NATURAL PRODUCTS AS SOURCES OF SPICES, DYES AND COSMETICS

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Contents

Summary

From early times, humans have learned to tame nature to extract important ingredients to address their basic needs, to express art and to cure their diseases. Egyptian Ebers Papyrus, Diocoride's manuscript Materia Medica, India Ayurveda, Chinese Traditional Medicine, Japanese Kampo and other traditional cultures and ancient manuscripts have all contributed to maintain and disseminate this primordial knowledge of the use of natural products. Much of this knowledge is still applied today. This chapter describes

the current uses of spices, natural dyes and natural ingredients for cosmetics, highlighting their sources and their historical aspects.

1. Spices

1.1. Introduction

The use of wild or human-cultivated spices has been reported since 50,000 BC. They were used for medicinal and food preservation purposes, but were also used in magic and religion. Today, spices are used mainly to promote flavor, color and taste in food, and they are present in nutritionally insignificant quantities. The essential oils present in the spices are responsible for their flavor due to the volatile constituents (mono-, di- and sesquiterpenes) of the essential oils. One of the most well-known spices is cinnamon, a bark of *Cinnamomum zeylanicum.*

Other well-known spices include mustard, black pepper and nutmeg, which are dried seeds of Brassicaceae family plants, *Piper nigrum* and *Myristica flagrans*. Roots and rhizomes are harvested for turmeric, ginger and garlic (*Curcuma longa, Zingiber officinale* and *Allium sativum,* respectively) and are used extensively as condiments around the world. Leaves, flowers and pods are widely used as spices, such as cloves (*Syzygium aromaticum*) and vanilla (*Vanilla* sp.).

A number of historical documents mention the use of spices by Egyptians long before the Ebers Papyrus (1550 BC) listed plants being used as medicines and for embalming, such as anise, mustard, saffron, cinnamon and cassia. Cinnamon and cassia are not native to Egypt; they are from southeastern Asia and China, which supported the existence of a spice trade over 3,500 years ago.

The spice trade increased in importance when Arabian merchants that traveled the Incense Route sold valuable spices to Greece from India, China, and southeastern Asia, using donkey caravans as transport. In Rome, the use of spices was not restricted to food and medicine; they were also used in lotions and perfumes.

For this reason, large amounts of gold and silver were traded for spices, which pushed the Romans to establish a direct trade route to India using the Red Sea, effectively breaking the Arab spice trade monopoly. This favored spice expansion around Europe. The decline of the Roman Empire facilitated the rise of the Goths, a tribe living near the Danube River that rose to power in 410 A.D. On that occasion, the Goths received gold, silver, silks, other valuables, and 3,000 pounds of pepper as ransom for the Romans' release.

During the Middle Ages, spices were among the most valuable products available in Europe, the most common being black pepper, cinnamon (and the cheaper alternative cassia), cumin, nutmeg, ginger and cloves. They were cultivated in Asia and Africa, which made them extremely expensive. From the 8th until the 15th century, after Marco Polo explored the exotic lands of Asia, the Republic of Venice (and the neighboring Italian city-states) monopolized the spice trade with the Middle East. The trade made

the region phenomenally rich; during the Venice domain, around 1,000 tons of pepper and 1,000 tons of the other common spices were imported from the East each year.

Figure 1. Picture of most common spices: 1) black pepper; 2) chili; 3) clove; 4) mustard; 5) bay leaf; 6) nutmeg; 7) cinnamon; 8) ginger; 9) saffron; 10)vanilla; 11) mint; 12) basil, 13) rosemary; 14) sage; 15) oregano. (Photo by LFY).

Starting around the 14th century, as a consequence of advances in ocean exploration, new sea routes from Europe to eastern Asia were discovered. In the 15th century, Vasco de Gama sailed around the Cape of Good Hope in Africa and reached Calicut in India, establishing a new route to Asia, thus overthrowing the Venetian monopoly. Finally, in 1492, Christopher Columbus discovered the New World during his challenge to map a shorter water route to find black pepper and cinnamon. Finally, in 1519, Spanish sailors discovered a water route to the Spice Islands (the Moluccas, near Indonesia), where cloves, nutmeg, mace, and pepper were produced. By the early 1800s, spice plantations were established in other locations around the world, ending the monopoly of spice trade. Currently, the spice market is still dominated by economically significant countries. The USA, the European Union and Japan lead the global spice trade, followed by Singapore, Saudi Arabia and Malaysia. The major spice suppliers are still China and India, but African countries, such as Madagascar and Indonesia, along with Vietnam, Brazil, Spain and Guatemala have contributed to addressing the spice demand.

