CHAPTER I

INTRODUCTION

It is a desire of any developing country to make researches in the overall utilization of biomass resources for valuable commercial products for application in the pharmaceutical, agricultural, and food industries. Sugar cane is one of the economic plants and very interesting one. Discovery of high value products from sugar cane is a strategy to increase income for sugar cane planters.

Sugar cane (<u>Saccharum officinarum</u> Linn.) is a giant perennial grass of the family Gramineae (1). It is cultivated in tropical and subtropical regions throughout the world. This plant begins as a single shoot(stalk) that develops from a seed (2). The cylindrical stalk is devided into nodes and internodes (Fig.1.1) with a lateral bud at each node. The lateral buds occur alternately on opposite sides of the stalk and there is an apical bud. A root band at each node includes several rows of root primordia. The internode is covered with wax and filled with parenchyma or storage cell (pith) and the vascular bundles. The leaf consists of a sheath (Fig.1.2) attached to the stalk at the node, an auricle, a dewlap, and a blade which tapers gradually from the base to the tip and is supported by a midrib extending almost its entire length. Edges of leaves of most varieties are serrated. The infloresence is a silky panicle at the apex of the stem (Fig.1.3) bearing many small spikelets which

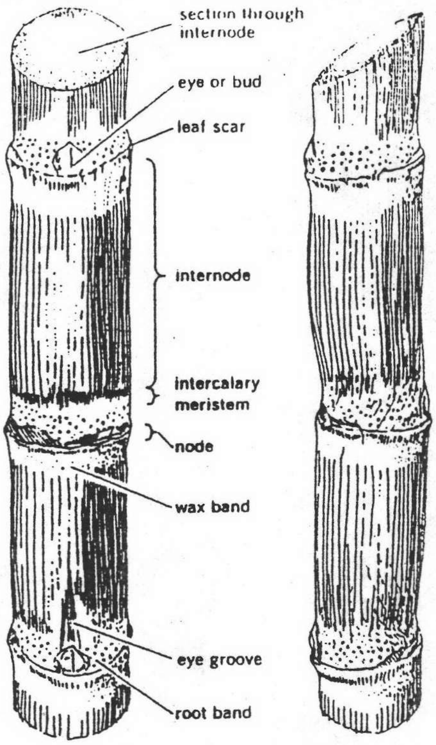


Figure 1.1 Sugar cane stalks

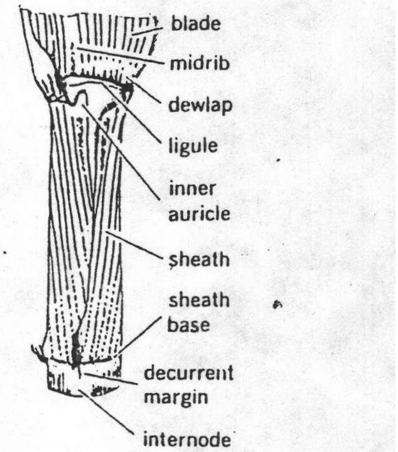


Figure 1.2 Structure of sheath

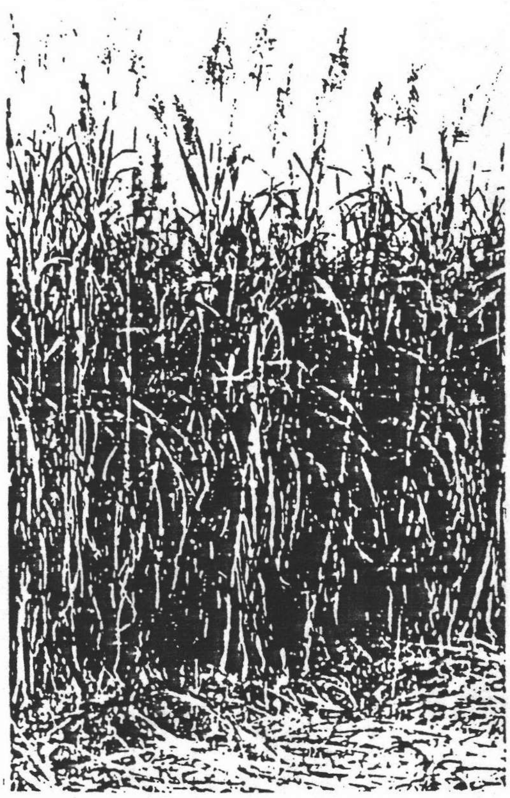


Figure 1.3 Flowering sugar cane

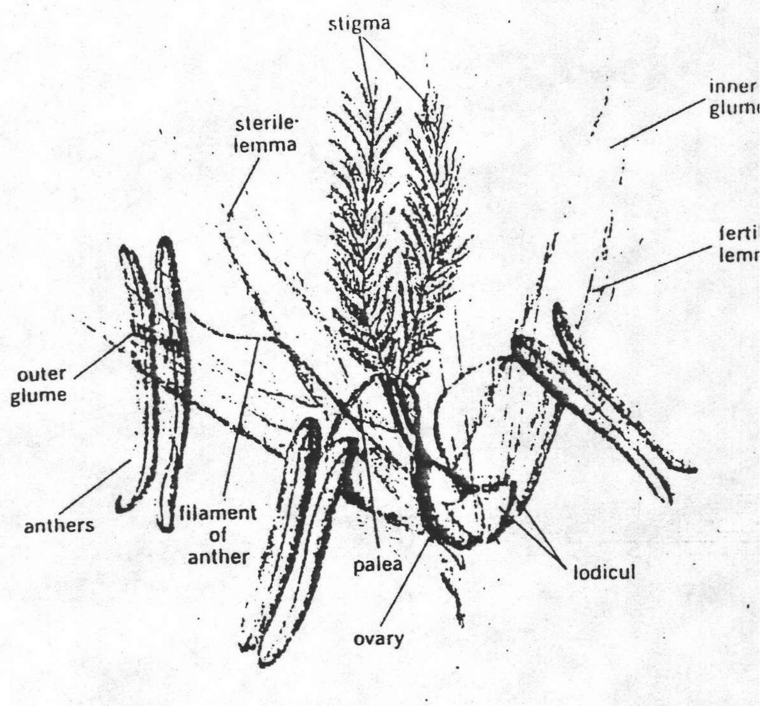


Figure 1.4 Sugar cane flower

are arranged in pair on the branches. Each spikelet contains a bisexual flower with three anthers and a single ovary surmounted by two plumelike stigma (Fig.1.4). The flower primodium is differentiated under the influence of length of night (or day).

