Natural waxes: past, present and future

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Animal and plant waxes are increasing in popularity as a result of concern over the use of synthetic materials. Some natural waxes are in widespread commercial use, while others are used locally and some are still under development.

Introduction

Natural waxes are one of the categories of natural products that are regaining popularity because they can replace synthetic equivalents. Chemical raw materials are being re-evaluated for safety and impact on the environment and those proved to be unsafe, or even perceived to be unsafe, are being removed from the market. Chemists are now faced with the task of reformulating products as a result of these changes.

Some natural waxes have been used for centuries and others are only now being evaluated. They are important raw materials for the cosmetic, pharmaceutical and food industry and for shoe, automobile and furniture care products, candles, coatings, waxed paper and inks. They also have many technical applications, ranging from explosives to precision investment casting.

A wax is a material with properties between those of a fat and a resin. The oldest wax known to man is beeswax, and other materials with the physical characteristics of beeswax also became known as waxes. Later, chemists recognized that beeswax and carnauba wax consisted mainly of esters of long chain alcohols and acids and this allowed the introduction of a chemically based definition.

Table 1 is included here to give an overview of the large variety of natural waxes and their classification according to origin. To complete the picture, mineral and synthetic waxes have been included. The physical and chemical properties of the most important commercial natural waxes are listed in *Table 2*. This article will deal with the composition of waxes, and the present trends and prospects for various waxes.

Animal waxes

The skin and hair greases of many animals are waxes and their physiological functions are mainly protective, such as maintenance of water balance. The whale employs wax as an energy depot lipid, a function that is performed in other animals by triacylglycerols

Table 1: Classification of waxes according to origin.

Natural			
Animal	**Plant**	**Mineral**[1]	**Synthetic and semi-synthetic**[1]
Insect	**Palm Tree**	**Petroleum**	**Fischer-Tropsch**
Beeswaxes[1]	Carnauba[1]	Paraffin	
Ghedda (low acid value beeswax)[2]	Ouricury[2]	Microcrystalline	**Polyethylene**
Chinese insect[2]	Caranday[2]	Semi-microcrystalline	**Polypropylene**
Shellac[2]	Bamboo Leaf[2]		**Synthetic ester**[7]
	Columbian palm[2]		
Marine mammal	**Shrubs & cane**	**Lignite (Brown Coal)**	
Spermaceti[4]	Candelilla[1]		**Oxidized hydrocarbon**
	Sugar cane[2]	Montan and derivatives	
	Rice bran[1]		
	Retamo[2]		**Modified montan**
	Sweet sorghum[3]		
Marine invertebrates:	**Fruit**	**Earth**	**Polyethylene glycol (carbowaxes)**
Copepod[3]	Japan[1]	Ozocerites[6]	
	Bayberry[2]	Ceresines[6]	
	Orange[3]		
Land mammal	**Fibre and grass**		**Amide**
Woolwax (Lanolin)[1]	Esparto[2]	**Peat**	
	Flax[2]		**Chlorinated naphthalene (halowaxes)**
	Raffia[3]		
			Fatty acids and alcohols from natural sources
	Bark		**Synthetic fatty acids and alcohols**
	Douglas fir bark[5]		
	Seed		**Hydrogenated vegetable/animal oils and fats**
	Chinese tallow		
	Sunflower seed[3]		
			Castor
	Floral		Rice
	Jasmine[2]		Jojoba
	Rose[2]		Fish oils
	Lavender[2]		Tallows

[1] Commercial wax. [2] Locally used and/or limited amounts on world market. [3] In development phase. [4] No longer available, replaced by synthetics. [5] Commercialization failed. [6] No longer available, replaced by petroleum wax blends. [7] For example: synthetic spermaceti

Table 2. Physical properties of major commercial natural waxes.

Physical properties	Beeswax	Wool wax	Spermaceti	Candelilla	Carnauba	Rice bran	Sugar cane	Japan
Melting point	61–65°C	38–44°C	45–49°C	66–71°C	82.5–86°C	79–82°C	70–79°C	50–56°C
Flash point	>240°C	–	>240°C	>240°C	≥290°C	–	–	>195°C
Specific gravity at 25°C	0.95–0.960	0.93–0.945	0.94–0.946	0.982–0.983	0.996–0.998	–	0.972–0.999	0.975–0.984
Acid value	17–24	5–20	0–1.5	11–19	2–6	5–13	8–30	6–20
Saponification value	87–104	80–120	116–125	44–66	78–88	70–95	55–100	210–237
Ester value	70–80	70–80	116–125	40–47	45–85	60–90	25–90	200–225
Unsaponifiables	45–55%	39–51%	45–50%	47–62%	50–55%	50–60%	50–55%	2–4%
Iodine value	7–12	18–36	<3.0	19–44	7–14	5–15	13–30	4–15
Hydroxyl value	~15	23–53	~3.0	–	50–54	–	–	27–31

(triglycerides). Remarkably, the honey bee uses wax, of a different composition to its skin wax, as a building material.

