# The Extraction of Natural Cashew Nut-Shell Liquid From the Cashew Nut (*Anacardium occidentale*)[1]

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**In the two-stage recovery of natural cashew nut-shell liquid (CNSL) by solvent extraction, the overall yields from half-shells obtained by mechanical cutting and from chilled fragmented shells (to solidify the phenols) by manual processing are identical, indicating that no physical loss of phenolic material occurs in the mechanical process. At the first stage, prior to comminution, the yield from intact half-shells of mechanical origin is considerably less than that from manually processed shells due to extensive internal fracturing of the shell structure and greater solvent penetration in the latter case. Static solvent extraction of macerated shells gave the same yield as Soxhlet extraction, but the filtration stage was difficult and large volumes of solvent were required. Soxhlet solvent extraction or ultrasound/solvent extraction of manually processed shells at ambient temperature gave similar yields and economy in solvent usage. Both were much superior to mechanical agitation. By catalyzed decarboxylation of the recovered natural CNSL an almost theoretical yield (25%) of phenolic lipid rich in cardanol was obtained, which is considerably higher than that (10%) in the traditional recovery of technical CNSL by the hot oil bath industrial method. Natural CNSL contains a predominant amount of anacardic acid and represents a novel phenolic lipid source. Chemical reduction with air/aqueous hydrazine gave saturated natural CNSL. Polymerization of natural CNSL was effected in alkaline solution with paraformaldehyde.**

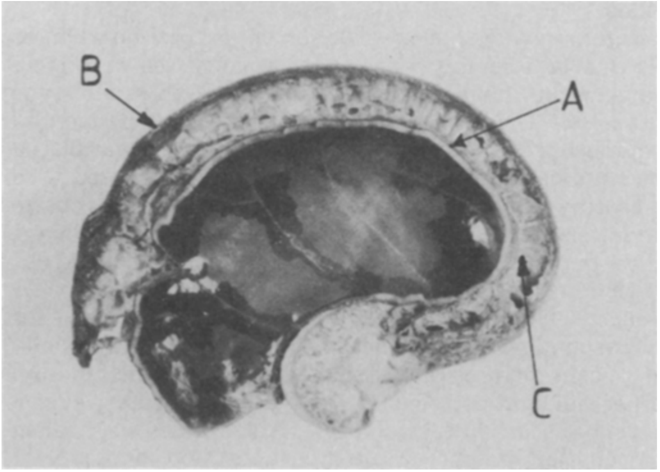
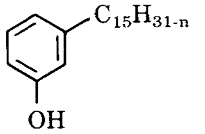


FIG. 1. Cross section of a cashew shell. A, inner shell; B, outer shell; C, membrane.

In a previous paper, the separation of cardanols (1; n = 0, 2, 3, 6) and cardols (2; n = 2, 4, 6) from technical cashew nut-shell liquid by a scaled-up chromatographic method was described (1). The present studies explore different techniques for the recovery of natural CNSL by solvent extraction. This is an aspect of lipid extraction and recovery which has been extensively reviewed (2,3). Solvent percolation and static immersion techniques have been discussed (4). Cashew nut-shell liquid (technical CNSL) is traditionally obtained by the hot oil bath method (5,6). In this, the constituent anacardic acids (3; n = 0, 2, 4, 6) in natural CNSL are decarboxylated by immersion of cashew nuts in technical CNSL preheated to 200°C. The pressure created bursts the outer shell (Fig. 1).



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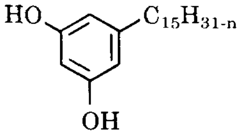

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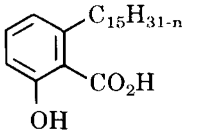

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After removal of some of the extraneous technical CNSL the inner shell is either cut by the Oltremare process, shattered by the Sturtevant/Tropical Products Institute method or removed manually in Indian practice to recover the cashew kernel. Numerous alternative methods have been tried to recover the intact kernel and the phenolic lipids separately and in high yield. In recent years the Buhler-Miag method (7) has been introduced in which the cashew nut is cut essentially in half lengthwise. Due to the greater value of the kernel portion, the recovery of natural CNSL from the half-shells has received almost no attention. New uses (8,9) for natural CNSL and anacardic acid have made it desirable to study more efficient recovery processes.

The present work is concerned with various techniques of solvent extraction and the influence of the degree of disintegration or subdivision of the shell material upon the recovery of natural CNSL. Because it seems likely that some physical loss of the shell liquid might accompany a mechanical cutting method, a parallel series of extractions was carried out by a cryogenic method (10). Intact shells were chilled at low temperature to solidify the phenols prior to manual disintegration, followed by the solvent treatment on the separated shell.

