LITERATURE REVIEW

The cashew tree (Figure 1), *Anacardium occidentale* Linn., is a native plant of Brazil, where it is called by its Portuguese name *Caju* (the fruit) or *Cajueiro* (the tree). The tree grows in the coastal areas of Asia and Africa. Nowadays, it can also be found widely in other parts of tropical climates. In Thailand, there is no evidence to confirm when cashew tree came. Presumably, in 1901, Payaratsadanupadit was the first who brought it from Malaysia to the southern part of Thailand. In present, the cashew trees are cultivated in vast amount of land of many provinces in Thailand. The production has grown to a point that it becomes an important economic factor of Thailand.

Figure 1 Cashew tree
Source: Morton (1987)

1. General detail

Common Name	Cashew
Botanical Name	Anacardium occidentale
Family	Anacardiaceae
Other Name	Casa, Maranon, Merey (Spanish), Noix d'anacarde, Pomme de caju (French), Caju (Portuguese), Kaju(Hind)

Cashew is essentially a tropical crop, grows best in the warm, moist and typically tropical climate. It can be grown from about 25° south of the equator to 25° north (Ohler, 1979). They require a good drainage, friable soils, low elevation (up to 1000 m or 3300 ft), and rainfall of about 1000-2000 mm (40-80 in) per year. The Propagation of cashew is often done by seed. Cashew plantations in Thailand and worldwide have been employed by this method.

Figure 2 Cashew apple and cashew nut

Source: Morton (1987)

The cashew nut tree consists of the cashew nut fruit, the apple, leaf and bark (Figure 2). The fruit has several components including an outer shell, inner shell and the kernel (Figure 3). The thickness of cashew nut shell is about 1/8 in. The soft honeycomb matrix, in between outer and inner shell, contains a dark brown liquid, which is known as cashew nut shell liquid (CNSL) (Das *et al* ., 2003).

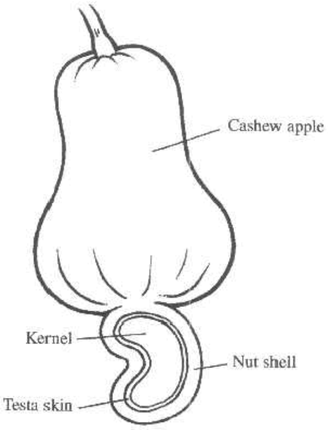


Figure 3 Cross-section of a Cashew Fruit

Source: Azam-Ali and Judge (2001)

2. Benefit of Cashew

Cashew is a multi-purpose tree. Many parts of the tree can be made use of such as cashew bark, cashew leaves cashew apple, cashew nut shell liquid, and cashew kernel.

Figure 4 Cashew kernel

Source: Morton (1987)

2.1 Cashew kernel

This part is used for diets (Figure 4). Researchers found that the vegetable proteins contained in cashew kernels stand at par with milk, eggs and meat. Besides, it also contains a high concentration of much needed acids in right proportions. A cashew kernel contains 47% fat, 82% of this fat is unsaturated fatty acids. Mostly of fatty acid in cashew kernel are oleic acid (73.8%), linoleic acid (7.7%) (Table1). This unsaturated fatty acid helps in lowering blood's cholesterol level.

Table 1 Fatty Acid Composition of Cashew Kernels (%)

Fatty Acid Composition	Percent (%)
Oleic Acid	73.80
Linoleic Acid	7.67
Palmitic Acid	0.89
Stearic Acid	11.24
Lignoseric Acid	0.15
Unsaponifiable Matter	0.42

Source: Azam-Ali and Judge (2001)

2.2 Cashew nut shell

Once removed from the kernel, cashew nut shell is subject to extraction of cashew nut shell liquid (CNSL). This liquid is caustic and causes blisters on the skin upon contact. On the other hand, CNSL plays an important role in industrial and medical fields. In industry, it is mainly used in the preparation of synthetic resins. In addition to its main application in brake lining of motor vehicles, it is used for manufacturing heat and waterproof paints, corrosion-resistant varnishes, insulating enamels and different types of surface coatings (Menon *et al.*, 1985). For medical fields, CNSL has been successfully applied to warts, ringworms, and even elephantiasis, and has been used in beauty culture to remove the skin of the face in order to grow a new one (David, 1999).

2.3 Cashew fruit or Cashew apple

Cashew apple is a bell-shaped pseudocarp which holds the nut below it. It is juicy, sweet, pungent, and high in vitamins A and C (Table 2). Per 100 g of fresh fruit, the cashew apple has more vitamin C than guavas, mangoes and oranges. However, they are quite perishable and only used locally unless preserved. It can be preserved in syrup, candied, sun-dried, stewed, and made into jams, chutneys, vinegar, pickles, and juices (David, 1999).

2.4 Cashew bark

Cashew bark is used for medical purposes to treat diabetes, eczema, psoriasis, hypertension, diarrhea, venereal diseases and gargle for mouth ulcers (David, 1999).

2.5 Cashew leaves

Cashew leaves is prepared as a mouthwash, throat problems and is used for washing wounds (Azam-Ali and Judge, 2001).

