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CASHEW NUT SHELL LIQUID. VI. THE OLEFINIC NATURE OF ANACARDIC ACID[1]

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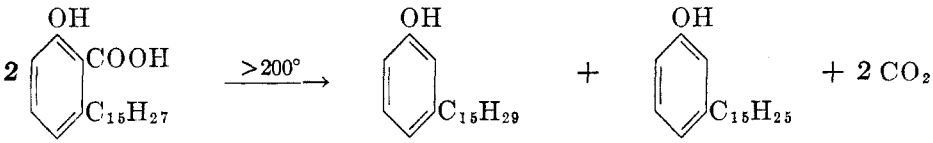
Commercial cashew nut shell liquid is a dark colored indefinite mixture containing three alkenyl phenolic components and certain decomposition and polymerization products. The phenolic components are a monophenol (cardanol),[3] a salicylic acid derivative (anacardic acid), and a resorcinol derivative (cardol) (2).

The monophenol, which is the major component of the commercial shell liquid is formed by decarboxylation of the anacardic acid component during the extraction of the shells at high temperature. The shell liquid when obtained by a low-temperature solvent-extraction process, contains only anacardic acid and cardol. The anacardic acid is the major component.

Although the carbon skeletons of these alkenyl phenols have been definitely established (3), the exact nature of the unsaturation of their fifteen carbon side chain has not yet been determined. Since the industrial uses (4) and the physiological functions (5, 6) of these types of phenolic compounds are intimately associated with their unsaturated character, the problem of clarifying their olefinic structure is one of considerable interest.

The phenolic components of the shell liquid show an unsaturation equivalent to about two olefinic bonds when freshly prepared, and previous investigators have assumed the phenols to be homogeneous diolefins. However, Sletzinger and Dawson (7), working with the monophenolic component of the commercial shell liquid, found that it was not a homogeneous diolefin, but a mixture of mono-, di-, and possibly tri- or higher olefins, having the fortuitous average unsaturation of two olefinic bonds. Qualitatively, the same results were obtained when a sample of the monophenol, resulting from the decarboxylation of a solvent-extracted anacardic acid, was investigated. However, in both cases investigated by Sletzinger and Dawson, the monophenol was subjected to temperatures of 200° or higher during its preparation. It is conceivable that such temperatures may have caused the observed olefinic heterogeneity by disproportionation reactions of the following type on a homogeneous diolefin. Higher olefinic com-



Anacardic Acid Monoölefin Triolefin

[1] For the fifth article in this series, see Sletzinger and Dawson, *J. Org. Chem.*, **14**, 849 (1949).

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[3] The monophenol has also been termed "anacardol". The reasons for preferring the name "cardanol" have been presented elsewhere (1).

ponents in the monophenol could conceivably arise by similar disproportionation reactions involving the monoölefin, triolefin, etc.

For the above reason, it seemed advisable to investigate the olefinic nature of anacardic acid obtained directly from the shells by a low-temperature solvent-extraction process. Consequently, during the investigation every effort was made to use conditions such that disproportionation reactions of the above type could be eliminated from consideration.

METHODS AND DISCUSSION OF RESULTS

In order to obtain anacardic acid from the shells of the cashew nut as close as possible to the form in which it exists naturally in the shell liquids, every precaution was taken during the isolation procedures to avoid temperatures above 100° and prolonged exposure of the anacardic acid to atmospheric oxidation. The same precautions were also observed during all the subsequent work on the olefinic material.

The shells of the nut were crushed and extracted with petroleum ether at the boiling point (60°). The extracted liquid was immediately treated with freshly precipitated lead hydroxide according to the method of Backer and Haack (3) which precipitated anacardic acid as lead anacardate. After decomposing the lead salt by heating with an aqueous solution of *p*-toluenesulfonic acid, the free anacardic acid was completely methylated with diazomethane. The resulting dimethyl-ether-ester, which was used in all of the structural investigations reported in this communication, was a light amber liquid possessing an unsaturation equivalent to 2.10 double bonds. The investigations were carried out using the methylated anacardic acid rather than the free acid to eliminate in large measure the vesicant properties of the free phenol (6), and to protect the phenolic hydroxyl group during oxidative operations on the alkenyl side chain.

Sletzinger and Dawson (7) established the heterogeneous olefinic character of the monophenol fraction of the commercial shell liquid by hydroxylating the olefinic mixture by means of the Prévost reagent, silver iodobenzoate (8), and separating the resulting glycols by fractional crystallization. Oxidative cleavage of a crystalline monoglycol with periodic acid established the position of the double bond in the monoölefinic component of the monophenol as being between carbons 8 and 9 of the fifteen carbon side chain.