Soxhlet extraction with light petroleum (40-60°C) was effected on comparatively large batches of half-shells obtained from the Buhler-Miag process and shells disintegrated to different levels of subdivision. Another solvent extraction technique examined used ultrasound to agitate the shell particles. Natural CNSL was decarboxylated catalytically with calcium hydroxide (11) at 135°C to give cardanols (equivalent to technical CNSL). The lower temperature (200°C is common in industrial practice) would be expected to minimize polymer formation and give an improved yield. Reduction of natural CNSL either chemically (12) or catalytically gave crude saturated anacardic acids.

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[1] Part 27. Part 26, ref. 1.

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## EXPERIMENTAL PROCEDURES

*Materials.* Half-shells and whole cashews were obtained from Buhler-Miag (Eng.), Barnet, London through the help of M. Grimminger. Reference phenolic lipids were available from previous work. All solvents were redistilled.

*Equipment.* For large-scale solvent extraction a Quickfit-Quartz assembly was used that consisted of a five-l, three-necked flask with a two-l flanged Soxhlet unit (type EX5/165/21) attached to the center neck. A flanged lid equipped with three double surface condensers was placed on the Soxhlet flange. The five-l flask was heated with a heating mantle. The material to be extracted was charged into a Soxhlet thimble prepared from Whatman No. 1 filter paper. Disintegration of half-shells was carried out with a Waring commercial Blender R (Model 8010S). A Jencons laboratory ultrasonic bath unit was used for ultrasound/solvent extraction. Solvent extracts initially were concentrated on a steam bath in the case of diethyl ether and light petroleum (40–60 °C) and by rotary evaporation for carbon tetrachloride. All residues were taken to constant weight by rotary evaporation in vacuo.

*Analysis.* Thin layer chromatography (TLC) on silica gel G (type 60, microslides) was carried out on commercial and self-prepared microslides with the solvent system chloroform-ethylacetate-formic acid (95:5:2, v/v/v) for natural CNSL and cardanol. Argentation TLC was effected on similar slides prepared from silica gel G with 10% silver nitrate (by weight) with the solvent system diethyl ether-light petroleum (40–60 °C)-formic acid (30:70:2). Higher performance liquid chromatography (HPLC) analysis on extracted and chemically transformed products was carried out as previously described (13). For quantitative analysis p-t-butylphenol was used as an internal standard.

*Methods of extraction. Static solvent extraction.* Experiments with carbon tetrachloride, light petroleum (40–60 °C) and diethyl ether were carried out by the static procedure with commercial half-shells, disintegrated commercial half-shells and shell material from manual disintegrations. In all these extractions, the shell material (100 g) was simply covered by the solvent (400 ml) and allowed to soak for one week in a stoppered flask at ambient temperature.

*Soxhlet extraction of commercial half-shells and disintegrated half-shells.* Commercial half-shells (1330 g) were finely disintegrated to an average particle size of 1–2 mm, together with fine dust. The total fragmented material was Soxhlet-extracted in the equipment described above with light petroleum (3000 ml) for 12 hr; by this time, the solvent in the barrel of the Soxhlet apparatus was colorless. The natural CNSL was recovered as a brown oil. Disintegration of half-shells for a shorter time gave particles 5–15 mm in size, with some material of 1–2 mm.

Intact cashew nuts (62.32 g) were chilled for a few minutes in liquid nitrogen in a Dewar flask rather than at −78 °C in acetone/carbon dioxide (10) and then lightly hammered to give shell fragments (10–20 mm) (43.86 g) which were Soxhlet extracted with light petroleum (40–60 °C) (120 ml) for six hr. Concentration gave natural CNSL (12.75 g; 29.0%). The shell material was then finely macerated in a blender and re-extracted for six hr with light petroleum (120 ml) to give further natural CNSL (3.24 g). The total yield was (15.99 g) 36.4%.

*Ultrasound/solvent extraction.* Cashew shells (45.2 g) from manual cracking of chilled raw nuts (62.9 g) were placed in light petroleum (120 ml) in a 250-ml B34 round-bottomed flask equipped with a water condenser and subjected to ultrasonic treatment for 17 hr. The bath water rose in temperature from 15 to 70 °C during this time. The mixture was then filtered and, from the filtrate, natural CNSL was obtained (11.04 g; 24% of the shell weight). The remaining shell material, damp with light petroleum (38.56 g), was macerated briefly to give material 2–3 mm in size. Further ultrasound treatment with petroleum (120 ml) gave, after a difficult filtration, more natural CNSL (4.61 g). The total yield was (15.65 g) 34.5%.

