[Contribution from the Department of Chemistry, Columbia University]

CASHEW NUT SHELL LIQUID. VII. THE HIGHER OLEFINIC COMPONENTS OF CARDANOL[1]

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Cardanol,[3] the monophenolic component of commercial cashew nut shell liquid, is the decarboxylation product of anacardic acid, an olefinic phenolic acid possessing the carbon skeleton and unsaturation of a pentadecadienylsalicylic acid. Recent investigations in this laboratory have revealed, however, that the unsaturation of cardanol (2) and of anacardic acid (3) represent an average of a complex mixture of mono-, di-, and poly-olefins. Consequently, the loss in unsaturation observed during the distillation of cardanol[4] can best be explained in terms of polymerization reactions involving selectively the more highly unsaturated components.

By the action of Prévost's reagent (silver iodobenzoate) on cardanol methyl ether containing 1.56 double bonds, Sletzinger and Dawson (2) isolated an iodinated monoglycol in which the OH groups were attached to the 8 and 9 positions of the 15-carbon side chain, thereby establishing the structure of the corresponding monoölefin as 3-(8′-pentadecenyl)anisole. An iodinated diglycol was also obtained in quantities too small to investigate.

The object of the present work, accordingly, was to develop a method for obtaining the diglycol in greater quantities in order that the structure of the corresponding diolefinic component might be established. For this purpose a cardanol methyl ether containing 1.76 double bonds was used.

Hydroxylation of the cardanol methyl ether with Prévost's reagent did not prove to be a feasible method for obtaining the diglycol in pure form. After removal of the monoglycol fraction (30–40% yield) the residual glycols proved to be very resistant to separation by fractional precipitation and by chromatographic adsorption techniques. The best product, obtained in low yield, appeared to be an associated compound composed of diglycol and triglycol in a 1:1 ratio. Incidentally, the oxidation of the monoglycol with periodate yielded not only heptaldehyde, as previously reported (2), but also a compound analyzing correctly for 2-iodo-5-methoxyphenylcaprylic acid—the aromatic fragment to be anticipated from previous studies in this laboratory (2).

As described elsewhere (3), hydroxylation by the 30% hydrogen peroxide-formic acid reagent of Swern and co-workers (4) produces glycols which can be

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[1] Previous paper, Izzo and Dawson, *J. Org. Chem.*, **14**, 1039 (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).

[4] A rapid, single distillation at 1.5 mm. usually yields a nearly colorless monophenolic fraction having an olefinic unsaturation value of about 1.9 double bonds, while a longer distillation at a higher temperature and 5 mm. may yield a monophenolic product containing as low as 1.26 double bonds.

partially separated by molecular distillation. Experience with the hydroxylated products of anacardic acid (methyl ether ester) indicated that the mono- and di-glycols were distillable whereas the triglycolic material was not. When this method was applied to the methyl ether of cardanol possessing 1.76 double bonds the hydroxylation reaction resulted in excellent yields of total glycolic material, and by molecular distillation it was possible to obtain a product analyzing correctly for a diglycol. This product along with monoglycolic material was found in the distillable fractions (usually about 75%) of the glycol mixture. No distillable fraction was ever obtained which gave analytical values for a triglycol; the latter apparently decomposed in the molecular still to a hard black residue.

It was not found possible to obtain a pure sample of the diglycolic material by a single molecular distillation. A preliminary rough separation into crude monoglycol and diglycol fractions (see Table I-A) proved to be a necessary first step. Subsequent redistillation of the crude diglycolic material at 10^{-5} mm. gave a fraction between 150–175° (in 27% yield) which analyzed correctly for the diglycol of methylcardanol.

Cleavage of the diglycol with periodic acid yielded formaldehyde which was characterized as its methone derivative. No other water-soluble aldehydes were detected, and the ether-soluble aldehydes could not be obtained in sufficient quantity for identification. Likewise, no success was had in attempts to isolate and identify the aromatic fragments of the molecule remaining after the cleavage. Formaldehyde was also identified as a lead tetraacetate cleavage product of the higher-boiling glycolic material (Fraction III, Table I-B).