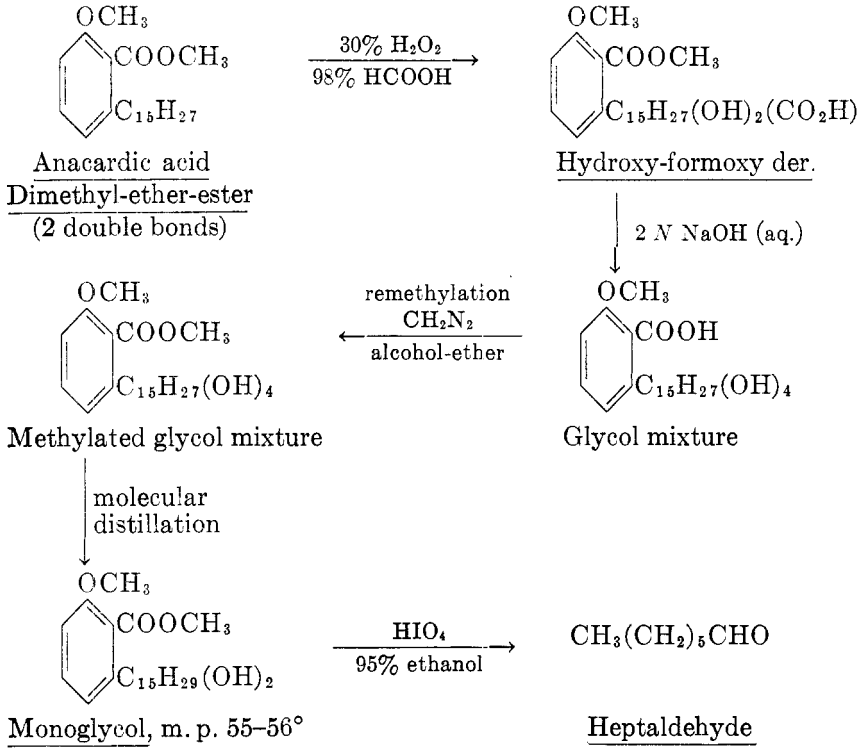
When the Prévost method of hydroxylation was applied to the dimethyl-ether-ester of anacardic acid described above, a mixture of iodinated glycols having the consistency of molasses was obtained. All attempts to obtain a crystalline glycol from the very dark colored mixture failed. Likewise, it was not possible to obtain the corresponding benzoates in crystalline form. The presence of iodine in the aromatic ring was established and this fact rendered unfeasible the separation of the glycols by molecular distillation.

Hydroxylation using the 30% hydrogen peroxide-formic acid reagent described by Swern and co-workers (9, 10) proved more successful in the sense that it was possible by this means to obtain a crystalline monoglycol (See Flow Sheet). The yield of hydroxylated material recovered from the reaction mass, however,

was never in excess of 57% of theory. Some of the loss was probably due to polymerization of the more highly unsaturated olefins in the acid-peroxide reaction mixture. Likewise, it is probable that some of the more highly hydroxylated material was not completely extracted from the reaction mass.

FLOW SHEET

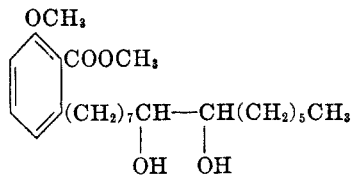
Preparation of Anacardic Acid Dimethyl-ether-ester Glycols



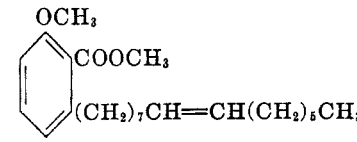
After removal of the solvent, the resulting mixture of glycols was fractionated, using a molecular still, and a fraction was obtained which could be crystallized. The crystalline material melted at 55–56°, and analyzed correctly for the monoglycol of the anacardic acid dimethyl-ether-ester.

Fractions which distilled at higher temperatures, with signs of decomposition, remained liquid even after repeated attempts at crystallization. They were presumably mixtures of monoglycol, diglycols, and decomposition products, for their analyses showed a lower carbon content. A considerable part of the mixture was not distillable and probably consisted of higher glycols.

Cleavage of the crystalline monoglycol with periodic acid yielded *n*-heptaldehyde. These results established the position of the glycol hydroxyl groups as being on carbons 8 and 9 of the fifteen carbon side chain. The corresponding monoölefin was therefore 1-methoxy-2-carbomethoxy-3-(8′-pentadecenyl)benzene.