There are many local names of sugar cane in Thailand such as Ka-thee (Karen - Mae Hong Son), Oi (General), Oi Khom, Oi Dam, Oi dang (Central), and Am-po (Khmer) (3). In Thailand, sugar cane is one of the important economic plants which is especially used in refined sugar industry. It is promoted throughout the country. Major plantations are in 5 parts covering 22 provinces (4). In the 5 parts, there are differences in climate and varieties of sugar cane which are shown in Table 1.1.

Table 1.1 Agricultural areas and varieties of sugar cane in Thailand

Part	Province	Varieties of sugar cane
Northern	Khamphaengphet,Lampang,Uttaradit Nakhonsawan,Uthaithani	F147, F156, Q83, Pindar
North-eastern	Karasin,Khon Kean,Burirum, Nakhonphanom,Udonthani	Q83, Pindar, especially F147, F156
Central	Lopburi,Chainad	all varieties
Eastern	Chachoengsau,Cholburi,Rayong	F156, Q83, Rogmar
Western	Kanchanaburi,Nakhonpathom, Petchburi,Prachaupkirikhan, Rajaburi,Suphanburi	all varieties

1.1 History

Historians disagree about whether sugar cane is native to India or New Guinea (5). They do agree that ancient people liked sugar cane and carried it with them wherever they migrated. It spread thoughout much of the South Pacific area, except for Australia, about 1000 BC. By 400 BC, it was known in Persia, Arabia, and Egypt. In the 7th to 10th centuries A.D., the Arabs spread sugar cane throughout their region of influence in the Mediterranean. At the same time, it was carried eastward across the Pacific Ocean to Fiji, Tonga, Samoa, Tahiti, Eastern Island, and Hawaii. By the 12th century, sugar cane had reached Europe, and Venice was the center of sugar trade and refining. Marco Polo reported advanced sugar refining in China toward the end of the 13th century. Columbus brought sugar cane to the new world on his second voyage. It spreads throughout the Western Hemisphere in the next 200 years and by about 1750 sugar cane had been introduced all over the world.

The process for extracting juice from the cane is also very old. In antiquity, the canes were undoubtedly sucked or chewed for their sweet taste. They were cut and crushed by heavy weights, ground with circular stones or by a heavy roller running on a flat surface, pounded in a mortar with a pestle or soaked in water to better extract the sweet juice. The term "grinding" survives to this day as the name of the process for extracting the cane juice, even though the process no longer involves a true "grinding". Parallel rolls, which are used today, were first used in Sicily in 1449.

The ancient process of obtaining sugar consisted of boiling the juice until solid formed as the syrup cooled. The product looked like gravel and the Sanskrit word for sugar, Shakkara, has that alternative meaning. Pliny, who traveled widely in the Roman Empire, wrote in 77 A.D. that sugar was "white and granular." He noted that Indian sugar was more esteemed than Arabian one, and that both were used in medicine. By the fourth century A.D., the Egyptians were using lime as a purifying agent, and carrying out recrystallization which is still the main step in refining.

Until quite recently, sugar was strickly a luxury item. Queen Elizabeth I was credited with putting it on the table in the now familiar sugarbowl, but it was so expensive that it was used only on the tables of royalty. Sugar production reached large volume at a reasonable price only by the 18th century.

The development of sugar industry from the 16th century onward was closely associated with slavery which supplied the large amount of labor used at the time. Low cost of labor and high price for sugar made many fortunes. So when the abolition of slavery occurred at various times in different countries between 1761 and 1865 profoundly affected the sugar industry. Upon the freeing of slaves, sugar production fell drastically in many production areas.

The first use of steam power as a replacement for animal or human power that drove the cane mills occurred in Jamaica in 1768. This first attempt worked only a short time, but steam drive was used successfully a few years later in Cuba. Steam drive for the mills soon spread throughout the world. The use of steam instead of direct firing was soon applied for evaporating the cane juice.

Probably the most essential piece of equipment in the modern process is the vacuum pan invented by Howard in 1813. This accomplishes the evaporation of water at low temperature and lessens thermal destruction of sucrose. The bone-char process for decolorization dates from 1820. The other essential piece of equipment is the centrifuge which was developed by Weston in 1852 and applied to sugar in 1867 in Hawaii. This machine reduces the time for draining the molasses from the sugar crystals from weeks to minutes by applying a force equal to 1000 G.

The manufacture of sugar was early understood to be an energy-intensive process. Cuba was essentially deforested to obtain the wood that fueled the evaporation of water from the cane juice. When the forests were gone, the bagasse burner was developed to use the otherwise waste dry cane pulp and bagasse for fuel. It is the everlasting credit of the cane-sugar industry that the greatest energy saver of all time was developed in the industry : the multiple-effect evaporator invented by Norbert Rillieux of Louisiana. The 1846 patents of Rillieux describe every detail of the process. The system is now used universally by every industry that has to evaporate water.