Beeswax

Of the many insects which produce wax, that of only one genus of bee, *Apis*, is used in industry. More specifically, *Apis mellifera* produces the only 'genuine beeswax' recognized by the British Pharmacopoeia and US Pharmacopoeia. The waxes of local bee species (*Apis dorsata, A. florea* and *A. indica*) have much lower acid values and different chemical compositions and are in use in several Asian countries.

Beeswax was first put to use by the peoples of ancient China and Egypt. The ancient Egyptians used beeswax for cosmetics, pomades and for holding their curls and braids in place. They also used beeswax to impregnate papyrus scrolls, thus helping to preserve the earliest written communications. In 55 BC, when the Romans reached Britain, they found that beekeeping was already practiced there. In the first and second century AD, beeswax was sun-bleached and sometime later the Catholic Church designated white beeswax candles to be used in religious services. In 1876, A.I. Root devised a roller mill with an embossed cylinder which made it possible to produce starter combs for mass production.

In general, when a country has a developed agricultural programme beeswax is usually commercially available. The main exporting areas are Africa, North and South America, China, and Australia and New Zealand. Only about 35% of the total world beeswax is exported and most is re-used locally in starter comb foundations.

The USA imported approximately 3 million pounds (1360 tonnes) and had domestic production of about 7 million pounds (3175 tonnes) of beeswax in 1990 (1). In comparison Germany imported 4.5 million pounds (2040 tonnes) from 25 countries in 1990.

Advances in technology have made the chemical analysis of beeswax and other waxes routine. Our preferred method is gas chromatography which has proven to be a powerful quality-control tool. In addition, it allows races of bees to be distinguished by the waxes they produce (2). Chromatograms of waxes from *Apis mellifera ligustica*, the Italian or Domestic bee, (*Figure 1*) and *Apis mellifera scutellata*, the East African or Brazilian 'killer' bee, (*Figure 2*) illustrate this elegant technique.

The two chromatograms show small differences in the hydrocarbon and the ester fractions, and concentration and ratio differences for the components are used as the basis for distinguishing between the races of bees. Importantly, the method has given us a better understanding of which geographical origin of beeswax works best for each application. Minor components in beeswax are responsible for some of its special properties as an antimicrobial, antioxidant and for protection from sunlight (2).

In contrast to most other natural waxes, only beeswax can be refined to a white colour. Various chemical and absorption bleaching techniques are employed for this purpose. Sun-bleaching was discontinued in the late 1950's due to increased cost.

Currently the main uses of beeswax in order of importance are cosmetics, pharmaceuticals, candles, food and polishes. There are also many lesser applications.

Beeswax derivatives

Derivatives were developed to increase the application range of beeswax, mainly for the cosmetic market, but retaining as much as possible of the natural wax properties. For one

Reutich), the free fatty acids have been converted to polyglycerol esters giving this derivative new physical and chemical properties (amorphous solid with very low acid value).

Enhanced application potential is claimed for Cera Bellina in cosmetic emulsions, decorative cosmetics and anhydrous gel uses (3). In the case of other products, beeswax is transesterified with polyethyleneglycol sorbitol (for instance, the 'Atlas G1702-G1734' series from ICI) or transesterified with a polyethylene glycol (for instance, 'Apifil' from Gattefosse). This creates derivatives with higher hydrophilic–lipophilic balance (HLB) values. Improved application potential in cosmetic emulsions is claimed for these products (3).

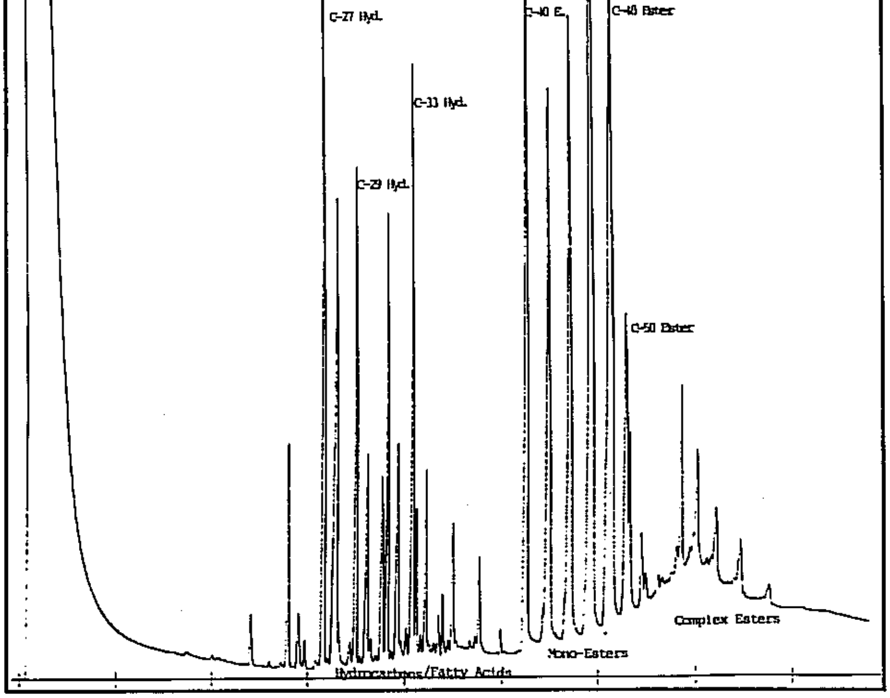

Figure 1: Gas chromatogram of domestic beeswax *Apis mellifera ligustica*.

