

True and common balsams

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Review

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Abstract: Balsams have been used since ancient times, due to their therapeutic and healing properties; in the perfume industry, they are used as fixatives, and in the cosmetics industry and in cookery, they are used as preservatives and aromatizers. They are generally defined as vegetable material with highly aromatic properties that supposedly have the ability to heal diseases, not only of the body, but also of the soul. When viewed according to this concept, many substances can be considered balsams. A more modern concept is based on its chemical composition and origin: a secretion or exudate of plants that contain cinnamic and benzoic acids, and their derivatives, in their composition. The most common naturally-occurring balsams (*i.e.* true balsams) are the Benzoin, Liquid Storax and the Balsams of Tolu and Peru. Many other aromatic exudates, such as Copaiba Oil and Canada Balsam, are wrongly called balsam. These usually belong to other classes of natural products, such as essential oils, resins and oleoresins. Despite the understanding of some plants, many plants are still called balsams. This article presents a chemical and pharmacological review of the most common balsams.

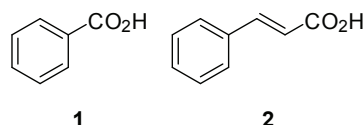
Introduction

The origin of the term balsam appears to go back to ancient civilizations, and the myth of an original, unique balsam called Egyptian Balsam, or Balsam of Judea. That time this balsam was already rare, a species difficult to cultivate. The first reference to this term is probably to be found in the biblical texts, where its fragrance and healing properties are described as unparalleled. (Genesis 37:25; Jeremiah 52:16). Arabic texts from the Medieval Era provide more details about this balsam, and the species from which it was extracted; a small tree of the Burseraceae family, called *Commiphora gileadense* (L.) C. Chr. (or *Commiphora opobalsamum*) (Alfonso-Goldfarb et al., 2010).

The alchemists introduced another ancient concept related to balsam; it was described as any substance, such as sulphur, that could act in the preservation of the dead body, avoiding putrefaction (Porto, 2008). These balsams were highly aromatic substances that contain, in their compositions, essential oils and resins spontaneously exuded by plants, water insoluble resinous and viscous liquids (Bährle-Rapp, 2007a; Wagner & Bladt, 1996). This definition has been commonly used to describe various groups of resinous substances, such as: Canada balsam, Copaiba balsam, Tolu balsam, Peru balsam, Gurjun balsam, balsam of Mecca, and balsam of Gilead (Cunha, 2005).

From a chemical perspective, the term balsam

is given only to exudates consisting mainly of benzoic (1) and cinnamic (2) acids and their respective esters and alcohol aromatic derivatives (Bruneton, 1995). They are mostly soluble, with a thick consistency (Liquid Storax and Peru balsam), that hardens, become thicker and solidify over time (Benzoin and Tolu balsam) (Robbers et al., 1996).



The preserving properties of balsams enable them to be used in the preservation of dead bodies, hence the term “embalming”. The ancient Egyptian used balsams to embalm and preserve the bodies from decaying, creating mummies. Since the balsams used were rare and expensive, this process was only used for Pharaohs and their immediate families. Different materials were used in this process, including bees’ wax, bitumen and resins of various species *Pistacia*, *Pinus*, *Abies*, *Cedrus*, *Boswellia* and *Commiphora* genus (Proefke et al., 1992; Koller et al., 2003; Buckley & Evershed, 2001, Colombini et al., 2000).

The first edition of the Official Brazilian Pharmacopoeia, published in 1929, already included some balsams, such as Copaiba balsam and Elemi balsam (Brandão et al., 2009). Both exudates are oleoresins and not real balsams, because they do not contain benzoic and

cinnamic acids in their composition.

The exudates that are often wrongly called balsams are usually oleoresins, and are composed only of terpenes, mono- and aromatic sesquiterpenes that solubilize the diterpenes and triterpenes. When the volatile terpenes evaporate, the residual part of the resin solidifies over time. Copaiba Oil, for example, is often called Copaiba balsam, but it is an oleoresin, due to its composition of sesquiterpene and diterpene acids (Veiga Jr & Pinto, 2002). Canada balsam is another oleoresin, which comes from a Pinaceae called *Abies balsamea*, in a clear reference to its aromatic mono- and sesquiterpenes (Lee et al., 1974). Oleoresins have been used as a varnish in paintings since ancient times, in various civilizations, such as the Persian, Indian, Chinese and Greek (Osete-Cortina & Doménech-Carbó, 2005). In the renaissance period, Copaiba Oil and Canada balsam were used by many artists, such as Cennino Cennini and Leonardo da Vinci, who described the process of varnish preparation, in which the resin was melted to obtain a clear liquid, and then poured into hot drying oil (Osete-Cortina & Doménech-Carbó, 2006).

The uncertainty as to what constitutes a true balsam, or which substances should be named as such, is not merely a matter of terminology, for which there is no clear definition. Another difficulty is the divergence between the names of the species that produce these substances, as in the case of the Cabreuva, Peru and Tolu balsams, all of which species belong to the *Myroxylon* genus. There is much confusion as to which species produces each balsam; whether they vary according to the different species, and whether they belong to different species, or to the same species but with different names or synonyms. A systematic study of the genus is clearly needed, to clarify each of these questions. The purpose of this article is to review the chemical composition and biological studies of the true balsam, and describe the exudates commonly known as balsams.

