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CASHEW NUT SHELL LIQUID. IV. ON THE HETEROGENEOUS NATURE OF THE MONOPHENOLIC FRACTION OF CASHEW NUT SHELL LIQUID. THE STRUCTURE OF THE MONO-OLEFINIC COMPONENT[1]

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The vesicatory properties of the saps of certain plants of the anacardiacea family, such as poison ivy, the Japanese lac tree, etc., and of the oily liquid which is extractable from the shell of the cashew nut (*Anacardium occidentale*), are due to the presence therein of phenolic compounds whose structures include a long unsaturated side chain attached to the phenol ring. Previous investigations (1, 2, 3) have in certain cases established the length and position of these alkenyl side chains, but little is known about the structural details of the unsaturation. There is no doubt, however, that the unsaturation of the side chain plays an important role both in the physiological properties (4, 5, 6) and the industrial uses (7) of these compounds.

In recent years large amounts of cashew nut shell liquid have been imported into this country from India and Brazil as a raw material for the manufacture of numerous industrial products (7). Thus there has become available a good source of the alkenyl phenols which can be used for structural investigations.

The oily liquid in the shell of the cashew nut appears to be almost completely phenolic in character; its major component is anacardic acid which is present to the extent of about 90% and the remainder is mainly cardol (8). Both Smit (9) and Backer and Haack (3), working with solvent-extracted cashew nut shell liquid, concluded that anacardic acid was a single substance with two olefinic bonds in the side chain, *i.e.*, a pentadecadienylsalicylic acid. The latter investigators reported it to be 2-carboxy-3-pentadecadienyl phenol. These authors also reported that anacardic acid readily loses carbon dioxide on heating to yield a single monophenol having the structure of a 1-hydroxy-3-pentadecadienyl benzene.

Cashew nut shell liquid has found important commercial usage as a raw material for the manufacture of certain resins and plastics. For commercial usage the liquid is obtained from the cashew nut shell by a process that involves heating the shell to a high temperature for several minutes in a vat of previously obtained shell liquid. During this process the shell liquid is held at a high temperature for several hours. Considerable decarboxylation of the anacardic acid takes place, and the product is a commercial raw cashew nut shell liquid which is mainly monophenolic in character, and contains a small amount [approximately 16%, (10)] of anacardic acid, cardol [a resorcinol derivative, (11)], and some

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[1] For the third article of this series, see Wasserman and Dawson, *J. Am. Chem. Soc.*, **70**, 3675 (1948).

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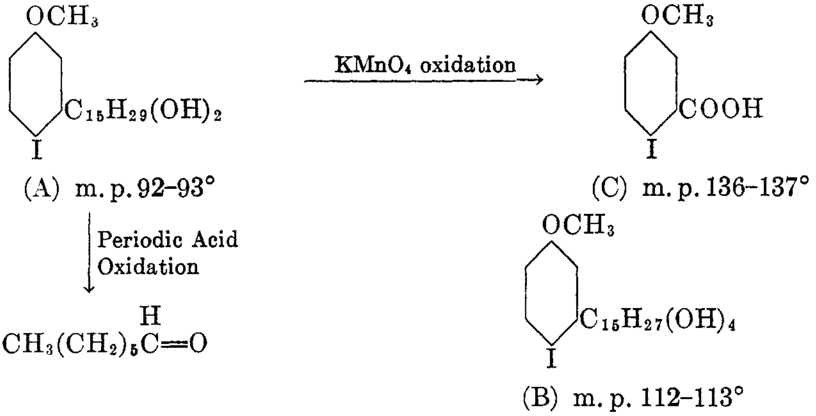
polymerized material. Wasserman and Dawson (12) have shown that the skeleton structure of the monophenol, cardanol, obtained by direct vacuum distillation of the raw commercial shell liquid, is the same as that established by Backer and Haack (3) for the monophenol obtained from solvent-extracted oil.[3]

It was the original purpose of this investigation to establish the positions of the two aliphatic double bonds in the side chain of the monophenolic component, cardanol, of the commercial shell liquid. However, attempts to obtain pure specimens of cardanol by repeated vacuum distillation of the commercial liquid gave products of continuously decreasing unsaturation. This observation, in conjunction with subsequent findings, suggested that the two double-bonded character of the monophenol, as originally isolated from the shell liquid, was the coincidental result of a mixture of monophenols having the same carbon structure but differing in their degree of unsaturation. The loss in unsaturation during distillation appeared to be due to selective polymerization of the more highly unsaturated components of the monophenolic mixture.

