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Essential Oils

III. Chemical Constituents of the Volatile Oil from the Bark of a Rare Variety of Cinnamon †

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Abstract : Gas liquid chromatographic studies on the steam-volatile bark oil of an exotic variety of cinnamon (probably *Cinnamomum capparu-coronde* Bl.) have revealed the presence in it of linalool (29%), eugenol (23%) and 1 : 8 cineole (16%) as major constituents. This variety has a totally different chemical composition to the bark oil of traditional cinnamon (*C. zeylanicum*). The plant is of interest with respect to the biosynthesis of these compounds and to the potential use of this oil and its constitutents in perfumery.

1. Introduction

The study of the steam-volatile bark oil of an exotic variety of cinnamon was initiated during a detailed study of the chemistry of the steam volatile oils from commercial cinnamon viz : *Cinnamomum zeylanicum* Blume.[7] During the collection of samples for this study,[7] bark of this exotic variety was supplied to us by a collector in the Karandeniya area in the Ambalangoda district. Authentic samples used for the present study were collected from the Bambarawana hills in the same district by one of us (A. L. Jayewardene). The exact botanical identification of the specimen was not available at this stage but it was introduced to us by the Sinhala name *Kapuru kurundu*. Recently, Kostermans[3] has described the botanical features of " a forgotton Ceylon cinnamon tree " to which he attributes the botanical name *Cinnamomum capparu-coronde* Bl., a variety first described by Blume in 1836. Kostermans has identified this variety as that bearing the Sinhala name *Kapuru kurundu* (or camphoraceous cinnamon) which name he contends had been distorted to " capparu-coronde " by Blume. Incidentally the odour attributed to the bark of this tree was that of " cloves " and strangely not that of camphor, which the Sinhala name would lead one to expect. The description of the leaf given by Kostermans tallies with our own herbarium pressing of the variety *Kapuru kurundu* investigated by us. However, Kostermans collected his specimens from Rasagalle near Balangoda, and along the Laxapana-Maskeliya road.

It is interesting that medicinal properties too have been attributed to this plant. The bark of the plant has an odour distinctly reminiscent of cloves and coriander and is quite different to that of commercial cinnamon.

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2. Experimental

2.1. Distillation of the bark

The bark was finely ground and the essential oil obtained by water-distillation. Both fresh bark and aged bark (stored for long periods after peeling) were distilled for oil. A Clevenger type apparatus was employed for fresh bark samples. A larger type still was used for distilling the older bark samples. The oil obtained was pale yellow, with a pleasant odour.

2.2. Gas-liquid chromatography

Gas liquid chromatographic analyses of the oil were carried out according to the methods previously described.[6,7] The typical chromatogram (Figure 1) was run on Carbowax 20 M phase (3m x 6 mm column). Gas liquid chromatography was performed on the dried neat oil and also the residual oil after treatment with sodium hydroxide and silica gel slurry.[7]

2.2.1. *Parameters employed for analytical GLC*

Instrument	—	*Varion* 1740 *Moduline*:
Column and packing	—	(i) 3m x 3mm ss with 10% FFAP
	—	(ii) 3m x 3mm ss with 15 %SE—30
Carrier gas	—	Argon 30 ml/min
Sample size	—	0.2 ul.
Detector dual	—	FID
Detector temperature	—	220°C
Injectors temperature	—	200°C
Column oven initial	—	70°C
Column oven final	—	210°C
Programme rate	—	2°/min linear
Chart speed	—	15″/h

Instrument	—	*Varian* 90 *P*—3:
Column and packing	—	3m x 6mm ss with 10% Carbowaz 20 M
Carrier gas	—	Helium 60 ml/min
Sample size	—	10 ul.
Detector Katharometer	—	(TC)
Detector temperature	—	220°C
Injector temperature	—	220°C
Column oven initial	—	60°C
Column oven final	—	220°C
Programme rate	—	4°/min
Chart	—	15″/h

2.2.2. *Operating parameters for preparative GLC — on a Varian 90/P3/TC instrument*

Column and packing	—	3m x 6mm 10% Carbowax 20M
Sample size	—	50 ul.
Carrier gas	—	55 ml/in Helium
Detector Katharometer	—	(TC)
Detector temperature	—	230°C
Injector temperature	—	200°C
Column oven temperature initial	—	80°C
Column oven temperature final	—	210°C
Programme rate	—	4°/min

2.3. Infra-Red Spectroscopy

IR spectroscopy of compounds isolated by preparative GLC was carried out as described previously.[6,7]

