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THE ESSENTIAL OIL OF *DIPTEROCARPUS KERRII*

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IBRAHIM BIN JANTAN. 1988. **The essential oil of *Dipterocarpus kerrii*.** The oleo-resins from *Dipterocarpus kerrii* (Dipterocarpaceae) were obtained by the bark-chipped method with aqueous sulfuric acid as stimulant and by the traditional method of the 'Orang Asli'. The essential oil fraction of the oleo-resin was investigated by capillary gas chromatography (GC), combined GC-mass spectrometry (GC-MS) and proton nuclear magnetic resonance (^{1}H-NMR). The two major components of the oil, α-gurjunene and allo-aromadendrene, were isolated by column chromatography on silica gel impregnated with silver nitrate.

Key words : Oleo resins – *Dipterocarpus kerrii* – gas chromatography – α-gurjunene.

Introduction

Dipterocarpus kerrii (family Dipterocarpaceae) is frequently tapped for its oleo-resin by the 'Orang Asli' (aborigines) in Peninsular Malaysia. The oleo-resins are used by the 'Orang Asli' for caulking boats, torches, coating wood as a protection against weather and for medicinal purposes (Burkill 1935). Today, the commercial demand for the essential oil, locally known as 'minyak keruing', distilled from the oleo-resin is encouraging. Its new use is as a fixative in perfumes (Gianno & Kochummen 1981, Gianno 1986). Presently the middlemen pay as much as M$60 to the 'Orang Asli' for a four-gallon tin of 'minyak keruing' (Ken Sew, personal communication). However, the essential oil sold is not hydro-distilled but only filtered with gunny and flour sacks to remove the resinous fraction.

Oleo-resins extracted from *Dipterocarpus* trees produce a high percentage of sesquiterpenoid essential oils (Gianno 1986). Essential oil containing sesquiterpenes as their major components are occasionally used as fixatives in the scenting of soaps and cosmetics and technical preparations. Their potential as medicinal agents have not been exploited yet although the 'Orang Asli' use 'minyak keruing' as one of the constituents in analgesic liniments (Ken Sew, personal communication). Investigations have shown that α-gurjunene and allo-aromadendrene are the major components of the essential oil of *D. dyeri* (Palmade *et al.* 1963) and α-gurjunene is the principal sesquiterpene of *Dipterocarpus* oleo-resins (Streith *et al.* 1962).

Previous work on the resin fraction was carried out at the Forest Research Institute Malaysia (FRIM) and dipterocarpol was identified as the major component (Azizol,

unpublished). As part of a systematic study of oleo-resin chemistry of the tree, the chemical constituents of the essential oil fraction of the oleo-resin extracted from *D. kerrii* by the traditional method of the 'Orang Asli' and by the bark-chipped method with aqueous sulfuric acid as stimulant are reported here.

Materials and methods

Collection of materials

The oleo-resins of *D. kerrii* were obtained by using the bark-chipped method with various concentrations of aqueous sulfuric acid (from 0 to 50%) as stimulant and by using the traditional method of the 'Orang Asli'. Tapping of the oleo-resins using the former method was done at FRIM and the latter at Buloh Nipis in Pahang (Ibrahim *et al.* unpublished). The traditional method involves cutting a hole in the trunk of the tree and the use of fire to stimulate further oleo-resin flow. In both methods, the trees were tapped once a week but the materials were collected daily at FRIM and once a week before the start of every new tapping, in the case of the traditional method of the 'Orang Asli'. At FRIM, the material was stored in an airtight glass container and kept in a cool and dark place.

Separation and purification of the essential oil

The essential oil was separated from the resinous fraction by dilution with petroleum ether and centrifugation. The supernatant layer was evaporated to give a yellow oil. Upon standing at room temperature for a few days, the crude oil turned brown. Purification of the oils by hydro-distillation gave a clear yellow oil amounting to 80% of the crude oil.

Isolation of pure components from the essential oil

The clear yellow oil was dried over anhydrous sodium sulfate overnight, d^{25°: 0.926, $\alpha_D^{25^\circ}$: –241 (methanol), boiling range : 230° – 260°C. Four grams of the oil was chromatographed on silica gel coated with silver nitrate which was eluted with petroleum ether. The column was prepared by dissolving 10 *g* silver nitrate in a small amount of water and adding 100 *g* silica gel (230 – 400 mesh) and an amount of water sufficient to form a fluid paste. Elution with petroleum ether (40° – 60°) yielded 2.85 *g* (71.3%) of **I** (colourless oil), 0.12 *g* (3%) of **II** (colourless oil) and 0.63 *g* (15.8%) of clear yellow oil. The specific rotations of **I** and **II** were – 230° (methanol) and – 42° (methanol) respectively.