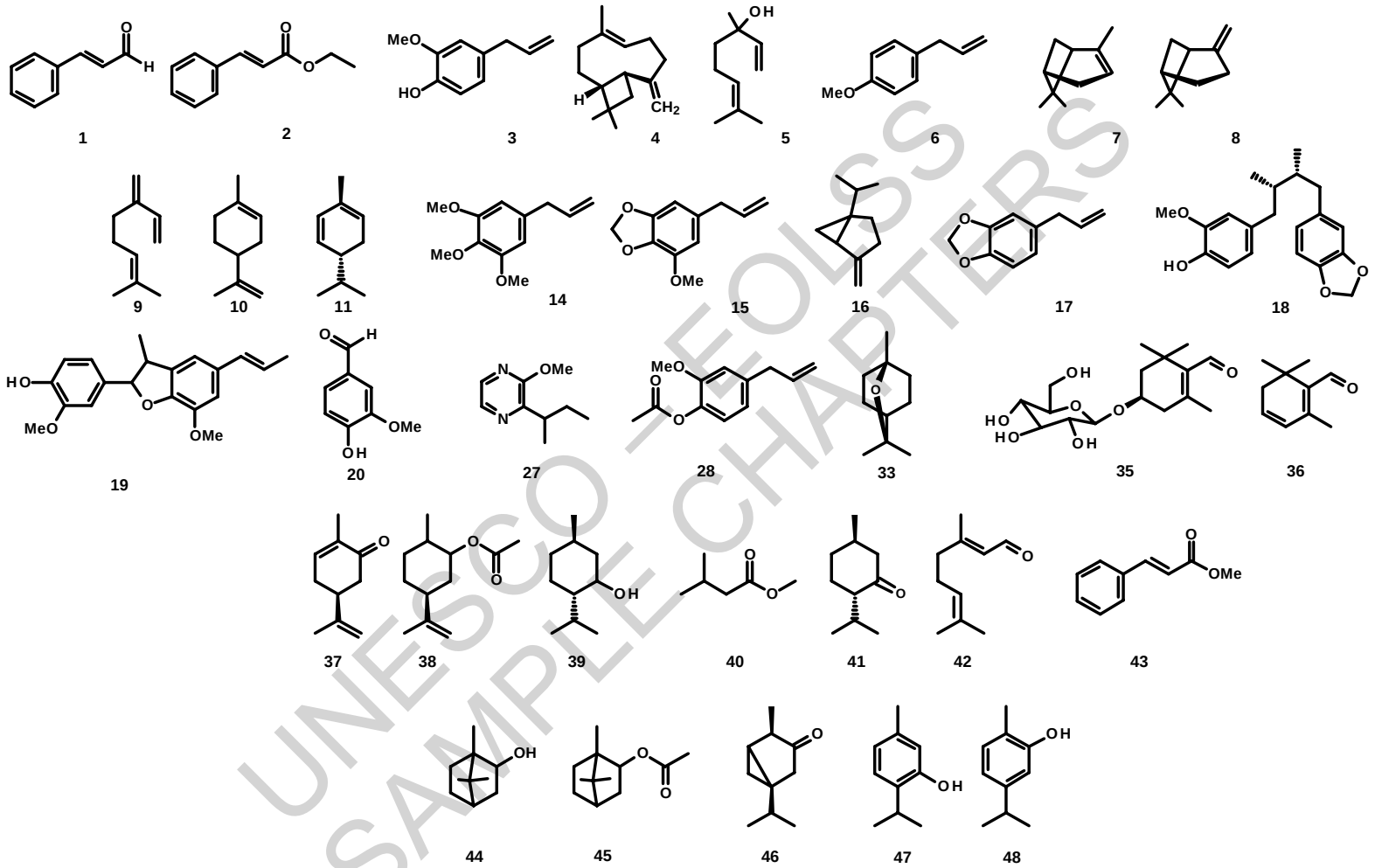

Figure 2. Chemical structures present in spices.

Spices have delighted the senses of humanity since early times, mostly because of their organoleptic characteristics. The presence of essential oils is responsible for their flavors, which are attributed to their volatile constituents (mono-, di- and sesquiterpenes). The characteristic tastes are promoted by the presence of other secondary products (amides, flavonoids, etc.) that, combined with the essential oils, give the spices their peculiar tastes and flavors.

The extraction of essential oil is performed using mostly steam distillation, but other extraction methods, such as enfleurage and solvent extraction, are also used. The secondary products are extracted using solvents and supercritical fluid extraction (SFE).