Monoglycol



Monoölefin

The isolation of a crystalline monoglycol from the dimethyl-ether-ester of anacardic acid, isolated from the shells as described above, clearly establishes that the two double bond unsaturated character of the anacardic acid as it exists in the shell fluids is the result of a mixture of several olefinic components of different degrees of unsaturation. Furthermore, the fact that the monoölefinic component has the same side chain structure as the monoölefinic component of cardanol obtained either from the commercial shell liquid or by decarboxylation of the anacardic acid, demonstrates that the heat processes used in obtaining the commercial liquid and in decarboxylating the anacardic acid do not cause disproportionation of the type suggested earlier. It seems likely, therefore, that the loss in unsaturation observed by previous workers (2, 7), when the various phenolic components of cashew nut shell liquid are subjected to distillation, is due to selective polymerization of the more highly unsaturated components naturally present in the phenols, rather than to the selective polymerization of olefins resulting from disproportionation reactions. It is of interest to note also that such heat processes apparently do not shift the position of the double bond in the monoöolefinic components.

In order to discuss the investigations carried out on the more highly hydroxylated material, it seems advisable to describe the molecular distillation in greater detail. During the molecular distillation at 10^{-5} mm. of several batches of hydroxylated dimethyl-ether-ester of anacardic acid prepared by the use of the formic acid-hydrogen peroxide reagent, it was observed that only about 60% of the material was distillable, and a very small portion of this was a forerun of presumably unhydroxylated material. The second and third fractions (see Table I), distilling between about 125° and 180° and accounting for about two-thirds of the distillable material, were always obtained as a clear, colorless oil which solidified on standing. It was from these combined fractions that the crystalline monoglycol of m.p. 55–56° was obtained in good yield after a single recrystallization. These results would indicate, therefore, that fractions II and III were made up almost completely of monoglycol, and that 40–45% of the sample of hydroxylated material taken for distillation was monoglycol in nature.

Beyond 180° the distillation was accompanied by visible signs of decomposition and the major portion of the fourth fraction (182–223°) actually distilled between 200° and 223°. The distillate was obtained as an amber-colored oil which did not solidify on standing and which could not be crystallized. This fraction, which accounted for about one-third of the distillable material, gave analytical figures for carbon and hydrogen about half-way between the theory for monoglycol and

diglycol. Presumably, it was a mixture of monoglycol, diglycol, and decomposition products.

The residue (about 2.1 g.) which failed to distill at 225°, and which accounted for about 35–40% of the original hydroxylated material, remained as a dark, highly viscous, sticky substance. It presumably contained more highly hydroxylated glycols and decomposition products. Further efforts to resolve this mixture were without success.

It seems likely from the nature of the distillation and the analytical data on the distillate, that fraction IV contained both diglycol and monoglycol and no significant amount of triglycol. When a sample of this fraction was cleaved with lead tetraacetate, formaldehyde was isolated in small amounts as the dimedon

TABLE I

MOLECULAR DISTILLATION AT 10^{-5} MM. OF A 5.4-GRAM SAMPLE OF THE MIXTURE OF GLYCOLS RESULTING FROM THE HYDROXYLATION OF ANACARDIC ACID DIMETHYL ETHER ESTER

FRACTION	TEMP. RANGE (°C.)	APPEARANCE	ANALYSIS[a]	AMOUNT (GRAMS)
I	Forerun up to 126	pale yellow liquid		0.1
II	126–139	white solid	C, 69.66 H, 9.23	0.8
III	139–182	yellowish semi-solid		1.5
IV	182–223	thick amber-colored liquid	C, 67.39 H, 8.86	0.9
Residue	undistillable	black tar		2.1

[a] Sample taken for analysis directly from distillation without further purification. Calc'd for monoglycol $C_{24}H_{40}O_5$: C, 70.55; H, 9.87; Calc'd for diglycol $C_{24}H_{40}O_7$: C, 65.43; H, 9.15.

derivative. No other water-soluble aldehydes were detected, but heptaldehyde arising from the cleavage of the monoglycol was evident from its odor. Since formaldehyde could only result from the cleavage of a glycol occupying the terminal position of the hydroxylated side chain, it may be concluded that fraction IV contained a diglycol component possessing a terminal glycol grouping. As previously pointed out, all attempts to crystallize such a diglycol from fraction IV were without success.