Table 2 Food value per 100 g of fresh cashew apple[*]

Nutrition content	Weight (g)
Moisture	84.4-88.7 g
Protein	0.101-0.162 g
Fat	0.05-0.50 g
Carbohydrates	9.08-9.75 g
Fiber	0.4-1.0 g
Ash	0.19-0.34 g
Calcium	0.9-5.4 mg
Phosphorus	6.1-21.4 mg
Iron	0.19-0.71 mg
Carotene	0.03-0.742 mg
Thiamin	0.023-0.03 mg
Riboflavin	0.13-0.4 mg
Niacin	0.13-0.539 mg
Ascorbic Acid	146.6-372.0 mg

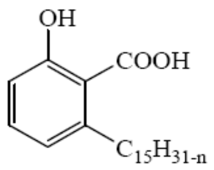
* Analyses made in Central America and Cuba.
Source: Morton (1987)

3. Cashew nut shell liquid

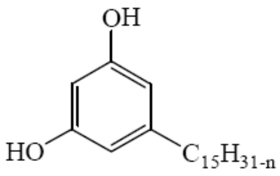
Cashew nut shell liquid (CNSL) is a by-product of cashew industry. It is obtained either by extraction in hot oil (or in solvents) or by mechanical expulsion from the shells. CNSL appears as a reddish brown viscous liquid in the soft honeycomb structure of the shell of cashew kernel. It is estimated that CNSL takes a significant proportion of about 15–20% by weight of the unshelled nut in Africa, 25–30% by weight in India. About 30–35% CNSL is present in the shell where the shells amount to approximately 67% of the nut. The world availability of CNSL is approximately 50 kiloton per annum (Das *et al*., 2003).

CNSL is essentially a mixture of phenolic compounds namely anacardic acid, cardol, cardanol and 2-methlycardol (Figure 5). These natural products could serve as alternative source of phenolic compounds from petrochemical industry. CNSL has found uses in areas such as in the manufacture of brake lining of automobiles, manufacturing of heat and waterproof paints, corrosion resistant varnishes, and insulating enamels for the electrical industry.

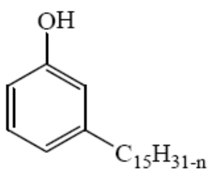
Ohler (1979) reported that fresh CNSL contains anacardic acid of about 90% by weight. Anacardic acid is a derivative of salicylic acid, which readily decarboxylates upon heating and converts to obtain anacardol or cardanol (Figure 6). Cardanol is the component that is responsible for the aforementioned applications of CNSL. The remaining 10% of CNSL consists of cardol, a resorcinol derivative having a long unsaturated hydrocarbon chain. The characteristics of cashew nut shell and International Standard (IS) Specification for CNSL is shown in Tables 3



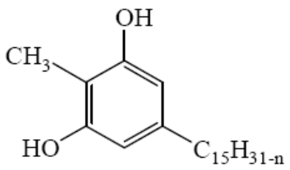
Anacardic acid
(6-pentadecenyl salicylic acid)



Cardol
(5-pentadecenyl resorcinol)



Cardanol
(3-pentadecenyl phenol)



2-Methyl Cardol
(2-methyl, 5-pentadecenyl resorcinol)

Where n = 0, 2, 4 or 6

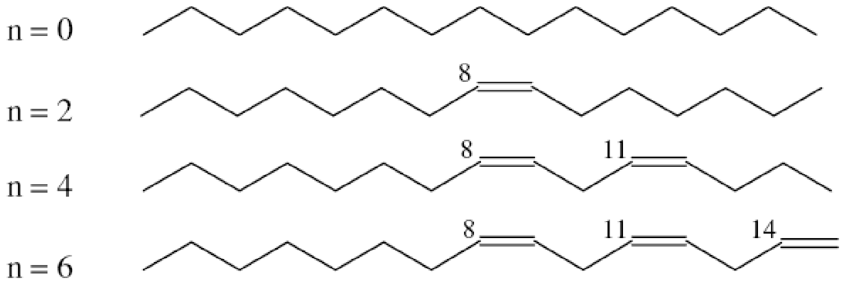


Figure 5 Chemical structures of major compounds in natural CNSL.

Source: Tyman and Bruce (2003)

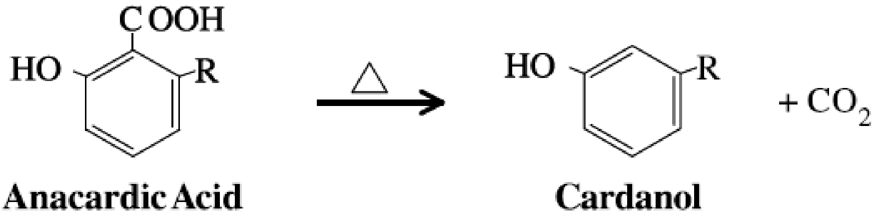


Figure 6 Decarboxylation of Anacardic acid

Source: Tychopoulas *et al*. (1990)

Table 3 International Standard (IS) Specification [*] for CNSL.

Properties	Specified Values
1. Specific gravity 30/30°C	0.950 to 0.970
2. Viscosity at 30°C, centipoises	550
3. Moisture content (% by weight)	1.0
4. Matter insoluble in toluene (% by weight)	1.0
5. Loss in weight on heating (% by weight)	2.0
6. Ash content (% by weight)	1.0
7. Iodine value	
Wij's method	250
Catalytic method	375
8. Polymerization	
Time in minutes	4
Viscosity at 30°C, centipoises	30
Viscosity after acid wash at 30°C, centipoise	200

[*] IS 840:1964

Source: Bola Raghvendra Kamath& Sons (2000)

4. Uses and Application of CNSL

The CNSL is a by-product of the cashew industry. CNSL is often described as a versatile industrial raw material. It has a wide range of applications in the manufacture of numerous products.

The CNSL is second only to the cashew kernel or nutmeat in economic importance. In the nature state, it serves as a protection to kernel against insect attacks. When used in combination with kerosene or diesel oil, it is an effective insecticide against mosquito larvae. Made into varnish, it is a preservation of wooden floors and fine carved woods, protecting them from insect destruction. For many years, fishermen have used this liquid to waterproof and preserve their fishnets, fishing lines and boats.