Analysis of the essential oil

TLC analysis of the oil was done on silica gel coated glass plates. GC analysis was carried out on Shimadzu gas chromatograph model GC-9A equipped with FID detector and a CR-3A Chromatopac data processor using a silicone GE SE-30 capillary column (25 *m*, 100 – 120 mesh); initial temperature, 80°C for 10 *min*, then 3°*C/min* to 250°*C* with N_2 as carrier gas. The GC-MS data were obtained with a Hewlett Packard model 5985A (70 *eV* direct inlet) using the HP-1 capillary column (30 *m*, 100 – 120 mesh) initially at 80°C for 10 *min*, then 3°*C/min* to 250°C with He as carrier gas. NMR spectra were obtained with a Jeol Fx 90.

Results and discussion

The essential oil obtained by the bark-chipped method with aqueous sulfuric acid as stimulant was clear yellow and the odour was pleasantly balsamic. GLC chromatogram of the hydro-distilled oil indicated the presence of 7 major components (Table 1). These were similar to the chromatogram of the oil obtained when no stimulant was employed indicating that there is no change in the composition of the oil when aqueous sulfuric acid of up to 50% is used.

Table 1. Composition of essential oil of *D. kerrii* obtained from FRIM (column capillary SE–30)

Peak No.	Retention time	Compound	Identified by	%
1	16.3	sesquiterpene	b	3.12
2	17.7	α-gurjunene	a, b & c	79.17
3	19.0	β-caryophyllene	b	1.10
4	19.6	α-humulene	b	0.32
5	20.1	allo-aromadendrene	a, b & c	5.25
6	20.7	sesquiterpene	b	0.58
7	21.1	β-gurjunene	b	0.79

(a – coinjection with authentic material; b – mass fragmentation; c – H–NMR; notations same for Table 2)

The essential oil obtained by the traditional method was dark brown in colour, the odour was less pleasant and the chromatogram from TLC showed the presence of the resinous fraction, indicating that there was no complete separation between the resinous and the essential oil fractions when filtered with gunny and flour sacks. The hydro-distilled oil still contained α-gurjunene and allo-aromadendrene as the major

components (Table 2). However, β-caryophyllene and humulene were absent. In addition there were two other unidentified compounds (peak 2 and 4, Table 2) and several minor ones. Compounds I and II isolated by the argentation column chromatography were identified as α-gurjunene and allo-aromadendrene respectively by comparing their 'H-NMR' spectra, mass spectral fragmentations and optical activities with those of authentic samples. Some other components were also identified as their mass spectral fragmentations were in complete agreement with the data available in the literature (Tables 1 & 2).

Table 2. Composition of essential oil of *D. kerrii* obtained from Buloh Nipis
(column capillary SE-30)

Peak No.	Retention time	Compound	Identified by	%
1	15.1	sesquiterpene	b	0.52
2	16.1	sesquiterpene	b	1.63
3	17.4	α-gurjunene	a, b & c	58.03
4	19.31	sesquiterpene	b	10.81
5	19.9	allo-aromadendrene	a, b & c	4.13
6	20.9	β-gurjunene	b	1.51
7	22.4	sesquiterpene	b	0.36
8	24.3	sesquiterpene	b	0.46
9	26.4	sesquiterpene	b	0.37

The essential oil obtained at FRIM showed a higher concentration of α-gurjunene and allo-aromadendrene than those obtained from Buloh Nipis. However the latter contained a significant amount of an unidentified sesquiterpene (10.81%, peak 4) which was absent in the former.

Conclusion

The results indicate that the essential oil of *D. kerrii* is composed entirely of sesquiterpene hydrocarbons in which α-gurjunene is the major component. However chemotaxonomic differences in *D. kerrii* at the two locations are observed: the essential oils differed in composition and percentage of each component. These differences can be attributed to the differences in the collection of the material, possibilities of pollution and other non-botanical factors. The method of tapping developed at FRIM gave a better quality oil. This suggests that the more drastic method of tapping by the 'Orang Asli' would result in the oxidation and resinification of the sesquiterpenes easily when exposed to air and light or under improper storing conditions.

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