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SESQUITERPENES OF *SANTALUM ALBUM* AND *SANTALUM SPICATUM*

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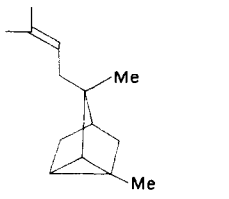
Key Word Index—*Santalum album*; *S. spicatum*; Santalaceae; essential oils; α and β-curcumene; dendrolasin; β-farnesene; sesquiterpenes; biosynthesis.

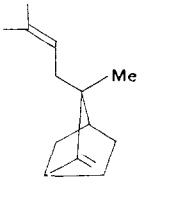
Santalum album and *S. spicatum* are grown chiefly in southern India and Western Australia respectively. The essential oils (especially from *Santalum album*) are highly prized for their organoleptic and medicinal properties, and on account of its importance in perfumery and medicine, sandalwood oil has been investigated by several workers [1]. The main constituents of the sandalwood oils have been found to be α and β-santalol (*ca* 90%) which are responsible for the general odour of the oils. In undertaking an analysis of both essential oils, our aim was to identify potentially important perfumery compounds present in the more volatile fractions.

Petrol extraction of both East Indian and Australian sandalwoods afforded *ca* 7% of essential oil. Both essential oils gave a "hydrocarbon fraction" (see Experimental) representing *ca* 6% of the total oil. A GLC analysis of the "hydrocarbon fraction" from Australian sandalwood on 5% carbowax, temperature programmed 80–200°, showed that it contained about ten components, of which α (**1**), β (**2**), and epi-β-santalene represented *ca* 21, 20 and 11% respectively of the total "hydrocarbon" content, identified initially by mass spectral data comparison with literature data [2]. The hydrocarbon fraction from East Indian sandalwood under the same GLC conditions was shown, however, to consist of about nine components of which α, β, and epi-β-santalene were *ca* 23, 36 and 21% of the total respectively. Both hydrocarbon fractions were subjected to preparative GLC on a 15% carbowax column, temperature programmed 80–200°. The components shown in Table 1 were isolated (unless indicated otherwise) and each gave a single peak when subjected to GLC analysis on two columns (5% carbowax and 5% OVI). All the compounds, where shown, were identified from their MS, NMR and IR spectral data by comparison with the literature [2, 3]. Several other trace components in the "hydrocarbon fraction" from East Indian sandalwood oil were detected and one was tentatively identified as β-farnesene from its mass spectrum [4].

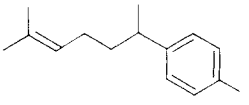
Although the chemical compositions of Australian and East Indian sandalwood oils are known to be different, the difference (Table 1) in santalene content has not been reported. The presence of α and β-curcumene (**3**) and (**4**) in sandalwood oil tends to support the proposed biosynthetic pathway for the formation of α and β-santalene (**1**) and (**2**) from farnesyl pyrophosphate [5].



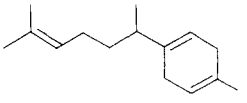
(1) α-Santalene



(2) β-Santalene



(3) α-Curcumene



(4) β-Curcumene

Dendrolasin is a new odour constituent of sandalwood oil (sweet lemon grass odour) and to the authors' knowledge, this is the first report of the presence of both dendrolasin and β-farnesene in sandalwood oil.

Table 1. Approx percentage in hydrocarbon fraction of sandalwood oil

Compound*	Australian I	Australian II†	East Indian
α-Santalene	21	24	23
Epi-β-santalene	11	14	21
β-Santalene	20	20	36
β-Curcumene	8	8	6
α-Curcumene	12	7	3
Dendrolasin	13	6	

* Four unknowns were found in all 3 samples, in amounts ranging from 2–10%.
† Volatile fractions supplied by Plaimar Ltd., Australia.

EXPERIMENTAL

NMR (100 MHz) spectra were recorded in CCl_4 with tetramethylsilane as reference: IR spectra were obtained from CCl_4 solutions. Analytical GLC were performed on a Pye Series 104 Chromatograph using 2 m × 4 mm glass columns containing (a) 5% carbowax 20M and (b) 5% OVI on 80–100 mesh Diatomite C and Diatomite CLQ (100–120 mesh) respectively. Preparative GLC was carried out using a 3 m × 6 mm glass column containing 15% carbowax 20M on 60–72 mesh Diatomite C.

(1) *East Indian sandalwood oil.* The dried heartwood (powdered) of *Santalum album* L (5 kg) (bought from the Govt. Sandalwood Depot, Mysore Forest Dept., Bangalore, India) was extracted with petrol (bp 40–60°) at 20° and the extract (350 g, 7%), after removal of petrol by rotary evaporation at 40°, was partitioned between petrol and 90% aq. MeOH in the usual way. The petrol fraction (60 g) was then chromatographed on basic alumina (3 kg) and continuous elution with petrol (40–60°) gave 20 fractions all containing hydrocarbons (21 g, 6%). Each fraction was subjected to preparative GLC and the components given in the Table were isolated and were shown to be single compounds (unless indicated otherwise) on analytical GLC [2 columns (a) and (b)].

Initial GLC–MS analysis on column (a) of the petrol fraction before column chromatography indicated the presence of β-farnesene, α and β-curcumene (**3**) and (**4**) as well as α (**1**), β (**2**) and epi-β-santalene. Isolation and subsequent MS, NMR and IR analysis of the components listed, confirmed the presence of α and β-curcumene and α, β and epi-β-santalene.

(2) *Australian sandalwood oil.* In the same way as described for East Indian sandalwood oil, the powdered heartwood from *Santalum spicatum* (R. Br.) A.DC (200 g) (kindly provided by the Ministry for Forests, Perth, Western Australia) afforded after efficient partitioning, a hydrocarbon fraction (1·0 g, *ca* 6% of total oil). This was not chromatographed but compared to the volatile fractions kindly given by Plaimar Limited, Australia, prepared by steam entrainment of the essential oil and subsequent distillation (see Table 1). This latter oil was subjected to preparative GLC and the components analysed in the same way as indicated for those obtained from East Indian sandalwood.

Acknowledgement We thank Union Carbide (U.K.) Limited for a Research Fellowship to D.R.A.

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