True balsams

Cabreuva balsam

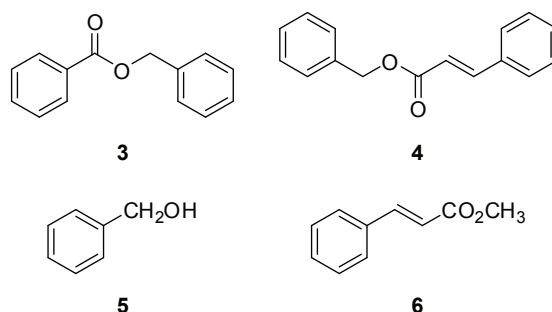
Myroxylon peruiferum L. f (synonyms *Myroxylon balsamum* (L.) Harms, *Toluifera peruifera* (L. f.) Bail) is a tree of the Fabaceae family, native to Brazil and other countries of South America. This species produces a balsam called Cabreuva balsam or Red Oil, which has been used for centuries by the native Indian peoples of Central America and Mexico to treat asthma, rheumatism, cold and external wounds, whilst the Amazon Indian use them to treat asthma, rheumatism, bronchitis, cold, tuberculosis, headaches and abscess (Lorenzi & Matos, 2008).

Morphological and histological studies of

the leaves and stem of *M. peruiferum*, showed the presence of the secretory canals and glands that are related to the physiological production of secretion of the plant. Different extraction methods are used to produce balsams of varied characteristics. In plants that have suffered injuries, a dark brown secretion can be observed, with a balsamic aroma. This secretion seems to be produced by injuries to the secondary bark shell, when it collects in sieved tube element (Akisue, 1971).

Phytochemical studies of this species are rare, although benzoic and cinnamic acids, vanillin, benzyl benzoate (**3**), benzyl cinnamate (**4**), nerolidol and benzyl alcohol (**5**) have been identified through specific chemical reactions (Akisue 1972a, 1977).

The volatile fraction of the balsam, obtained by hydrodistillation (4.5% yield), was fractionated in preparative thin-layer chromatographic plate to obtain benzoic acid, vanillin, benzyl benzoate, benzyl cinnamate, methyl cinnamate (**6**), nerolidol, farnesol and benzyl alcohol, identified through specific chemical reactions and compared to known patterns. In this study, the author observed similar physical constants to Tolu balsam (Akisue, 1972b, 1977).



The last-published study on this species (1979), analysis of the stem extracts was performed and eleven flavonoids were found, two of them new natural substances at the time: 2'-hydroxy-7,3',4'-trimethoxyflavone and 2'-hydroxy-7,3',4'-trimethoxyflavone (Maranduba et al., 1979).

Tolu balsam

Tolu balsam is obtained from *Myroxylon balsamum* (L.) Harms. var. *genuinum* Baill. (sin. *Toluifera balsamum* L., *Myroxylon toluiferum* H. B. et K.), a tree of the Fabaceae family, native to Colombia and Venezuela. It also grows in the Antilles, mainly in Cuba. The balsam is produced by making incisions in the bark of the tree, in the form of canals (Bährle-Rapp, 2007b). This balsam was included in the British Pharmacopoeia in 1820 with indication for the treatment of bronchitis, laryngitis, diarrhoea, and leucorrhoea, and as a food aromatizer. It is widely used as a lotion

to treat wounds, ulcers, and scabies, and in hair lotions and conditioners, anti-dandruff products, deodorants, soaps, creams, lotions, sprays, and tablets for common cold (Taylor, 1998; Bährle-Rapp, 2007b, Heinrich et al., 2008).

Tolu balsam presents approximately 70 to 80% resinous fraction, comprised mainly of cinnamic and benzoic esters of a resinous oil known as toluresinotanol ($C_{17}H_{18}O_5$). The balsam has 35% acids (20% free and 5% combined), with 12 to 15% cinnamic acid (**2**) and 8% benzoic acid (**1**). The volatile fraction (7.5%) is composed by benzyl cinnamate, benzyl benzoate, vanillin, farnesol and terpenes (Costa, 1994).

The hexane-soluble volatile fraction obtained by an ethanol solution from Tolu balsam has been shown to be the most aromatic fraction, with a mixture of terpenic and aromatic substances. These include benzoic and cinnamic acids, their alcohols and aldehydes, the ethyl, benzyl and cinnamyl esters, methyl cinnamate, styrene, eugenol, vanillin, benzyl ferulate or isoferulate, ferulic acid, and 1,2-diphenylethane were also identified (Wahlberg et al., 1971; Boelens et al., 1982). Sesquiterpenes such as α and β -bourbonene, cadalene, β -caryophyllene, α -copaene (**7**), and the triterpenes 20S-dammarenediol, hydroxyhopanone, oleanolic acid, sumaresinolic acid, 3-oxo-6 β -hydroxylean-12-en-28-oic acid, urs-12-en-3-on-28-al, and 20R,24 ξ 2-ocotillone were also identified (Wahlberg et al., 1971).

Since Tolu balsam is extracted by making a slit in the bark of the tree, some researchers have investigated both the bark and the stem, seeking to identify substances in these structures, and their possible role in producing the balsam. Research carried out on stem of *Myroxylon balsamum* resulted in a series of flavonoids that were biogenetically related in a series, including (\pm)-7-hidroxy-4'-methoxyisoflavone, (\pm)-7,3'-dihidroxy-4'-methoxyisoflavone, and 2-(2',4'-dihidroxyphenyl)-5,6-dimethoxybenzofuran (Oliveira et al., 1978). Cabreuvin, the terpenes farnesol, nerolidol, α and β -pinene, carvone, geraniol, menthol, citronellal, linalool; and the phenylpropanoids cinnamaldehyde (**8**), eugenol and safrole were isolated from the hexane fraction, obtained from an ethanol extract of the bark (Naves, 1949; Gottlieb & Magalhães, 1959; Harborne et al., 1963; Cheng et al., 1996 and Simas et al., 2004).

