cashew nutshell liquid were placed in a one-liter round-bottom flask and decarboxylated by heating on a Wood's metal bath at 130-200° C. for 2 hours under 4 mm. pressure. The ground-glass jointed flask was equipped with an electrically heated Vigreux column, condenser, and multiple receiver, and the brown oil distilled at 1.5 mm. The main fraction boiling at 205-219° (Wood's metal bath at 260-292° C.) amounted to 393 grams of a yellow oil which darkened on standing. Upon redistillation at 1.4 mm., a pale yellow middle fraction was cut at 204-204.5° (Wood's metal bath at 250-259° C.). A small sample of clear colorless oil was obtained for analysis by another fractionation at 1.0 mm. with a boiling range of 186-187° (Wood's metal bath at 260-264° C.).

CALCULATED FOR $C_{21}H_{32}O$: molecular weight, 300.5; C, 83.94; H, 10.76.

 $n_{\rm D}^{27-2}$ 1.5060.

The water-insoluble colorless phenol was found to be soluble in acetone, benzene, ethyl acetate, ethanol, methanol, and petroleum ether at room temperature.

3-PENTADECYLPHENOL (II). Seventy grams of the 3-pentadecadienylphenol (I) in 150 cc. of ethanol were hydrogenated in the presence of 1.2 grams of palladium oxide catalyst at room temperature under 1-3 atmospheres of hydrogen. After filtering the solution free of catalyst and removing the alcohol by distillation, the residue was distilled at 1.5 mm. and cut at 195-200° (Wood's metal bath at 241-245° C.), yielding 66.5 grams (95% of theory) of a colorless oil which crystallized as white needles. A middle fraction boiling at 197° and 1.5 mm. (Wood's metal bath at 244° C.) was collected for analysis; its melting point was $51-51.5^{\circ}$ C. [Backer and Haack (1) reported a melting point of $51.5-52.5^{\circ}$ for this compound, and Furukawa (2) reported 50° C.]

CALCULATED FOR C21H360: molecular weight 304.5; C, 82.80; H, 11.95. FOUND: C, 82.51; H, 11.80.

3-Pentadecylphenol was found to be water-insoluble, but was soluble in acetone, benzene, ethyl acetate, ethanol and methanol

Found: C, 83.89; H, 10.91.

at 0° and 25° C. It was insoluble in petroleum ether at 0° but soluble at 25° C.

For the quantitative hydrogenation of the unsaturated phenol, 2.037 grams of the 3-pentadecadienylphenol (I), 75 cc. of ethanol, and 0.2 gram of palladium oxide were placed in a 250-cc. shaker and hydrogenated at atmospheric pressure. The compound absorbed a total of 334.3 cc. of hydrogen in 3.5 hours at 30° C. and 758 mm. The theoretical uptake for the above amount of 3pentadecadienylphenol, based on the presence of two double bonds in the side chain, is 335.0 cc. at 30° C. and 758 mm.

OXIDATION OF 3-PENTADECYLPHENOL (II) AND ISOLATION OF PALMITIC ACID. The method of Furukawa (2) was used. Three grams of compound II dissolved in 150 cc. of acetone were oxidized with a mixture of 10.5 grams of potassium permanganate in 60 cc. of water and 450 cc. of acetone. After filtering free of manganese dioxide, concentrating the filtrate, acidifying, and cooling, a small amount of a reddish colored solid was isolated. This was recrystallized once from ethanol and three times from petroleum ether to yield an acid melting at 61-62° C. Palmitic acid (melting point 61.5-62.5° C.), obtained from Eastman Kodak Company, was mixed with the unknown acid in several proportions, and a constant mixed melting point of 61-61.5° was obtained. Mixed melting points of the acid with myristic acid and stearic acid (Eastman) gave depressions of 5-11° C.