The experimental observations that definitely established the heterogeneous nature of the monophenolic fraction obtained by vacuum distillation of commercial cashew nut shell liquid were the result of an attempt to prepare a glycol derivative of the double bond by means of the Prévost reagent, silver iodobenzoate (14, 15, 16). As briefly reported elsewhere (17), treatment of the methyl ether of the monophenol from cashew nut shell liquid with silver iodobenzoate and subsequent hydrolysis of the benzoates, yielded on fractional crystallization from aqueous methanol two crystalline glycols (A and B) both of which contained iodine.



(A) m.p. 92–93°

(C) m.p. 136–137°

(B) m.p. 112–113°

Both glycols showed no discoloration of bromine in carbon tetrachloride. Oxidation of the monoglycol (A) with periodic acid gave *n*-heptaldehyde which

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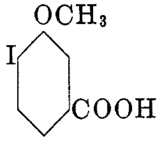
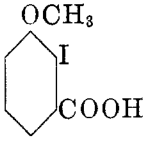
[3] Backer and Haack referred to the monophenol as "anacardol". However, the name "cardanol" is to be preferred for the monophenolic fraction resulting from the decarboxylation of anacardic acid, since Naidu (13) had previously used the name "anacardol" for a different phenol, $C_{18}H_{30}O$, found in marking-nut shell liquid. Additional reasons for preferring the name cardanol have been presented elsewhere (11).

was identified as the 2,4-dinitrophenylhydrazone, while oxidation with alkaline permanganate gave an aromatic acid (C) containing one iodine atom in the nucleus.

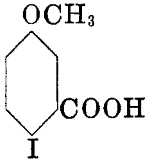
Since it was known from previous work that the aliphatic side chain was *meta* to the methoxyl group in (A), four possibilities existed for the position of the iodine atom in the aromatic acid resulting from the oxidation. These were:



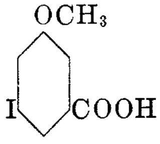
(a)



(b)



(c)

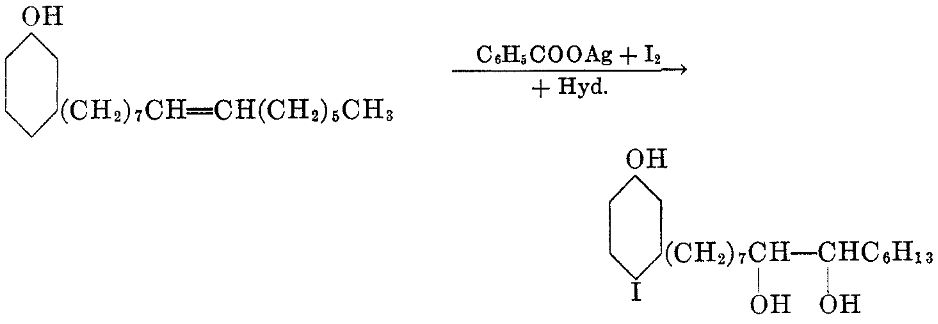


(d)

Of the four possible structures, (d) could be almost definitely eliminated because of the *ortho-para*-directing influence of both the methoxyl group and the alkyl side chain. Structure (b) seemed unlikely because it had been previously synthesized (18, 19) and reported as melting at 148–151°. For these reasons the two iodinated methoxybenzoic acids (a) and (c) were selected for synthesis, in order to establish the structure of the iodinated oxidation product.