Keeping in mind that only a little over 50% of the original olefinic mixture was recovered in hydroxylated form and that 40–45% of the latter was found to be monoglycol in nature, it may be concluded that at least 20–25% of the original olefinic mixture was monoölefin. To account for the unsaturation equivalent to two double bonds, one must assume, therefore, that the anacardic acid contained appreciable amounts of higher olefins.

SOME CHEMICAL PROPERTIES OF ANACARDIC ACID

All of the hydroxylation experiments discussed above were carried out using completely methylated anacardic acid, for it was observed that the free acid is very sensitive to oxidizing agents. Attempts to hydroxylate the sodium salt with very dilute solutions of $KMnO_4$ at 5–10° resulted only in a black granular substance which was insoluble in water and organic solvents. The free acid is quite stable to oxygen, however, for after ten hours of bubbling oxygen through a benzene solution of the acid at 33° no significant change in the double bond value was observed. The most highly purified sample of the free acid was obtained by chromatographing the dark brown product obtained by the lead precipitation process described earlier. This procedure produced a white waxy solid, m.p. 33–36°, which showed a hydrogenation value of 1.96 double bonds. Anacardic acid forms a lead salt when its alcoholic solution is treated with freshly precipitated lead hydroxide. The lead anacardate thus formed is easily decomposed with sulfuric acid, *p*-toluenesulfonic acid or hydrogen sulfide. If the solid lead anacardate, however, is allowed to stand for a long time (1 year or more) at room temperature, it undergoes a change (presumably polymerization). Attempts to decompose such a salt with one of the above acids produces only a nondescript gum and no anacardic acid.

EXPERIMENTAL

Isolation of anacardic acid. Anacardic acid was obtained from the shells of the cashew nut *Anacardium occidentale*, by solvent extraction and lead precipitation as previously described (3, 1) except for the following modifications. All steps in the procedure were carried out at steam-bath temperatures or lower, and under an atmosphere of nitrogen. The lead precipitations were carried out employing an equimolar quantity of $Pb(OH)_2$ in order to minimize the co-precipitation of cardol. The anacardic acid obtained was a chocolate-colored solid melting at 28–30°.

Anacardic acid dimethyl-ether-ester. A 20-g. sample (0.06 mole) of anacardic acid, prepared as described above, was dissolved in 100 ml. of peroxide-free ether and treated slowly with a cold ether solution of diazomethane (11) until the vigorous evolution of nitrogen had stopped. A small excess of the diazomethane solution was then added and the mixture was allowed to stand for 1 hour at ice-bath temperature.

At the end of this time, a small amount of ether was carefully distilled off in a hood. A greenish-yellow distillate indicated the presence of excess diazomethane and therefore complete methylation. The ether was distilled until the distillate ran colorless (about 50 ml.). The remaining ether solution of the methylated acid was then treated with 4 g. of Darco, refluxed, filtered, and the ether was finally completely removed under a high vacuum. A light amber oil remained in quantitative yield (22 g.).

Anal. Calc'd for $C_{24}H_{36}O_3$: C, 77.37; H, 9.74.

Found: C, 77.58; H, 9.82.

A 2-g. sample of the oil was catalytically hydrogenated using 5% Pd on Darco in ethyl acetate, during which a volume of hydrogen equivalent to 2.1 double bonds was absorbed.

The dimethyl-ether-ester glycols (10). A 9.5-g. sample (0.025 mole) of the dimethyl-ether-ester of anacardic acid (0.05 mole of double bonds) was added to 42 ml. of 95–100% formic acid (m.p. 8°). The two substances did not form a homogeneous mixture; the anacardic acid compound floated to the top. After cooling to about 10°, 7 g. of 29–30% H_2O_2 was added all at once. This amount represents 0.059 mole of potential performic acid. The mixture was then stirred mechanically. After a time lag of about 10 minutes, the reaction rapidly heated up,

reaching a temperature of 70°, and the mixture slowly turned reddish-brown. A cold-water bath was initially used to bring the temperature down to 40°; thereafter, a warm-water bath served to keep the reaction at 40° for four hours during which the reaction mixture was continuously stirred. The mixture on standing separated again into two immiscible phases, the hydroxy-formoxy derivatives of the dimethyl anacardic acid separating on top as a brown oil.