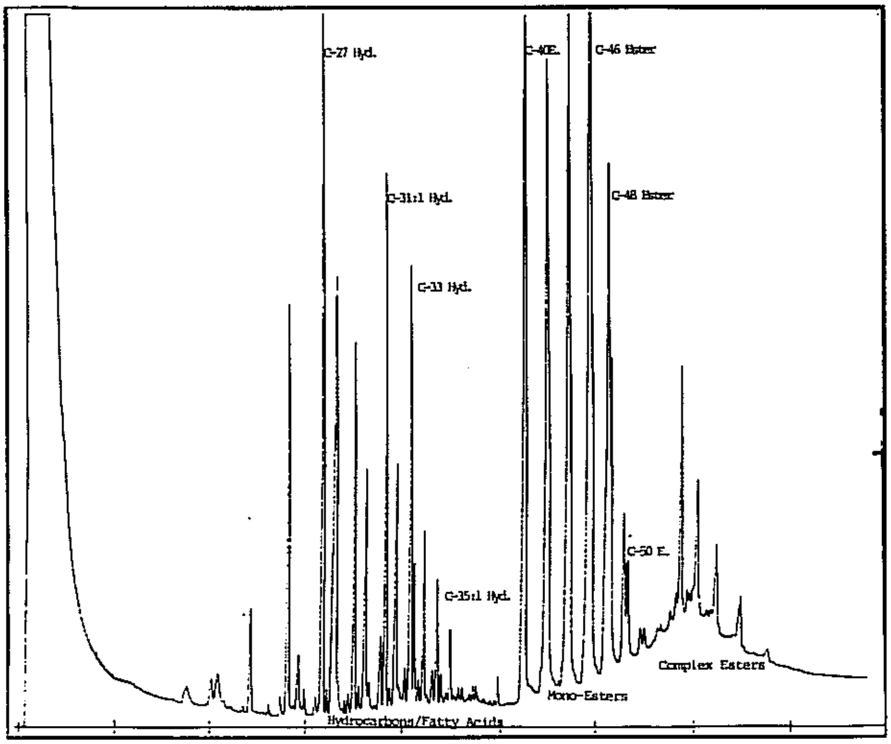

Figure 2: Gas chromatogram of African or Brazilian beeswax *Apis mellifera scutellata*.

Wool wax (lanolin)

Wool wax (wool fat or lanolin containing 25% water) is obtained as a by-product of washing sheep wool. The raw wool may contain as much as 25% wool grease. The Egyptians used this product in cosmetics 4000 years ago and it has been a commodity ever since, with average world production now at 40 million pounds (18 000 tonnes) a year. Its chemistry and toxicity have been extensively investigated.

The chromatogram (*Figure 3*) of anhydrous lanolin illustrates the major functional components: aliphatic monoesters (mainly branched and unsaturated or containing extra hydroxyl functions) 48–49%, sterol esters of cholesterol and isocholesterol 32–33%, lactones 6–7%, free triterpenoid alcohols 4–6%, free fatty acids 3–4% and free sterols 1%. The high content of sterol esters and the branched nature of the acids and alcohols are responsible for the special character of lanolin.

Among the natural waxes lanolin is special because of the truly remarkable number of derivatives prepared commercially. Derivatives of the whole wax are important, such as acetylated, hydrogenated and hydroxylated lanolin, and polyethylene glycol lanolins. Fractions of wool wax are also important and are obtained by physical and/or chemical separation steps and with or without subsequent derivatization. Examples are lanolin alcohols, acetylated lanolin alcohols, lanolin fatty acids, isopropyl lanolate and higher ester fractions.

Safety in use is essential to the future success of lanolin and there has been concern about the possible presence of pesticide residues. However, evidence has accumulated confirming that lanolin is safe.

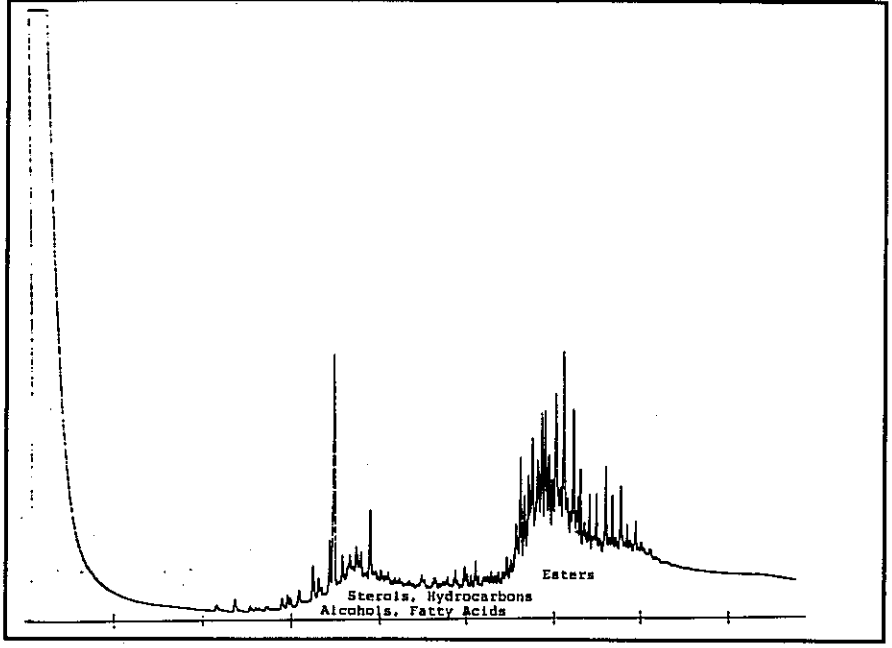

Figure 3: Gas chromatogram of lanolin.