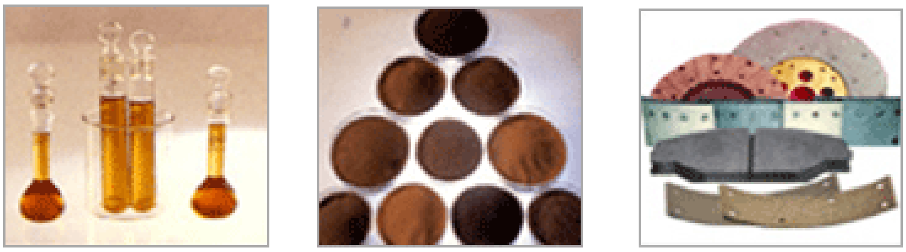


Figure 7 Application of CNSL
Source: Palmer International, Inc. (2000)

With recent advances in chemical technology, CNSL is finding many new industrial applications. It is used commercially as a phenolic raw material for the manufacture of resins and plastics. In particular, it is used as a friction modifier in the manufacture of brake lining and clutch facing (Figure 7). It has the property of absorbing the heat generated by friction in the braking action while retaining their braking efficiency longer. It is also used in rubber compounds, where it acts as reinforcing fillers, which tensile strength, hardness and abrasion resistance are improved. The resins from CNSL are used in laminating for papers, cloths and glass fibers, or impregnating materials where oil or acid resistance is required. Other uses include the manufacture of lacquers, paints, printing inks, electrical insulation material, an anti-corrosive for metals, water proofing compounds and adhesives (Menon *et al.*, 1985).

5. Extraction of CNSL from cashew nut shell

In the production of cashew kernels for edible purposes, CNSL is extracted from the outer shell of the cashew nuts before they are decorticated in order that the kernels may be removed without becoming contaminated by the liquid. There are three main methods to obtain this liquid.

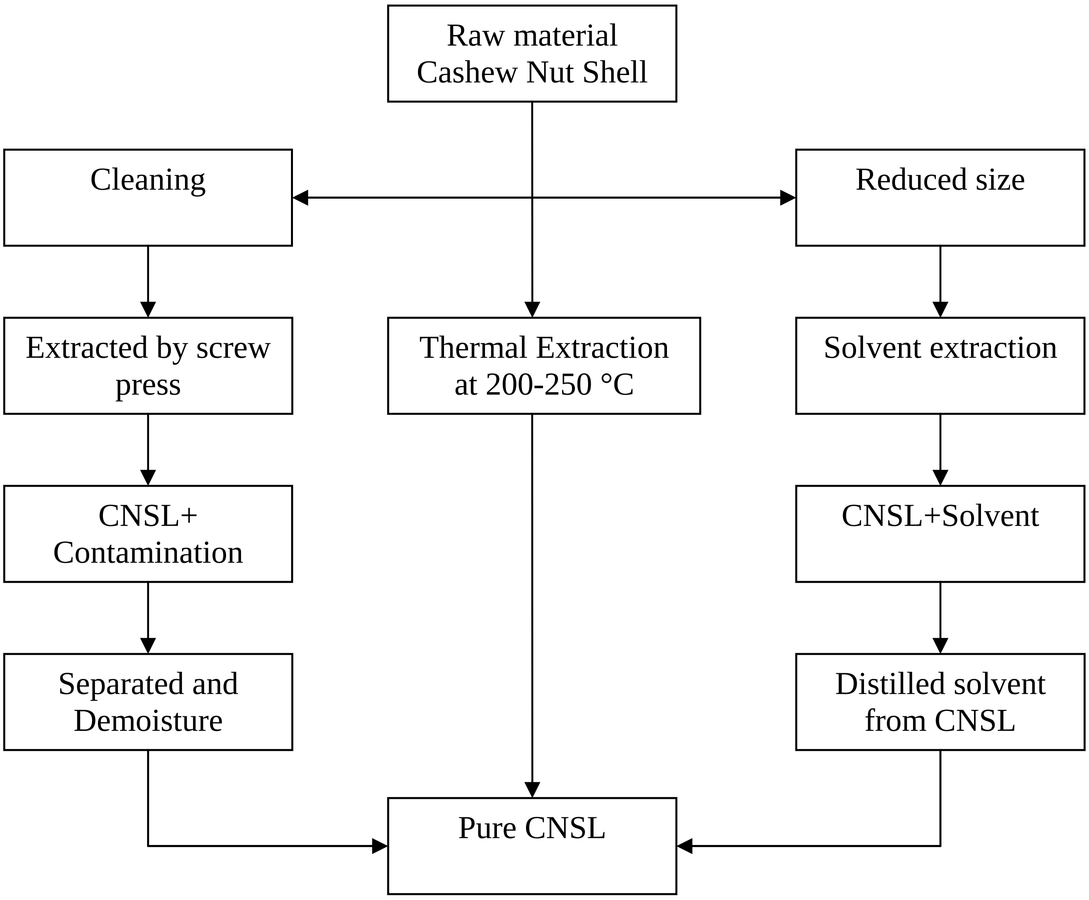


Figure 8 Methods for extraction of CNSL from cashew nut shell

Source: Wilson (1975)

5.1 Thermal extraction

5.1.1 Roasting method

In East Africa, the traditional method of removing CNSL involves roasting the nut in drums or baths. The roasting process not only removes the corrosive CNSL but also makes the shell brittle, thereby aiding the cracking process. This method causes the loss of most of CNSL. In order to extract the retained CNSL, the nuts are roasted in baths at a temperature of 180–185ºC. Vents in the equipment dispel the unpleasant fumes. This method recovers 85–90% of the liquid (Acland, 1977).

In India, method of extracting CNSL involves roasting the nuts in a shallow pan over open charcoal fires and uses constant agitation to prevent the nuts from becoming scorched. This method is extremely unpleasant as the shells burst releasing CNSL and fumes with resulting losses (Woodroof, 1967).