Some of these substances were also observed in the balsam by the two authors previously cited, such as α and β -pinene and cinnamaldehyde, observed by Wahlberg et al. (1971); and farnesol and eugenol, observed by Boelens et al. (1982). Other substances such as 1(5),6-guaiadiene and five derivatives aromadendene 1-*epi*- α -gurjunene, 1,2-didehydroaromadendrane, 9,10-didehydro aromadendene, 1(5),3-aromadendradiene and 1(10),4-aromadendene were also observed in Tolu

balsam (Friedel & Matusch, 1987a, 1987b).

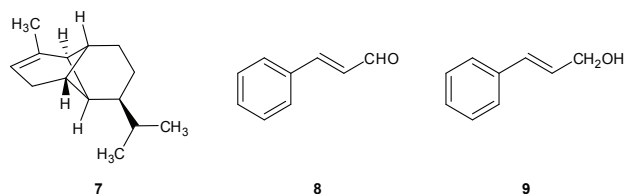
Tolu balsam is a well-known sun block agent that presents a good sun protection factor (FPS) when compared with aminobenzoic acid (El-Shaer, 2006). In addition, the *Myroxylon balsamum* hexane extract showed good activity against multi-resistant bacteria, revealing a very important medicinal usage, as well as methicillin-resistant *Staphylococcus aureus* and *Pseudomonas aeruginosa*. Bioassay-guided fractionation of its hexane extract led to the identification of the chalcone isoliquiritigenin, an antimicrobial compound (Machado et al., 2005).

Peru balsam

Myroxylon pereirae Klotzsch. (sin. *Myroxylon balsamum* (L.) Harms. var. *pereirae* (Royle) Baill., *Myrospermum sonsonatense* Per.) is a native Fabaceae of Central America. This species produces a balsam called Peru balsam-so-named because one of the first places it was sold was at Galahao Port in Peru (Robbers et al., 1996). The leaves and stem have been used by the Indian tribes of Mexico and Central America for the treatment of asthma, catarrh, rheumatism and external wounds (Taylor, 1998).

Peru balsam has a very complex composition, but with some differences from Tolu balsam (Chart 1). Of the hydrocarbons, only styrene and stilbene were observed, and only one sesquiterpene, δ -cadinene. Other substances such as benzyl alcohol, cinnamyl alcohol (**9**), elemol, vanillin, farnesol, (+)-nerolidol, previously called peruvial, and benzoic and cinnamic acids, have also been identified in its composition (Boelens et al., 1982). A resinous substance called peruresinotanol ($C_{18}H_{20}O_5$) was observed, both free and in the form of esters from the benzoic and cinnamic acids, these being the main constituents of the resinous fraction (28%) (Costa, 1994).

Peru balsam has been widely studied as an allergenic agent in many areas, and its substances are found in many products used by humans, including food and hygiene products, like soaps, deodorants, perfumes and others. Research on systemic contact dermatitis has shown that almost half of those who had positive results in the epicutaneous tests for Peru balsam and a mixture of fragrances, which followed a diet on reduction of Peru balsam, saw a complete healing of their dermatitis (Salam & Fowler, 2001). Other Studies used Peru balsam as an allergenic agent, comparing it with other products such as vegetal extract, perfumes, deodorants, and shaving lotions, to observe the frequency of the sensitization (Schnuch et al., 2004; Tanaka et al., 2004; Avalos-Peralta et al., 2005; Paulsen & Andersen 2005; Uter et al., 2007). Farnesol, a substance present in this balsam, showed a high percentage of contact allergies (Schnuch et al. 2004).



Benzoins

Benzoins have been used since ancient times by the Romans, the Egyptians and the Phoenicians for the treatment of respiratory infections, due to their antiseptic and expectorant properties (Modugno et al., 2006). Nowadays, they are used in perfumes, as fixatives, and as preservatives and aromatizers in food and cosmetics, due to their antioxidant and organoleptic properties (Castel et al., 2006, Fernandez et al. 2006).

Benzoins can be divided in two groups; those that contain cinnamic acid (Sumatra Benzoin and Penang Benzoin), and those that do not contain this acid (Benzoin of Siam and Benzoin of Palembang) (Costa, 1994). The Siam and Sumatra Benzoins are produced by species of the *Styracaceae* family, and represent the main categories of commercially available balsams (Hovaneissian et al., 2008).

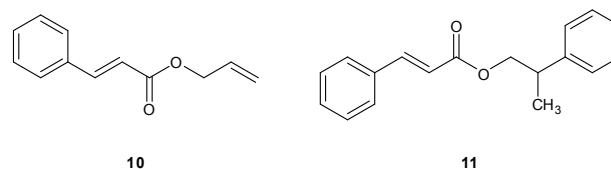
The Siam Benzoin or Siam balsam is obtained from *Styrax tokinensis*, a native species of Indochina. Related to this benzoin are the species *Styrax benzoides* and *Styrax finlaysonianum*, both from Thailand. *Styrax benzoin* and *S. paralleloneurum*, species found in Java, Sumatra and Borneo, produce the Sumatra Benzoin (Robbers et al., 1996).