3-PENTADECYLANISOLE (III). Saturated phenol II was methylated by a modification of the method found in Organic Syntheses (4). Twenty grams of 3-pentadecylphenol (II) and 60 cc. of absolute methanol were placed in a 200-cc. three-neck round-bottom flask, equipped with stirrer, condenser, and dropping funnel. An alcoholic solution of potassium hydroxide was prepared by dissolving 15.7 grams of potassium hydroxide in 15 cc. of water and diluting with methanol to a total volume of 60 cc.; 19.3 cc. of this solution were added to the flask. The flask was heated on the steam bath, and 10.4 grams of dimethyl sulfate were added at a rate to maintain an ebullition of the reaction mixture. After the above portion of dimethyl sulfate had been added, the flask was heated for 15 minutes; then 2.2 grams of dimethyl sulfate were added, and the flask was again heated. At this point the acid reaction mixture was made basic by the addition of 3.2 cc. of the alkali solution and then more of the sulfate (2.2 grams) added. This procedure of adding the alkali solution and sulfate portionwise and heating was repeated twice more; after the remainder of the alkali had been added, the entire mixture was refluxed for 15 minutes. Because of its low solubility in dilute methanol the methylated phenol separated as an oil early in the reaction. The reaction mixture was cooled and diluted with water, and the substituted anisole layer was separated, dried by distillation of benzene from the mixture, and distilled in a 25-cc. Vigreux conical-bottom flask under vacuum. A middle fraction, boiling at 175-177° and 1.5 mm. (Wood's metal bath at 223-231° C.) which solidified on cooling (melting point 29-30° C.) was cut for analysis. Backer and Haack (1) also reported the melting point of this compound to be 29-30° C.

CALCULATED FOR C22H38O: C, 82.95; H, 12.03. FOUND: C, 82.95; H, 11.86.

3-Pentadecylanisole was found to be soluble in acetone, benzene, ethyl acetate, hot ethanol and methanol, and petroleum ether, but insoluble in water and cold ethanol and methanol.

3-PENTADECADIENYLANISOLE (IV). The methyl ether of unsaturated phenol IV was obtained directly from the raw commercial shell liquid by decarboxylating the liquid and then methylating it before distilling. The decarboxylation was carried out by heating the liquid at 3 mm. for 45 minutes on a Wood's metal bath maintained at 150-210° C. The oil was then methylated according to the method of Perkin and Weizmann (6) by adding 252 grams (2 moles) of dimethyl sulfate to 308 grams of the decarboxylated oil dissolved in 600 cc. of methanol. The reaction was carried out in a 2-liter three-neck flask equipped with

stirrer, reflux condenser, and dropping funnel. After the flask was chilled, the reaction was initiated by adding 100 grams (2.5 moles) of sodium hydroxide in 180 cc. of water, with continuous cooling and stirring. After refluxing for about 30 minutes, more dimethyl sulfate (120 grams) was added and then 30 grams of sodium hydroxide in 60 cc. of water. After refluxing one hour, the mixture was diluted with water; the oily layer separated and was dried by the addition and distillation of benzene from the residue. Vacuum distillation of the dark brown oily residue at 1 mm, yielded 244 grams of yellow liquid boiling between 186° and 198° (Wood's metal bath at 262-270° C.). This fraction was again distilled at 1-1.5 mm. in a 30-cm. electrically heated Vigreux column, and a middle fraction boiling at 195–195.5° (Wood's metal bath at 247° C.) was taken. Because this fraction gave a slight positive sodium test, a portion (20 grams) was remethylated as described above. The remethylated oil, on distillation at 1.0 mm. in a 25-cc. Vigreux conical-bottom flask, yielded 5 grams of clear colorless middle fraction boiling at 188.5° (Wood's metal bath at 242-251° C.) which was used for analysis.

CALCULATED FOR C22H34O: molecular weight, 314.5; C, 84.01; H, 10.91; OCH₃, 9.86. FOUND: C, 84.10; H, 11.13; OCH₃, 10.02. $n_{\rm D}^{28.5}$ 1.5008.

3-Pentadecadienylanisole was found to be insoluble in water, cold ethanol and methanol, slightly soluble in hot methanol and soluble in acetone, benzene, ethyl acetate, petroleum ether, and hot ethanol.