Major essential oil constituents are determined using chromatographic and spectroscopic analyses. The most common way to characterize essential oils is to use gas chromatography (GC) coupled with mass spectrometry (MS), which easily allows the separation and identification of the components. Moreover, comparison to the mass spectrometry profile library allows the unequivocal determination of the components of a compound. The advent of analysis methods, such as high performance liquid chromatography (HPLC), GC coupled to MS or nuclear magnetic resonance (NMR), has favored the rapid determination of secondary metabolites, enabling the purification and identification of major plant constituents.

1.2. Cinnamon

For centuries, cinnamon has pleasured the human senses with its unique aroma and warm taste. It is the dried bark of a tree from the Lauraceae family native to Ceylon (Sri Lanka). The use of *Cinnamomum zeylanicum* Blume (true cinnamon) (Figure 1) dates back to Chinese writings in 2800 B.C. Cinnamon derives from the Hebraic and Arabic term “amomon”, meaning fragrant spice plant; Italians called it canella, meaning "little tube."

Ancient Egyptians used cinnamon in their embalming process because of its pleasant odor and its preservative qualities. Cinnamon was also considered one of the most important medicinal spices for the treatment of colds and flu, along with digestive system problems. Even in the Bible, there are mentions that Moses used it as an ingredient in the famous anointing oils. Romans employed it in funerals and burned it to avoid the odor of a dead body. As for culinary purposes, the spice was also valued for meat preservation, due to its phenol contents that inhibit bacterial growth. The strong scent of cinnamon provided the aged meat with a reasonable aroma.

Today, cinnamon is considered to be a very popular spice. In the past, cinnamon was the most traded product, generating high profits to anyone who controlled its production or negotiation. The interest for trading was so elevated that in the 15th century, it led the Portuguese to find their way to Ceylon (around the southern tip of Africa). In fact, the search for new cinnamon sources was one of the reasons guiding the New World exploration in the 15th century. Cinnamon was affordable only to select people at that time, due to the high cost of ship voyages and the virtual monopoly on the overland trade route that was controlled by the Venetians. Soon, the Dutch wanted a share of the profits and by 1640, the Portuguese were deposed, and control of the cinnamon

monopoly had fallen into Dutch hands. In 1796, English control of the seas allowed them to take Ceylon from the Dutch.

By 1796, the production of cinnamon had spread to other areas, and the downfall of the cinnamon monopoly had begun. Today, cinnamon is cultivated in many places in the tropical regions, such as Java, Sumatra, Borneo, Mauritius, Réunion and Guyana. This has led to an abundant supply in a free market, making it affordable to most people.

Cinnamon's flavor is due to an aromatic essential oil that makes up 0.5% to 1% of its composition. This oil can be prepared by pounding the bark and distilling it over water. It is of a golden-yellow color, with the characteristic odor of cinnamon and a very hot aromatic taste. This characteristic compound that confers the taste and scent of cinnamon comes from cinnamaldehyde (1) (about 60 % of the bark oil); by reaction with oxygen as it ages, it darkens in color and develops resinous compounds. Other chemical components of the essential oil include ethyl cinnamate (2), eugenol (3) (found mostly in the leaves), β-caryophyllene (4), linalool (5), and methyl chavicol (6) (Figure 2).

1.3. Pepper

Pepper, the dried fruit of *Piper nigrum*, is one of the most commonly used spices (Figure 1). Its remarkable characteristics include a pungent and biting taste and an unmistakable aroma. Depending on harvest time and processing, peppercorns can be black (unripe dried seeds), white (the same as black pepper but unpeeled), green and red (unripe and mature seeds, respectively). Different types of peppers have different characteristics: white pepper has the strongest pungency, while green pepper has the weakest. Black and green peppercorns are more aromatic than white ones.

Pepper originated in Malabar, a region on the Western Coast of South India, and it has been cultivated for more than two thousand years. Pepper production spread around the tropical world, and new cultivars in Thailand, Vietnam, China and Sri Lanka were settled. In the 1930s, Brazil became an important (and the sole) producer in the Americas.