It is not clear how long sugar cane has been wide spread in Thailand. From several evidences, sugar production was reported since Sukhothai period (B.E.1920) in the regions of Sukhothai, Phitsanuloke and Kumphaengphet. It was only produced in the form of muscovado propagated by the chinese (6,7). The

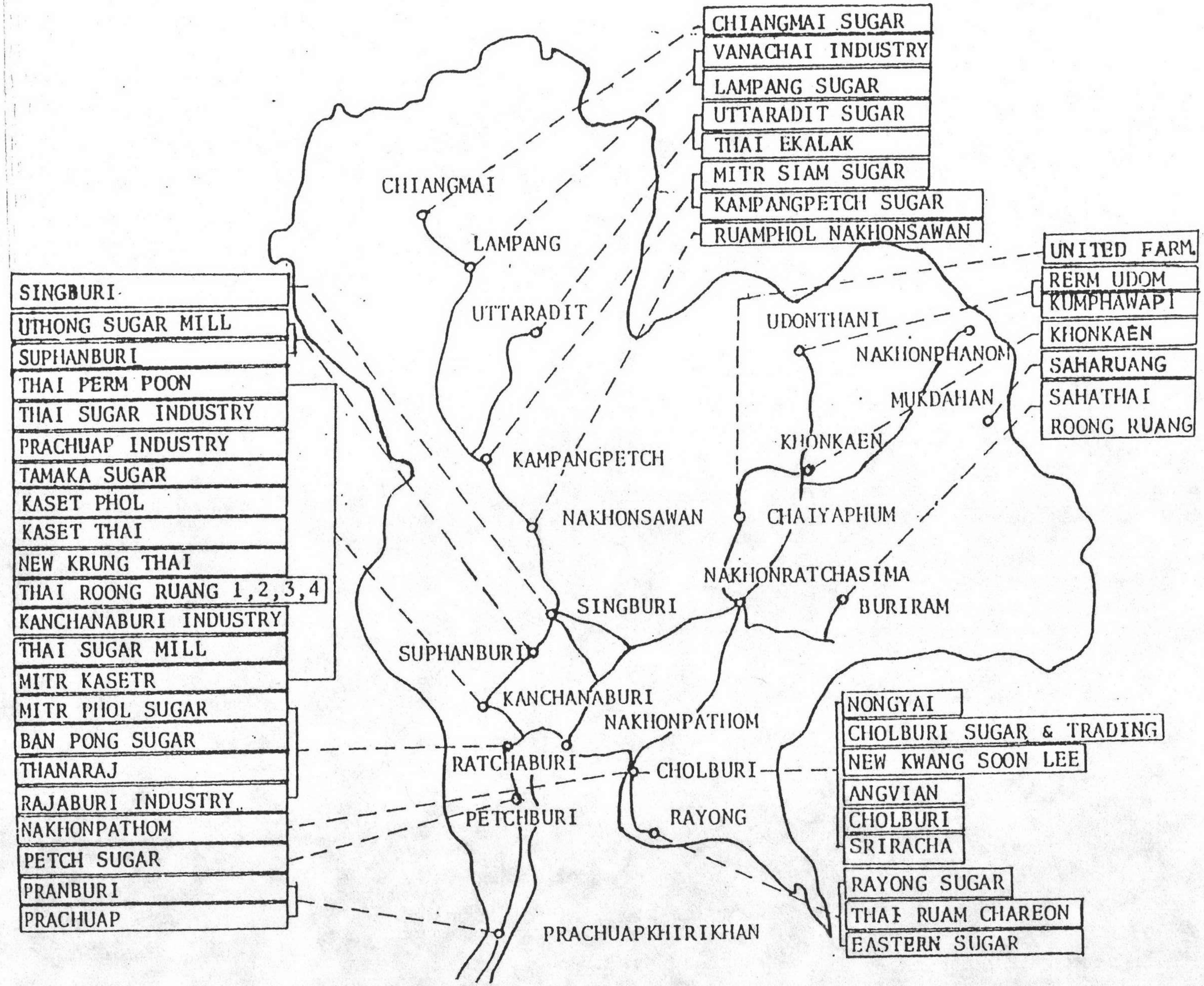


Figure 1.5 The refined sugar factories in Thailand

muscovado production was widely spread since the King Rama III era and depreciated later because of high taxes, low price of sugar in the world market and the introduction of more favorable sugar. Nowadays, muscovado factories are decreased while refined sugar factories are increased.

The first refined sugar factory in Thailand was Thai-Lampang refined sugar factory which was constructed at Amphur Koaka, Lampang Province in B.E.2479 by Chao Soi Na-Lampang and Mr.Sai Nithinunda. At present, there are 46 refined sugar factories in Thailand situated in various parts of the country, e.g. Northern, Central, Eastern and Northeastern regions. Of mentioned factories, 4 factories belong to the Government situated at Lampang, Uttaradit, Suphanburi and Cholburi provinces. The name and situation of various factories are shown in figure 1.5 (8).

1.2 Cane Sugar Manufacture

The sugar cane is planted in tropical or subtropical areas (9). The production of raw cane sugar begins when cane is harvested after a season varying from 7 months in subtropical areas to 12 - 22 months in the tropics. The cane stalks are harvested either mechanically or by heavy hand-knives and then transported to a mill by oxcart, rail or truck.

At the mill, the stalks are crushed and macerated between heavy grooved iron rollers while being sprayed continuously with water to dilute the residual juice. The expressed juice contains 95% or more of the sucrose present. The