OXIDATION OF 3-PENTADECADIENYLANISOLE (IV) AND ISOLA-TION OF *m*-METHOXYBENZOIC ACID. In a 500-cc. round-bottom flask equipped with a reflux condenser were placed 5 grams of compound IV, 500 cc. of water, 2.0 grams of potassium permanganate, and 3 cc. of 0.2 N sodium hydroxide, and the mixture was refluxed overnight. The manganese dioxide was filtered off, and the filtrate was concentrated, acidified with hydrochloric acid, and cooled in the refrigerator. The milky mixture yielded white crystals (melting at 105-106° C.) that were isolated and recrystallized twice with petroleum ether. Mixtures of this product with several proportions of a known sample of mmethoxybenzoic acid (melting at 106-7°; Beilstein melting point, 105-106.6° C.) gave constant mixed melting points of 105-107°; the identity of the product was thereby established as m-methoxybenzoic acid.

CONVERSION OF 3-PENTADECADIENYLANISOLE (IV) TO 3-PENTADECYLANISOLE (III). Eight grams of compound IV in 75 cc. of glass-distilled ethanol and 25 cc. of acetone were hydrogenated at atmospheric pressure and room temperature in the presence of 0.4 gram of palladium oxide catalyst. After the absorption of 2 moles of hydrogen, the reaction ceased and the catalyst was removed by filtration. After removal of the solvent by evaporation, the oil was washed three times with Claissen's solution (an equivolume mixture of 50% potassium hydroxide and methanol) to remove free phenol and once with water. and was then dried by the addition and distillation of benzene. Final purification was achieved by two distillations at 2 mm., using in the last distillation a 25-cc. Vigreux conical-bottom flask. A middle fraction of clear colorless oil boiling at 196-8° (Wood's metal bath at 237° C.) which solidified to a white solid, melting at 29-30°, was taken for analysis:

CALCULATED FOR C22H28O: C, 82.95; H, 12.03. FOUND: C, 82.80; H, 11.80.

MONOPHENOL (VI) FROM COMMERCIAL CARDANOL. Commercial Cardanol was redistilled three times under vacuum. In the first distillation about 85% of the oil was found to distill between 42° and 245° at 1.5–4.0 mm. (Wood's metal bath at 178–305° C.), leaving a black semi-liquid residue in the flask. About 65-70% of the oil was collected between 204° and 236° (Wood's metal bath at 258-290° C.). Two more distillations of this fraction yielded a light yellow oil, the major portion of which distilled at $198-205^{\circ}$ and 1.0 mm. (Wood's metal bath at $233-236^{\circ}$ C.). This oil darkened slightly on standing to a reddish orange color. A fraction boiling constantly at 205° at 1.0 mm. (Wood's metal bath at $233-236^{\circ}$ C.) was taken for analysis:

CALCD. FOR C21H32O (ANACARDOL)	CALCD. FOR C21H34O	FOUND
Mol. wt. 300.5	Mol. wt. 302.5	•••••
bonds C 82 04	bond	C 82.39
H, 10.76	H, 11.34	H, 11.23
$n^{25} n^{2} 1.5070$		

DIHYDRO-CARDANOL (II) OR TETRAHYDROANACARDOL. The presence of one double bond in the fifteen-carbon side chain of the above purified monophenol (VI) from Cardanol was verified by quantitative hydrogenation; 1.688 grams of (VI) in 60 cc. of ethanol were reduced with hydrogen at 30° C. and 763 mm. pressure, using 0.3 gram of palladium on carbon as a catalyst. A total volume of 161.4 cc. of hydrogen was absorbed. The theoretical absorption for this amount of the phenol, based on one double bond in the side chain, is 140.5 cc. Thus an equivalent of 1.15 double bonds was indicated in the purified phenol (VI).

To prepare a larger amount of the dihydro-Cardanol for preparative purposes, 100 grams of (VI) dissolved in 160 cc. of ethanol were reduced under a pressure of 2 atmospheres of hydrogen, using 2.0 grams of palladium on carbon as catalyst. After the absorption of hydrogen had ceased with an uptake of 1.1 equivalents, an additional gram of catalyst was added but no more hydrogen was absorbed. After filtering off the catalyst, the solvent was removed by distillation and the residue was vacuumdistilled at 1.0 mm. in a 250-cc. flask equipped with an electrically heated Vigreux column. The fraction taken at 202.5-205.0° (Wood's metal bath at 232.4° C.) solidified on cooling to yield a light yellow solid melting at 47-48° C. After four recrystallizations from petroleum ether, the melting point of the pure white crystals remained constant at $51.0-51.5^{\circ}$ C. The yield was 21.5 grams.