According to an Italian patent, the shells are scraped in a rotary apparatus with sand and steel wool, heated at 100–300ºC for 1 h and then roasted at 400–700ºC in an inert atmosphere, when the oil again oozes out (Gedam *et al*., 1986).

5.1.2 Hot oil bath method

By and large, this is the most common method of commercial extraction of CNSL in practice nowadays. The technique can be different depending upon the raw material, which is either raw cashew nut or cashew nut shell. For the first, cashew nut shell are collected in the cylinder, where steam heating is applied at temperatures around 200-250ºC for 2-3 minutes. CNSL is then released from the shells and the process is repeated. This method yields CNSL of around 7-12% by weigh. For the latter, the raw nuts are passed through a bath of hot CNSL itself, when the outer part of the shell bursts open and releases CNSL. This method produces CNSL around 6-12 % by weight of nut.

5.2 Screw pressing method

The raw cashew nut shells are put in the hydraulic press or screw pressing and then exert high pressure in order to release CNSL from the shells. This method is rather straightforward and quick among others. However, the residue from this method still retains significant proportion of CNSL around 10-15%.

5.3 Solvent extraction method

This method gives off most of CNSL compared to other methods. The oil remains in the residue is less than 1% by weight. In the preparation step, the contamination is removed by the use of magnetic device. Cashew nut shell is then reduced to small sizes to facilitate drying and extraction. The organic solvent is added to the cashew nut shell. CNSL is then extracted in the solution. The solution is separated from the solid particles and brought to boil off the solvent, which is subsequently condensed for reuse in the process. The boiling solution will be distilled further until all solvent is separated.

The percentage yield of CNSL varies with the extraction process. Indian native method of roasting nuts and collecting the expelled liquid is reported to yield about 50% of total oil content. Extraction with hot oil bath method gives about 85–90% of total CNSL in India. Superheated steam treatment and collection of condensate method improves the yield further by 2% (Hartley, 1998).

6. Advances for extraction of CNSL from cashew nut shell

The actual composition of CNSL may vary with the origin of the shells, their climatic conditions, and mostly with the process of extraction. Many researchers tried with various techniques of extraction such as pyrolysis, solvent extraction, and heat extraction. The cashew nut was first examined by Cadet, who found in it gallic acid and an acrid resin. Afterward, De Mattos (1831), by a more careful investigation, found, in addition, tannin, an extractive substance, a gum-resin, and some green coloring matter. But the most interesting investigation was made by Staedeler (1847), who examined the viscid liquid contained between the two shells of the nut, having extracted it by means of ether. This liquid is fluid at 15.5°C, congeals at 10°C, is soluble in alcohol and ether, but insoluble in water, and is bitter and caustic; when placed upon the skin, it promptly produces vesication. Staedeler separated this liquid into two constituents, one of which was an oily substance constituting about 10 percent, fluid at even low temperatures, and forming the vesicating part of the liquid, which he named cardot ($C_{21}H_{30}O_2$). This was associated with an acid substance, white and crystalline, when pure, capable of forming salts with bases, some being crystalline, and others amorphous, and to which Staedeler gave the name anacardic acid. This acid is not vesicating. Cardol was subsequently investigated by Spiegel and Dobrin (1895), who established there for the formula $C_{32}H_{50}O_3.H_2O$.

Recent advances of analytical instrumentation in past decades have allowed scientists to further their investigation and to gain more insight into the chemical composition of various constituents in CNSL obtained from different methods.

Tyman *et al*. (1989) investigated liquid extraction of the shell material with carbon tetrachloride, light petroleum, or diethyl ether and found that these solvents could give 15–30% of the total nut-in-shell (NIS) weight. When this is combined with catalytic decarboxylation to prevent polymerization, near theoretical yields of technical grade CNSL can be obtained. However, long extraction times (22–336 h), large amounts of solvent, harsh mechanical pretreatment, and low yield of whole kernels make this process unattractive. Furthermore, solvent extraction of CNSL tends to extract undesirable colored compounds from the shell material (Tyman, 1996).

Shobha and Ravindranath (1991) investigated the extraction of cashew nut shell liquid (CNSL) by using supercritical carbon dioxide. By flowing carbon dioxide 4-5 kg/h and maintaining at 40ºC and 250 bar for the extraction. The yield was 18.7% in 17.5 h.

For pyrolysis extraction, Das *et al*. (2004) extracted CNSL from cashew nut shell by using vacuum pyrolysis. It was found that the composition of CNSL obtained in this study mainly contained cardanol, cardol, substituted phenols, di-n-octyl phthalate, bis (2-ethyl hexyl) phthalate, etc.

Ganesh *et al*. (2006) employed supercritical carbon dioxide for the extraction of cashew nut shell liquid (CNSL). Under the pressure ranging from 200-300 bar, at 60°C, and mass flow rate ranging from 0.8-1.3 kg/h, it was found that the yield of CNSL increased as pressure, temperature and mass flow rate of supercritical carbon dioxide increased. The CNSL obtained by this method has unique characteristics, which has excellent solubility in diesel oils and light lubricating oils. The main product was cardanol (70–90%). It hardly contained anacardic acid, while traces of cardol were found only at high pressures.

For solvent extraction, Edoga *et al*. (2006) extracted CNSL from cashew nut shell by using hexane (n-hexane) in a soxhlet solvent extraction. The extraction was carried out at 680°C and atmospheric pressure. The product mainly contained 10% cardol, 50% cardanol and 30% anacardic acid (With the remainder being made up of other substances).

For heat-extracted CNSL, the heating process leads to decarboxylation of the anacardic acid to form cardanol. Typically, the composition of heat-extracted CNSL is approximately 52% cardanol, 10% cardol and 30% polymeric material. Heat-extracted CNSL is often further processed by distillation at reduced pressure to remove the polymeric material. The composition of the distilled CNSL is about 78% cardanol, 8% cardol, and 2% polymeric material.

