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Wood essential oils of two endemic trees from New Caledonia: *Callitris sulcata* (Parl.) Schltr. and *Callitris neocaledonica* Dummer

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ABSTRACT

The essential oils obtained by hydrodistillation of pieces of dead trunks of *Callitris sulcata* (Parlatore) Schlechter and *Callitris neocaledonica* Dummer were investigated by gas chromatography, mass spectrometry and NMR spectroscopy. Analyses evidenced the presence of rare natural compounds: both essential oils are exclusively sesquiterpenic with nevertheless remarkable difference: *C. sulcata* essential oil was dominated by β-barbatene and thujopsene while *C. neocaledonica* was characterized by high levels of guaiane- and eudesmane-type structures (eudesmols, guaiol and related components). The biochemical correlations between the major components of each species are discussed and the relationship between the two species is commented.

1. Introduction

The Cupressaceae include 30 genera and 142 species of principally evergreen coniferous trees, and shrubs in 19 genera of cosmopolitan distribution.

This family, which is the most widely distributed of all Gymnosperm families, occurs in diverse habitats on all continents except Antarctica. However, all genera except *Juniperus* show strongly relictual distribution with a large number of localised, rare and endangered taxa. Most of the generic diversity is within the southern hemisphere, but the largest genus, *Juniperus* is mainly north temperate.

The flora of New Caledonia is of special interest, because it holds three endemic conifer genera and 43 endemic conifer species, of which six are species of Cupressaceae, and some of them are among the rarest conifers in the world (Lowry, 1996).

Callitris is a genus of 19 species, of which 17 are native to Australia (Richer de Forges et al., 1998) and only two are endemic in New Caledonia: *Callitris sulcata* (Parlatore) Schlechter and *Callitris neocaledonica* Dummer (Jaffré et al., 2001). The members of genus *Callitris* are monoecious and evergreen trees or shrubs with erected branches that spread or fastigiate. The persistent bark is hard and compact. The branchlets consist of triangular or cylindrical joints owing to the decurrent leaf bases.

Many of the most abundant species have been and are still used because of their durable and insect-resistant wood for diverse purposes like the fabrication of oars, spears, glues, etc., and are treated with very high regard by the traditional societies.

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C. sulcata is a very slow growing tree reaching from 5 to 12 m high with densely standing branches and a hard, compact bark. The juvenile leaves are reduced to scales which attain 26 × 1.2 mm with joints owing to the leaf base. At a height of about 1 m they turn suddenly into adult leafs. Adults leafs are needle-like and present a 4–6 mm long edge on their back. The terminal standing pollen cones are ovoid, 3–5 mm long and about 1.5–2 mm large and contain triangular microsporophylls. The seed cones are to be found at the end of the short branches and look like 10 × 10 mm onions or even larger, because the cones open when the six triangular seeds are set free.

C. sulcata is found in the south of the main island of New Caledonia in the three valleys of Camboui, where it is particularly common, in that of the upper Tontouta River and in the valley of Dumbea, where it is growing at an altitude of 15–300 m. Traditionally it was used in the construction of wooden houses, as posts made of *ngié* (vernacular name of *C. sulcata* in xârâguré language, Thio region). It is in danger of extinction and only about 150 examples are there still left on the islands of New Caledonia (De Laubenfels, 1972).

C. neocaledonica (syn. *C. sulcata* var. *alpina*) is a small tree reaching from 3 to 7 m high with densely standing branches. It has the shape of a candelabrum, that's why it is also called candelabra pine. The juvenile leaves are 5–9 mm long, about 0.8 mm large, linear and needle-like and stand vertically decussate in groups of four. Adult leafs have 2–4 mm edges on their dorsal side. The round pollen cones are 2–3 mm long, 2–2.5 mm large and contain about 1 mm long triangular microsporophylls and stand terminal position on the branches. The seed cones stand in terminal position on the short branches. In contrast to all *Callitris* species, where the scales joining in the center are the largest, the largest scales of the *C. neocaledonica*'s cones are the ones joining at the peak of the cone. The seeds are of pyramidal shape with a size of 6 × 7 × 2 mm (De Laubenfels, 1972).

C. neocaledonica is found in the south of the main island of New Caledonia. However, the plant is in great danger of extinction and therefore on the red list of the IUNC (International Union for Nature Conservation).

Neocallitropsis pancheri (Carrière) de Laubenfels, which has also previously been described by different botanical names: *Callitropsis araucarioides* Compton and *Neocallitropsis auraucarioides* (Compton) Florin (De Laubenfels, 1972 and Jaffré et al., 1987) is another species native to New Caledonia belonging to the Cupressaceae family; it looks like *C. neocaledonica* on account of its candelabra form; this single known species of *Neocallitropsis* is considered as strongly associated with *Callitris* and has been included in the Callitroid clade (Gadek et al., 2000).

Over the last hundred years, a substantial number of chemical investigations have been carried out on the Australian *Callitris* species. Undoubtedly, the classic work on the essential oils is that of Baker and Smith dating from almost a century ago (Baker and Smith, 1910). These authors examined the oils obtained from both leaves and wood and they succeeded to isolate and identify some mono and sesquiterpenes. From this time, the results of numerous other chemical investigations can be found in the literature: in particular, the investigations performed on *Callitris columellaris* with the identification of new sesquiterpene lactones are worth knowing (Brecknell and Carman, 1979); an exhaustive review of these previous works was recently published by Brophy et al. (2007) who have surveyed the leaf essential oils of 17 species and four subspecies of the genus *Callitris* endemic to Australia, which were all dominated by monoterpenes, mainly pinenes and/or limonene, with some exceptions: samples of *Callitris drummondi* and *Callitris rhomboidea* essential oils, characterized by high levels of monoterpenic esters (geranyl, neryl and bornyl/or citronellyl acetates) and *Callitris monticola* and *Callitris muelleri* essential oils which contained more than 25% of spathulenol.

On the other hand, the only chemical investigation on the two New Caledonian *Callitris* species concern the solvent extracts of their leafy twigs which were examined only once for their flavonoid content (Gadek and Quinn, 1983). To the best of our knowledge, the essential oils obtained from the wood of *C. neocaledonica* and *C. sulcata* were never previously described, whereas the essential oil obtained from the heartwood of *N. pancheri* was submitted to various chemical analyses. The volatile extract of the latter is characterized by a sesquiterpenic composition, dominated by eudesmols (Raharivelomanana et al., 1993b) accompanied by various oxygenated sesquiterpenes, mainly elemol, guaiol, bulnesol and carissone (Raharivelomanana et al., 1995), bisabolenol and bisabolenal (Raharivelomanana et al., 1993a,b), jinkoholic acid, a prezizane sesquiterpene (Raharivelomanana et al., 1994) or pancherione and eudesm-4(14)-en-3α,11-diol (Raharivelomanana et al., 1996). Recently, two new sesquiterpenic components, one epimere of α-acoradiene (α-neocallitropsene) and its hydroxylated derivative (neocallitropsenol), were also identified in the essential oil of this species (Joulain and Waikedre, 2007).

The aim of the present study was to compare the chemical compositions of the volatile fractions of the wood part of *C. neocaledonica* and *C. sulcata* from New Caledonia, in order to get a better characterization of these two endemic species and possibly to ratify their classification within the Cupressaceae family.

2. Materials and methods

2.1. Plant material

Dried wood pieces of dead trees located in New Caledonia near Thio for *C. sulcata* and on the peak of Mount Humboldt at an altitude of 1452 m for *C. neocaledonica* were collected in January 2002. The wood pieces were finely chopped before hydrodistillation procedure.