Calculated for $C_{21}H_{36}O$: C, 82.80; H, 11.95. Found: C, 82.74; H, 11.98.

Mixtures of these crystals with varying proportions of pure 3-pentadecylphenol (II) obtained as previously described from the raw commercial shell liquid melted at $51.0-51.5^{\circ}$ C. with no depression.

OXIDATION OF DIHYDRO-CARDANOL (II) AND ISOLATION OF PALMITIC ACID. To verify further the identity of dihydro-Cardanol as 3-pentadecylphenol, the length of the side chain of dihydro-Cardanol was established by the method used with the 3-pentadecylphenol that was obtained from the raw commercial shell liquid. Oxidation of the dihydro-Cardanol with permanganate in acetone yielded a white crystalline product which, after three recrystallizations from ethanol, melted at $61.5-62.0^{\circ}$ C. Just as in the former case, mixtures of these crystals with varying proportions of pure palmitic acid (melting point $61.5-62.5^{\circ}$) melted constantly at $61.0-62.0^{\circ}$ C.

LITERATURE CITED

- (1) Backer and Haack, Rec. trav. chim., 60, 661-77 (1941).
- (2) Furukawa, Sci. Papers Inst. Phys. Chem. Research (Tokyo), 24, 304 (1934).
- (3) Harvey and Caplan, IND. ENG. CHEM., 32, 1306 (1940).
- (4) Organic Syntheses, Coll. Vol. II, 619 (1943).
- (5) Patel, J. Indian Inst. Sci., 5, 152 (1922).
- (6) Perkin and Weizmann, J. Chem. Soc., 89, 1649 (1906).
- (7) Smit, Proc. Acad. Sci. Amsterdam, 34, 165 (1931).
- (8) Städeler, Ann., 63, 137-64 (1847).

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Red Lead-Alkyd Resin Reactions

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ED lead-alkyd resin paints have been used for the protection of structural iron and steel for approximately fifteen years. Many specifications (7, 13, 14, 15) have been written to cover paints of this type. Red lead is a pigment of basic character. It is known that all basic pigments react to some degree with oleoresinous vehicles. The presence of limited amounts of reaction compounds formed from red lead and oleoresinous vehicles has been found to impart beneficial properties to the paint film. This investigation concerns the factors influencing the reaction between red lead and alkyd (phthalic) resin vehicles. In order to study these factors, the following points were considered: variations in degree of reactivity of red leads of varying true red lead (Pb₃O₄) content; effect of time and temperature on the formation of these reaction compounds; degree of reaction between red lead and the alkyd resin vehicles; solubility of the reaction compounds in the vehicle.

Analytical methods for determining phthalates in such paint systems presented a problem; therefore special attention was given to the methods involved. The important steps in determining phthalic reaction products are the centrifugal separation of the pigment from the vehicle and the determination of the phthalic anhydride content of the pigment and vehicle portions. The extent to which reaction products formed was determined by analysis of pigments and vehicles extracted from paints of known composition and history.

Several methods have been described for the quantitative determination of phthalic anhydride in alkyd resin varnishes. The two in general use are the Kappelmeier (3) and the U. S. Navy method (8), which were discussed by Sanderson (9). The Kappelmeier method has been modified (5, 6), but the original method (3) was used in this investigation for the analysis of extracted vehicles. It was necessary to determine the volatile portion since the phthalic anhydride in the vehicle should be reported on the solids basis. Here, again, various methods were used. They include the A.S.T.M. standard method (1), a vacuum method (10), and a method using castor oil (4).

The determination of the phthalate in the pigment portion presented a still different problem. The Kappelmeier (3) and Navy (3) methods were modified by the authors; the Kappelmeier modified method was found to be more satisfactory.

A qualitative method for phthalic anhydride in extracted pigments has been reported (12). Reference has been made to the reaction between red lead and alkyd resin vehicles (11). No quantitative method for determining phthalate was given.

For simplicity, paints were made according to the formulation given under "Experimental Work". Six samples of each