The identification of formaldehyde as a cleavage product of the diglycol definitely establishes the presence of a terminal glycol structure, and consequently establishes the presence of a terminal olefinic double bond in the diolefinic component (or components) of cardanol. The yields of formaldehyde obtained, however, were so low (usually about 10%) that it raises a question as to the homogeneity of the diglycolic material. It appears probable that there is more than one isomeric diglycol in the diglycol fraction and some of the diglycols (possibly most of them) do not possess a terminal glycol grouping.

Formaldehyde was recovered in only about 50% yield when model compounds such as ethylene glycol and phenylpropylene glycol were cleaved with $Pb(OAc)_4$ or with HIO_4 under the same conditions as used above. It made little difference which oxidizing agent was employed. Judging from these model experiments one might expect to obtain formaldehyde in about a 50% yield on cleavage of a homogeneous diglycol. Furthermore, a homogeneous diglycol would be expected to produce a recognizable dialdehyde fragment as one of the other cleavage products.

Particular attention was paid to the possibility that the diglycolic material might have the structure of 3-(8′,9′,14′,15′-tetrahydroxypentadecyl)methoxybenzene, for it will be recalled that the monoglycol structure was established as that of 3-(8′,9′-dihydroxypentadecyl)methoxybenzene. The cleavage of a homogeneous diglycol having the 8′,9′,14′,15′-tetrahydroxy structure would yield formaldehyde and adipic aldehyde as the aliphatic fragments. Model experiments with adipic aldehyde established that no difficulty would be expected in isolating and identifying it as a cleavage reaction product. However, all attempts to isolate adipic aldehyde or any other dialdehyde were without success.

TABLE I

FRACTIONATION OF THE METHYL CARDANOL GLYCOLS INTO MONO- AND DI-GLYCOL COMPONENTS BY MOLECULAR DISTILLATION AT 10^{-5} MM.

A. FIRST STEP: Rough Fractionation of 20 grams of Crude Glycol Mixture in Three Separate Batches

BATCH NO.	CRUDE GLYCOL, GRAMS	FRACTION	TEMP. RANGE, °C.	HOURS	APPEARANCE OF DISTILLATE	DISTILLATE	
						Grams	%
1	7.5	I	126–170	10	White solid	3.5	47
		II	170–250	15	Reddish liquid	1.8	24
						5.3	71
2	8.2	I	126–160	14	White solid	4.2	51
		II	160–250	14	Reddish liquid	1.9	23
						6.1	74
3	4.3	I	126–165	8	White solid	2.5	60
		II	165–240	8	Reddish liquid	1.0	23
						3.5	83
Totals and Summary	20	I	Crude Monoglycol Fraction[a]			10.2	52
		II	Crude Diglycol Fraction[b]			4.7	23

B. SECOND STEP: Redistillation of 4.4 g. of the Above Crude Diglycol Fraction (II)

FRACTION	TEMP. RANGE, °C.	HOURS	APPEARANCE OF DISTILLATE	ANALYSIS[c]		AMOUNT	
				C	H	Grams	%
I	126–150	7	Yellow oil	73.03	9.86	2.0	45
II[d]	150–175	7	Yellowish semi-solid	69.26	9.86	1.2	27
III	175–245	8	Reddish glassy liquid	70.05	9.83	0.7	16
Residue	Undistillable		Black tar			0.5	12

[a] Main part distilled in the vicinity of 146°. [b] Main part distilled in the vicinity of 225°. [c] Samples taken for analysis directly from distillation without further purification. Calc'd for monoglycol, $C_{22}H_{38}O_3$: C, 75.38; H, 10.93. Calc'd for diglycol, $C_{22}H_{38}O_5$: C, 69.07; H, 10.01. [d] Solidified on cold-finger.

Although such arguments are far from conclusive, and are not intended as such, they do lend some support to the view that the diglycolic material resulting from the hydroxylation of cardanol is not a single, homogeneous diglycol possessing a terminal glycol grouping, but is more likely a mixture of isomeric diglycols with one or more of the isomers possessing the terminal glycol grouping.