7. Isolation of anacardic acid

According to an Indian patent Rye (1946) CNSL was purified to the anacardic acid as calcium anacardate by adding Calcium hydroxide to CNSL dissolved in isopropyl alcohol. The pure calcium salt of anacardic acid was dried and treated with HCl to release free anacardic acid ene mixture (n=0, 2, 4, 6). Although this method is efficient, the purity of the product was not supported by any modern chromatographic or spectral data.

Wasserman and Dawson (1948) isolated the constituents of the cashew nut shell liquid 200 g by dissolving in 750 ml of 95% ethanol and 211 g of lead hydroxide to precipitate the lead anacardate. The pure lead salt of anacardic acid was washed with alcohol and then suspended in water and decomposed with the use of p-toluenemlfonic acid at 100°C for one hour. The brown oil which floated to the top was extracted with ether, washed with saturated sodium chloride solution, and dried with anhydrous magnesium sulfate.

Kubo *et al.* (1986) investigated the isolation of the constituents of the cashew nut shell liquid by using column chromatography of silica gel (Merck; 230-400 mesh) and eluted with n-hexane-ethyl acetate-acetic acid (90:10:1, v/v/v, 1 L; 80:20:1, v/v/v, 1 L; 50:50:1; v/v/v,1 L). The product mainly contained 6.5 g of anacardic acid, 510 mg of cardanol, 980 mg of 2-methylcardol, and 3.3 g of cardol.

Tyman *et al.* (1989) used carbon tetrachloride to extract cashew nut shell 400 g. It was found that CNSL 91.08 g, (32.6%) was recovered and purified by lead salt precipitation, filtration and regeneration with cold dilute nitric acid. The anacardic acid was obtained as a viscous brown liquid 26.68 g (29.3%).

Nagabhushana and Ravindranath (1995) investigated the means for isolation of anacardic acid from CNSL by column chromatography. CNSL 100 g was loaded onto a silica gel bed, prepared in a solvent system comprising ethyl acetate-hexane (25:75) and 0.5% triethylaminel. It was found that 70 g of the product consisting of anacardic acids and 27 g of cardols and the identity of the compounds was confirmed by HPLC (Figure 9).

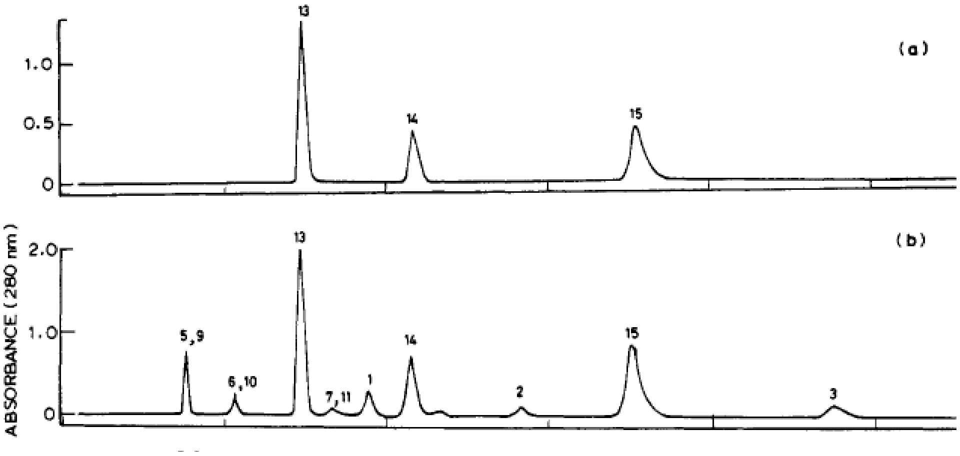


Figure 9 HPLC of (a) anacardic acid fraction, (b) solvent-extracted CNSL

Source: Nagabhushana and Ravindranath (1995)

Where numbers 1-3 represent cardanol
numbers 5-8 represent cardol
numbers 9-11 represent 2-methylcardol
numbers 13-15 represent anacardic acid

Tsunetaro *et al.* (1995) isolated anacardic acid on ion-exchange resin using organic solvents (nonaqueous) as a mobile phase. This method is not ideal for industrial isolation, however, as the use of nonaqueous solvent affects the life of ion-exchange resins.

Paramashivappa *et al.* (2001) isolated anacardic acid as calcium anacardate from CNSL 100 g. The pure calcium salt of anacardic acid was dried and treated with HCl to release free anacardic acid ene mixture. The acid-free CNSL was treated with liquor ammonia and extracted with hexane/ethyl acetate (98:2) to separate the mono phenolic component, cardanol. Subsequently, ammonia solution was extracted with ethyl acetate/hexane (80:20) to obtain cardol. (Figure 10-11)

Tyman and Bruce (2003) extracted CNSL from the shells 348.7 g by solvent extraction. CNSL was extracted with carbon tetrachloride 1000 ml for 6 h. Further crushing of the shells and extraction for 12 h with carbon tetrachloride 1500 ml, followed by filtration and evaporation of the combined extracts, gave CNSL 145.7 g, (29.1%). They also isolated anacardic acid by means precipitation as lead anacardate. The lead salt of anacardic acid was dried and treated with HCl to release free anacardic acid ene mixture (84.1 g, 58%).

