Seeking a Sustainable Alternative to Brazilian Rosewood*

Linalool enantiomers in the essential oils of aromatic plants from Brazil: *Aniba rosaeodora* (rosewood), *Lippia alba* (erva cidreira) and *Ocimum basilicum* (basil)

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Brazil was the 10th largest essential oil importer in 2004 ($42 million), and the fourth largest exporter ($98 million) after the United States, France and the United Kingdom. Chief Brazilian oil exports in 2005–2006 were orange (80%; citrus oils comprised 91% of the total exports), lemon, lime, eucalyptus and rosewood. Exported products are characterized by high volume, low price and reduced aggregated value, at an average price of $2.60/kg. However, the average growth was 8.2% in the period 2000–2004. This year, the value of Brazil's essential oil production is expected to reach $82 million, a fall of 16% attributable to the lack of citrus oils in production. Brazil imported 2.761 million tons of essential oils in 2004 at a price of $15,235 per ton of product, and exported 32,000 tons of essential oils (August 2005 to August 2006).[1] Exported products from the Brazilian biodiversity contributed just 0.07% to the total Brazilian market. Meanwhile, rosewood oil comprised 3%—or US$2.80 million—of the market, the majority of which ended up in the fine fragrance industry.

The commercial essential oil of rosewood (*A. rosaeodora*) comes from a tree at risk of extinction. Beginning in the 1900s and ramping up between the 1940s and 1970s, the oil of rosewood has been used on a large scale as a fragrance material.[2] The oil is comprised of linalool (70-90%), linalool esters such as linalyl acetate, and linalool oxides, which are odoriferous substances with very intense and pleasant aromas. The olfactive analysis of linalool enantiomers has been described as woody, flowery and lavenderlike, with fresh notes of *laevo*; on the other hand, *dextro* linalool has a sweet, citrus and herbaceous impression.[3] Linalool is mostly used in floral fragrant products, but it also finds use in detergents and soaps (which typically use synthetic linalool) and as an important intermediary in vitamin E synthesis.

The rosewood oil world trade market has experienced a long downward trend since the 1960s, when synthetic linalool replaced it in the lower-grade perfumery product market. In the 1970s, the rosewood oil market share was further eclipsed in the international market by the entry of the Chinese ho (*Cinnamomum camphora* L.) wood and leaf oil, which contains approximately 95% linalool—all in the *laevo* form—therefore replacing rosewood oil in mid-range perfumes, cosmetics and household products.

As a result of this competition and dwindling supplies, the export of rosewood oil, which constituted on average 75% of the total rosewood oil production in the heyday of the industry, has decreased. From an average of 360 tons in the period between 1945 and 1974, rosewood oil exports declined sharply during the 1990s to only 36 tons on average in the period 1997–1999, and 38.5 tons from August 2005 to August 2006. As a result, today's average prices are on the rise, climbing to $72.89 (August 2005 to August 2006).

Today, rosewood oil and its derivatives are used as the main fragrance component in just a few top-of-the-line perfumes, and as a component of "bouquets" in a wider range of scents.[2] Recently, the perfume industry reduced rosewood oil applications due not only to high cost,

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At a Glance

Rosewood is an endangered species; consequently, its oil is at risk of serious shortage. Some authors claimed that the essential oils of *Lippia alba* and *Ocimum basilicum* could substitute rosewood oil (*Aniba rosaeodora* Ducke). Based in comparisons among linalool chirality in the oils of *L. alba* (Mill. N.E. Brown), *O. basilicum* (L.) and in the leaf oil of *A. rosaeodora*, this work presents rosewood leaf oil as the most probable source to replace commercial rosewood oil from the wood.

approximately $80/kg, but also environmental issues.[2] The oil production has traditionally relied on tree harvesting; one ton of wood is needed for the production of 9–13 L of oil. In consequence, more than 2 million trees have been destroyed since the commencement of oil production.[4] Therefore, Brazilian scientists concerned with the exhaustion of rosewood natural reserves have been searching for alternative sources of linalool-rich oils. Studies have examined *Ocimum basilicum* as a possible alternative for rosewood oil, since it contains considerable linalool concentrations (31%) and is easily cultivated.[5] Other studies have pointed out that the aerial parts of *Lippia alba* may produce an alternative oil due to its high linalool concentration (60%).[6]

Our own studies began in 2001 with 60 rosewood leaf samples collected from crops and forest rosewood trees growing in different Amazonian regions. The GC/MS analysis of the leaf oils showed that the relative linalool percentage varied as much as 50–91%.[7] A trial with 200 kg of wild Amazonian rosewood leaves has indicated that leaf oil production would be industrially feasible. Analysis showed that linalool enantiomers were distributed in the ratio of 60% *laevo* to 40% *dextro* in the leaf oil from the forest. The aim of this work is to compare rosewood leaf oil with *L. alba* and *O. basilicum* oils, considered by the authors to be reasonable replacements for rosewood oil.[5,6]

Experimental

Plant material and oil isolation: Rosewood leaf oil (*A. rosaeodora*) was obtained from an industrial assemblage experiment of 200 kg of leaves collected in the Amazon forest. Rosewood wood oil was obtained from a commercial sample. *Lippia alba* (A) were grown at the CPQBA (Research Center of Chemistry, Biology and Agronomy); the leaves were then steam distilled. *Lippia alba* (B) were obtained from plants grown at UNICAMP and hydro-distillated in our laboratory. *Ocimum basilicum* oil from aerial parts of the plant was obtained from industrial sample from the Agronomic Institute of Campinas (IAC).