Clark (4) has evaluated hypersensitivity and allergy cases related to lanolin products from many studies spanning over 50 years of testing and there are only minor incidents, from mild irritations to erythema, recorded.

Lanolin and its derivatives have made their way into a great range of products, to the extent of 2 billion pounds (900 tonnes) a year. They include ointment bases, skin care emollients, emulsifiers, stabilizers, plasticizers, solubilizers, texturizers, lubricants, conditioners, and agents for pigment wetting and dispersion.

Marine waxes

Waxes are a major constituent of many marine animals, from zooplankton to higher vertebrates. The harvesting of marine waxes from the sperm whale by people in settlements on the Alaskan coast goes back as far as 100–200 AD.

The marine organism most exploited is the sperm whale. An average whale would produce about three tonnes of oil and 230 kg of wax (spermaceti). Until protection of the sperm whale began in 1954, the Antarctic whaling industry had processed 66 000 tonnes of spermaceti. Today, commercially available synthetic spermaceti reproduces the major chemical and physical properties of the natural product (*Table 2*).

Synthetic spermaceti contains 98% monoesters, with the remainder being free fatty acids and alcohols. Cetyl palmitate represents 90–93% of the monoesters.

Spermaceti and its synthetic equivalents have applications in a variety of products including cosmetics, food, pharmaceuticals, soaps, textiles, lubricants, polishes, adhesives and printing inks.

Plant waxes

The leaves, fruit, bark and roots of plants all contain waxes, but it is the fatty substance (epicuticular wax) of the leaves and fruits which protect from dehydration and are of commercial importance. Carnauba wax and candelilla wax are primary products: in contrast, most newer plant waxes are secondary products from the refining of what would otherwise be waste materials. *Table 1* gives a breakdown of plant wax categories.

Candelilla wax

Candelilla wax is obtained from the surface coating of the succulent plant *Euphorbia antisyphylitica* and related species. This shrub grows from 0.5–1.5 m in height along the canyons and gorges of river banks. Mexico is the only true commercial source of the wax. Imports into the USA of candelilla wax amounted to 1.24 million pounds (560 tonnes) in 1990, an increase of 57% over 1989 and the highest level of import since 1982 (1).

Compared with other plant waxes candelilla has a high hydrocarbon content, as shown by *Figure 4*. The product is 50% paraffins (consisting of C29, C31 and C33 hydrocarbons), 30% esters, 12–14% free alcohols, sterols and neutral resins, and 7–9% free acids.

Candelilla wax has a long history of use in leather, furniture and other polishes, sealing wax, electrical insulators, paper sizing, inks, rubber, waterproofing, lubricants, adhesives, candles, explosives and cosmetics.

Carnauba wax

Among commercial natural waxes carnauba is the hardest and has the highest melting point; prime yellow No.1 (T1) is the most expensive. Brazil is the exclusive producer of carnauba wax, the source being a palm-like tree, *Copernicia cerifera*. The tree grows on dry ground that is subject to only periodic flooding. Imports of carnauba wax into the USA amounted to 6.18 million pounds (2800 tonnes) in 1990, down from the peak of 9 million pounds (4100 tonnes) in 1987 (1).

Another palm-like tree (*Attalea excelsa*) produces ouricury wax. Ouricury is similar in composition to carnauba (but with a somewhat lower melting point) and was used principally as a substitute for carnauba wax in certain applications. Due to high pricing, the consumption of ouricury has declined to less than 10 000 pounds (4.5 tonnes) a year in the USA (6).

High molecular weight esters and free fatty alcohols are the main functional components of carnauba wax (*Figure 5*). Esters with an average carbon chain length of 56 represent 80–85% of carnauba wax. Remarkable aspects of the composition include high free alcohol content, lack of hydrocarbons, resin content and the fact that many of the esters contain an aromatic ring.