The excess formic acid was distilled off as completely as possible at reduced pressure and at a temperature not exceeding 60°. To the dark brown oily residue was then added 100 ml. of 2 *N* NaOH and the mixture was refluxed for 1½ hours during which the hydroxy-formate and the methyl ester groups were hydrolyzed. Towards the end of this period, a small amount of ethanol was added to produce a homogeneous solution. The alkaline solution was extracted once with ether, to remove polymerized material, and then was carefully acidified with dilute H_2SO_4 to *p*H 4. A very dark brown, viscous oil, which was extracted several times with ethyl acetate, separated.

The ethyl acetate was distilled off thoroughly at reduced pressure, leaving a thick oily residue sparingly soluble in organic solvents such as ether and benzene. To remove unhydroxylated olefinic material, the residue was rapidly washed once with ether. The residual methyl-ether-anacardic acid glycols thus obtained were dissolved in 100 ml. of 95% ethanol and re-methylated at the carboxyl groups by slowly adding an ether solution of diazomethane in slight excess. After standing for two hours, the ether was removed by distillation (hood). The remaining alcohol solution of the glycols was decolorized somewhat by refluxing with Darco and filtering. After the alcohol had been completely removed at reduced pressure, the residue was dried by adding 50 ml. of anhydrous benzene and distilling off the benzene *in vacuo*. The resulting crude mixture of glycols remained as a dark brown, very viscous oil weighing 5.5 g. (50%).

Molecular distillation of the glycols. A 5.4-g. sample of glycols prepared as described above was placed in a small, cylindrically-shaped molecular still having a cold finger extending to within about 1 cm. of the surface of the distilling substance. The distillate, after having condensed on the cold finger, dropped into a 6-tube fraction cutter which could be easily turned by hand. The distillation was carried out at 10^{-5} mm. (mercury vapor pump) while the still was heated by a Variac-controlled electrical heater. The distillation data are summarized in Table I.

From each of the fractions II and III a colorless crystalline monoglycol was obtained in good yield by recrystallization from 60% ethyl alcohol; m.p. 55–56°.

Anal. Calc'd for monoglycol $C_{24}H_{40}O_5$: C, 70.55; H, 9.87.

Found: C, 70.30; H, 9.54.

The crystalline monoglycol was very readily soluble in benzene, ether, alcohol, and chloroform, but insoluble in petroleum ether.

All attempts to obtain a crystalline product from fraction IV proved unsuccessful.

Cleavage of monoglycol with periodic acid (12). A 1.0-g. sample (0.0024 mole) of the monoglycol was dissolved in 60 ml. of aldehyde-free 95% ethanol, and to this solution was added 546 mg. of paraperiodic acid (H_5IO_6, equivalent to 0.0024 mole of HIO_4) dissolved in 5 ml. of water. Some heat was evolved and the solution turned a light yellow color. The reaction mixture was allowed to stand at room temperature for four hours; it was then diluted with twice its volume of water and shaken six or seven times with small portions of ether to extract the ether-soluble aldehydes.

The combined ether extracts were evaporated to a small volume which was added to 100 ml. of hot water and immediately steam-distilled. The distillate (about 200 ml.) was extracted with ether as above and on evaporation yielded a small oily residue which smelled strongly of aldehyde. To the residue was added 250 mg. of 2,4-dinitrophenylhydrazine dissolved in 75 ml. of 95% ethanol, and 1.0 ml. of conc'd HCl. The mixture was refluxed on the steam-bath for 30 minutes. After distilling off about 10 ml. of alcohol, the solution was cooled and 270 mg. of a yellow crystalline 2,4-dinitrophenylhydrazone was obtained. The material was recrystallized to constant melting point (103–104° corr.) using ethyl alcohol acidified

with HCl. Several mixed melting points with an authentic sample of *n*-heptaldehyde 2,4-dinitrophenylhydrazone (m.p. 104–105° corr.) showed no depression.

Anal. Calc'd for $C_{13}H_{18}N_4O_4$: C, 53.06; H, 6.12; N, 19.05.

Found: C, 52.78; H, 5.93; N, 18.84.

In another experiment in which the monoglycol was cleaved with periodic acid as above, the aldehydic residue was treated with 500 mg. of dimedon (5,5-dimethyldihydroresorcinol) in 40 ml. of a 50% aqueous ethanol solution. After heating on the steam-bath two hours, and standing at room temperature for about a day, glistening mica-like flakes settled out on shaking and cooling. During two recrystallizations from 95% alcohol the melting point remained constant (100–101° corr.), and a mixed melting point with an authentic sample of heptaldehyde dimedon derivative (m.p. 102–103° corr.) melted sharply at 101–102°.

Anal. Calc'd for $C_{23}H_{36}O_4$: C, 73.36; H, 9.64.