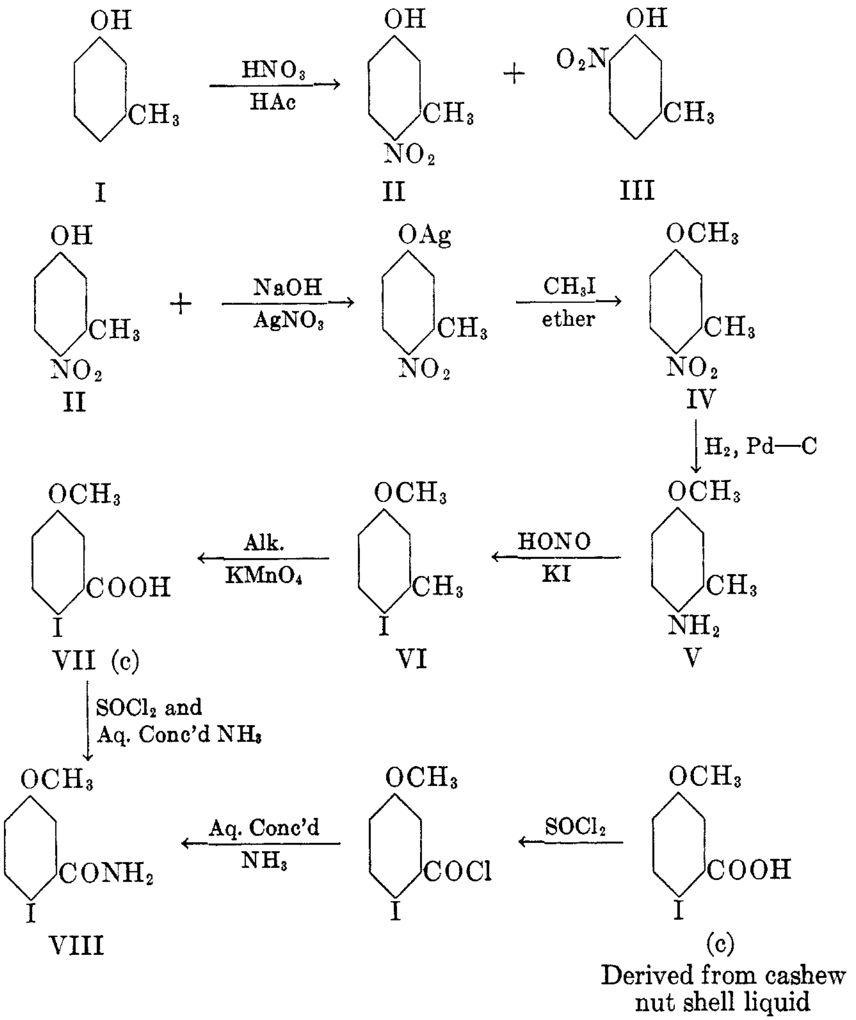
Neither (a) nor (c) had been previously synthesized and the sequence of reactions used to prepare (c) from *meta*-cresol is illustrated in the Flow Sheet. By similar reactions the isomeric acid (a) was prepared from the nitrocresol (III) which had been separated from (II) by steam distillation (20, 21). The iodinated acid derived from the cashew nut shell liquid proved to be identical with the synthetic acid (c) as revealed by mixed melting points of the free acids and their amides (VIII).

The above results establish that the monophenolic fraction of commercial cashew nut shell liquid contains at least two different olefinic components: one a monoölefin and the other a diölefin. The monoölefin is unsaturated in the 8–9 position of the side chain. During the hydroxylation of the double bonds by the Prévost reagent the benzene ring is iodinated in the *para* position to the methoxyl group as shown by the following reaction for the monoölefin:



In order to account for the average of two double bonds in the original monophenolic fraction of the shell liquid, it must be presumed that higher olefinic components were also present. Although no serious attempt was made during the present investigation to isolate in pure form other glycols from the Prévost reaction mother liquors, these liquors on long standing deposited more crystalline material which melted differently than (A) or (B).

FLOW SHEET



As previously pointed out, Backer and Haack (3) working with a solvent-extracted oil, came to the conclusion that the monophenolic fraction was composed of a single compound possessing two aliphatic double bonds in its side chain. In view of the observed heterogeneous olefinic nature of the vacuum-distilled monophenolic fraction of commercial (heat-treated) cashew nut shell liquid, it seemed advisable to investigate the action of the Prévost reagent on the monophenolic fraction of a solvent-extracted oil. Following the procedure described by Backer and Haack for the isolation of the monophenol, a phenolic fraction was obtained possessing an unsaturation equivalent to two aliphatic double bonds. Treatment with the Prévost reagent in the manner described above yielded a crystalline iodomonoglycol which proved to be identical with that obtained from the monophenolic fraction of the commercial (heat-treated) oil. These results establish the presence of a monoölefin in the vacuum-distilled monophenolic fraction of solvent-extracted oil possessing an average of two double bonds, and reveal, therefore, that the monophenolic fraction obtained by vacuum distillation of either the commercial (heat-treated) shell liquid or the solvent-extracted shell liquid is, in actuality, an olefinic mixture so composed as to possess under certain conditions an average of two double bonds.