Gas chromatography/mass spectrometry: Samples were analyzed in an HP5890-II GC equipped with a HP-5 fused silica column (30 m x 0.25 mm; 0.25 µm film thickness) interfaced with a quadrupole detector HP-5870-B. The column gradient temperature ranged from 60°C to 240°C at 3°C min^{-1}; the injector was operated at split mode at 220°C. Helium was used as carrier gas at the flow rate of 1.0 mL min^{-1}; the mass spectrometer was operated at 70 eV.

Identification of components: Constituent identification was conducted by comparing their retention indices and their spectra in the Wiley Library and literature.[8]

Results and Discussion

The fragrance sensorial analysis of the oils considered three main factors: linalool enantiomeric composition, linalool concentration and minor substances in the oils, which give the fragrances a complexity that makes them unique.

Samples of the oils of *L. alba* (A) and (B), *O. basilicum* and rosewood (leaf and wood) have been compared in this study (**T-1**). *Lippia alba* possessed a variable linalool composition of 59–75% probably due to genetic differences and/or soil quality. *Ocimum basilicum* contained about 40% linalool when derived from commercial field cultivars. Rosewood leaf oil obtained from an industrial assemblage experiment of leaves collected in the Amazon forest was comprised 81% linalool. Finally, rosewood oil from wood was represented by a commercial sample containing 85% linalool. Rosewood leaf oil possessed a strong herbal, floral rose/petit grainlike and green woody scent. The rosewood commercial sample from the wood was sweet, woody, floral and spicy.

Essential oil composition of *Ocimum basilicum, Lippia alba* and *Aniba rosaeodora* by GC/MS **T-1**

Constituents	RI	*O. basilicum* leaf oil	*L. alba* leaf oil (A)	*L. alba* leaf oil (B)	*A. rosaeodora* leaf oil	*A. rosaeodora* wood oil
1-octen-3-ol	974	–	1.3	1.6	–	–
myrcene	984	5.2	–	–	–	–
1,8 cineole	1017	24.4	4.2	5.3	–	–
δ-3-carene	1019	–	2.3	–	–	–
limonene	1031	–	–	–	0.5	2.4
linalool oxide*	1076	–	–	–	5.4	14.1
linalool	1090	40.0	59.2	75.3	81.4	85.0
camphor	1140	10.0	–	–	–	–
pulegone	1227	–	2.6	8.7	–	–
eugenol	1350	9.6	–	–	–	–
β-caryophyllene	1419	–	–	3.0	–	–
α-selinene	1485	–	–	–	2.7	2.0
β-selinene	1487	–	–	–	1.0	4.4
germacrene D	1488	10.8	9.7	3.6	–	–
eicosane	2000	–	8.6	–	–	–
Total		100	94.1	97.5	60.1	75.1

*correct isomer not identified; RI = retention indices on an HP-5 column; A = collected at CPQBA field; B = collected at UNICAMP, Campinas

Using a chiral column we showed that rosewood oil contains a mixture of linalool enantiomers in a ratio of approximately 40% (-) linalool and 60% (+) linalool (**T-2**).[9] *Lippia alba* oil analysis showed that, besides presenting exclusively *dextro* linalool, the material contained minor substances that influence the final fragrance composition, including 1,8-cineole, which presents a camphor-like, penetrating odor characteristic.[10] Considering these findings, we can establish that *L. alba* oil is hardly a candidate to replace rosewood oil from wood due to significant differences in olfactive analysis.

Enantiomers of linalool from *Ocimum basilicum*, *Lippia alba* and *Aniba rosaeodora* oils **T-2**

Oil	(-) Linalool	(+) Linalool
O. basilicum leaves	100	–
L. alba leaves (UNICAMP)	–	100
L. alba leaves (CPQBA)	–	100
A. rosaeodora leaves	20	80
A. rosaeodora wood	40	60

On the other hand, *O. basilicum* oil analysis presented *laevo* linalool in abundance. Moreover, the presence of other substances such as eugenol (clove-like odor), germacrene D, 1,8-cineole (eucalyptus-like odor) and camphor (camphor-like odor) confers to *O. basilicum* oil an olfactive characteristic (herbal, spicy, woody) very distinct when compared to rosewood oil fragrance. Considering these factors, we can establish that *O. basilicum* oil also cannot substitute rosewood oil.

In addition, from a commercial point of view, basil oil—though rich in *dextro* linalool—cannot substitute ho oil, because the analysis detected linalool levels of just 40% (**T-1**). As a consequence, to obtain pure linalool it would be necessary to conduct a fractional distillation of *O. basilicum* oil, which is a relatively complex and expensive process, as well as making it unattractive as a final product when compared to Chinese ho. Studies conducted in our laboratory showed that minor fragrant substances are frequently isolated along with the main distilled oil, which even in small concentrations can substantially alter the final product.

We observed through chiral GC/MS analysis that the leaf oil of *A. roseadora* contained linalool enantiomers at an average of 20% (-) linalool and 80% (+) linalool. We then concluded that *A. rosaeodora* leaf oil has the closest composition profile when compared to rosewood oil from wood, making it a possible new substitute for materials from the Brazilian biodiversity.

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