There are other species of *Styrax* present in the Americas that are also used in the preparations of benzoins, for example *Styrax pearcei* var. *bolivianum*, which produces the Bolivia Benzoin and *Styrax aureum*, which produces the Bogota Storaque. The specie *Styrax officinale*, found in the Mediterranean and the Middle East, produces Solid Storaque, a balsam commonly used in the production of perfumes (Costa, 1994).

Benzoins are considered a pathologic secretion, and are produced by squizogenous cavities originated in the bark incision of the species of *Styrax* from many regions (Hovaneissian et al., 2008). It is necessary to make very deep incisions to obtain the benzoin from the innermost part of the stem. The balsam that forms tears-called high degree balsam-is collected separately, while the material obtained in the end as craps, next to the stem, is considered of lower quality (Costa, 1994).

The Siam Benzoin contains coniferyl benzoate (60 to 70%), 10 to 15% of *p*-coumaryl benzoate, 0.5 to 6% cinnamyl cinnamate, with lower proportions of free benzoic acid (10%), as well as the triterpene siasinol (6%)

and vanillin. The Sumatra Benzoin, obtained from *Styrax benzoin*, is composed of the free cinnamic acid (10%) and benzoic acid (6%), and their esters derivatives. Triterpenes, such as 19-hydroxyoleanolic and 6-hydroxyoleanolic acids, and other substances in lower quantities, such as the myristic acid, styrene, benzyl alcohol, cinnamyl alcohol, vanillin, propyl cinnamate (**10**) 3-phenylpropyl cinnamate (**11**), cinnamyl cinnamate and phenylethylene were also observed in its composition (Robbers et al., 1996; Schroeder, 1968).



In the Siam and Sumatra Benzoins, it was observed that coniferyl benzoate was an excellent biomarker fluorescent of Siam Benzoin. Other substances were identified in this balsam, such as benzoic acid, isovanillin, lubanol benzoate, and *p*-coumaryl benzoate (Hovaneissian et al., 2008). These authors observed the absence of free cinnamic acid, as previously reported by Schroeder (1968) and Costa (1994); a different observation from that Boelens et al. (1982) made in this balsam. In Sumatra Benzoin, the presence of styrene, isovanillin, high quantity of cinnamic acid, *p*-coumaryl cinnamate, and traces of benzoic acid and *p*-coumaryl benzoate were observed (Hovaneissian et al., 2008).

As the benzoins are produced by the stem, studies have been carried out on species of *Styrax* with the purpose of identifying other substances present in this species that can be related to benzoins. Triterpenes isolated from the bark of the stem of *Styrax japonica* were identified as 3 β -acetoxy-28-hydroxyolean-12-en, 3 β -acetoxyolean-12-en-28-oic acid, 3 β -acetoxyolean-12-en-28-aldehyde, 3 β -acetoxy-17 β -hidroxy-28-norolean-12-en and taraxerol, together with stigmasterol, through spectroscopic techniques such as RMN 2D. The inhibitory activity of the protein tyrosine phosphate 1B (PTP1B) of the isolated substances was determined *in vitro*. Among the isolated substances, the acid 3 β -acetoxyolean-12-en-28-oic acid and the 3 β -acetoxyolean-12-en-28-aldehyde presented more powerful activity in relation to PTP1B, with IC₅₀ of 7.8 and 9.3 μ M, respectively (Kwon et al. 2008).

Benzoin tincture is also an allergenic of contact. In a study involving 447 patients, 45 showed positive reactions, whilst only fourteen had severe positive reactions to the tincture (Scardamaglia et al., 2003).

Liquid Storaque

Liquid Storaque is obtained from the arboreal species *Liquidambar orientalis* Mill., Altingiaceae, native to the forest regions of the Middle East and Turkey and extending to northeastern Syria. It is known that the balsam is produced by secretory structures of secondary origin formed internally in the young stem, as a result of the incision made in the plant. The balsam accumulates between the bark and the internal part of the stem, and is extracted by peeling the external part of the bark, several days after the incision is made. This material is put in boiling water, squeezed, and the fluid removed, in order to separate the Liquid Storaque. It was also obtained by the extraction of the bark with benzene, after making the incision (Costa, 1994).

The composition of Liquid Storaque includes a high quantity of cinnamic acid (17 a 23%), combined in the form of esters (24 to 25%), hydrocarbons, benzenoids, mono- and sesquiterpenes, alcohol, carbonyl substances, carboxylic acids, including benzoic acid, many esters and some phenolic skeleton (Boelens et al., 1982; Costa, 1994).

Another study was carried out with a volatile fraction of the American Storaque (*L. styraciflua*), from Honduras and the Asian Storaque (*L. orientalis* Mill.), from Turkey. The volatile fraction was obtained by hydrodistillation using a Clevenger device (4 h) with a yield of 0.6% (Asian Storaque) to 0.8% (American Storaque). The GC-MS analysis showed that the oil of the Asian Storaque presented six esters (0.6%), eleven monoterpenes (26.1%) and seventeen sesquiterpenes (0.6%), while the American oil presented eight esters (0.8%), twelve monoterpenes (26.4%) and sixteen sesquiterpenes (29.9%). Despite their similar chemical compositions, significant differences were found in relation to the percentage of the major components. Styrene is the major component in both oils, but it is more abundant in the Asian Storaque (70.4%) than in the American one (30.9%). On the other hand, β -caryophyllene is more abundant in the American Storaque (20.2%) together with α -pinene (19.6%), than in the Asian Storaque (0.2%) (Fernandez et al., 2005). Some of the substances identified by Fernandez et al. (2005) were also observed by Boelens et al. (1982) in the same balsam, such as the styrene, *p*-cymene, limonene, terpinolene, cinnamyl alcohol, α -cubebene, and other substances in minor quantities.