TABLE 1

FRACTIONATION DATA

FRACTION	RATE OF DISTILLATION	BOILING POINT,[a]	VOLUME OF DISTILLATE	n_D^{30}	COLOR OF DISTILLATE	NO. DOUBLE BONDS
		°C.	*cc.*			
I[b, c]	1 drop/sec.	184	30	1.5040	light lemon	1.57
II[b, c]	1 drop/sec.	186	200	1.5050	light lemon	1.56
III[b, c]	1 drop/sec.	186	150	1.5050	light lemon	1.57
IV[b, c]	1 drop/sec.	188	200	1.5060	light lemon	1.58
V[b, c]	1 drop/sec.	190	150	1.5075	light lemon	1.57

[a] At 1.5 mm. pressure.

[b] Mantle temperature, 260°.

[c] Column temperature, 145°.

EXPERIMENTAL

RAW COMMERCIAL CASHEW NUT SHELL LIQUID

Decarboxylation and distillation. In order to decarboxylate the brown colored raw commercial cashew nut shell liquid, 1597 cc. of material was heated in a flask under 3 mm. pressure with an electrically heated mantle for one hour at 200°. The ground glass jointed flask was equipped with an electrically heated Vigreux column, condenser, and receiver. After the decarboxylation was finished, as evidenced by stoppage of bumping and splattering in the flask, the distillation was begun by raising the bath temperature to 260°. The material, boiling at 187–205° at 1.5 mm., was then collected. The volume of distillate collected which was yellowish in color was 860 cc.

In order to determine the unsaturation value of the distillate a 2.00-gram sample of the material in 50 cc. of ethyl acetate was reduced in an Adams shaker using 10% palladium on carbon as catalyst at 31° and 764 mm. pressure. The reduction came to a complete stop after 329 cc. of hydrogen had been absorbed which is in agreement with the theoretical value (328.4 cc.) for the reduction of two aliphatic double bonds under these conditions.

Fractionation of the monophenol. The fractionation was accomplished using a 34-in. Fenske helix-packed column, which was electrically heated and had a direct take-off.

An 850-cc. sample of the crude monophenol described above was fractionated at a rate of one drop per second by maintaining the mantle temperature at about 240° and the column temperature at about 140° at a pressure of 1.5 mm. The distillation yielded 20 cc. of fore-run boiling at 180–187° and 800 cc. of yellowish oil, which boiled at 187–194° at 1.5 mm. The main fraction (800 cc.) was fractionated again at 1.5 mm. and yielded a fore-run of 40 cc boiling at 190–194° and 740 cc. of light lemon yellow-colored oil of b.p. 194–195° at 1.5 mm. The bath temperature was 240° throughout both distillations.

The above material (740 cc.) was then distilled for a third time yielding two fractions (II and III) having the same index of refraction. The fractionation data are given in Table I.

In order to determine if Fractions II and III were contaminated with any resorcinol compound, which is present to a small extent in raw commercial cashew nut shell liquid, each fraction was hydrogenated as described above and the hydrogenated mixture was processed as follows. The reduction mixture was filtered from the catalyst and the filtrate was concentrated by evaporation. The residue on cooling yielded white hairlike crystals of m.p. 51–51.5° in quantitative yield. Since a quantitative yield of saturated phenol of excellent melting point was obtainable from the hydrogenation of Fractions II and III, thus indicating that no contaminant was present, these fractions were therefore selected for further work.