Found: C, 73.45; H, 10.45 (one recryst.); C, 73.39; H, 10.25 (two recryst.).

Cleavage of higher glycol fraction with lead tetraacetate, (12, 13). Preliminary cleavage experiments with the higher glycol material obtained in fraction IV (Table I) revealed that better yields of formaldehyde could be more easily obtained using lead tetraacetate than with periodic acid as the cleavage agent. In a typical experiment a 0.7-g. sample of fraction IV was dissolved in 50 ml. of glacial acetic acid which had previously been distilled from $KMnO_4$. To this solution was added 1.0 g. of pure lead tetraacetate, which had been recrystallized several times from glacial acetic acid, and the mixture was shaken gently until homogeneous and then allowed to stand at room temperature for 3–4 hours.

The water-soluble aldehydes were then extracted by shaking the reaction mixture several times with small portions of water, during which the solution turned brown due to the hydrolysis of the excess lead tetraacetate. The combined water extracts were then steam-distilled directly into 20 ml. of 95% aldehyde-free ethanol containing 0.5 g. of the dimedon reagent. The dimedon-distillate mixture was heated to 60° for 2 hours and then allowed to stand at room temperature over night. The next day long white needles melting at 186–187° were obtained (yield, 35 mg.). A mixed melting point with an authentic sample of formaldehyde dimedon compound (m.p. 188–189°) showed no depression.

Anal. Calc'd for $C_{17}H_{24}O_4$: C, 69.83; H, 8.27.

Found: C, 69.56; H, 8.38.

Purification of anacardic acid by chromatography. A glass column, 3 ft. long and $\frac{3}{4}''$ in diameter, was packed to a height of 30″ using 30–35 g. of a 50–50 mixture of Darco and Celite. After washing the column with benzene, a solution of 5 g. of crude anacardic acid (2.10 double bonds) dissolved in 50 ml. of benzene was slowly forced through the column under 5 lbs. of nitrogen pressure. Successive portions of benzene were then passed through the column, and 25-ml. eluate-samples were collected. The first three fractions showed no residue on evaporation of the benzene, but the fourth fraction contained 0.8 g. of a brown oil which did not crystallize on cooling. The next four fractions each contained a small amount of colorless oily liquid (total yield about 2 grams) which solidified to a white, wax-like substance on standing in the refrigerator. Each sample of this material melted at 33–36° and showed an unsaturation equivalent to 1.96 aliphatic double bonds when catalytically hydrogenated using 5% palladium on charcoal in ethyl acetate. After filtering off the catalyst, the solution was evaporated and the white residue without further purification melted at 86–88°, and analyzed correctly for tetrahydroanacardic acid:

Anal. Calc'd for $C_{22}H_{36}O_3$: C, 75.81; H, 10.41.

Found: C, 75.64; H, 10.15.

Acknowledgment. The authors are indebted to the Irvington Varnish and Insulator Company of Irvington, New Jersey, for the supply of cashew nut shell liquid and for their helpful interest in this investigation. The authors also wish to thank Miss Lois May who carried out the microanalyses reported in this communication.

SUMMARY

It has been established that the anacardic acid component of the oil of the shell of the cashew nut *Anacardium occidentale*, is not a homogeneous compound having the structure of a 3-pentadecadienylsalicyclic acid as heretofore believed. The anacardic acid as it occurs naturally in the cashew nut shell and which may be obtained from such shells by cold solvent-extraction, has been found to consist of a mixture of several olefinic components possessing an average unsaturation equivalent to about two double bonds. It has been estimated that at least 25% of the anacardic acid is a monoölefinic component.

Using conditions throughout which would not be expected to alter the olefinic nature of the anacardic acid, the free acid was first methylated with diazomethane and the resulting dimethyl-ether-ester, possessing an average unsaturation equivalent to two double bonds, was hydroxylated using a mixture of 30% hydrogen peroxide-formic acid at low temperatures. The resulting mixture of glycols was partially separated by molecular distillation and a pure monoglycol was obtained.

The crystalline monoglycol on cleavage with periodic acid yielded *n*-heptaldehyde, thereby establishing the monoölefin present in the natural anacardic acid mixture as 1-hydroxy-2-carboxy-3-(8′-pentadecenyl)benzene. The higher-boiling glycol fraction yielded formaldehyde on cleavage with periodic acid or lead tetraacetate, thereby establishing the existence of a terminal olefinic linkage in one or more of the higher olefinic components of anacardic acid.

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