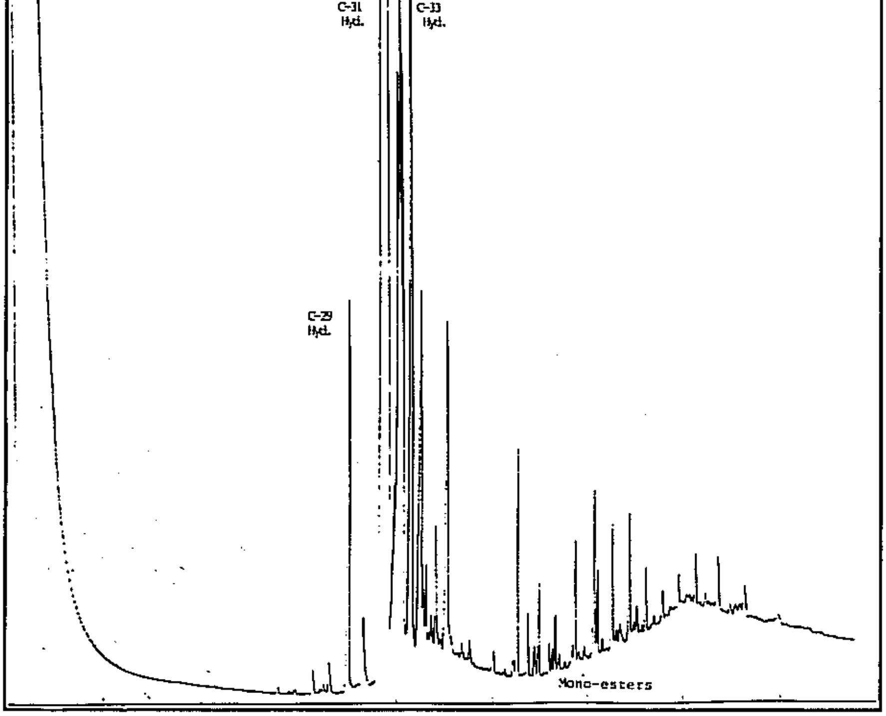

Figure 4: Gas chromatogram of candelilla wax.

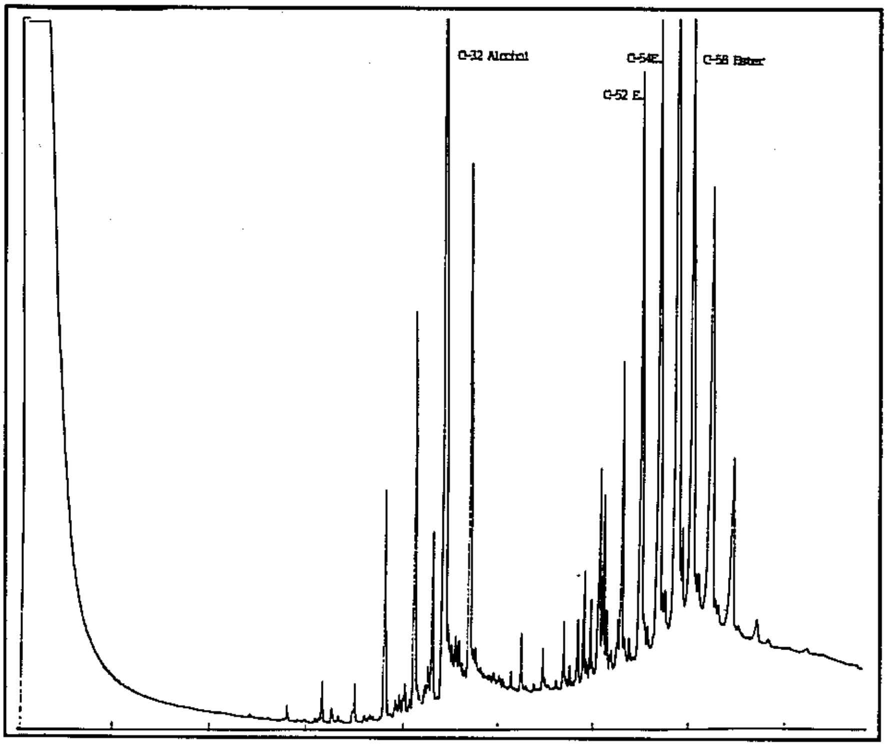

Figure 5: Gas chromatogram of carnauba wax No 1 yellow.

Several grades are available: prime yellow (T1), extra light fatty gray (T3) and fatty gray (T4). The prime yellow is an important ingredient in cosmetics and foods. The well-known disc-shaped chocolate candies owe much of their success to a thin layer of carnauba (T1). The other grades of carnauba (T3 and T4) are more important in terms of volume, are lower-priced and are extensively used in polishes for cars, floors, furniture and shoes, and for making carbon paper.

We have found many users of prime yellow carnauba (T1) changing to synthetic carnauba and wax blends due to price volatility.

Rice bran wax

Japan has been the principal rice-producing country manufacturing rice by-products.

edible oil to solid waxes and from vitamins to phospholipids. The initial waxy by-product of rice bran oil refining is a soft, pliable material consisting of two wax fractions. The most desirable is the hard saturated ester wax obtained by solvent extraction. The most abundant fraction is unsaturated ester wax which is usually hydrogenated to a product called rice wax.

Imports of rice products to the USA have increased many times over the last three years. The USA is itself a large producer of rice and is expected to produce commercially-available rice by-products in the near future. Other rice producing countries, notably India, may follow this trend.