Methylation of phenolic fractions II and III. A 150-g. sample of the monophenol of 1.57 double bonds was methylated in the customary manner using dimethyl sulfate and alkali. The oily product was extracted with Claisen solution to remove unmethylated phenol, dissolved in benzene, dried over magnesium sulfate and then fractionated. The fraction boiling at 195–196° at 2.5 mm. was collected. The yield was 120 g. (77%) of a colorless oil. The hydrogenation value indicated 1.56 double bonds.

Isolation of an iodomonoglycol (A) from the methyl ether of fractions II and III. A 10 g. sample of the methyl ether described above was added to a suspension of 35 g. of silver benzoate in 300 cc. of an anhydrous, thiophene-free benzene solution of 21 g. of iodine. The addition of the methyl ether was accompanied by the liberation of some heat and the violet iodine color soon changed to a lemon yellow on shaking. The resulting mixture was refluxed for two hours with occasional stirring and then cooled and filtered from the insoluble silver iodide. The benzene solution containing the benzoate esters was evaporated on a steam-bath *in vacuo* to leave a viscous oil. The oil was dissolved in 375 cc. of 80% ethanol containing 25 g. of KOH and refluxed for three hours on a steam-bath to hydrolyze the esters. The alcohol was then distilled until a heavy precipitate deposited in the flask. The residue was diluted with 50 cc. of water and extracted with three 50-cc. portions of ether. The ether extracts were washed with water until alkali free and then dried over magnesium sulfate, filtered, and evaporated. The oily residue was dissolved in a hot 4:1 methanol–water solution and allowed to cool slowly. Within a short time crystals appeared. The crystals were filtered and washed with cold methanol. The yield was 5.2 g. of material of m.p. 87–89° (the mother liquors were set aside for the isolation of the *diglycol* described below). Four recrystallizations from methanol gave a white, crystalline substance of m.p. 92–93° which showed no unsaturation with bromine in carbon tetrachloride. The presence of iodine in the molecule was established by qualitative tests and the analytical data given below. The compound analyzed for an *iodomonoglycol*.

Anal. Calc'd for $C_{22}H_{37}IO_3$: C, 55.35; H, 7.74; Mol. wt., 476.

Found: C, 55.55; H, 7.51; Mol. wt., (ebulliometric in CCl_4) 478.

Isolation of an iododiglycol (B). The methanol–water mother liquors from the previous reaction were evaporated to a small volume under vacuum on the steam-bath. The oily residue was dissolved in 50 cc. of benzene and dried over magnesium sulfate and filtered. The benzene was distilled off and the dried, residual oil was again dissolved in 10–15 cc. of benzene. The benzene solution was diluted with Skellysolve A[4] until precipitation was complete. A gummy precipitate separated which on standing in an icebox for two days turned semi-solid. The material was filtered and sucked as dry as possible. The solid was recrystallized three times from methanol and finally yielded a very small amount of white solid of m.p. 112–113°. The presence of iodine was established by qualitative tests and the analytical data given below for an iododiglycol.

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[4] Hydrocarbon solvent, b.p. 83–100°F., supplied by Skelly Oil Co.

Anal. Calc'd for $C_{22}H_{37}IO_5$: C, 51.96; H, 7.28.
Found: C, 51.92; 52.01; H, 7.50; 7.43.

Oxidation of the iodomonoglycol (A) with potassium permanganate. Isolation of (c). In order to oxidize the iodomonoglycol (A) to an iodomethoxybenzoic acid and thereby locate the position of the iodine in the ring, 2.0 g. of the iodoglycol (A) was suspended in 250 cc. of water containing 10 g. of $KMnO_4$ and 2 cc. of 0.2 *N* NaOH. The mixture was refluxed for two hours or until the supernatant liquid was colorless. The hot solution was filtered through a Büchner funnel using Celite[5] as a filter aid. The MnO_2 precipitate was well washed with hot water. The colorless filtrate was acidified with conc'd H_2SO_4 until definitely acid to Congo Red paper and then cooled. Crystals appeared, which were filtered and then recrystallized from hot water. The yield of white needles of m.p. 136–137° was 380 mg. (32%). The analysis conformed to an *iodomethoxybenzoic acid.*

Anal. Calc'd for $C_8H_7IO_3$: C, 34.54; H, 2.51.
Found: C, 34.71; H, 2.77.