*Chemical reduction of natural CNSL.* Natural CNSL (20.0 g) in methanol (200 ml) in a 500-ml flask equipped with a water condenser, thermometer and delivery tube for compressed air, was stirred and treated with hydrazine hydrate (8.71 g; 0.1739 g mol). The temperature of the mixture was raised to 50 °C and vigorous aeration was commenced. After 53 hr, it was established by argentation TLC that the unsaturation had been removed. The mixture was acidified with dilute hydrochloric acid to give a pale yellowish precipitate which was extracted with diethyl ether. The combined extracts were dried with magnesium sulphate and evaporated to a light brown solid (17.85 g) rich in (15:0)-anacardic acid, (15:0)-cardol and (15:0)-cardanol. The yield was 87.0% (on the assumption of an average starting mol wt of 344 and a final mol wt of 348).

*Decarboxylation of natural cashew nut-shell liquid.* A considerable number of experiments with different proportions of alkaline earth hydroxides was carried out and the following general procedure established (cf. ref. 11): Natural CNSL (20.0 g) and calcium hydroxide (0.40 g, 2%, $5.41 \times 10^{-3}$ mol) were mixed in a 200-ml B24-necked boiling tube which was held at an angle of 60 °C and rotated while immersed in an oil-bath at 135–140 °C for two hr. A vigorous effervescence was observed during the first hour. The mixture was allowed to cool to ambient temperature and extracted with light petroleum (60–80 °C) (50 ml), filtered and concentrated to give a dark brown oil (17.40 g, 98.9%). TLC showed the presence of cardanols, cardols, 2-methylcardols and only traces of anacardic acids.

*Separation of mixed anacardic acids from natural CLSL.* Lead hydroxide was used with an ethanolic solution of natural CNSL to precipitate lead anacardates which were collected by filtration. After thorough washing of the solid with ethanol, anacardic acids were regenerated by acidification with ice-cold dilute nitric acid. The combined ethereal extracts were washed with brine until neutral, dried with magnesium sulphate, and evaporated to give mixed anacardic acids.

## RESULTS AND DISCUSSION

*Static solvent extraction of mechanically halved shells.* Static extraction experiments over at least 16 hr with carbon tetrachloride, light petroleum (40–60 °C) or diethyl ether were similar and gave a recovery of approximately 35% provided maceration and solvent washing of the subdivided filtered material were used. Example 1 is typical

**TABLE 1**

**Solvent Extraction by Various Techniques from Mechanically and Manually Shelled Cashews**

| | Experiment 1 | Experiment 2 | Experiment 3 | Experiment 4 |
|---|---|---|---|---|
| Type of extraction | Static | Soxhlet | Ultrasonic | Soxhlet |
| Shell weight (g) | 100 | 800 | 45.2* | 43.08** |
| Treatments | | | | |
| 1st extraction | Intact half shells | Intact half shells | Manually shelled (10–20 mm) | Manually shelled (10–20 mm) |
| 2nd extraction | Disintegrated (1–2 mm) | Disintegrated (1–2 mm) | Disintegrated (2–3 mm) | Disintegrated (1–2 mm) |
| Solvent type | Ethyl ether | Light petroleum | Light petroleum | Light petroleum |
| Solvent volume (ml) | 400 + 400 | 3000 | 120 + 120 | 120 + 120 |
| Extract times (hr) | 168 + 168 | 12 + 10 | 17 + 17 | 6 + 16 |
| Yield (g) | 10.29 + 24.01 | 48.5 + 226.0 | 11.04 + 4.61 | 11.15 + 4.06 |
| Yield (%) | 10.29 + 24.01 | 6.1 + 28.3 | 24.4 + 10.2 | 26.0 + 9.4 |
| Total yield (%) | 34.3 | 34.4 | 34.6 | 35.4 |

*Weight of intact raw cashew nut, 62.90 g; **weight of intact raw cashew nut, 63.39 g.

with diethyl ether as solvent (Table 1). Where blender-disintegrated shells were used throughout, the 35% yield was equal to that where half-shells were used initially and then disintegrated. The cashew shell is relatively elastic and requires chilling in order for subdivision by hammering to be effective. Although the shell fragments were large, they were internally fractured sufficiently to permit substantial solvent penetration. The 28.5% yield obtained with diethyl ether as solvent was nevertheless lower and is attributed to a nonuniform level of subdivision. In all of these experiments the filtration was slow and large volumes of solvent were involved so that Soxhlet extraction was examined.