Rice bran wax consists almost exclusively of saturated monoesters with a typical carbon chain length distribution of C46 to C60. It also contains small amounts of fatty acids, sitosterol and stigmasterol, squalene, tocopherol and trace amounts of phospholipids (*Figure 6*). This monoester distribution makes it intermediate between the ranges of the esters found in beeswax and carnauba. However, the low level of unsaturation (low iodine value) makes rice bran wax nearly as hard as carnauba, with almost the same melting point.

Rice bran wax has uses in food, fruit and vegetable coatings, polishes, carbon paper, lubricants and cosmetics.

Sugar cane wax

Sugar cane wax is a by-product of the manufacture of cane sugar. It is obtained by direct extraction of the cane, from raw juice and from filter waste (bagasse). Cuba is a major producer of this wax but since the trade embargo with the USA there is much greater use in the European market. The wax by-product has not been recovered in the USA because there it has been easier and less expensive to dispose of the unextracted material. However, the increased cost of waste disposal in the USA may soon cause a resurgence of this raw material. Other cane producers

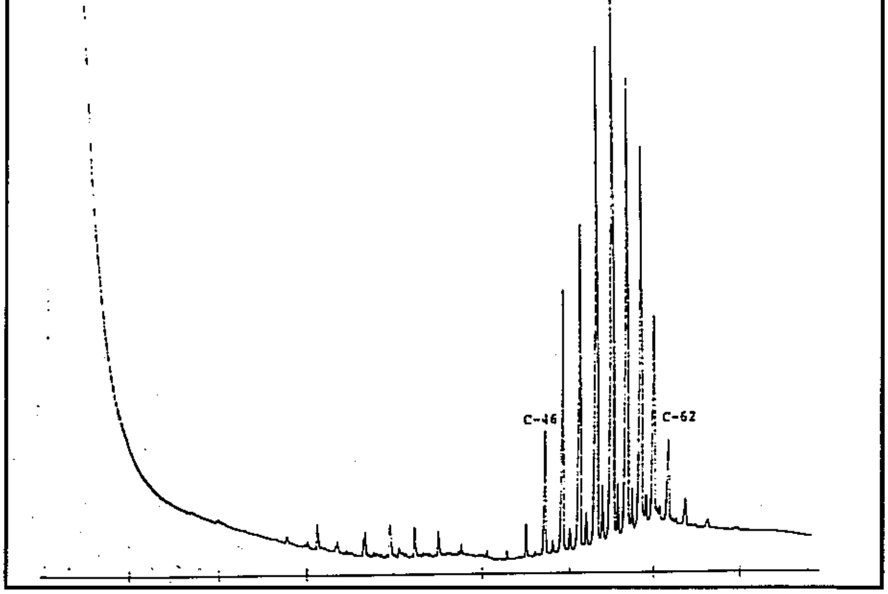

Figure 6: Gas chromatogram of rice bran wax.

and potential producers of wax are Africa, Argentina, Australia, Brazil, India and the Philippines.

The major functional components of sugar cane wax are esters (73%), fatty acids (15%), alcohols (7%) and hydrocarbons (3%). It also contains 2–3% stigmasterol and sitosterol. *Figure 7* shows a chromatogram of a hexane extract of the cane and filter waste (bagasse). The total extract contains approximately 20% resinous matter which is removed in a subsequent step.

The chemical and physical properties of cane wax are similar to those of other vegetable waxes. If this wax was fully commercialized, world production could far exceed that of any other vegetable wax. The uses of sugar cane wax would be similar to those of candelilla, carnauba and rice bran waxes, but until now sugar cane wax has been mainly used locally in carbon paper, candles and polishes for instance.

Fruit waxes

Fruits yielding wax can be divided into two categories: berries and large fleshy fruits. Examples of the berries are bayberry, raspberry and cranberry; those of large fruits are apples, pears, pineapples, grapefruit and orange. We will discuss Japan wax and orange wax as examples of the two categories.

Japan wax

Vegetable tallow may be a more correct term for Japan wax because it consists mainly of triacylglycerols (triglycerides). It is found between the kernel and the outer skin of the berries of the small sumac tree (genus *Rhus*). The tree grows in China, Indo-China, India and Japan.

Annual imports into the US market have been estimated at 10 000 pounds (4.5 tonnes) a year (6). This conflicts with a recent inquiry from a US company with an annual requirement of 50 tonnes. Apparently, companies are paying for a synthetic Japan wax thinking they are receiving a natural wax. The cost of the natural wax may exceed whereas the cost of the synthetic is approximately $1.50/pound ($3.30)/kg). The ease of synthesis is the reason that synthetic wax is supplied in place of natural Japan wax. Distinguishing between the natural product and a good synthetic wax can be difficult.

The chief chemical component of Japan wax is a triacylglycerol of palmitic acid and *Figure 8* shows the simple composition. The wax can be easily synthesized, with the exceptions of the di-acids and higher molecular weight alcohols. In our experience, a high percentage of the Japan wax being sold is really a synthetic equivalent. Japan wax is widely used in cosmetic stick pencils, candles, crayons, finishes for textiles and leather, pharmaceuticals and an assortment of industrial applications.

Orange wax

The rinds of oranges are a source of both oils and wax. Though oranges have been exploited for many years, and the by-products have long been used in food, fragrance and industrial applications, the rind products have been only partially exploited. D-limonene is a terpene obtained from the rind and can be used as a natural solvent.