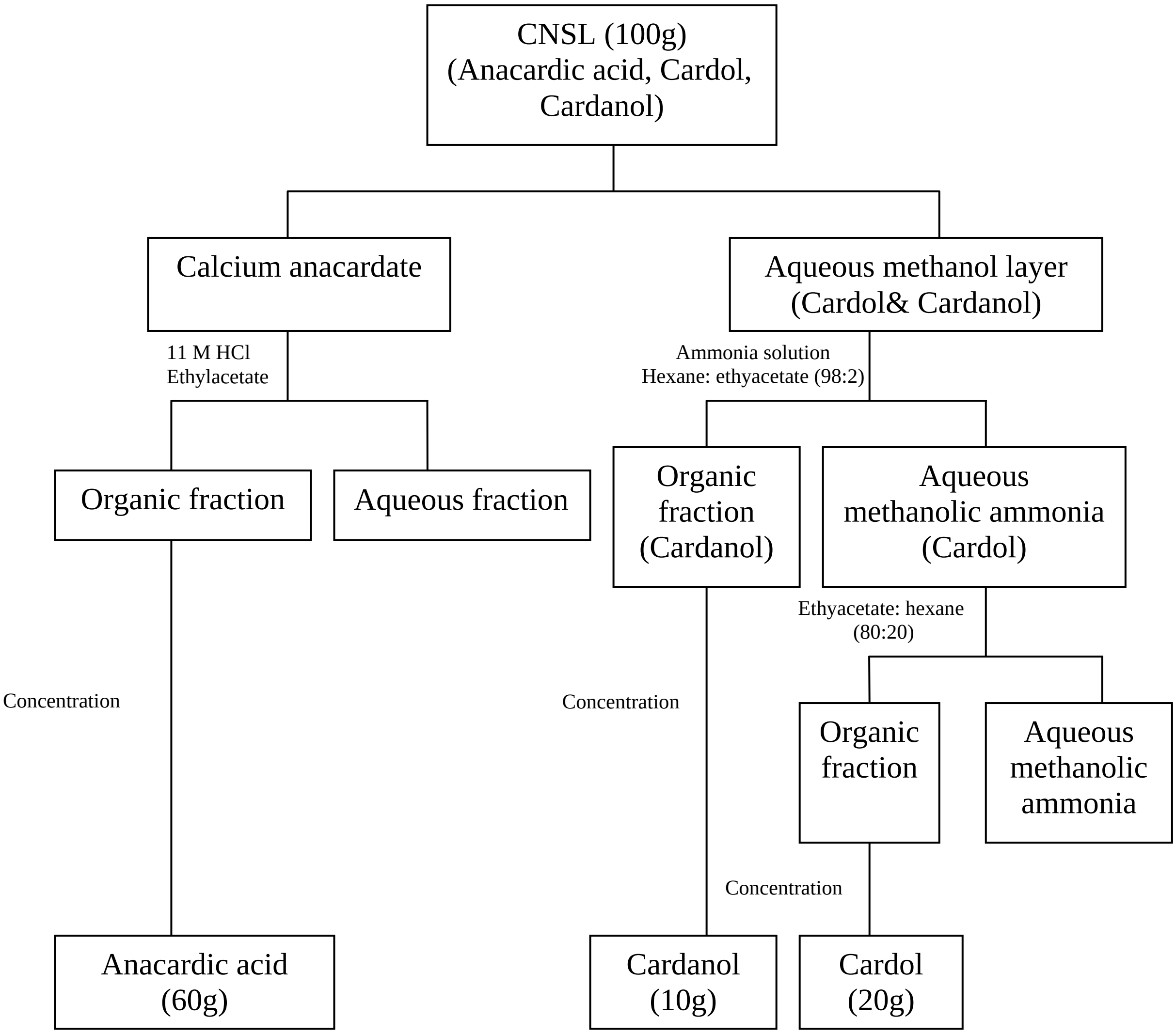


Figure 10 Flow diagram for separation of anacardic acid, cardol, and cardanol from CNSL.

Source: Paramashivappa *et al.* (2001)