3. Results and Discussion

Kapuru kurundu bark oil had a most acceptable odour. The chromatogram of the oil was quite different to that of commercial cinnamon. There were 3 major peaks which were quite readily identified as 1 : 8 cineole, linalool and eugenol (in order of elution) by comparison with a chart of commercial cinnamon bark oil.[7] These identifications were confirmed by trapping the eluates in precooled capillary tubes followed by IR spectroscopy.[6] Apart from these 3 major constituents, there were over 40 comparatively minor ones. These were identified by peak enhancement, retention data, chemical reaction on tlc, etc. as previously described.[6,7] Table 1 gives the percentage composition and the peak identities based on resolution on 2 different liquid phases of the constituents of the bark oil of *Kapuru kurundu*.

The oil of *Kapuru kurundu* displayed several remarkable features. It possessed a relatively large percentage of terpenoid constituents (> 60%) when compared with *C. zeylanicum* (7.0%). The major constituent is linalool and this contributes markedly to the pleasant odour of the oil. The high content of eugenol as well as the significantly small amount of cinnamaldehyde — the major constituent of the bark oil of *C. zeylanicum* — is also evidence of the operation of a rather different biogenetic system to that of normal cinnamon. The biosynthesis of linalool in the *Cinnamomum camphora var. linaloolifera* has recently received attention.[4] It has been found that the labelling pattern in linalool biosynthesised from mevalonic [2 — ^{14}C] acid in this plant was consistent with the predicted biosynthetic pathway involving the condensation of isopentenyl pyrophosphate with 3,3 — dimethylallylpyrophosphate.[2]

TABLE 1. Chemical composition of *Kapuru kurundu* and *C. zeylanicum*.

Component	*Kapuru kurundu* bark	*Cinnamomum zeylanicum*
α Pinene	2.1	0.2
Camphene	0.25	—
β Pinene	1.1	+
Sabinene		+
α Phellandrene	2.2	+
α Terpinene	4.0	+
Limonene	15.8	+
1 : 8 Cineole		1.65
Ocimene	1.6	+
γ Terpinene		
p - Cymene	4.00	0.55
α Ylangene	0.4	+
Camphor	0.3	trace
Linalool	29.1	2.3
β Caryophyllene	3.0	1.35
4 - Terpineol	0.65	—
Piperitone	+	+
α Terpineol	2.4	0.4
Cuminaldehyde	1.05	0.25
Safrole	0.25	+
Cinnamaldehyde	0.55	74.0
Eugenol	23.0	8.8

