



New insights in the chemical composition of benzoin balsams



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ABSTRACT

Benzoin balsam is an anthropic exudate obtained from the bark of several species of *Styrax* trees that is mainly used as a perfume fixative as well as a flavouring agent. Benzoe tonkinensis Laos (also commercialized under the denomination Siam benzoin balsam) displaying characteristic vanilla notes and already being largely used to flavour all kinds of edible goods, was intended to be proposed by Agroforex Company to the Codex Committee on Food Additives for evaluation as a food additive. For this purpose, the present paper reports the phytochemical characterisation of both the volatile and non-volatile fractions of benzoin balsams and the quantitation of some of the major components by gas and liquid chromatography techniques. Four coniferyl and two morinol derivatives were characterised for the first time in Benzoe tonkinensis Laos. Finally, two liquid chromatographic methods used to easily discriminate Siam from Sumatra balsam (also known as Benzoe sumatranus Indonesia) were developed.

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1. Introduction

Benzoin – not to be confused with ‘benjamin gum’ or Benzoin – is a balsamic resin or balsam (AFNOR NF T 75-006, 1998) exuding from *Styrax* species (Styracaceae) that was employed since ancient time. First evidences confirmed that benzoin balsam was traded to China about A.D. 800 to be used notably as a fixative for perfumes (Arctander, 1960; Langenheim, 2003). In the Mediterranean basin, it was valued for its therapeutic, pharmacological and odoriferous properties: it was notably used in the Middle-East as a substitute to incense in religious ceremonies, often in combination with frankincense (Hovaneissian, Archier, Mathe, Culioli, & Vieillescazes, 2008; Hovaneissian, Archier, Mathe, & Vieillescazes, 2006; Modugno, Ribechini, & Colombini 2006).

The *Styrax* trees and shrubs originated from regions displaying warm and temperate climates mainly from Southeast Asia (Hovaneissian et al., 2006). Nowadays, the main benzoin producers are the deciduous *Styrax tonkinensis* (Pierre) Craib ex Hartwich. on one hand, and the evergreen *Styrax benzoin* Dryander and *Styrax*

paralleoneurum Perkins on the other hand. *Styrax tonkinensis* was tapped for centuries mainly in Laos and probably also in Thailand to obtain the so called Siam benzoin balsam. *S. benzoin* and *S. paralleoneurum* are essentially native to Indonesia (Sumatra and Java) and produce Sumatra benzoin balsam (Fernández, 2004; Supplementary material 1). The generic term ‘benzoin’ either consists in the exudate of one or the other of the two sources or in their mixture (WHO technical report 966, 2011).

Benzoin balsam does not exude naturally from the trunk, but is rather a pathological product resulting from tapping *Styrax* trees, e.g. cutting multiple superficial incisions through the cambium of these trees (Langenheim, 2003; Pauletti, Teles, Silva, Araújo, & Bolzani, 2006). As excessive tapping often induce the death of the tree, this traditional practice is nowadays well-defined: *S. tonkinensis* tree may be tapped once a year for about ten years once it is 7 years old, whereas *S. benzoin* and *S. paralleoneurum* may be tapped twice a year for about twenty years once they are 8–10 years old (Chagnaud, pers. comm.). After the yellowish exudate hardens upon exposition to air, it is collected by scraping the cut in the trunk (79th JECFA – CTA, 2014; Langenheim, 2003). Once collected, benzoin balsam is cleaned, sorted into four different grades according to the size and the homogeneity of the pieces, and then matured. The production remains nowadays entirely manual, from tapping to packaging (79th JECFA – CTA, 2014).

These three *Styrax* species are the most significant producers of balsam in terms of tonnage per year (Kashio & Johnson, 2001).

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Apart from them, several other minor species that yield benzoin to lesser extent and quality are also common in these regions (Burkill, 1966). Another minor source of benzoin is *Styrax officinalis* from the Mediterranean region that was already known by the Greeks Herodotus (5th c. A.D.) and Theophrastus (4th–3rd c. A.D.) and recommended by Hippocrates (5th–4th c. A.D.) as a remedy (Langenheim, 2003). It is worthwhile to note that the term *Styrax* deriving from ‘*astirax*’, an Arabic locution meaning ‘sweet-smelling exudation’ (Langenheim, 2003), has generated a nomenclatural confusion quite frequent in the resin terminology: gums from *Liquidambar* spp. (Hamamelidaceae), so-called storax, are often marketed as benzoin but are not to be considered as such from botanical and chemical points of view (Hovaneissian et al., 2006; Langenheim, 1996).

In the present paper, we focus on Siam (also known as Benzoe tonkinensis Laos, BTL; Eur. Ph. 2016) and Sumatra (also known as Benzoe sumatranus Indonesia, BSI; Eur. Ph. 2008) benzoin balsams. Their chemical compositions have been widely studied over the last decades (Supplementary material 2). A hundred years ago, Reinitzer found that the major constituent of Siam balsam was coniferyl benzoate **1** (75–80%) (Reinitzer, 1914). Later, Schroeder's work shows that Siam benzoin balsam was composed of coniferyl benzoate **1** (65–75%), *p*-coumaryl benzoate **2** (10–15%), cinnamyl cinnamate **3** (0.5–6%), benzoic acid **10** (12%), and siarresinolic acid **17** (6%) (Schroeder, 1968). On the other hand, cinnamic acid **11** and its esters, mainly cinnamyl cinnamate **3** and coniferyl cinnamate **16**, and pinoresinol have been characterised as components of Sumatra benzoin balsam (Bruneton, 2009; Pastorova, de Koster, & Boon, 1997). Vanillin, prevalent in Siam balsam, is nevertheless present in Sumatra balsam and gives rise to their familiar vanilla odour (Kashio & Johnson, 2001).