The waxes had been discarded until Koster Keunen

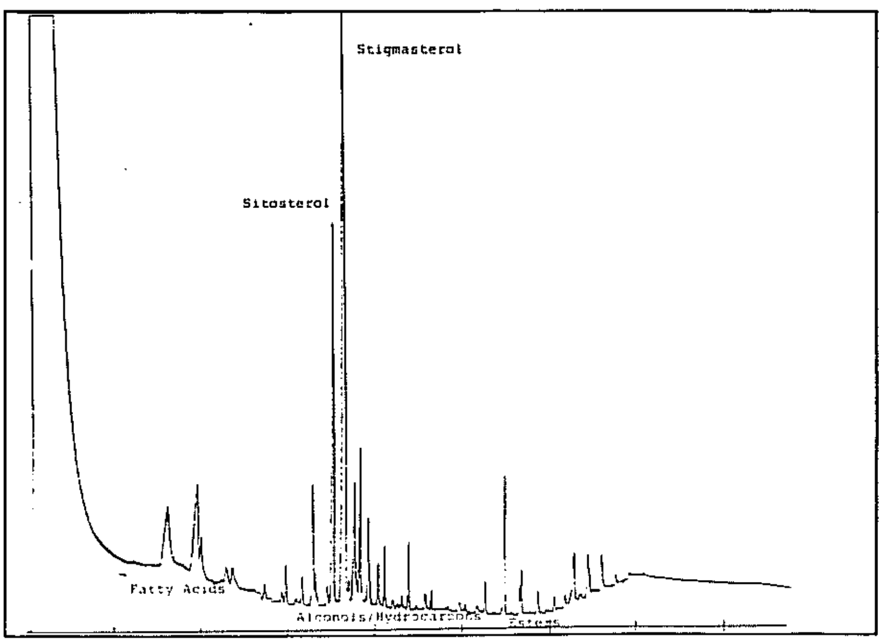

Figure 7: Gas chromatogram of sugar cane wax.

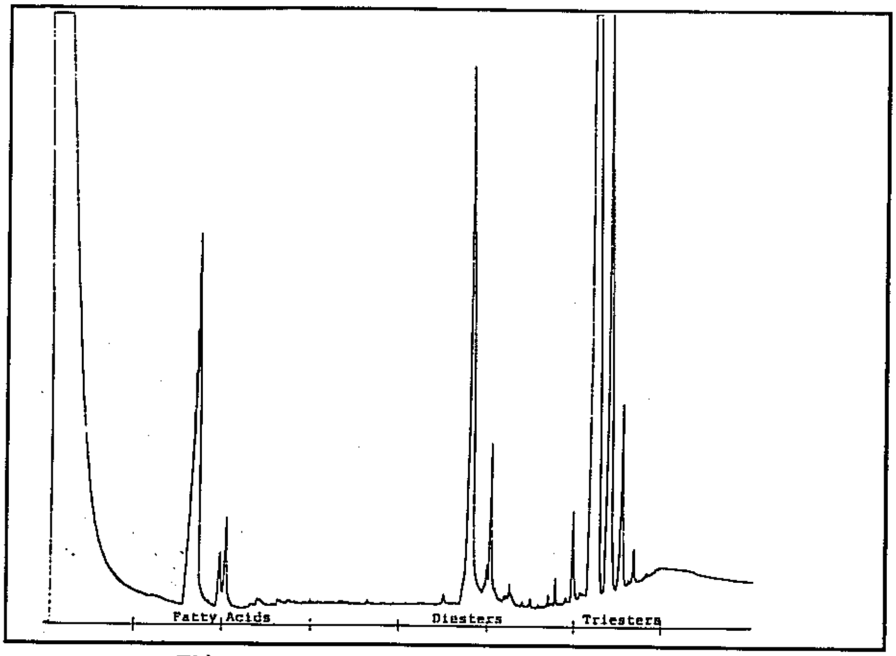

Figure 8: Gas chromatogram of Japan wax.

developed a process for the mild extraction of the wax while retaining the natural properties. The oil is easily separated from the wax using a cold-press, producing a semi-solid material with reddish-brown colour and characteristic odour for subsequent refining. The properties of orange wax are similar to those of lanolin.

Some typical chemical and physical properties of a semi-refined orange wax are: melting point of 38–47 °C, congealing point 38–45°C, acid value 8–20, saponification value 70–110, ester value about 80, iodine number approximately 115, hydroxyl value 50.

The major functional components, branched and unsaturated esters, alcohols, sterols, free fatty acids and hydrocarbons, are illustrated by a chromatogram of a semi-refined orange wax (*Figure 9*). With citrus products, a major concern is the presence of certain types of terpene, for example 5-methyl-psoralens which are phototoxic. However, when we analysed semi-refined orange wax by using gas chromatography–mass spectrometry, we did not find any photo-toxic compounds and only low concentrations of assorted terpenes.

Although available only on a pilot plant scale now, orange wax will soon become commercially available for use in such applications as creams lotions, makeups, shampoos, conditioners, anhydrous gels, lipsticks, surface-treated pigments, shaving creams and soaps.