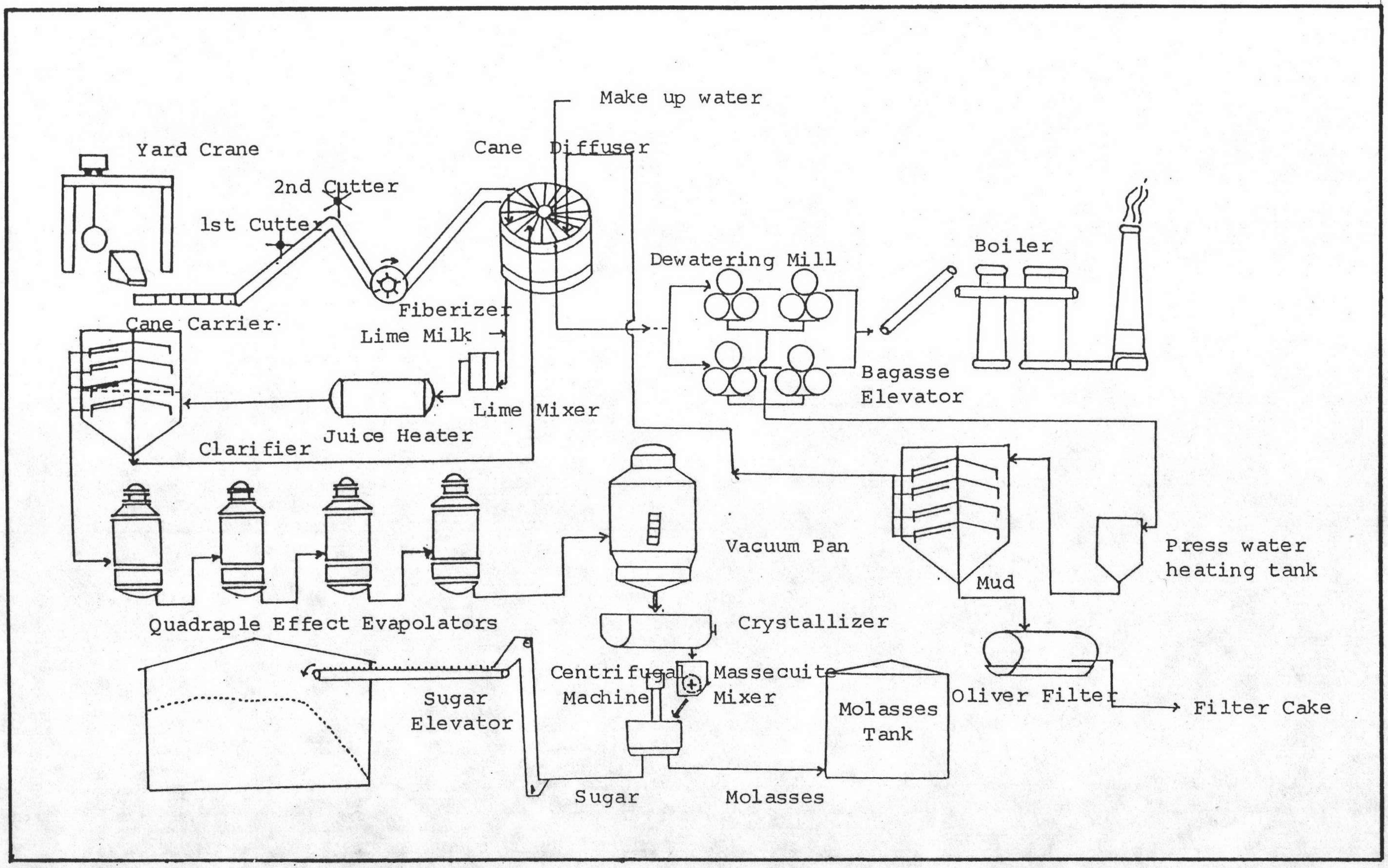


Figure 1.6 Cane sugar manufacture (Defication process)

fibrous residue or bagasse is usually used as fuel for boilers, although increasing amounts are being made into paper, insulating board, and hardboard as well as furfural, which is chemical intermediate for the synthesis of furan and tetrahydrofuran.

The cane juice is treated with lime to bring its pH to about 8.2 to prevent the inversion reaction, which is favored by heat and acid and would lower the yield of crystallizable sugar. The juice is then heat to facilitate the precipitation of impurities, which are removed by continuous filtration. (filter cake, filter mud)

After concentrated by multiple stage vacuum evaporation (usually four or five stages), the purified juice will be boiled to grain or seeded with sucrose crystals in a single-stage vacuum pan. Usually there successive crops of crystals are grown, cooled, and centrifuged. The final mother liquor, which is resistant to further crystallization, is called blackstrap molasses. It is used principally as a feed for cattle. Relatively small amounts are still fermented to produce industrial alcohol and rum.

The refining of raw sugar begins with dissolution of the molasses which remains as a thin film on the crystals in spite of the centrifugation. This step, called affination, brings the purify from about 98 to 99 %. The crystals are dissolved in hot water and percolated through bone char columns to remove color by adsorption. The sucrose is finally concentrated by vacuum evaporation, crystallized by seeding, centrifuged, and dried.

A major step forward has been the use of bone char in a continuous countercurrent manner (Grosvenor patent). The bone char is washed, dried, and burned to remove impurities, it is reused until it wears out mechanically and is discarded as fines. Even the fines have value as fertilizer because of their high calcium phosphate content.

In some plants, in place of bone char activated, vegetable charcoal is used. The fragility of this material requires the employment of filter presses rather than char columns. An activated char made from coal that is sufficiently strong to be used in columns has become available. Ion-exchange resins reduce the ash content of sugar solutions and thus increase sucrose recovery with a lowering of molasses production. They are employed to a limited but increasing extent.

1.3 The Utilization of Sugar Cane

Various parts of sugar cane have been used as Thai herbal medicine such as juice and stem are used as diuretic, expectorant, antitussive, and hang over; peels for marasmus, malnutrition; and bagasse as a drug for chronic ulcer (3).

In refined sugar industry, not only sugar which is the main product, but also by-products such as bagasses, filter cakes, and molasses are produced in large quantities. The commercial value of those by-products is indicated as well as the value upgrading that would result from further processing. Bagasses are used primarily as fuel for factories and for the manufacture of building boards and paper products (2). Molasses have various utilizations such as alcohol, citric acid,