Oxidation of (A) with periodic acid. Isolation of n-heptaldehyde 2,4-dinitrophenylhydrazone. One gram of the iodomonoglycol (A) was dissolved in 100 cc. of ethanol. To this solution in a glass-stoppered Erlenmeyer flask at 35° was added 0.480 g. of periodic acid dissolved in 3 cc. of water. An immediate odor of aldehyde was detected. The reaction was allowed to stand at 35° for 15 minutes and then at room temperature (29°) for 2 hours. The solution was then diluted with twice its volume of water and an oil settled to the bottom of the mixture. This oil was extracted with ether and the extracts were evaporated to a small volume. The yellowish oil residue was then steam-distilled. A total of 150 cc. of distillate was collected and the aldehyde was extracted from this distillate using ether. The ether extract was evaporated and the residue remaining was dissolved in 100 cc. of 95% ethanol to which 0.50 g. of 2,4-dinitrophenylhydrazine was added. The mixture was refluxed until all was in solution. At this point 1 cc. of conc'd hydrochloric acid was added; the color then changed from red to yellow. Refluxing was continued for an additional 15 minutes, and the solution was cooled. A copious crop of yellow crystals deposited which were filtered, washed with cold ethanol, and dried. Yield 410 mg.; m.p. 106–107°. The mother liquors after concentration to one-half their volume gave an additional 60 mg. of material of m.p. 105°. Total yield 470 mg. (76%). Recrystallization of Crop I from 95% ethanol gave material of m.p. 106.5–107°. A mixed melting point with an authentic sample of the 2,4-dinitrophenylhydrazone of *n*-heptaldehyde of m.p. 105–108° 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, 53.23; H, 6.21; N, 19.10.

EXTRACTED CASHEW NUT SHELL LIQUID

The monophenol (methyl ether). Anacardic acid was obtained from the shells of the cashew nut, *Anacardium occidentale*, by solvent extraction and lead precipitation as previously described (3, 11). The resulting brown solid (m.p. 25–26°) absorbed 80.0 cc. of hydrogen per 0.555 gram in dioxane at 764 mm. pressure and 24° using Raney nickel as the catalyst (theoretical for two olefinic bonds, 79.0 cc.).

A 115-g. sample of the anacardic acid was decarboxylated in a small distilling-flask at 200° at 3 mm. pressure. The decarboxylation was finished after twenty minutes and the distillation of the phenol was begun by raising the bath temperature to 260°. The material boiling at 185–205° at 1.5 mm. was collected. The yield of yellowish oil was 50 g. or 50% (based on 115 g. of acid).

The decarboxylated yellow oil absorbed 334.4 cc. of hydrogen per 2.04 g. in 75 cc. of ethyl acetate at 758 mm. pressure and 30° in 3.5 hours using 0.5 g. of 10% Pd-carbon as catalyst (theoretical for two olefinic bonds, 335.0 cc.).

The monophenol was converted into the methyl ether using the same procedure as described previously for the methylation of the phenol obtained by fractionation of the commercial heat-treated oil. The hydrogenation of this methylated material also indicated

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[5] A diatomaceous earth made by Johns-Manville and Co.

the presence of an average of two double bonds. (2.02 grams of methyl ether in 50 cc. of ethyl acetate using 0.2 g. of 10% Pd-carbon absorbed 325 cc. of hydrogen at 29° and 764 mm. of pressure; theory, for two double bonds, 326 cc.).

Isolation of iodomonoglycol (*A*). A 10 g. sample of the methyl ether just described was added to a suspension of 37 g. of silver benzoate in 250 cc. of dry, thiophene-free benzene containing 24.3 g. of I_2. By the procedure previously used for the isolation of the iodomonoglycol from the methyl ether obtained from heat-treated oil, a crystalline material melting at 92–93° was obtained in a yield of 1.5 g. A mixed melting point with the iodomonoglycol (m.p. 92–93°) resulting from the commercial oil showed no depression. This therefore proved the identity of the two materials and also established that the solvent extracted oil contained a monoölefinic component and therefore must also be a mixture.

SYNTHESIS OF IODOMETHOXYBENZOIC ACIDS

4-Nitro-5-methylphenol (*II*) *and 2-nitro-5-methylphenol* (*III*). The nitration of *meta*-cresol (I) and the separation of the nitro isomers (II and III) were carried out according to the directions of Staedel (20, 21).