*Soxhlet extraction of mechanically halved shells.* In very early batches with different half-shells yields up to 41% had been encountered; such yields may have been due to seepage and sampling difficulties. The present series was conducted with a 7.5 k sample, and the yields were equal to those in the static extraction series. Fine maceration to give particles 1–2 mm in size, and partial maceration giving particles 5–15 mm with some finer material present, resulted in yields of 31% and 33.7%, respectively, upon solvent extraction. Evidently, partial maceration results in extensive internal fracturing because unmacerated (intact half-shells) material gave a yield of only 6.1%, as een in example 2 (Table 1). A second maceration of the shell material was needed to obtain a total yield of 34.4%. Soxhlet extraction overcame the filtration problem encountered in the static series, and a considerable economy in solvent usage was achieved by comparison with those experiments. It has been shown that in the extraction of oils and fats, the rate of solution of the oil undergoing extraction is more important than resistance to its diffusion (14). Therefore, Soxhlet extraction with warm solvent is likely to be better than static conditions at ambient temperature. Even greater economy of solvent could probably be effected by the technique of supercritical fluid extraction in a closed system (15,16).

*Ultrasonic extraction of manually shelled cashews.* Ultrasonic treatment (Table 1, experiment 3) gave a yield comparable (24%) to the first step in experiment 4, representing a control Soxhlet extraction, although maceration was essential to give a total yield of 34.6%. The disadvantage of this procedure was the need for filtration. By contrast, mechanical agitation techniques on unmacerated shells yielded only half (15.6%) the natural CNSL. Experiments with manually shelled cashews enabled the static and Soxhlet methods to be compared. It was not feassible to conduct an operation similar to the Buhler-Miag process with chilled shells. Instead, the chilled shells containing the solidified cashew phenols were manually shelled by light hammering to give fragments in the range of 10–20 mm. These particles evidently were internally fractured to a considerable degree, allowing good solvent penetration. As seen in the control Soxhlet experiment 4 (Table 1), a substantial initial extraction (26%) was obtained, which was increased to a total of 35.4% after maceration of the shell material. The failure to recover a high yield of natural CNSL from unmacerated half-shells is evident from the photograph of a broken shell shown in Figure 1. The presence of a fairly continuous membrane can be seen. It is thought that cutting (sawing) of the soft shell as in the Buhler-Miag process is less likely to result in internal fracturing of the shell structure than the hammering of chilled, brittle shell material from the manual process. It is evident from Table 1 that the total yields from mechanically and manually shelled cashews are comparable. Therefore, loss of natural CNSL is not significant in the Buhler-Miag process. The average yield of shell portion from the intact raw nut (Table 1) was 71.6%, and from an average total yield (35.65%) the average yield of natural CNSL from the original raw cashew (experiments 3 and 4) was therefore 25.5% (35.65 × 0.716). This yield is comparable with the previous values (17).

*Analysis of recovered natural CNSL.* Previous work has established that natural CNSL contains some polymeric material (13). The proportion of polymer in mechanically shelled cashews was determined because some deterioration could be expected at the surface of half-shells after storage. Table 2 summarizes some HPLC analyses carried out on Soxhlet-extracted natural CNSL from the mechanically shelled source, from manually processed cashews, and on the cardanols/cardols obtained by decarboxylation. The average value for each constituent was corrected by applying the relative molar response values (13), and the polymer value was determined by difference

**TABLE 2**

**Composition of Natural CNSL and of Transformation Products**

| | Natural CNSL (manual shelling) | Natural CNSL (mechanical shelling, Soxhlet extraction) | Decarboxylated CNSL (mechanical shelling) | Chemically reduced natural CNSL |
|---|---|---|---|---|
| Cardols | | | | |
| 15:3 | 15.15 (±0.37)[b] | 13.31 | 14.26 | |
| 15:2 | 4.82 (±0.26) | 4.41 | 4.58 | |
| 15:1 | 2.14 (±0.58) | 2.00 | 1.37 | |
| 15:0 | — | — | — | 8.80 |
| Anacardic acids[c] | | | | |
| 15:3 | 26.49 (±1.07) | 24.03 | 1.37 | |
| 15:2 | 15.18 (±1.98) | 13.47 | — | |
| 15:1 | 21.44 (±0.31) | 19.20 | 0.66 | |
| 15:0 | 1.44 | 1.44[d] | — | 62.0 |
| Cardanols | | | | |
| 15:3 | 0.80[d] | 0.78 | 24.14 | |
| 15:2 | 0.45[d] | 0.36 | 9.38 | |
| 15:1 | 0.80[d] | 0.78 | 19.20 | |
| 15:0 | — | — | 1.44[d] | 4.9 |
| Polymer (by difference) | 11.55 | 20.52[e] | 24.10 | 24.3 |

[a] All percent compositions are corrected [for different molar responses in HPLC analysis (13)].