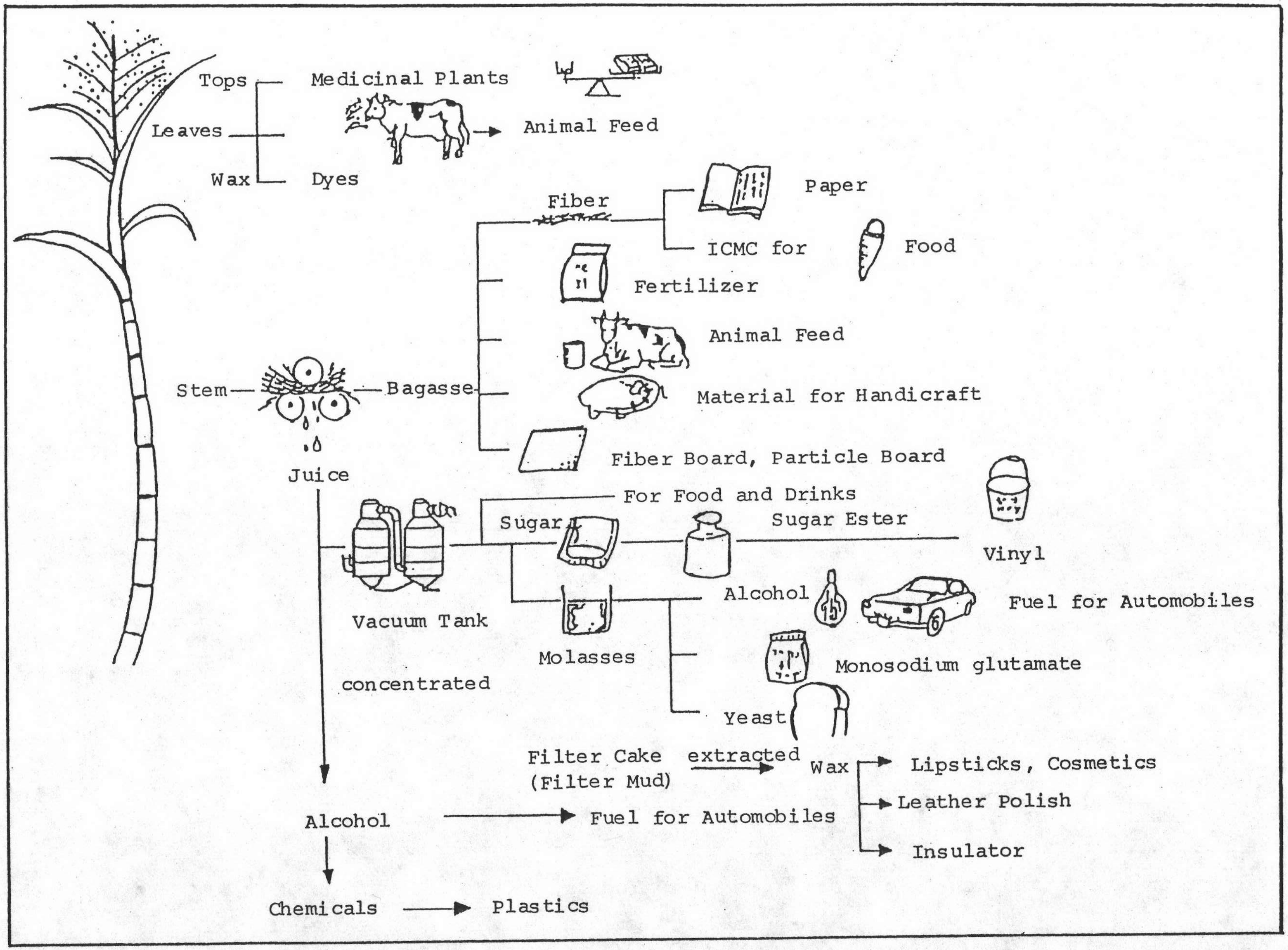


Figure 1.7 Total utilization of sugar cane

monosodium glutamate, and feed yeast. Filter cakes and cane tops are mostly returned to, or left in the field as fertilizer or soil conditioner. Moreover, wax separated from filter cakes is used in cosmetic and pharmaceutical industries (10). Nearly every part of sugar cane can be utilized. The total utilization of all parts of sugar cane is proposed in Fig. 1.7 (11).

1.4 **Sugar Cane Wax** (12)

Sugar cane wax occurs on the surface of the sugar cane stem. The wax of commerce is obtained as a by-product in the production of raw sugar. Much of the cuticular wax is carried into the juice stream in the cane crushing and washing operation along with the sugar, other cellular material, and dirt. Separated from the juice, the suspended materials including the wax are concentrated in a mudlike layer in the lower portion of the large clarifies, or filter cake. After the mud is filtered and washed for residual sugar, the wax is extracted from the filter cake with oils and resins by the use of solvents such as petroleum naphthas. Because of differences in the varieties of cane, the season, the flocculating treatments, the storage condition, and the age of the pressed cake, there are some wide variations in the character of different crude wax production. Some steps such as the use of fresh press cake to increase the uniformity of the crude wax are practical and both deoiling and deresinating can be carried out. The economic of the production of cane wax, however, is likely to be marginal when encountered by strong price competition from other hard waxes.

The first commercial development of cane wax probably was at Natal, South Africa during the first World War. Several million pounds of the wax were produced, and records indicated that as much as twelve million pounds were exported from Natal in 1924. Cane wax has been produced since then in different places at different times. Examination of the products, however, nearly always indicated that some of the changes had taken place that are to be expected if there has been prolonged atmospheric exposure and drying out of the press cake before extraction. In Cuba in 1946 and 1947 continuous feed liquid-liquid extractors were installed to operate on fresh press cake during the crushing season. They were used at two mills for several years, and the crude wax, containing about 33% of a fluid fraction and 17% resin, was refined at Gramercy, Louisiana, USA. A light colored hard wax and other products were produced through the 1950s. In the early 1960s, there was a substantial drop in price of carnauba wax and for this reason and on account of political developments the sale of the products was gradually discontinued.

1.5 The Study of Wax Extracted from Filter Cake in Thailand(10)

In 1975, Wasuvat and coworkers reported the extraction of sugar cane wax in filter mud from sugar factories and its use in (industrial) production of cosmetics and drugs. The result of this report was shown that cane wax was extracted from filter mud about 7 %. The lipstick production and coating tablet production using sugar cane wax extracted from filter mud were similar to the production produced from carnauba wax. The sugar cane wax was used as a component in producing gelatin capsules and their quality could be standardized to United States Pharmacopoeia (U.S.P.).

1.6 The Chemical Constituents of Sugar Cane and By-products

Some compounds in sugar cane and by-products from refined sugar industry are useful in industry and medicine in foreign countries. The literature survey of chemical constituents of sugar cane and by-products are shown in Table 1.2.