Black pepper is considered to be the king of spices; it has always been highly valued all over the world. Europe was introduced to pepper through Alexander the Great who, in the 4th century BC, established new trading routes with India. Right away, its popularity grew, as it figured as a highly commercially important item. Later, the pepper trade was monopolized by Arabs, who transported the spice through the Arab peninsula and Egypt to their European customers. The pepper reached the status of a fine gastronomic ingredient in the Early Middle Ages in Rome, when the Venetians solely controlled the trade with Arabs, as they monopolized the Indian production. This monopoly allowed only a few cooks in Europe to appreciate pepper at all; but when Europe stabilized economically in the 15th century, increasing demand for pepper led to the Age of Exploration. To bypass the Arabian and Venetian monopoly, Spanish and Portuguese sailors found alternative routes to India to obtain the spice directly from the producers. At that time, an ounce of fragrant black pepper could be as valuable as an ounce of gold. In 1487, Bartholomeu Diaz, a Portuguese explorer, discovered the passage around

Africa via the Cape of Good Hope, which provides a way to Asia. Eleven years later, that passage allowed Vasco de Gama to circumnavigate the Cape and continue the route to India, where he founded several Portuguese outposts and established permanent trade relations with local traders.

By the end of the 15th century, America was accidentally discovered when Christopher Columbus, an Italian who found support for his unconventional plans at the Spanish court, failed in his own quest for a route to the East Indies.

Today, India is still a leading producer, consumer and exporter of black pepper in the world. From 2005-06, 16,700 tons of black pepper products were exported to various countries, accounting for 6.0% of export earnings among spices.

The aroma of black pepper is due to the essential oil (3% of the product). The constituents of the essential oil can change according to the varieties and cultivars. The main compounds present are α-pinene (7), β-pinene (8), myrcene (9), limonene (10) and β-caryophyllene (4). White pepper does not have the same scent as black pepper because of the low essential oil content (1%), in which the major compounds are monoterpene hydrocarbons, such as limonene (10), β-pinene (8), α-pinene (7) and α-phellandrene (11) (Figure 2).

Amides, which are alkaloid-analog compounds, make up the pungent principles of peppers. Piperine (12) is the major compound, followed by azinane (piperidine) (13). The total content of piperine analogs in black pepper is about 5%. Pepper is commonly used as a condiment, and it is also important in the food industry, perfumery, traditional medicine and as an insecticide (Figure 3).

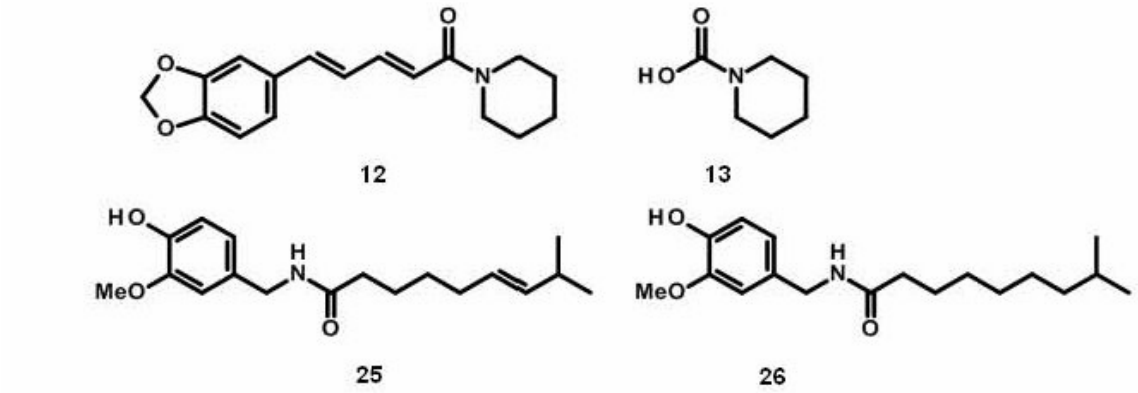

Figure 3. Chemical structures of pungent amides present in spices.

1.4. Mustard

From earlier times, mustard has been known by Europeans as a condiment and for its medicinal properties. Mustard seeds have been found in Stone Age settlements in the Northern hemisphere. One of the treasures found inside the Tutankhamun tomb was a large supply of mustard seeds. The Sumerian verjus, the juice from unripe grapes, was spiced with ground mustard paste, and it is mentioned in the Bible for use in cooking. The Europeans used mustard as a condiment before the introduction of the Asian spice

trade. Greeks used mustard to season meat and as a medicine. Pythagoras (570 to ca. 490 BC), a famous mathematician, prescribed mustard for scorpion stings. Hippocrates (460-377 BC), a pioneer physician, employed it in poultices for inflammations and toothaches, a use that has continued until recent times (as mustard plasters).

Mustard was not an everyday condiment in ancient Greece or Rome, though a recipe for mustard appears in Apicius, a collection of Roman cookery recipes from the late 4th or early 5th century. The recipe calls for a mixture of ground mustard, pepper, caraway, lovage, grilled coriander seeds, dill, celery, thyme, oregano, onion, honey, vinegar, fish stock, and oil.