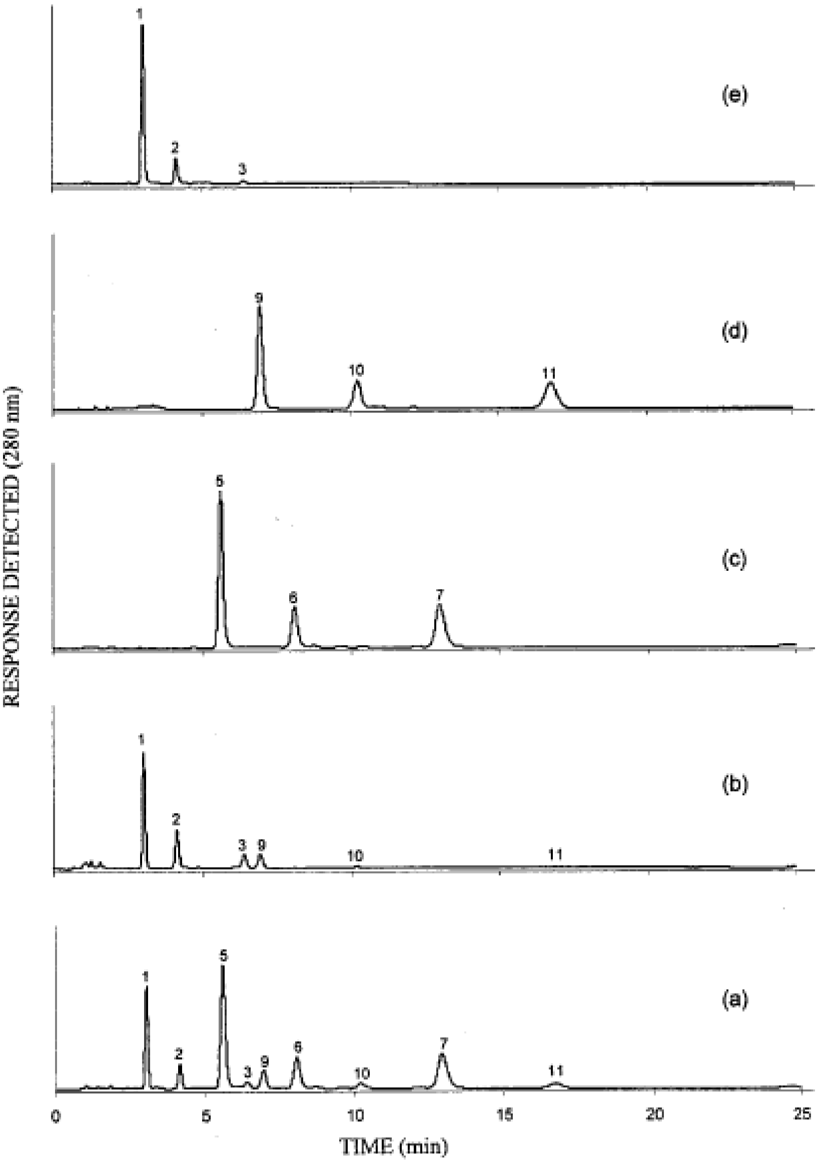


Figure 11 HPLC profiles of (a) CNSL, (b) anacardic acid free CNSL, (c) anacardic acid, (d) cardanol, (e) cardol; using Supelcosil, LC-18 and acetonitrile/ water/acetic acid (80:20:1) as mobile phase at 280 nm.

Source: Paramashivappa *et al.* (2001)

Where numbers 1-3 represent cardols
numbers 5-7 represent anacardic acid
numbers 9-11 represent cardanol

8. Extraction theory

Extraction is a physical process by which a compound (solute) is transferred from one phase to another, usually from a liquid or a solid to another liquid. The solute is removed from one phase by adding to it an immiscible solvent in which the solute is more soluble.

8.1 Liquid-liquid extraction

Liquid-liquid extraction involves the distribution, or partitioning, of a solute between two immiscible liquid phases. In the organic laboratory, the most common process involves the extraction of an organic compound from one liquid phase to the other. The two liquid phases are usually, but not always, an aqueous solution and an organic solvent. A simple extraction is often used in the work-up of an organic reaction mixture (the isolation and purification of a reaction product is often called the "work-up" of the reaction mixture), but extraction can also be used to separate and purify organic compounds. Most extraction operations in the organic laboratory are carried out in separatory funnels.

In nearly all synthetic experiments, a series of operations involving extractions are used after the actual reaction has been concluded. These extractions form an important part of the purification. Using them, the desired product is separated from unreacted starting materials or from undesired side products in the reaction mixture. Such extractions, primarily intended to remove unwanted chemicals, are referred to as washes. Several types of washes are commonly used:

(1) Water, for removing salts and organics with reasonably good water solubility. Water washes are also used immediately following extractions of the mixture with either acid or base to ensure that all traces of acid or base have been removed.

(2) Saturated aqueous salt (e.g. NaCl, Na_2SO_4), for removing salts and organics when a salting-out effect is desirable (the effect of decreasing the solubility of molecular species by increasing salt concentration is known as the "salting-out effect") or to help prevent emulsions.

(3) Aqueous acid (e.g. HCl, CH_3CO_2H), for extracting basic compounds.

(4) Aqueous base (e.g. NaOH, Na_2CO_3, $NaHCO_3$), for extracting acid compounds.

On the other hand, mixtures of acidic, basic and neutral compounds can be easily separated by extraction techniques. Organic bases can be made more water soluble by treating the organic solution with dilute inorganic acids and alternatively, organic acids can be more water soluble by treating the organic solution with a dilute base. In both cases, the organic compound is converted to its corresponding salt, which is usually soluble in the aqueous phase and can therefore be extracted from the organic solution.

After extraction, materials can be regenerated by neutralizing the extraction reagent. If an acidic material has been extracted with aqueous base, the material can be regenerated by acidifying the extract. A basic material can be recovered from an acidic extract by adding base to the extract. These substances can then be removed from the neutralized aqueous solutions. If the compounds are solid, they can be filtered from the aqueous solution; if they are liquid, they can be extracted from the water into an organic solvent. The solvent can then be evaporated using a rotatory evaporator which will yield the isolated compounds.

8.2 Choice of extraction solvent

Although water is almost always one of the liquids in the liquid-liquid extraction process, the choice of organic solvent is quite wide. A good extraction solvent needs four essential features:

(1) It has to be practically immiscible with water.

(2) It has to have a different density to water.

(3) It needs good stability and volatility so that it can easily be removed from the organic compound by evaporation.

(4) The solute has to dissolve easily in it.

Ideally an extraction solvent should also be nontoxic and nonflammable, but these two criteria are less easy to meet.

Extraction solvents fall into two groups; those which are less dense than water and those which are denser. Commonly used extraction solvents which fall into the first group include diethyl ether (the most common extraction solvent of all), ethyl acetate and hydrocarbons, such as light petroleum, hexane or toluene. The second group comprises chlorinated solvents, such as dichloromethane and chloroform, with dichloromethane being the preferred solvent because of its lower toxicity. However, chlorinated solvents do have a greater tendency to form emulsions than non chlorinated solvents. Emulsions are suspensions of small droplets of one immiscible liquid in another. The properties of some common extraction solvents, listed in order of increasing dielectric constant, are given in Table 4

Table 4 Common extraction solvents

Solvent	Dielectric Constant	B.p. (°C)	Density (g mL^{-1})	Flammability	Toxicity	Suitability
Hexane	1.9	68.7	0.65	+++	+	Poor solvent for polar compounds
Benzene	2.3	80.1	0.87	+++	+++	Too toxic general use; prone to emulsion
Ether	4.3	34.6	0.71	+++	+	Good general extraction solvent, especially for oxygen-containing compound; dissolves up to 1.5% water.
Chloroform	4.8	61.7	1.48	Nonflammable	+++	Easily dried, toxic; prone to emulsion
Ethyl acetate	6.0	77.1	0.89	+++	+	Good for polar compound; absorbs a large amount of water
Dichloro-Methane	8.9	39.7	1.31	Nonflammable	++	Good general extraction solvent; easily dried, but slight tendency to emulsify
1-butanol	17.5	117.7	0.81	++	+	"Last resort" for extraction of very polar compound; dissolves up to 20% water

+ = least flammable/toxic, +++ = most flammable/toxic.