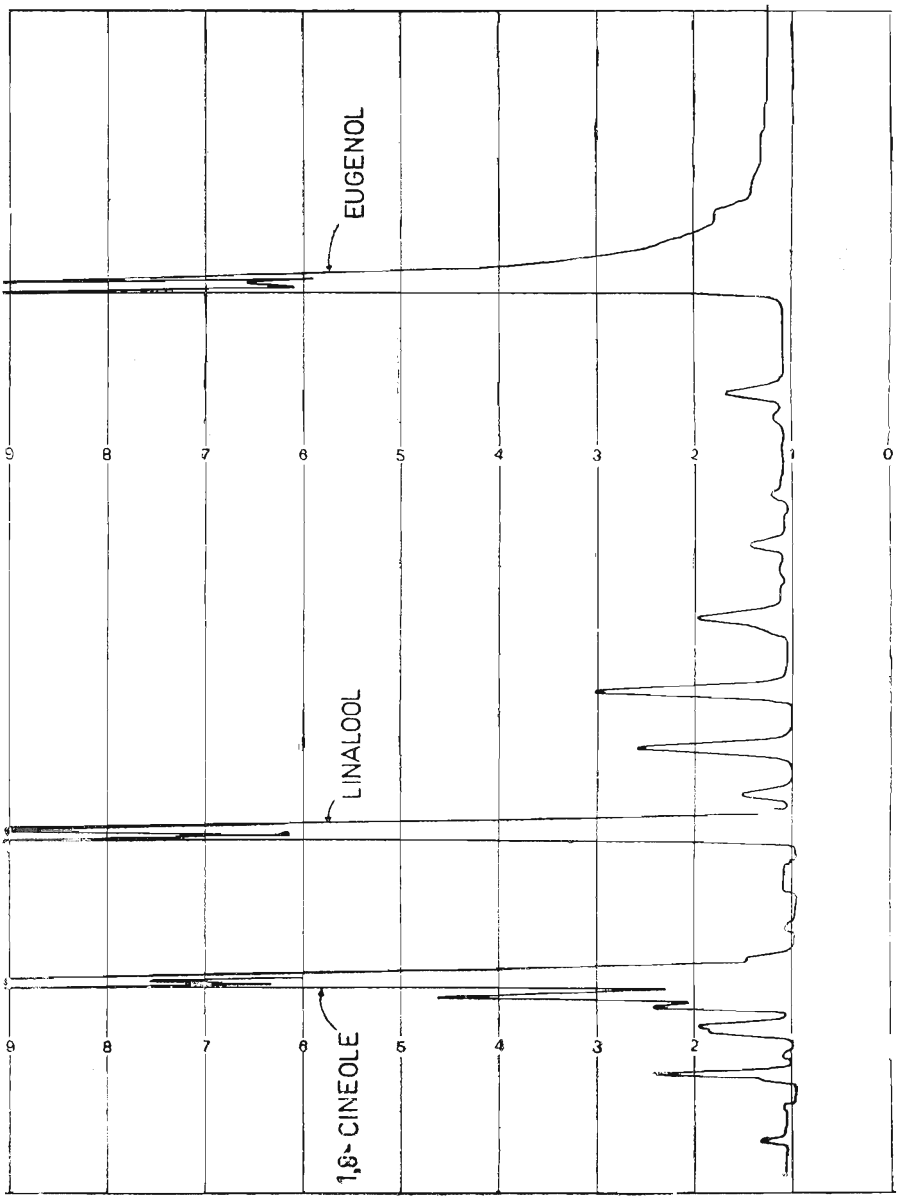

FIGURE 1. Gas-liquid chromatogram of bark oil.

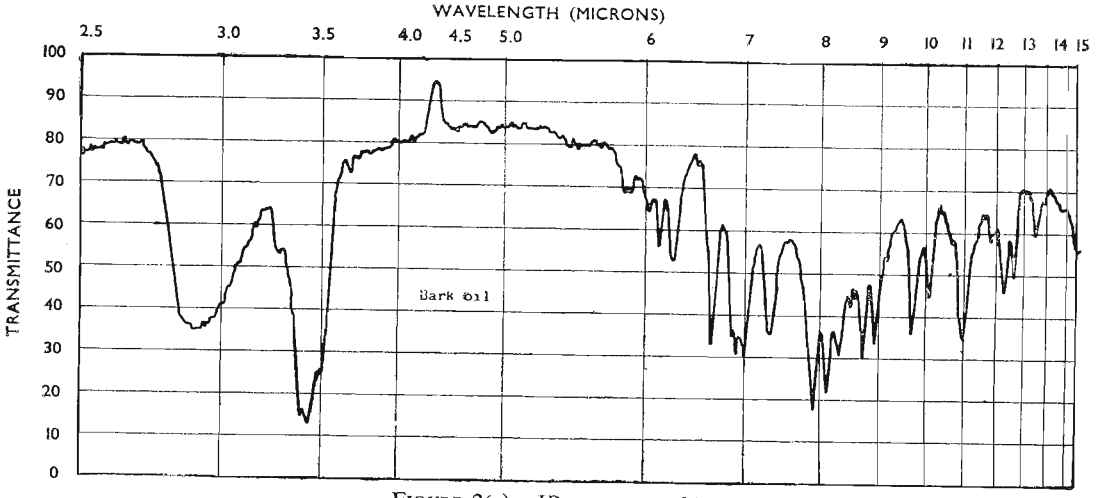

FIGURE 2(a). IR spectrum of bark oil.