The Romans introduced the mustard seed to Gaul, where it was cultivated by monks and became a popular condiment. The seeds were also mixed with crawfish powder to treat war wounds and to rub on lesions. In the 9th century, the French monasteries made significant earnings by selling mustard and becoming the hub of mustard production. In the 13th century, Dijon was considered the center of the world for mustard, even maintaining the famous Dijon mustard until today.

Mustard belongs to Brassicaceae family, and there are various types of mustard. The most common, white or yellow *Sinapsis alba* L., is native to the Mediterranean region. A brown variety from the Himalayan region (*Brassica juncea* L.) is not as frequently found as black mustard (*Brassica nigra* L.), which is hotter than the others. The seeds are used as condiments, but the leaves are consumed as a tasty vegetable (Figure 1).

Crushed mustard releases an enzyme, myrosinase, which hydrolyzes glucosinolates, cleaving off the glucose moiety to form isothiocyanate, the hot principle of mustard (Figure 4). Isothiocyanate is heat-labile, which requires attention in preparation. The use of cold water is recommended, and the pungency, which should be avoided when it is added to a dish during cooking, is reduced by heating.

In the USA, mustard is the second-most consumed spice, exceeded by black pepper. It was introduced by Benjamin Franklin when he returned from France to the USA after his activities as an ambassador in 1758. Today, mustard is cultivated in several parts of the USA and in Canada.

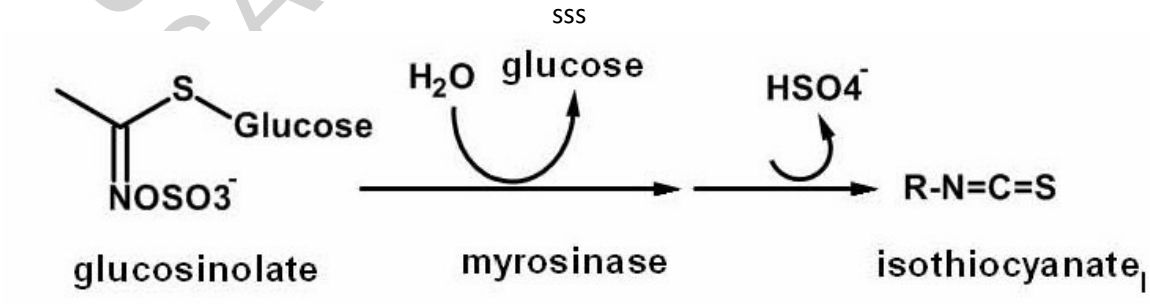

Figure 4. Scheme of isothiocyanate (pungent principle of mustard) formation from hydrolysis of glucosinolate.

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Biographical Sketches

Paolo Di Mascio: Dr. Paolo Di Mascio is full professor of biochemistry at São Paulo University, Brazil. His main research activities deal with various aspects of the chemistry and biochemistry of oxidatively generated and photo-induced damage to biomolecules. His research focuses on the chemical sources and the noxious behaviors of molecular oxygen/nitrogen-derived free radicals in biological systems. Studies have focused on identifying the mechanism by which singlet molecular oxygen and other reactive oxygen/nitrogen species play their physiological and pathological roles. He has devoted efforts to develop suitable singlet molecular oxygen generators based on the thermolysis of endoperoxides (e.g., the synthesis of the first water-soluble naphthalene endoperoxide, isotopically labeled as a source of singlet molecular oxygen-18). The application of sensitive and specific methods, using mass spectrometry with electrospray ionization/MALDI-ToF developed in his laboratory, allows for the study of reactive species reactions in biological media. His work aims to respond to the strong interest in the role of nutrition in the prevention and pathogenesis of cancer.

Lydia F. Yamaguchi: Dr. Lydia F. Yamaguchi finished her undergraduate degree in Pharmacy at the University of São Paulo, Brazil. Her PhD in Sciences was mentored under Prof. Paolo Di Mascio, in the Biochemistry Department of the Chemical Institute of the University of São Paulo. The theme of her PhD was the study of the biological activities of bioflavonoids from the Brazilian pine *Araucaria angustifolia*. The activities addressed included those as antioxidants, along with the singlet oxygen quencher and photoprotection capacities of these compounds. *Araucaria angustifolia* is endemic to South America and is an ancient Araucariaceae species that was endangered by the extensive logging process in the 30'. After completion of her PhD, she began a new approach as a postdoc, studying the biosynthesis of bioflavonoids in *A. angustifolia*, which is her current pursuit.