Studies carried out on the balsam of *Liquidambar orientalis* Mill. (Liquid Storaque) to investigate its antibacterial activity related to the *Aeromonas hydrophila*, *Bacillus amyloliquefaciens*, *B. brevis*, *B. cereus*, *B. megaterium*, *B. subtilis*, *Corynebacterium xerosis*, *Enterobacter aerogenes*, *Enterococcus faecalis*, *Escherichia coli*, *E. coli* O157:H7, *Klebsiella pneumoniae*, *Listeria monocytogenes*, *Micrococcus luteus*, *Mycobacterium*

smegmatis, *Proteus vulgaris*, *Pseudomonas aeruginosa*, *P. fluorescens*, *Staphylococcus aureus* and *Yersinia enterocolitica* showed that the growth of *A. hydrophila*, *B. amyloliquefaciens*, *B. megaterium*, *E. coli*, *E. coli* O157:H7, *L. monocytogenes* and *Y. enterocolitica* was not inhibited by any concentration of Liquid Storaque tested. The results showed that the Liquid Storaque has antibacterial activity against many bacteria at concentrations of 10% and against other bacteria at concentrations of 1%, 0.4% and 0.2% (Sağdıç et al., 2005). The essential oil obtained from the Liquid Storaque also presented nematicide activity against the nematode of the pine bark, *Bursaphelenchus xylophilus* (Kim et al., 2008).

A very strong antifungal activity related to the *Phytophthora cactorum*, a fungus phytopathogenic, was found in the essential oil obtained from *Liquidambar orientalis* (sweet Oriental gum) at the concentration of 28 ng/mL of air. GC-MS analysis led to the identification of eleven substances in the oil, including cinnamaldehyde and benzaldehyde, both with inhibition of 100% related to *P. cactorum* at the same concentration (Lee et al., 2009).

Some fake balsams

In terms of chemical composition, various aromatic oils are, in fact, oleoresins. Among these are Egyptian, Gurjun, Canada and Copaiba.

Egyptian balsam or Balsam of Judea

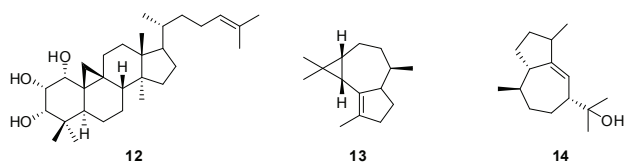
Chemical studies of resin exudates of *Commiphora opobalsamum*, Burseraceae, showed that it is, in fact, a complex oleoresin, with many substances, such as octadecane-1, 2S, 3S, 4R-tetrol 1-*O*- α -1-L-rhamnopyranoside, eudesmane-1 β ,5 α ,11-triol, guaia-6 α ,7 α -epoxy-4 α ,10 α -diol, guaianediol, mirrone, dihydropyrocuzerenone, 2-metoxo-5-acetoxo-furangermacren-1(10)-en-6-one, (1(10)*E*,2*R*,4*R*)-2-metoxo-8,12-epoxygermacr-1(10),7,11-trien-6-one and curzerenone (Shen et al., 2007; Shen et al., 2008).

Antioxidant and hepatoprotective effects were observed in the ethanol extract of *C. opobalsamum* (Al-Howiriny et al., 2004), while for cicloartan-24-ene-1 α ,2 α ,3 α -triol (**12**) and octadecane-1,2*S*, 3*S*, 4*R*-tetrol 1-*O*- α -1-L-ramnopiranoside, moderate antiproliferative effect was observed in progeny of cancer cells in the human prostate (IC₅₀ of 5.7 to 23.6 μ M), with inhibition of the androgen receptor (AR) expression inhibition in LNCaP and moderate cytotoxicity related to the cell progeny PC3 or DU145 (IC₅₀ from 10.1 to 37.2 μ M) (Shen et al., 2007; Shen et al., 2008). Recent studies with *C. gileadensis* (syn. *C. opobalsamum*) stems showed to be an apoptosis inducer that acts selectively against tumor cell lines and not against normal cells. According to the authors, the activity would

be associated with β -caryophyllene, that was obtained from the ethanol-based extracts and from the essential oils, and already have many properties known, as antifungal, local anesthetic and anti-inflammatory (Amiel et al., 2012).

Gurjun balsam

Gurjun balsam is an oleoresin exuded from species of *Dipterocarpus*, Dipterocarpaceae, originated in the forest regions of Southeast Asia. This oil is a pathological product formed after incisions or other damage to the bark of the trees. Historically, this oil is known for its use in the adulteration of some essential oils such as ylang-ylang, patchouli, vetiver, and others. Gurjun balsam consists of 60 to 80% of an essential sticky oil used in perfume for its sweet, woody, balsamic aroma (Bombarda et al., 1997). In the essential oil of Gurjun balsam obtained from *Dipterocarpus dyeri*, a high concentration of α -gurjunene (**13**) was found, and various sesquiterpenes, including calarene, alloaromadendrene and γ -gurjunene (Ehret & Ourisson, 1969). Rucker & Hefendehl (1978) also found guaianic alcohol in this balsam; guaien-(5)-ol-(11) (**14**).