Floral waxes

Floral waxes are by-products of the extraction of fragrance oils from flowers. The process leaves an insoluble wax residue with low odour and light colour. Typical flowers used for extraction are jasmine, rose and lavender. It takes an enormous mass of flowers to produce any sufficient quantities of these waxes; world production of jasmine wax is a few tonnes a year and the cost is approximately $130/kg. Jasmine wax is a semi-solid, yellow to tan in colour and has a mild characteristic odour.

When we examined a sample of 'Ester De Jasmin' wax from Creations Couleurs of France we found the major functional components to be unsaturated and branched triacylglycerols (60–65%), saturated hydrocarbons from C25 to C33 (15–25%) and free fatty acids (5–10%). We did not investigate the minor compounds, but a product of this type should be rich in antioxidants and bioactive compounds.

Jasmine wax is expensive and, as far as we are aware, it is only being marketed to the cosmetic industry, for applications such as make-up powders, lipsticks, creams, lotions and surface treatment of pigments.

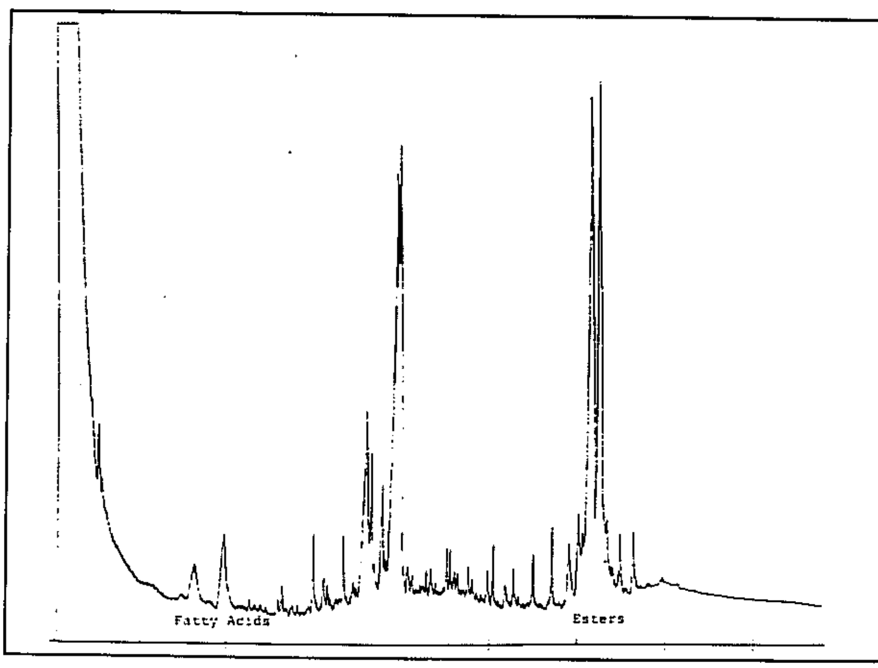

Figure 9: Gas chromatogram of orange wax.

Natural waxes are being used, despite their higher prices, to replace synthetic equivalents. Beeswax is being used in a larger number of natural consumer products and many all-natural cosmetics take advantage of its popularity. A large proportion of cosmetics formulas patented in Japan contain beeswax.

The use of lanolin is changing due to regulatory and social issues and this has stimulated a search for alternatives, preferably of plant origin. Nevertheless, the large quantities used mean there will be a demand for lanolin for many years yet. The special properties of lanolin derivatives and the diverse application range mean that substitutes and replacements may be difficult to produce.

Marine waxes and by-products obtained from aquaculture are materials with increasing potential uses. Some countries, such as Japan, have used aquaculture technology for hundreds of years and we expect food and chemical raw materials increasingly to come from a well-managed coastal eco-system. Aquaculture may prove to be more socially acceptable than simply using marine products from animal sources.

Plants are renewable and predictable sources of raw

ensure that it obtains supplies from more than one geographical region. For example, carnauba and candelilla waxes are each from one geographical region and the supply of carnauba is controlled by the government. Jojoba yields oil and, if hydrogenated, a wax. It is sourced from one geographical region, the south-west USA, and if weather patterns change the raw material supply is affected. A 'synthetic' version of jojoba wax from natural products is obtained when behenyl alcohol and behenic acid of plant origin are esterified to produce behenylbehenate.

The outlook is promising for relatively new waxes, such as rice bran and sugar cane waxes and developmental waxes like sweet sorghum, sunflower seed, orange wax and marine waxes, if they prove their value in competition, availability and applications. Rice bran and sugar cane waxes, and their blends with other natural waxes, may one day provide reliable alternatives to carnauba and candelilla.

Waxes such as orange wax will eventually replace lanolin in some applications. Grass waxes may be harvested as farmers realize the potential economic value. Coupled with current

will yield a wide array of waxes and raw materials that will contribute to society without unduly affecting the environment.

Acknowledgments

Special thanks are due to Fred Koster for his helpful discussions and to Bernadette Uzzi of Koster Keunen Inc in New York, USA, for the gas chromatograms.

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REPRINTED FROM LIPID TECHNOLOGY JULY/AUGUST 1992 ISSUE