Source: Linstromberg *et al.* (1987)

8.3 Solid-liquid extraction

Solids can also be extracted using organic solvents. One very simple way of doing this is to place the solid in an erlenmeyer flask, cover the solid with the organic solvent and allow the flask to stand with occasional swirling. The organic compound of interest will be slowly leached out of the solid. The unwanted solid can then be removed from the organic solution containing the desired compound by simple filtration. This is, however, a fairly inefficient technique in terms of extracting all of the organic compound in question, although the efficiency of the extraction can be improved by using hot solvents.

A much more efficient way to extract solids is to use a soxhlet apparatus (Figure 12). In this technique, the solid to be extracted is placed into a special “thimble” made of thick filter paper. The thimble is placed in the apparatus as shown, and the whole soxhlet extractor is placed on top of a well-supported round-bottomed flask containing the organic solvent. A reflux condenser is placed on top of the soxhlet extractor. The flask is heated using water, or steam bath (for flammable solvents) or some form of electrical heating, so that the solvent boils. Solvent vapor passes up the large diameter outer tube of the apparatus, and condensed solvent then drips down through the thimble containing the solid. Material is extracted out of the solid into the hot solvent. When the solution level reaches the top of the siphon tube, the solution is automatically siphoned through the narrow tube and returns to the flask where the extracted material accumulates.

The process is highly efficient, since the same batch of solvent is repeatedly recycled through the solid. If the extraction is run for prolonged periods, it is possible to extract materials that are only very slightly soluble in organic solvents. The technique is often used for the extraction of natural products from biological materials such as crushed leaves or seeds.

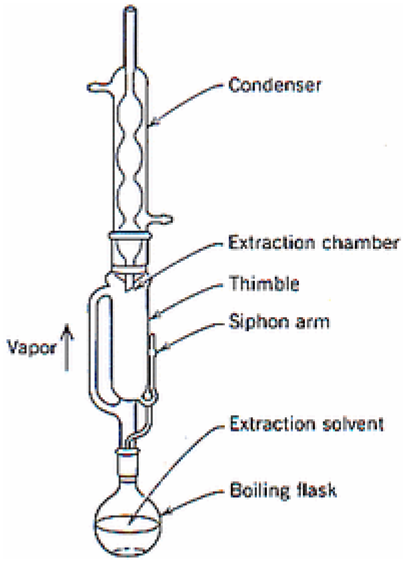


Figure 12 Soxhlet extractor
Source: Linstromberg *et al.* (1987)

8.4 Solution drying

After completing the isolation or purification of an organic compound by some form of extraction, or after completing the work-up of the reaction mixture, an organic solution containing the required compound is obtained. Since the organic solution is extracted or washed with aqueous solutions, it contains some water within. Although the amount of water can sometimes be reduced by washing the organic solution with saturated sodium chloride solution, the last traces of water have to be removed by treatment with a drying agent. Common drying agents are anhydrous inorganic salts which readily take up water to become hydrated. At the end of the drying process, the hydrated salt is removed from the organic solutions by filtration.

The procedure is as follows: at the end of the extraction, pour the final organic solution out of the separatory funnel into a dry Erlenmeyer flask. Add the solid drying agent and swirl the flask. Allow the flask to stand for at least 15 minutes. The time depends on the speed with which the drying agent takes up water. After a period of standing, remove the drying agent by filtration and evaporate the solvent on a rotary evaporator.

Several simple observations allow one to determine whether a solution is “dry”. If a solution is still wet, the drying agent usually forms clumps and sticks to the flask. In extreme cases, the drying agent may even be seen to dissolve in the aqueous phase that has formed at the bottom of the flask. If the solution is dry, the drying agent shifts or moves freely on the bottom of the flask. A wet solution usually appears cloudy; a dry one is clear.

The most important factor in drying an organic solution is the choice of drying agent. Ideally, the solid drying agent should be totally insoluble in organic solvents, inert to a wide range of organic compounds (including solvents) and able to take up water quickly and efficiently to give a hydrated form which is an easily filterable solid. Table 5 shows the most commonly used drying agents and gives information on their capacity (how much water they can take up), speed (rate of water uptake), efficiency (how dry they leave the solution) and applicability (suitability for different classes of compounds). As a good general purpose drying agent, magnesium sulfate is the most widely used.

Table 5 Common drying agents for organic solutions

Drying agent	Capacity	Speed	Efficiency	Applicability
Calcium chloride	High	Slow	Poor	Use only for hydrocarbons or halides; reacts with most oxygen and nitrogen containing compounds
Calcium Sulfate	Low	Very fast	Very good	Generally useful; neutral
Magnesium sulfate	High	Fast	Good	Excellent general purpose drying agent; a weak Lewis acid and should not be used for very acid-sensitive compounds
Molecular sieves	Moderate	Fast	Good	When freshly activated, excellent for removing most of the water, but solutions should be pre-dried with a higher capacity agent first
Potassium carbonate	Quite high	Quite fast	Quite good	Basic; reacts with acid compounds
Sodium sulfate	High	Slow	Poor	Mild, generally useful, but less efficient than $MgSO_4$

Source: Linstromberg *et al.* (1987)