Canada balsam

Canada balsam is an oleoresin produced by the species *Abies balsamea* (L.) Mill. Trunk., Pinaceae. Among the oleoresins of *Abies*, Canada balsam is the most widely commercialized. It is collected mainly in Eastern Canada. Locally, it is used as a remedy for the common cold, but its main usage is as mounting medium in microscopy (Lee et al., 1974).

Chemical studies with this oleoresin has shown a very complex composition, with monoterpenes (21%), such as β -pinene, α -pinene, β -phellandrene, limonene, 3-carene, myrcene and camphene; and oxygenated monoterpenes (0.4%), mainly 4,4-dimethyl-2-cyclohepten-1-one, linalol, bornyl acetate, methyltimol, citronellyl acetate, α -terpineol, piperitone, citronellal, borneol, citronellol and geraniol. Sesquiterpenes (1.1%) such as longifolene, β -bisabolene, longipinene, sativene, cyclosativene, cis- α -bisabolene, β -himachalene, α -himachalene, β -caryophyllene, γ -humulene, farnesene, longicyclene, and β -selinene were also observed. (Lee et al., 1974).

The oleoresin of cortical origin of *Abies magnifica* showed the presence of nineteen monoterpenes and 26 sesquiterpenes, including two

new substances in the species; γ -humulene and the cyclosativene. Acyclic monoterpenes such as myrcene, geraniol, geraniol acetate, citronellool, citronellyl acetate; monocyclic monoterpenes such as α e β -phellandrene, limonene, terpinolene, α -terpineol, borneol, bornyl acetate, bicyclic monoterpenes such as α and β -pinene, 3-carene, α -thujene, sabinene, camphene and the tricyclic monoterpene tricyclene were identified. Among the monoterpenes, β -phellandrene was the most prevalent, with 48.3%. Among the sesquiterpenes, acyclic (farnesene), monocyclic (β and δ -elemene, α and γ -humulene and β -bisabolene), bicyclic (α -guaiene, guaiazulene, α and β -selinene, selin-4(14),7(17)-diene, selin-3,7(11)-dien, caryophyllene, β -santalene, β -bergamotene, γ and δ -cadinene and γ -muurolene), tricyclic (α -cubebene, α and β -copaene, sativene, α and β -ylangene, α -longipinene and longifolene) and tetracyclic (cyclosativene and longicyclene) were observed. Of the sesquiterpenes, longifolene was the most representative, with 47% (Smedman et al., 1969a).

Other species of *Abies* have also been studied due to their oleoresin chemical composition. A comparison between the oxygenated monoterpenes of twelve samples of cortical oleoresins showed great chemical differences between the species and varieties studied. The species *Abies magnifica* and *Abies procera* are difficult to identify morphologically but the chemical differences in δ -elemene and longifolene amounts were observed and helps to perform the differentiation. A similar situation was observed for the quantities of farnesene, α -muurolene, α -cubebene, α -copaene and longifolene between the species *Abies concolor* var. *concolor* and var. *lowiana* (Smedman et al. (1969b).

Besides resinous substances, the Pinaceae species also present a fraction of fatty acids. *Pinus silvestris* L., *Pinus sibirica* R. Mayr. and *Larix sibirica* present fatty acids with 11 to 22 carbons, with oleic and linoleic acids being the main unsaturated ones and palmitic acid the main saturated one (Bardyshev et al., 1970). These acids, as well as stearic acid, were also observed in *Picea excelsa*, *P. obovata*, *P. ajanensis*, *P. tianschanica*, *Pinus pityusa* and *P. dahurica* (Bardyshev et al., 1974).

Copaiba balsam

The *Copaifera*, Fabaceae, genus consists of seventy-two arboreal species native to the tropical regions of Latin America and West Africa. Among the species of this genus, the main producers of oleoresins are *C. reticulata* (70%), *C. guianensis* (10%), *C. multijuga* (5%) and *C. officinalis* (5%). Copaiba Oil is found in secretory canals distributed all over the plant, and is formed by a

mixture of sesquiterpenes and diterpenes (Veiga Jr & Pinto, 2002).

The first mention of Copaiba Oil was in a letter written by Petrus Martius to Leo X, the Pope, published in Strasbourg in 1534, in which he mentions that the drug, called "Copei" was used by the native Indians. In 1606, the work "De Naturali Novi Orbis", written by José Acosta, a Jesuit Priest, was translated from Latin to French. In a Portuguese translation by Joseph Maffeu, entitled "História Natural e Moral das Índias", the Copaiba Oil is called as a balsam that presents excellent aromatic and healing properties (Acosta, 1792).

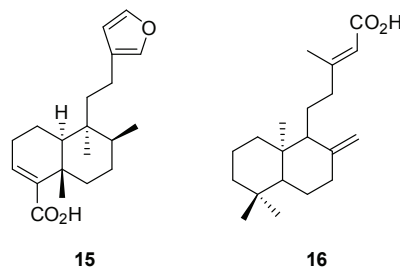
Copaiba Oil receives different names in the regions of Latin America where it is used. In the Amazon region, its usage is so widespread that copaiba trees are the most commonly used medicinal species among the population (Ming, 1995). The oil is sold in local markets, where it is known as *Copahyba*, *Copaibarana*, *Copaúba*, *Copaiba*, *Copal*, *Maram*, *Marimari* and Jesuit balsam (Rodrigues, 1989; Ducke, 1939).