4-Nitro-5-methylanisole (*IV*). A 5.0-g. sample of the 4-nitro-5-methylphenol prepared as described above was dissolved in 50 cc. of water containing 1.4 g. of sodium hydroxide. It was necessary to heat the mixture to 45° in order to attain complete solution. To this red solution was added slowly with stirring a solution of 6.0 g. of $AgNO_3$ in 15 cc. of water. A reddish precipitate formed. The mixture was then cooled to 5°, filtered, and the precipitate washed successively with cold water, methanol, and ether and finally dried in an air-drier.

The brownish precipitate of the silver salt of 4-nitro-5-methylphenol was suspended in 100 cc. of anhydrous ether and to this was added 8.4 g. of methyl iodide. The mixture was refluxed for 16 hours. The precipitate of AgI which at the end of this time had changed to a black color, was filtered and washed with ether. The filtrate was concentrated on the steam-bath to remove the ether and 10 cc. of 10% NaOH was added to the concentrate. This mixture was steam-distilled. A colorless oil separated from the steam-distillate and solidified on cooling (m.p. 52°). Recrystallization from Skellysolve A gave 5.0 g. (95%) of crystalline material melting at 55–56° as reported for 4-nitro-5-methylanisole (22).

4-Amino-5-methylanisole (*V*). A 5 g. sample of IV was reduced in 50 cc. of ethanol using 0.5 g. of 5% Pd-carbon. The reduction took up the theoretical amount of hydrogen (three moles of hydrogen for each mole of nitro compound) and was complete in 30 minutes. The solution was filtered from the catalyst and evaporated under reduced pressure to a yellowish oil. This material was not purified any further but used directly for the next step.

4-Iodo-5-methylanisole (*VI*). The yellowish oil (V) was dissolved in 36 cc. of water containing 8.8 g. of conc'd H_2SO_4. The solution was cooled to −5° and to it was added a cold solution of 2.3 g. of $NaNO_2$ in 15 cc. of water over a period of one hour with constant stirring and maintenance of temperature below 1°. After all was added, stirring and cooling was continued for an additional hour. To the cold solution of the diazonium salt was next added 9.96 g. of KI and the reaction mixture was allowed to stand overnight at room temperature. The next day the brownish solution was treated with an excess of sodium bisulfite to remove the excess iodine and then extracted with ether. The ether solution was evaporated to a reddish oil which was steam-distilled after the addition of 1.0 cc. of 10% NaOH. A yellowish oil separated in the distillate which on cooling solidified to a crystalline mass of m.p. 44–45°; yield, 4.7 g. or 60%.

4-Iodo-5-carboxyanisole (*VII*). To convert the methyl side chain of VI into a carboxyl group a 2.0 g. sample of VI was added to a solution of 2.6 g. $KMnO_4$ in 150 cc. of water containing 0.5 g. of NaOH, and the resulting solution was then refluxed until the supernatant liquid was decolorized. This took about three hours. The alkaline solution was filtered while hot from the manganese dioxide and the latter was well washed with hot water. The combined filtrates (alkaline) were then distilled under atmospheric pressure until no more oily drops of unreacted material were observed in the distillate. In this way, 1.5 g. of starting material was recovered. The water residue was made acid (*p*H 2) with conc'd hydrochloric acid and cooled to 0° for three hours. Needles separated which were washed well with cold water. Yield, 300 mg. of white crystalline material, m.p. 135–136°. After two recrystallizations from hot water, it had m.p. 136–137°. The yield based on recovered starting material was 53.5%.

4-Iodo-5-amidoanisole (VIII). To convert the acid (VII) to the amide a 200-mg. sample was refluxed with 3 cc. of thionyl chloride for 30 minutes. The yellow solution was then added dropwise with stirring to 15 cc. of conc'd ammonia cooled to 0° with a Dry Ice-bath. A white precipitate settled out. This was filtered, washed well with cold water and recrystallized twice from water. Yield 195 mg. (98%); m.p. 189.5–190°.