Table 1.2 The chemical constituents of sugar cane and by-products from sugar industry

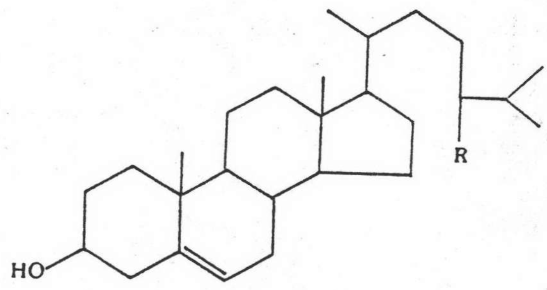
Plant Part	Type of Compound	Compound	Ref.
flower	flavonoids	5-O-methylapigenin, 5,7,3',4'-tetrahydroxy-6,3'-dimethoxyflavone	18
leaf	flavonoids	5,7-dimethylapigenin-4'-O-β-D-glucopyranoside	20
	acids	vitamin C, aconitic acid	3
	steroids and triterpenoids	β-sitosterol, stigmasterol campesterol	3
		4 -methyl-24-methylene-lophenol, α_1-sitosterol (24-ethylidene-lophenol)	25

Plant Part	Type of Compound	Compound	Ref.
root	enzymes	nitrogenase	25
juice	elements	Ca, K, Mg, P, S	25
	amino acids		25
	acids	mesaconic acid, fumaric acid, succinic acid, glycolic acid,malic acid, citric acid, oxalic acid, aconitic acid	25
peel	anthocyanins	peonidin-3-monogalactoside	19
	flavonoids	5,7-dimethylapigenin-4'-O-β-D-glucopyranoside	
leaf wax	sterols and triterpenoids	arundoin (fernenol methyl ether), sawamilletin (taraxerol methyl ether)	21
stem	amino acids		25
	carbohydrates	D-arabinose, D-xylose, D-fructose, D-galactose, D-glucose, sucrose,starch	25
	coumarins		25
	acids	mesaconic acid, succinic acid, citric acid, oxalic acid, fumalic acid,d-(+)-malic acid,aconitic acid, glycolic acid , p-hydroxybenzoic acid	25

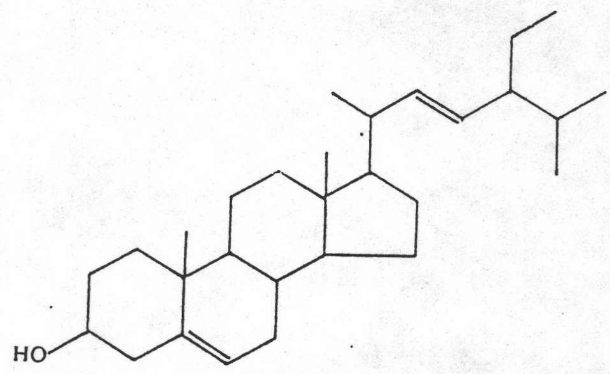
Plant Part	Type of Compound	Compound	Ref.
	enzymes		25
	lignins		25
	elements		25
	gum		25
	hemicelluloses		25
	celluloses		25
	waxes		25
	sterols and triterpenoids	campesterol, β-sitosterol, stigmasterol	25
	flavonoids	5,7-dimethoxyflavone 3"-O-β-D-glucoside, 7-hydroxy-5-methoxy-flavone 3"-O-β-D-galac-toside	25
mill syrup	flavonoids	tricin-7-(2"-rhamnosyl)-α-galacturonide, orientin-7,3'-dimethyl ether, swertisin, schaftoside, isoschaftoside, isoorientin-7,3'-dimethyl ether, tricin-7-glucoside	22
filter cake	phytosterols	β-sitosterol, campesterol, stigmasterol	23
	sterols and	α-saccharostanediol,	24

Plant Part	Type of Compound	Compound	Ref.
	sterol ketones	β-saccharostenone	
	acids	caproic acid, palmitic acid, arachidic acid, stearic acid, oleic acid,	25
		$C_{13}H_{27}COOH$-$C_{23}H_{47}COOH$ and	26
		$C_{29}H_{59}COOH$-$C_{35}H_{71}COOH$	
	alcohols	myricyl alcohol,	25
		$C_{24}H_{49}OH$-$C_{34}H_{69}OH$	27
	hydrocarbons	$C_{14}H_{30}$-$C_{37}H_{76}$	27
	aldehydes	$C_{22}H_{45}CHO$-$C_{36}H_{73}CHO$	28

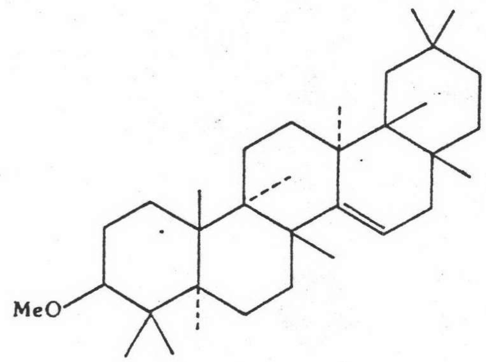
Recently, Kimura and Okuda reported that the non-sugar fraction of crude black sugar caused reduction of serum triglyceride, lipid peroxides, and insulin levels in rat (13). Further more, it was found that the non-sugar fraction of crude black sugar reduced the level of plasma insulin without elevating plasma glucose in the glucose tolerance test, suggesting that non-sugar fraction might inhibit absorption of glucose and fructose from small intestine (14). Sho reported that Okinawan sugar cane rind materials as well as black sugar showed effect on weight control and lowering serum cholesterol levels of rats (15,16,17). The significant effect of dietary fiber (sugar cane bagasse) on the bone metabolism of the diabetic rat was also observed and reported by the researchers of Tsukuba University, Japan.