Copaiba Oil is also known as Maracaibo balsam, being described as a liquor with a syrupy consistency, composed of essential oils, crystallizable substances, and amorphous acid resins. (Strauss, 1865). In terms of appearance, it is described as a transparent, white or yellowish liquid, and it is generally mixed with other substances, such as Juniper Oil or Canada balsam, to disguise the bitter unpleasant taste (Pinto, 1836). Other studies mention the adulteration of the Copaiba Oil with beaver oil and other fatty oils, probably due to its similarity to these oils (Muter, 1862). Copaiba Oil is obtained through an incision made in the tree stem. Sometimes, oleoresin exudates so abundantly that almost two kilograms of oil can be collected in one hour. Adult trees produce oil twice or three times a year (Hempel, 1865).

Copaiba balsam is an oleoresin; an exudate formed by resin acid (46.9%) and volatile substances (53.0%) (Gottlieb & Iachan, 1945). The commonly used term Oil or Copaiba balsam is, in fact, incorrect, since it contains neither cinnamic nor benzoic acids, or their derivatives (Veiga Jr & Pinto, 2002).

Among the sesquiterpenes found in the Copaiba Oil are: β -bisabolene, δ -cadinene, β -caryophyllene, α and β -copaene, α and β -cubebene, β -farnesene, α and β -humulene, longifolene, α -multijugenol, α and β -selinene, among others. In relation to the diterpenes fraction, kaurane skeleton was observed (*ent*-16- β -kauran-19-oic acid and *ent*-kaur-16-en-19-oic acid), clerodanes (*ent*-15,16-epoxy-13(16),14-clerodadien-18-oic acid, or chlorechinic acid, *ent*-15,16-epoxy-3,13(16),14-clerodatrien-18-oic acid, or hardwickiic acid (**15**) and 3,13-clerodadien-15-oic acid covalenic acid) and labdanes ((13*S*)-7-labden-15-oic acid or cativic acid, *ent*-8(17),13-labdadien-15,19-dioic acid or *ent*-agathic acid, *ent*-8(17)-labden-15-oic acid or eperuic acid, and *ent*-8(17)-13*E*-labdadien-15-oic acid or copalic

acid (**16**)) (Veiga Jr & Pinto, 2002).



This oleoresin has been used since ancient times as a remedy for gonorrhea and chronic infections of the mucus and other membranes (particularly bronchitis and chronic diarrhea) (Comfort, 1853). Many other folkloric uses are reported in the literature, including its use as an anti-inflammatory (Ferreira, 1980; Vieira, 1992), antiseptic (Bruneton, 1987; Oliveira, 1905; Goodman & Gilman, 1945), expectorant (Oliveira, 1905), and stimulant (Grieve, 1994; Peckolt, 1942), and for the treatment of asthma (Barros, 1982), headaches (Ribeiro, 1971), snakebites (Rosa, 1964; Barléu, 1974), dermatitis and eczemas (Lewis & Elvin-Lewis, 1977), and leishmaniasis (Grenand & Moretti, 1987). It is also reported as having aphrodisiac properties (Ribeiro, 1971).

Some of these ethnopharmacological properties have been confirmed in pharmacological studies, including its anti-inflammatory (Basile et al., 1988; Veiga Jr et al., 2001), analgesic (Fernandes et al., 1992), antitumor (Ohsaki et al., 1994), antimicrobial and antibacterial (Opdyke, 1976; Marussella & Scirella, 1960 Cascon et al., 2000) properties. It also protects against the penetration of larva of *Schistosoma mansoni* cercaries (Gilbert et al., 1972) and is effective as an insect repellent (Lacey et al., 1981; Jones et al., 1983), besides its healing properties in wounds and ulcers (Brito et al., 1998; Brito et al., 1999; Paiva et al., 2002).

Balsam constituents

All the true balsams mentioned above present a very complex composition, with some components in common and others different in each one. The compilation showed at Chart 1 helps to observe the differences.

The aromatic substances cinnamic acid, benzyl alcohol, benzyl benzoate, methyl cinnamate and vanillin were observed in all the balsams described in this study, although benzoic acid was not detected in Liquid Storaque.

Besides cinnamic and benzoic acid and their derivatives, the balsams present many other components that contribute to their aroma, such as monoterpenes, sesquiterpenes and phenylpropanoids. The Liquid Storaque presented a greater variety of

monoterpenes, among them limonene, α and β -pinene, terpinolene, geraniol, α -terpineol, camphor, carvone and fenchone. Tolu balsam was found to contain *cis* and *trans*-ocimene, α and β -pinene, *p*-cimene and eugenol, whilst in the Siam Benzoin, menthone and eugenol were observed.

Chart 1. Substances presents in the Cabreúva balsam (CB) described by Akissue (1972b), in the Tolu balsam (TB) described by Boelens et al. (1982) (^b) and Wahlberg et al. (1971) (^w), in the Peru balsam (PB), in the Siam Benzoin (SB) and in the Liquid Storake (LS) described by Boelens et al. (1982).