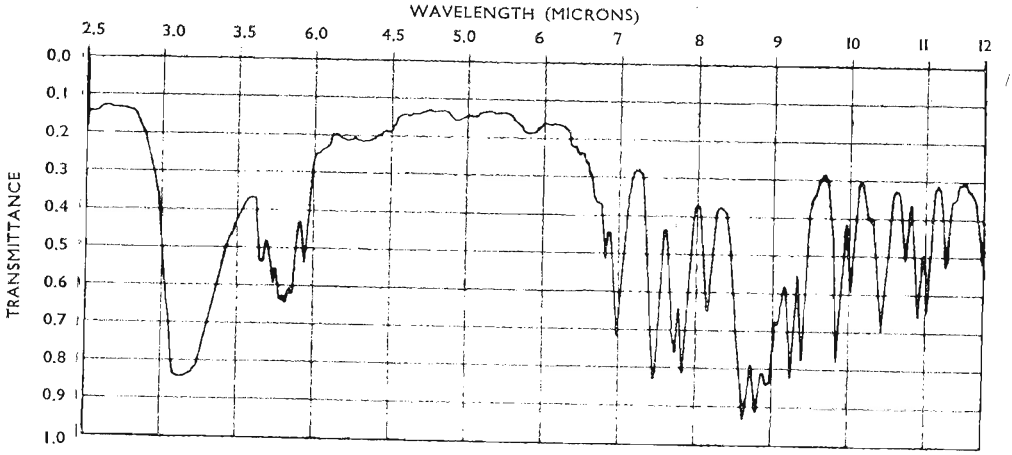

FIGURE 2(b). IR spectrum of eugenol.

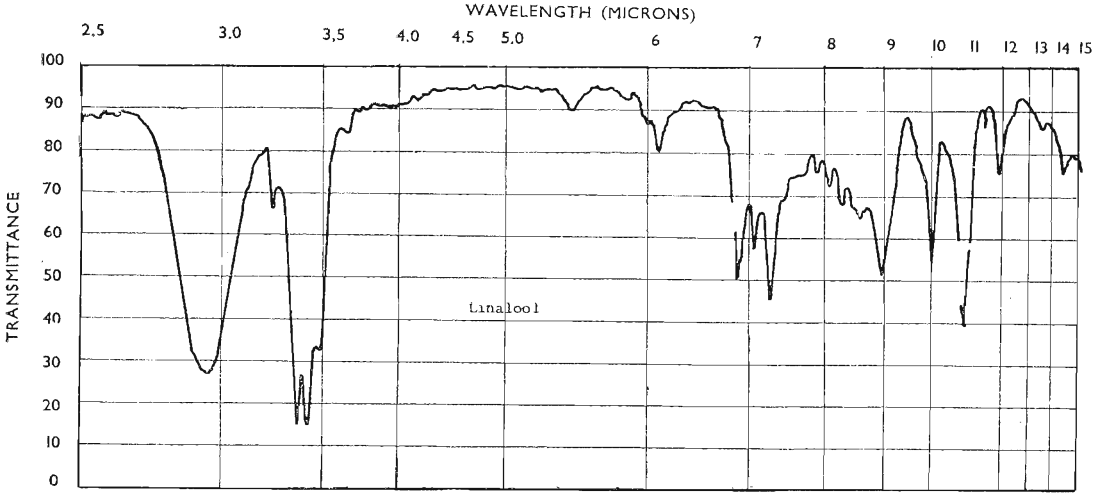

FIGURE 2(c). IR specturm of linalool.

It has been accepted that geranylpyrophosphate or nerylpyrophosphate is the phosphorylated intermediate which by hydrolysis leads to the common constituent of essential oils, geraniol ; under other conditions and via a different mode of enzymic hydrolysis it also leads to linalool.[1,2,3] It is evident that in *C.capparu-coronde* Bl. the enzyme system that operates the hydrolysis to linalool is the predominant one. Aside of linalool, the phenolic constituent eugenol is the major component but cinnamaldehyde is found only to the extent of about 1 %. The IR spectrum of the oil (Figure 2) displays the characteristics of both linalool and eugenol. The peaks due to each major constituent can be identified by differential IR spectrophotometry and employed to estimate each constituent in a sample of the oil by the technique recently described.[5]

The leaf oil of the new variety was also examined and this again was quite different from the leaf oil of *C. zeylanicum*.[7] The major constituent of this leaf oil was 1:8 cineole and the eugenol content, in contrast, was negligible.

4. Conclusion

The exotic variety of cinnamon investigated, which is in all probability identical with Kostermans' sample, has a bark oil with interesting possibilities. Biosynthetic considerations apart, the oil has a pleasant odour and affords a new source of the important perfumery ingredient linalool. The main source of linalool presently is oil of coriander which is expensive, particularly so, in Sri Lanka. This variety of cinnamon according to Kostermans[3] has medicinal uses. There is also the grave possibility of the variety going extinct ; presently it is rare and occurs only in remote areas. There is a case for its cultivation. The presence of linalool poses the possibility that its use in native medicine may be analogous to the use of coriander whose major constituent is also linalool. The pleasant smelling oil itself may have possibilities as a soap perfume, particularly due to its linalool — eugenol mixed notes. Preliminary attempts to use it as such directly revealed that the odour was somewhat fugitive. Work on the identification of the minor constituents of the bark and leaf oil are in progress.

Acknowledgements

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