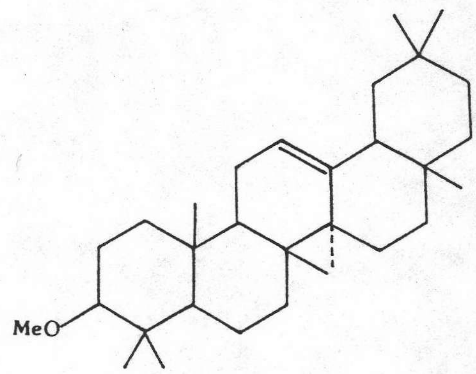
R=Et, β-sitosterol
R=Me, campesterol



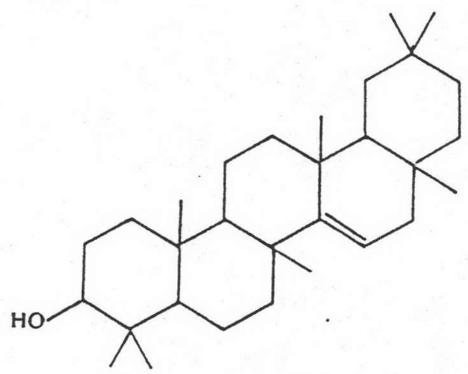
stigmasterol



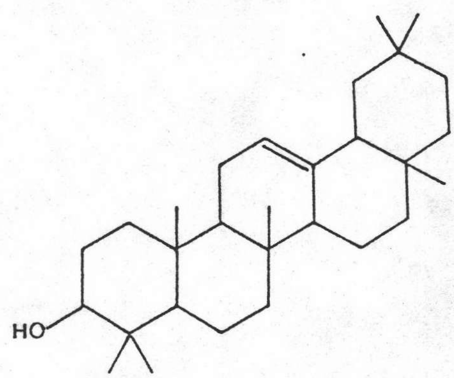
sawamilletin



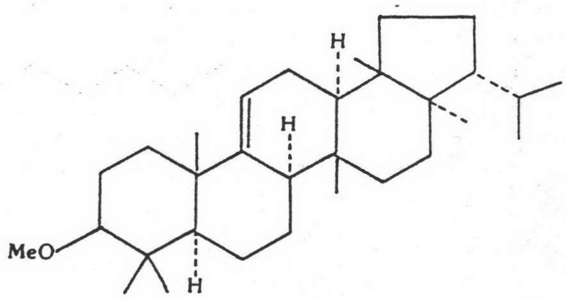
isosawamilletin



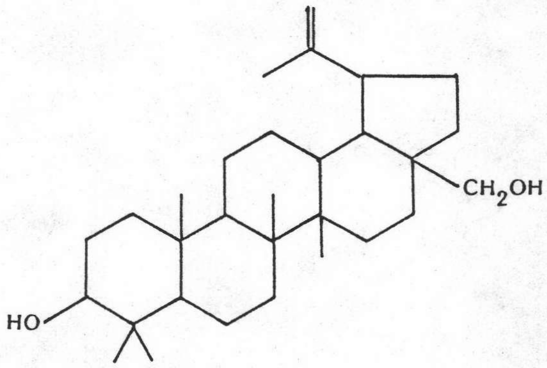
taraxerol



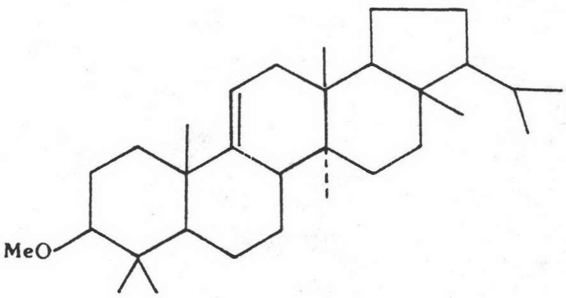
β-amyrin



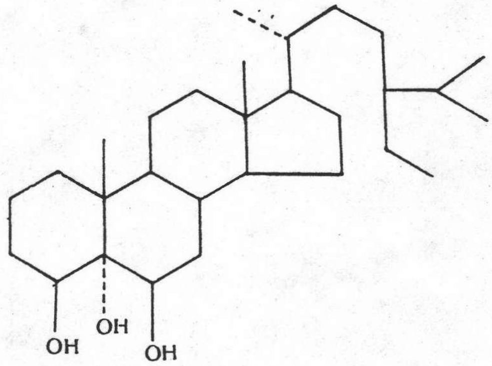
arundoin



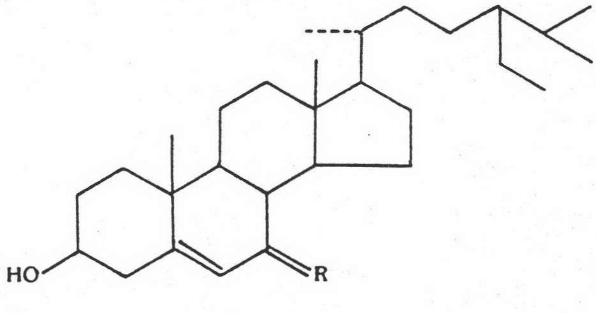
betulin



cylindrin

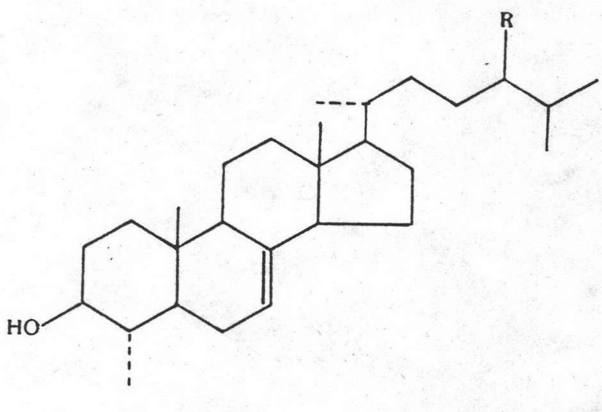


stigmastan-3β,5α,6β-triol



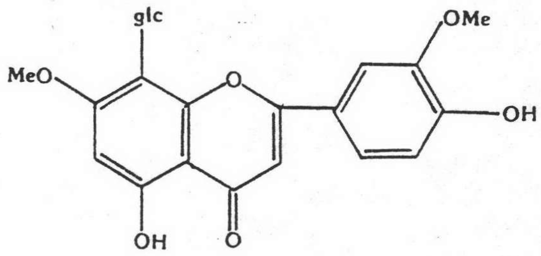
R=H, α-OH, ikshusterol

R=H, β-OH, epi-ikshusterol

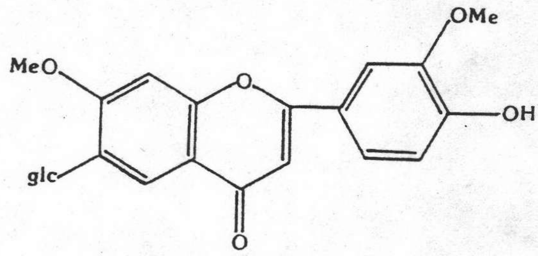


R=Me, 24-methyllophenol

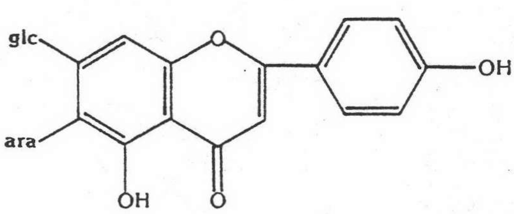
R=Et, 24-ethyllophenol



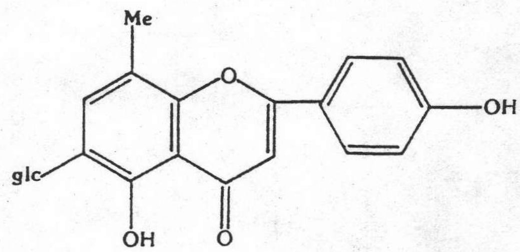
orientin-7,3'-dimethylether



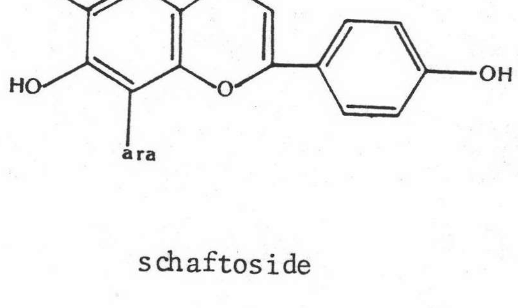
isoorientin-7,3'-dimethylether



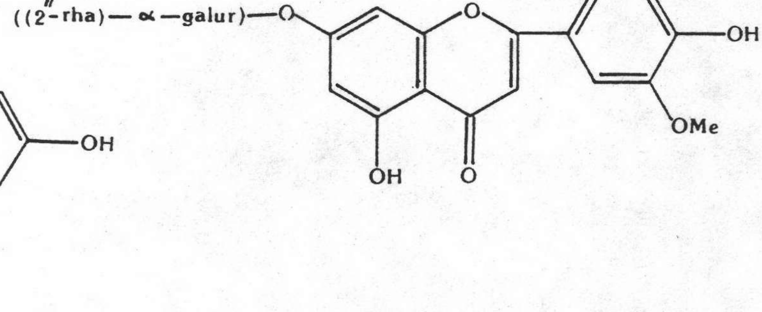
isoschaftoside



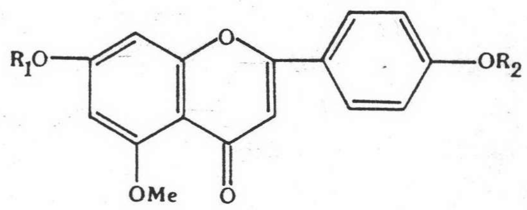
swertisin



schaftoside

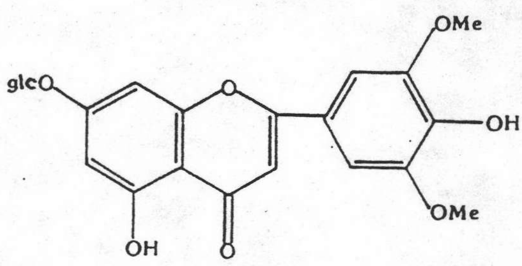


tricin-7-(2"-rhamnosyl)-
-α-galacturonide