Substance	Balsam				
	CB	TB	PB	SB	LS
benzoic and cinnamic acids and derivatives					
cinnamic acid	x	x ^{b,w}	x	x	x
benzyl alcohol	x	x ^{b,w}	x	x	x
benzyl benzoate	x	x ^{b,w}	x	x	x
methyl cinnamate	x	x ^{b,w}	x	x	x
benzoic acid	x	x ^{b,w}	x	x	
benzaldehyde		x ^{b,w}	x	x	x
ethyl benzoate		x ^{b,w}	x	x	x
ethyl cinnamate		x ^{b,w}	x	x	x
benzyl cinnamate	x	x ^w	x	x	x
cinnamic alcohol		x ^w	x	x	x
cinnamic aldehyde		x ^{b,w}		x	x
methyl benzoate		x ^b	x	x	
cinnamyl benzoate		x ^w	x	x	
cinnamyl cinnamate			x		x
3-phenylpropyl cinnamate		x ^b			x
allyl benzoate				x	
propyl cinnamate				x	
benzyl ferulate		x ^w			
terpenoids					
monoterpenoids					
limonene					x
<i>cis</i> and <i>trans</i> -ocimene		x ^w			
α and β -pinene		x ^w			x
terpinolene					x
<i>p</i> -cymene		x ^w			x
geraniol					x
α -terpineol					x
camphor					x
carvone					x
fenchone					x
menthone				x	
bornyl acetate					x
sesquiterpenoids					
α and β -bourbulene		x ^w			

cadalene	x ^w				
δ -cadinene	x ^w	x			x
calacorene	x ^w				
calamarene	x ^w				
β -caryophyllene	x ^w				x
α -copaene	x ^w				
α -cubebene					x
β and γ elemene	x ^w				
humulene					x
α and γ muurolene	x ^w				
β -selinene	x ^w				
δ -cadinol					x
elemol					x
farnesol		x	x ^b	x	
nerolidol		x			x
phenylpropanoids					
eugenol			x ^{b,w}		x
other compounds					
styrene			x ^{b,w}	x	x
stilbene				x	
1,2-diphenylmethane			x ^w		
α -phenylethanol					x
3-phenylpropanol			x ^b	x	x
acetophenone				x	x
1-phenyl-2-methyl-1,3-butanedione				x	
vanillin		x	x ^{b,w}	x	x
acetovanillone				x	
(3-methoxy-4-hydroxyphenyl)-2-propanone				x	
miristic acid				x	
3-phenylpropionic acid					x
bornyl acetate					x
4-ethyl phenol				x	x
4-vinyl phenol					x
<i>p</i> -ethyl guaiacol				x	

Cabreúva balsam presents a unique composition, as shown in Chart 1, since it does not contain any of the substances found in other balsam. This fact may be due to the type of analysis performed for its identification. The authors used specific chemical reactions, and it may be that this method did not enable all the substances in the balsam to be detected, or perhaps these substances were in such small quantities as to be undetectable in this method of analysis.

In relation to the sesquiterpenes, these were observed in the highest concentrations in Tolu balsam such as α and β -bourbulene, cadalene, δ -cadinene, calacorene, calamarene, β -caryophyllene, α -copaene, β and γ elemene, α and γ muurolene, β -selinene and

nerolidol. Only two sesquiterpenes, farnesol and nerolidol were observed in Cabreuva balsam, while in the Liquid Storaque, α -cubebene, β and γ -elemene, δ -cadinol and elemol were detected. In Peru balsam was only found in δ -cadinene, which was also found in the Tolu balsam and in Liquid Storaque, and farnesol, that was related to the Cabreuva and Tolu balsam. Meanwhile, the Siam Benzoin was found to contain menthone and eugenol, but no sesquiterpenes were observed.

Monoterpenes and sesquiterpenes are found in greater amount in false balsams, such as Gurjun, balsam of Canada, and Copaiba balsam, and are related to the aromas present in the oleoresins. For example, Gurjun balsam was found to contain α -gurjunene, calarene, allo-aromadendrene and γ -gurjunene. In Canada balsam, many monoterpenes were identified, such as α and β -pinene, which were also present in the Tolu balsam and in Liquid Storaque, and geraniol also found in Liquid Storaque. β -caryophyllene, observed in Tolu balsam and in Liquid Storaque, was also found in the Copaiba and Canada balsams. Meanwhile, δ -cadinene was found in the Copaiba Oil, and was also observed in Tolu balsam, Peru balsam and in the Liquid Storaque.

Based on the data presented in this work, it can be observed that balsams have many substances in common, such as styrene, benzyl alcohol, benzaldehyde, vanillin, cinnamic acid, ethyl benzoate, benzyl benzoate, methyl cinnamate and ethyl cinnamate. On the other hand, some substances were found only in one balsam, and these maybe be used as markers to aid identification. This was the case, for example, of stilbene in Peru balsam, limonene, terpinolene and geraniol in Liquid Storaque, β -selinene in Tolu balsam, and menthone in Siam balsam.

Conclusion

Considering the data presented, it can be concluded that knowledge of balsams is scant, and new studies are needed on these substances. It can be observed that the balsams described contain benzoic and cinnamic acids and their derivatives. In general, the balsams have various components in common, but with different overall compositions. Another difficulty in identifying their compositions is the lack of information about the percentage of each component of the balsams, which could be very helpful for identifying each one of them, from different places. In relation to the producer species, some of them previously considered different species are now considered to be the same species, with one of the names being used, and the other names considered synonyms.

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