It is of interest to note that the first step in the fractionation of the crude methyl cardanol glycol mixture (see Table I-A) showed about 75% of the glycolic material to be distillable. About 50% was obtained as monoglycol fraction and 25% as a diglycol fraction. Further distillation of the diglycol fraction (Table I-B) resulted in the separation (Fraction I) of more monoglycolic material. Starting with 20 g. of the crude hydroxylated material, the distillation results (shown in Table I) may be broken down about as follows:

Monoglycol—12 g. (60%)—Combined from first and second steps.
Diglycol—2 g. (10%)—Fractions II and III of second step.
Polyglycol—6 g. (30%)—(By difference) non-distillable.

These percentages are representative of the relative amounts of mono-, di-, and poly-olefinic components present in the original methylcardanol mixture. A simple calculation, assuming the polyglycol to be essentially triglycol, reveals that such a proportion of olefinic components corresponds in striking fashion to the degree of unsaturation of the starting cardanol (1.76 double bonds).

EXPERIMENTAL

Distillation of raw commercial cashew nut shell liquid. In order to shorten the heating period and minimize polymerization reactions, a 550-ml. sample of commercial cashew nut shell liquid was simultaneously decarboxylated and distilled *in vacuo*, rather than in separate stages as previously reported from this laboratory (2, 5). The dark brown liquid was placed in a two-liter flask fitted with an electrically-heated modified Claisen still-head and was rapidly heated. The distillation was carried out rapidly at a pressure of about 2 mm., during which carbon dioxide was continuously bubbled through the capillary. The process was marked by much foaming and vaporous spraying as decarboxylation occurred simultaneously with distillation. The main fraction distilled at 218-224° and was obtained as a clear, pale, yellow oil. From a total of 1100 ml. of raw oil, distilled in two charges of 550 ml. each, 600 ml. of the above fraction was obtained, leaving in the flask about 400 ml. of a black dense liquid residue which on standing soon set to a hard, tacky mass.

The distilled cardanol darkened slightly on standing in air, but this change in color did not significantly change its degree of unsaturation, for after standing one year, though its color had turned almost black, the unsaturation decreased but slightly. The freshly-distilled oil possessed 1.91 olefinic bonds as revealed by quantitative hydrogenation using ethyl acetate as solvent and 5% palladium-on-carbon as catalyst.

Methyl cardanol. A 360-gram sample of the above monophenol (1.2 mole) was methylated using dimethyl sulfate (6). After distilling off about one-half of the methanol solvent, one liter of water was added. The oil was separated and the solution was extracted twice with 200-ml. portions of benzene and dried over magnesium sulfate. During the extraction, troublesome emulsions were formed.

After removing the benzene under diminished pressure the oil was treated with 200 ml. of Claisen solution (50% aqueous KOH in an equal volume of methanol) to remove unmethylated cardanol. The mixture was shaken vigorously, and on standing three well-defined layers appeared: the bottom of a light yellow color, the middle a dark brown, and the top, amber. The top layer was separated and shaken again with Claisen solution, but the second time, no middle layer appeared. The top layer was separated, dissolved in 100 ml. of benzene, and dried over magnesium sulfate. The benzene was removed *in vacuo* and the 400 ml. of amber-colored oil remaining (crude cardanol methyl ether) was fractionated at 1.5 mm. using a 19-inch electrically-heated Fenske column under an atmosphere of CO_2. The distillation data are summarized as follows:

FRACTION	DISTILLATION TEMP., °C.	VOLUME, ML. APPEARANCE
I	133–147°	25 Light yellow
II	147–151°	300 Colorless oil
Residue	—	75 Amber-colored oil

The main fraction (II) weighed 280 g. (73% yield on the methylation). It gave a negative test for a free phenolic hydroxyl group when tested with phosphorus pentachloride. A quantitative hydrogenation showed an unsaturation equivalent to 1.76 olefinic bonds. This material, used in all the investigations to be described, remained a clear, colorless oil without any significant change in the degree of unsaturation during a period of over 1½ years when stored in a glass-stoppered, brown bottle at room temperature.