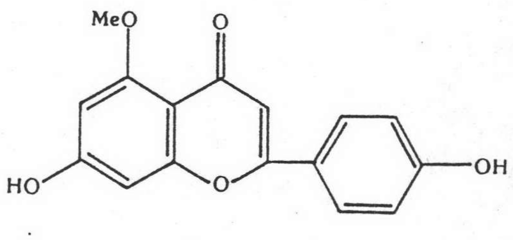


R_1=Me,R_2=glu, 5,7-dimethylapigenin-
-4'-O-β-D-glucopyranoside

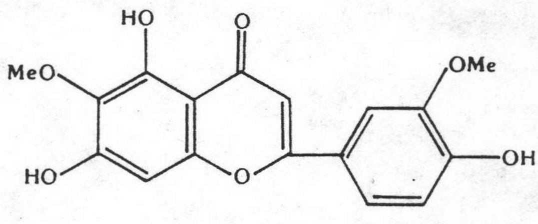
R_1=H,R_2=gal, 5-methylapigenin-
-4'-O-galactoside



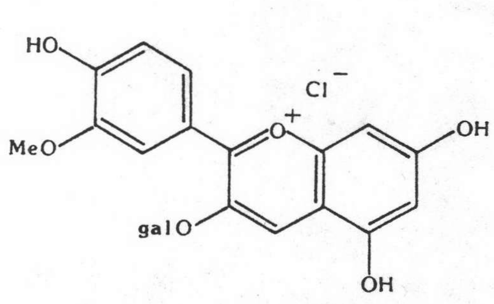
tricin-7-glucoside



5-O-methylapigenin



5,7,3',4'-tetrahydroxy-
-6,3'-dimethoxyflavone



peonidin-3-monogalactoside

1.7 The Goal of the Research

In Thailand, large amount of filter cake is left as the waste of refined sugar factories every year. Some compounds in filter cake and sugar cane rind are useful in industry and medicine in foreign countries. It is better to study the utilization of those economic compounds.

The goal of this research can be summarized as follows :

1. To extract and isolate the organic constituents from filter cake and sugar cane rind.

2. To elucidate the structural formulae of the isolated substances from filter cake and sugar cane rind.

3. To compare quantity of each compound isolated from filter cake from different factories and rind of different sugar cane varieties.

4. To propose the utilization of compounds isolated from filter cake and sugar cane.