Anal. Calc'd for $C_8H_8INO_2$: C, 34.65; H, 2.52.
Found: C, 34.60; H, 2.73.

2-Amino-5-methylphenol (IX). In order to convert III to the amine a 12 g. sample was reduced catalytically in 50 cc. of ethanol using 0.15 g. of 5% Pd-carbon. The reduction was completed in two hours and took up the theoretical amount of hydrogen. The solution was filtered from the catalyst and was colorless. However, as soon as the solution came into contact with the atmosphere it turned red. Nitrogen was then bubbled through to prevent any further oxidation. The solution was evaporated under reduced pressure to dryness and a brown solid was deposited in practically a quantitative yield.

2-Iodo-5-methylphenol (X). A 10-gram sample of IX was dissolved in 72 cc. of water containing 17 g. of conc'd sulfuric acid. The solution was cooled to −5° and a cold solution of 4.6 g. $NaNO_2$ in 30 cc. of water was added slowly with stirring in the course of one hour with maintenance of temperature below 1°. Stirring and cooling were continued for an additional hour after all of the nitrite had been added. To the cold solution of the diazonium salt 21 g. of potassium iodide in 20 cc. of water was next added. A large amount of foaming occurred and the solution was left standing overnight. The following day, the solution was treated with an excess of $NaHSO_3$ to remove the excess iodine and it was then extracted with ether. The ethereal solution was washed with aqueous potassium hydroxide and concentrated to an oil which was then steam-distilled. The steam-distillate was extracted with ether, dried over magnesium sulfate, filtered, and concentrated. A semi-solid deposited which weighed 10.5 g. This semi-solid was used directly for conversion to 2-iodo-5-methylanisole.

2-Iodo-5-methylanisole (XI). The crude phenolic compound (X) was methylated by dissolving an 8.0-g. portion in a hot alkaline solution containing 1.38 g. of NaOH in 50 cc. of water. To this was added slowly with stirring a solution of 5.5 g. of $AgNO_3$ in 15 cc. of water. A white precipitate separated which darkened on standing. The insoluble silver salt was filtered, washed with water, methanol, and ether and dried in air.

The dry silver salt was suspended in 100 cc. of anhydrous ether containing 12 g. of methyl iodide and refluxed for 8 hours. The solution was filtered and the yellowish filtrate evaporated to an oil which weighed 9.0 g.

The residual oil was treated with 1.0 cc. of 10% NaOH solution and steam-distilled. A colorless oil collected in the distillate. A large amount of a yellow insoluble solid remained in the distilling flask. The distillate was extracted with ether and the ether extracts dried over magnesium sulfate, filtered, and evaporated to dryness. The yield of colorless oil was 2.0 g.

2-Iodo-5-carboxyanisole (XII). The methyl side chain of XI was oxidized by suspending 2 g. of the material in 250 cc. of water containing 2.57 g. $KMnO_4$ and 0.2 g. of KOH. The mixture was refluxed for 12 hours or until the color in the supernatant liquid had disappeared. The hot solution was filtered and extracted with benzene to remove any unreacted material. The excess benzene was removed from the water solution under vacuum. Conc'd hydrochloric acid was added to the aqueous solution until it was definitely acid to Congo Red paper and then it was cooled to 0°. White crystals deposited, which were washed with water, and recrystallized from hot water. Yield 2.0 g. (86%); m.p. 210–213°.

Anal. Calc'd for $C_8H_7IO_3$: C, 34.56; H, 2.52.
Found: C, 34.67; H, 2.64.

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SUMMARY

The methylated monophenol obtained from commercial cashew nut shell liquid both by vacuum-distillation and by solvent-extraction contains the same monoölefinic component. The isolation of an iodomonoglycol, by means of the Prévost reagent, proves the heterogeneous nature of these substances, for it must be assumed that higher olefinic components were also present in the oil in order to account for the average of two double bonds in the starting material.

The monoölefinic component is unsaturated in the 8–9 position since *n*-heptaldehyde was isolated after periodic acid oxidation of the corresponding glycol.

The complete structure of the iodomonoglycol was shown to be 3-(8′,9′-dihydroxypentadecyl)-4-iodoanisole. The position of each of the substituents on the benzenoid ring was proven by degradation and synthesis.

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