Our research group recently studied more particularly the volatile fraction of both benzoin types. For this, volatile extracts obtained by hydrodistillation of 50 kg of each benzoin gum were analysed using High Temperature-Gas Chromatography (HT-GC), Gas Chromatography coupled to Mass Spectrometry (GC/MS) and electronic nose using different sample pre-treatment strategies (Castel et al., 2006; Fernandez, Castel, Lizzani-Cuvelier, Delbecque, & Puech Venzal, 2006; Fernandez, Lizzani-Cuvelier, Loiseau, Perichet, & Delbecque, 2003). The GC/MS study of these extracts led respectively to the identification of 20 and 29 compounds. The major compound identified in benzoin balsams of both botanical origins was benzyl benzoate **12** (76.1–80.1%). Yet, while Siam benzoin balsam was characterised by benzoic acid **10** (12.5%), methyl benzoate (1.5%) and allyl benzoate (1.5%), Sumatra balsam was defined by its content of cinnamic acid **11** (3.5%) and benzyl cinnamate **13** (3.3%). This work also led to the detection and identification of an unusual acenaphthylene-type sesquiterpene hydrocarbon in these volatile extracts (Filippi et al., 2009). Besides aromatic compounds, Siam balsam also contains several triterpenoids (siarresinolic and sumaresinolic acids, etc.).

Despite their traditional uses, benzoin balsams are well known for their characteristic scents. Siam benzoin balsam has a pleasant sweet-balsamic odour with distinct notes of vanilla, amber, chocolate, caramel and nuts while Sumatra benzoin balsam presents a strong styrax-like odour (Castel et al., 2006). Hence, benzoin balsam of both botanical origins is widely used in the fragrance industry as perfume fixatives and preservatives with a slight prevalence for the Siam product (Langenheim, 2003).

Benzoin balsam is also largely priced in the flavour industry: the Siam one was notably widely used to flavour all kinds of beverages, confectioneries, etc. to add characteristic vanilla notes (Burdock, 1995; Burdock, 1997; Leung & Foster, 1996; Moyler, 1998). In fact, the warm, soft and sweet notes of natural vanilla are among the world's favourite scents and vanillin is a compound of high interest for the flavour industry. However, its popularity among consumers

also means that supplies of natural vanilla must be carefully and sustainably managed over the long-term. The necessity of alternative vanilla sources has long been explored: vanillin was first synthesized in 1874 from coniferin (Tiemann & Haarmann, 1874), and “vanilla extract” was invented as a cost effective substitute for the real vanilla. Furthermore, over the last decades, food and drink manufacturers were seeking for cheaper alternatives to meet the pressing consumer demand for more natural products: benzoin balsam being a natural source of vanillin was a perfect candidate.

Siam benzoin balsam was intended to be proposed by Agroforex Company to the Codex Committee on Food Additives (CCFA, Codex Alimentarius) for evaluation as an authorized food additive. Hence, the necessity to meet the JECFA (Joint FAO/WHO Expert Committee on Food Additives) regulations implied to get a better knowledge of the composition of benzoin balsam. In fact, despite the number of studies reporting chemical investigations of benzoin balsam, analytical techniques frequently used do not take into account the whole material and issues with botanical and geographical origins are often reported.

Agroforex Company already submitted a file summarizing the requested information about characterisation and toxicological data on Benzoe tonkinensis Laos (September 2010), an Activity Report (May 2011), Complementary Data (December 2012) and a Report (January 2014) to JECFA (79th JECFA – CTA, 2014). Finally, BTL was concluded not to be of safety concern regarding the ‘no observed adverse effect level’ (NOAEL) criteria (WHO technical report 990, 2014). However, the previous evaluations of the question of the BTL registration as a food flavour evidenced some missing information and particularly additional data about its overall chemical composition, including quantitation of benzoin balsam constituents, were requested (FAO JECFA monograph, 2011; WHO technical report 983, 2013). The development of relevant analytical methodology to distinguish between benzoin of both botanical origins was also claimed.

For this purpose, analytical and semi-preparative HPLC-DAD-ELSD (High-Performance Liquid Chromatography coupled to Diode Array and Evaporative Light Scattering Detectors), GC-FID (Gas Chromatography with a Flame Ionization Detector), GC/MS, NMR (Nuclear Magnetic Resonance), and UPLC-QToF (Ultra-Performance Liquid Chromatography–Quadrupole Time of Flight mass spectrometry) were used to characterise these balsamic exudates *via* both the identification of new aromatic compounds of the phenylpropanoids family, and the quantitation of some of their main constituents.

2. Materials and methods

The complete experimental procedure employed for this study is summarized in Fig. 1.

2.1. Material and sample preparation

Benzoin samples of both botanical origins were provided by Agroforex Company in 2011: Siam benzoin balsam (BTL Grade 3) was collected in Laos and Sumatra balsam (BSI Grade B) in Indonesia. Siam and Sumatra samples are respectively referred to as BSiam and BSum in the current article (Supplementary material 1).

All the samples were solubilized in ethanol, filtered and evaporated to obtain ethanol extracts at a final concentration of 30 mg/mL (extraction yield: 98%).

2.2. Chemicals

Acetonitrile (ACN, Chromasolv[®] for HPLC), water (H₂O, Chromasolv[®] for HPLC), dichloromethane (DCM, Chromasolv[®] for HPLC),

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