Hydroxylation of methyl cardanol with the Prévost reagent(2,7). The methyl ether, iodine, and silver benzoate were used in the ratio of 1:2:3. The iodine (28 g., 0.112 mole) was dissolved in 300 ml. of hot, anhydrous thiophene-free benzene, and to this was added 38 g. (0.167 mole) of silver benzoate. An immediate yellow precipitate appeared. The mixture was stirred and 10 g. (0.031 mole; 0.055 mole of double bonds) of methyl cardanol was added at 60°. Heat was evolved and the reaction became vigorous. After shaking until most of the iodine color had disappeared, the mixture was refluxed for three hours, cooled, and filtered from the insoluble silver iodide. The slight excess of iodine was removed by shaking the benzene solution with saturated sodium bisulfite, followed by washing with saturated sodium bicarbonate until neutral, and then twice with water.

After removing the benzene at reduced pressure, the brown oil was taken up in a solution of 25 g. of potassium hydroxide in 250 ml. of ethanol and refluxed on the steam-bath for one hour with occasional stirring. About 150 ml. of ethanol was then distilled off, and the precipitated potassium benzoate was separated. The clear solution was diluted with 200 ml. of water, extracted several times with benzene, and dried over magnesium sulfate. Evaporation left a residue of 12 g. (75%) of crude glycol mixture (brown oil).

This material was dissolved in 150 ml. of methanol, treated with 3 g. of Darco, refluxed and filtered. The resulting light brown solution on standing in the refrigerator for a few hours precipitated 4 grams of a white amorphous-appearing material (m.p. 71–74°). After three recrystallizations from methanol, it had m.p. 87–89° and analyzed for an iodinated monoglycol.

Anal. Calc'd for $C_{22}H_{37}IO_3$: C, 55.46; H, 7.77.
Found: C, 55.33; H, 7.94.

The methanol mother liquor from the first crystallization was evaporated. The residual brown oil was then treated with hot benzene which dissolved the major portion. The benzene-insoluble material was filtered off and recrystallized three times from methanol to yield finally 100 mg. (0.6%) of white crystals containing iodine and melting at 102–107°. The benzene-soluble material was precipitated as a gummy semi-solid by Skellysolve D as described by Sletzinger and Dawson (2) but no success was had in obtaining high-melting crystals on recrystallization from methanol. For this reason, subsequent efforts were concentrated on the benzene-insoluble fraction.

A series of Prévost reactions like the one described above was carried out on batches of 10 g. and 20 g. Altogether 100 g. of methyl cardanol was hydroxylated, which theoretically should yield 160 g. of glycolic material. From the total hydroxylated material 1.7 g. (about 1%) of glycols melting at 100–106° were finally obtained as described above. This combined yield was recrystallized from methanol, and a white powdery material was obtained, m.p. 106–108°.

Anal. Calc'd for $C_{22}H_{37}IO_5$ (diglycol): C, 51.96; H, 7.28.
Found: C, 49.27; H, 7.00.

Another methanol recrystallization gave m.p. 106–108°.

Anal. Found: C, 50.18; H, 6.83.

A recrystallization from carbon tetrachloride (in which the material was soluble with great difficulty at refluxing temperature) did not significantly change the melting point nor the analytical data.

Anal. Found: C, 50.31; H, 6.82.

An ebulliometric molecular weight determination in trichloroethane gave a value of 552. This substance was finally placed in a micro-Soxhlet and washed with hot carbon tetrachloride for one hour. The substance now melted at 109–111°.

Anal. Found:[5] C, 50.47, 50.54; H, 6.84, 6.82.

