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Lignans from a hybrid *Paulownia* wood

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1. Subject and source

Paulownia species are fast growing hardwood trees indigenous from the south east of China recorded as far back as 1049 BC for the production of high quality timber. In the Iberian Peninsula, the first experimental *Paulownia* plantation (more specifically the natural hybrid of *Paulownia elongate* S.Y. Hu and *Paulownia fortunei* Hemsl.) was introduced two years ago. The present paper reports the study of the chemical composition of the dichloromethane extract of the referred hybrid wood.

2. Previous work

Paulownia produce versatile, dimensionally stable, consistently knot-free wood, marketed primarily for specialty solid wood products, oriented for strand board, veneer (Bergmann, 1998) and also for pulping to produce fine papers (Olson and Carpenter, 1985). The climate of most South European countries is suitable for *Paulownia* plantation. Under the appropriate conditions, a five-year-old tree can reach about 15–20 m high. The number of publications reporting the presence of

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lignans in *Paulownia* species is scarce: their presence was reported only in *Paulownia tomentosa* (Takahash and Nakagawa, 1966; Plouvier, 1971; Ayres and Loike, 1990; Okazaki et al., 1997) and recently in *Paulownia kawakamii* (Ping et al., 2004).

3. Present study

3.1. Extraction and GC–MS analysis

The hybrid *P. elongata*/*P. fortunei* wood was harvested from a plantation in north of Portugal. Six trees (2 years old) of about 4.0–4.5 m high were cut down and the part of the stem between 0.5 and 1.5 m high was air dyed, powdered and submitted to Soxhlet extraction with CH_2Cl_2 for 6 h (0.81% yield). Aliquots of the dried extract were trimethylsilylated and analysed by GC–MS under the following conditions (Freire et al., 2002): helium as carrier gas (35 cm/s), and a DB-1 J&W capillary column (15 m × 0.32 mm i.d., 0.25 μm film thickness); temperature programme: initial: 100 °C (3 min); rate: 5 °C/min; final: 340 °C (12 min); injector: 320 °C; transfer-line: 290 °C; split ratio: 1:100. Quantitative analysis was carried out based on the multiplication factors relative to tetracosane previously calculated for fatty acids, aliphatic alcohols and sterols (Freire et al., 2002). For sesamin and paulownin, multiplication factors were calculated by injection of aliquots of the isolated compounds.

The dichloromethane extract is mainly composed of fatty acids and sterols, minor amounts of fatty alcohols (Fig. 1, Table 1) and a very intense chromatographic peak around 48.8 min (peak 16). The fragmentation profile of the peak has demonstrated that it was a mixture of two compounds; the base peak at $m/z = 149$ characteristic of an $Ar-C{\equiv}O^{\cdot +}$ ion (Ar being a piperonyl group) suggests the presence of furofuran lignan structures with piperonyl substituents (Gunatilaka et al., 1982; Ayres and Loike, 1990). The presence of a fragment at $m/z = 73$ suggests that, at least one compound would have a TMS derivatized OH. The GC–MS analysis of the extract without derivatization allowed to detect a chromatographic peak at the same retention time referred above with an $M^{+\cdot}$ ion at $m/z = 354$ and a new broad peak (49.9 min) with an $M^{+\cdot}$ ion at $m/z = 370$, which would be compatible with the structures of sesamin and paulownin (Fig. 2). Their unambiguous identification was confirmed after isolation by preparative chromatography and NMR characterization. Results of the quantitative analysis show that sesamin and paulownin represent 2.1 g/kg and 0.4 g/kg of dry wood, respectively.

3.2. Isolation of lignans

The CH_2Cl_2 wood extract was fractionated by preparative thin layer chromatography on silica gel (TLC). Eluting with ethyl acetate:hexane (4:6); a fraction only composed of sesamin and paulownin was isolated. This fraction was further fractionated by TLC eluting the plates several times with ethyl acetate:hexane (1:9) allowing the isolation of sesamin and paulownin as pure pale yellow solids. NMR spectra were recorded on a Bruker Avance 300 spectrometer (300.13 and 75.47 MHz, for ^1H and ^{13}C, respectively), using $CDCl_3$ as solvent and TMS as internal reference.