[b] Standard deviations are shown in parentheses. They are representative of all the analyses.

[c] This does not include traces of C13 and C17 anacardic acids reported by J. Gellerman and H. Schlenk [*Anal. Chem. 40*:739 (1978)].

[d] These values are estimated due to difficulties in integration of small peaks.

[e] The higher percent polymer is due to aging rather than deterioration during extraction, because the shells were believed to be more than one year old.

(from 100%). The value for both analyses of natural CNSL in Table 2 is probably an overestimate, because a number of minor constituents such as 2-methylcardols remain undetermined. The higher polymer value in the mechanically cut material is consistent with the slightly lower proportions of the triene and diene constituents, which are most vulnerable to deterioration. Both the age and open nature of the shells were probably contributory factors to the amount of polymer found, and it is unlikely that any significant polymerization of natural CNSL occurred in the extraction experiments. Natural CNSL obtained from manual processing contained less polymer, presumably because the intact shell protected the components. TLC analysis gave a clear indication of the composition of mixtures (Fig. 2). In III compared with I, the presence of formic acid in the TLC solvent enhanced the resolution of anacardic acid, while in II and IV the major component was cardanol at high $R_f$ value.

*Transformation products of natural CNSL.* Natural CNSL is a useful raw material for several applications where anacardic acids fulfill functions not achievable by cardanols. Through polymerization with paraformaldehyde in alkaline solution, natural CNSL is a raw material for the preparation of particle board (8). It can be converted to an aldoxime, which is valuable as a solvent extractant for copper (II) (18) and, after further chemical transformation, it can be used as an extractant for other anions (Tyman, J.H.P., and S. Mehet, private communication).

In the major use of technical CNSL, the manufacture of friction dusts, the component phenols are polymerized with formaldehyde. The catalyzed decarboxylation of natural CNSL gives, in effect, technical CNSL. Natural CNSL decarboxylated by heating with 2% calcium

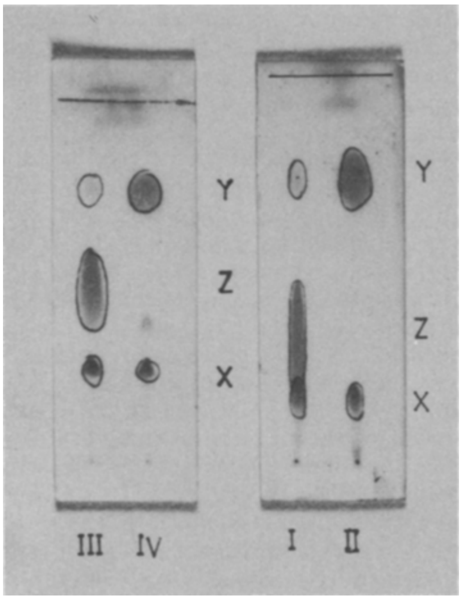

**FIG. 2. An analytical TLC plate (silica gel G). I, III, Natural CNSL from solvent extraction of mechanically cut shells. II, IV, Decarboxylated natural CNSL. X, Cardol; Y, cardanol; Z, anacardic acid. Solvent (I, II) $CHCl_3$:EtOAc (95:5); (III, IV) $CHCl_3$:EtOAc:$HCO_2H$ (95:5:2).**

hydroxide at 135-140°C yielded cardanols and cardols, traces of other phenolic lipids and polymeric material having the analysis shown in Table 2. Only a small increase in polymer was found. In principle, the yield of technical CNSL from natural CNSL should be approximately 25%, considerably greater than the 10% currently obtained from the industrial hot oil bath method.

Chemical reduction of natural CNSL with hydrazine hydrate in the presence of air by the di-imide method (12) gave from HPLC analysis primarily (15:0)-anacardic acid (62.0%), (15:0)-cardol with smaller amounts of (15:0)-2-methylcardol (8.8%), (15:0)-cardanol (4.9%) and polymeric material (24.3%). Some deterioration of the cardol and formation of cardanol by decarboxylation are apparent. If individual constituents are required, mixed anacardic acids obtained from natural CNSL by metal salt precipitation (10) can be separated by argentation TLC with a 'Chromatotron' and the solvent system, chloroform-ethyl acetate-acetic acid (Tyman, J.H.P., and A. Findon, private communcations).

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