Cleavage of the monoglycol with periodic acid (8); *2-iodo-5-methoxyphenylcaprylic acid.* The monoglycol of m.p. 87–89° (1.0 g., 0.0021 mole) was cleaved with 0.5 g. of paraperiodic acid (equivalent to 0.0022 mole HIO_4) (2, 3) in the usual way. *n*-Heptaldehyde was recovered from the reaction mixture by steam-distillation and identified as its 2,4-dinitrophenylhydrazone (9). The residue left in the flask from the steam-distillation was extracted with ether. The ether was evaporated and the residue was oxidized with 3% hydrogen peroxide in alkaline medium (9). After acidification, extraction with ether and evaporation of the ether, an oily residue was left which was recrystallized from aqueous alcohol; m.p. 69–71°. The white crystalline material analyzed for 2-iodo-5-methoxyphenylcaprylic acid.

Anal. Calc'd for $C_{15}H_{21}IO_3$: C, 47.88; H, 5.63.
Found: C, 48.15; H, 5.82.

Cleavage of the crude iodinated glycols with lead tetraacetate (8, 10); *isolation of 2-iodo-5-methoxyphenylcaprylic acid and formaldehyde.* The above caprylic acid was also obtained when the mixture of crude glycols, obtained after a preliminary crystallization from methanol to remove excess of monoglycol, was cleaved with lead tetraacetate. A one-gram sample of the crude glycols was dissolved in 50 ml. of glacial acetic acid and 1.7 g. of lead tetraacetate was added. The mixture was shaken until all was in solution. After standing at room temperature for two hours, the solution was diluted with water until addition of ether no longer produced a homogeneous solution. The aldehydes were extracted with ether, the ether evaporated, and the residue oxidized with 3% hydrogen peroxide as described above. The mixture of acids was steam-distilled to remove the steam-volatile aliphatic acids.[6] The residue left in the flask from the distillation was extracted with ether, the ether evaporated, and the residue recrystallized from aqueous ethanol. A colorless crystalline acid, m.p. 71–73° was obtained.

Anal. Calc'd for $C_{15}H_{21}IO_3$: C, 47.88; H, 5.63.
Found: C, 47.72; H, 5.51.

The aqueous acetic acid solution remaining after extracting the ether-soluble aldehydes was steam-distilled directly into an alcoholic solution of methone (9) and a small amount of the formaldehyde methone derivative crystallized; m.p. 183–186° without further purification.

Anal. Calc'd for $C_{17}H_{24}O_4$: C, 69.83; H, 8.27.
Found: C, 69.88; H, 8.25.

Hydroxylation with 30% hydrogen peroxide in formic acid (4). A 20-g. sample (0.062 mole) of methyl cardanol (0.11 mole of double bonds) was mixed with 85 ml. of 98–100% formic acid (m.p. 8°) and 14 g. of 29–30% hydrogen peroxide (0.12 mole). The mixture was vigorously stirred for four hours at 40°. An initial heat effect was observed after a time lag of 5–10 minutes, the temperature reaching 70° and the mixture turning dark brown. Thereafter

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[5] Calc'd for triglycol, $C_{22}H_{37}IO_7$: C, 48.89; H, 6.90.
Calc'd for associated compound (di-tri-glycol, 1:1): C, 50.38; H, 7.11.

[6] The pungent odor of the steam-distillate indicated the presence of small amounts of fatty acids; however, it was not feasible to attempt their separation.

temperature was maintained at 40° by means of a warm-water bath. At the end of four hours, the excess formic acid was distilled off *in vacuo* and the amber oil residue was taken up in a solution of 3 *N* NaOH in 70% ethanol, and refluxed for one hour. About 50 ml. of alcohol was then distilled off and 100 ml. of water was added, followed by acidification to *p*H 2 with dilute sulfuric acid. The black sticky suspension was extracted several times with ethyl acetate, until the extracts were only faintly colored yellow. The ethyl-acetate extracts were combined and the solvent removed *in vacuo*. The dense residue was dissolved in 50 ml. of benzene and slowly distilled until the distillate ran clear. The solution was then filtered and evaporated *in vacuo* leaving a very viscous, black, glycol mixture weighing 22.5 g. (95% yield).

Molecular distillation of the methyl cardanol glycols. In three separate batches (see Table I-A) a total of 20 g. of the above material was fractionated using a large molecular still of the type used previously for anacardic acid glycols (3). Previously a single fractionation had revealed that collecting the various fractions over short temperature intervals did not lead to good separation of the higher glycol fractions.

The first fraction (126–160° or 170°) obtained as a white waxy solid was recrystallized once from aqueous ethanol. The white crystalline product melted at 53–54° and analyzed for the monoglycol.

Anal. Calc'd for $C_{22}H_{38}O_3$: C, 75.38; H, 10.93.
Found: C, 75.36; H, 11.06.

The combined second fractions (160–250°) obtained from three distillations (see Table I-A) were refractionated into three fractions (Table I-B) collected at 25°-intervals. Fraction II from this distillation which solidified entirely on the cold finger, was a semi-solid resembling petroleum jelly and analyzed for a diglycol.

Anal. Calc'd for $C_{22}H_{38}O_5$: C, 69.07; H, 10.01.
Found: C, 69.26; H, 9.86.

Fraction III of this distillation was a clear, reddish, glassy liquid analyzing 1% higher in carbon than the theory for diglycol.

Cleavage of diglycol fractions. A 1-g. sample of fraction II (Table I-B) (0.0026 mole) was dissolved in 75 ml. of aldehyde-free ethanol and 1.2 g. of paraperiodic acid (equivalent to 0.0052 mole of HIO_4) was added in 19 ml. of water. The solution immediately turned red, but no test for liberated iodine could be obtained. After standing for four hours the solution was diluted with twice its volume of water and worked up as usual [see cleavages of anacardic acid glycols (3)]. From the water extract 30 mg. (10%) of formaldehyde methone derivative was obtained. After one recrystallization from aqueous ethanol, the crystals melted at 183–185°. Mixed melting points with an authentic sample of *formaldehyde methone derivative* showed no depression.

Anal. Calc'd for $C_{17}H_{24}O_4$: C, 69.83; H, 8.27.
Found: C, 69.76; H, 8.28.

The ether-soluble aldehydes were steam-distilled directly into a methone solution which became cloudy. On centrifuging, after long standing, a small amount of non-crystalline oily residue was deposited. Repeated attempts to crystallize this material were without success.

A 1-g. sample of fraction III (Table I-B) was dissolved in 50 ml. of anhydrous, thiophene-free benzene and 1.8 g. of lead tetraacetate (0.0047 mole) was added. The reddish-brown solution became turbid due to the separation of lead acetate, but this turbidity disappeared on adding 10 ml. of glacial acetic acid. The reddish-brown color, however, persisted throughout the cleavage reaction. After five-hours standing at room temperature, the benzene solution was extracted repeatedly with small portions of water and the water extracts were steam-distilled directly into a methone solution. Formaldehyde methone derivative was obtained, m.p. 182–183° without recrystallization (35 mg.).

The benzene solution was evaporated to a small volume and steam-distilled directly into a methone solution. No crystalline material could be recovered, although the solution developed a cloudiness almost immediately.

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SUMMARY

The mono- and di-olefinic components of commercial cardanol have been separated by means of their glycol derivatives. The monophenolic fraction obtained by distillation of the commercial cashew nut shell liquid was methylated and then hydroxylated in good yield with a 30% hydrogen peroxide-formic acid mixture. The resulting glycols were "fractionated" in a molecular still.

The monoglycol was obtained in crystalline form and on periodate cleavage gave rise to *n*-heptaldehyde, thereby confirming the identity of the corresponding monoölefin as 3-(8′-pentadecenyl)anisole.

The diglycol, obtained as a semi-solid, gave small amounts of formaldehyde as the sole identifiable cleavage fragment, thereby establishing the presence of a terminal glycol structure in some of the diglycolic material.

The evidence is interpreted as supporting the view that the "diglycol" is probably a mixture of isomeric diglycols rather than a homogeneous diglycol.

A cardanol sample possessing an unsaturation equivalent to 1.76 olefinic bonds has been shown to have approximately the following olefinic composition: Monoölefin, 60%; diolefin, 10%; and tri- and poly-olefins 30%.

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