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Essential Oils IV

Recent Studies on the Volatile Oils of Cinnamon*

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Abstract : Cinnamon is a uniquely interesting plant that gives rise to three different essential oils viz : bark oil, leaf oil and root bark oil, whose principal constituents are cinnamaldehyde, eugenol and camphor respectively. Bark and leaf oil are important commercial products. Recently GLC has been used to make a comparative study of the detailed composition of Sri Lanka grown cinnamon oils. The three oils were found to contain the same array of monoterpene hydrocarbons but in differing proportions. The root bark oil has a large monoterpene fraction of which 1 : 8 cineole is the major constituent. All three oils contained the sesquiterpenes β—caryophyllene, α— ylangene and α—humulene. Prefractionation by chemical separation methods and column chromatography on silica gel followed by preparative GLC enabled many of the major constituents of each oil to be isolated for identification by IR spectroscopy. In addition an IR spectrophotometric technique was developed for the direct analysis of samples of each oil. By this technique a quantitative estimate of eugenol, cinnamaldehyde, acetyl eugenol, benzyl benzoate, cinnamyl acetate, camphor and 1 : 8 cineole in a sample of an oil could be made with a single spectrum.

1. Introduction

The commercial plant *Cinnamomum zeylanicum* has been recognised since very early times as a valuable spice and flavouring agent.[6] It is a uniquely interesting plant, in that it gives rise to three different essential oils, namely, bark oil, leaf oil and root-bark oil. Each has a different chemical composition. The methods of classical chemical analysis have revealed the principal differences among them.[5] Each one of these oils has a major constituent that is different from the others. In the bark oil this is cinnamaldehyde, in the leaf oil it is eugenol, while in the root-bark oil it is camphor. These early studies on the chemical composition of the cinnamon oils were based on the comparatively drastic separation procedures of fractional distillation. The comparatively recent developments in chromatographic techniques have enabled more searching studies to be made on the chemical composition of cinnamon oils. Such studies have been made on Indian cinnamon leaf oil,[3] and on the composition of the oil from *C.zeylanicum* grown in Ghana.[1] Sri Lanka has been the major producer of cinnamon in the world, since antiquity.[7] Detailed studies on the chemical composition of cinnamon oils, obtained from plantations in Sri Lanka, have been recently carried out.[9, 10] These studies, which are based on GLC and IR spectroscopic techniques have revealed interesting results, which are discussed here.

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2. Experimental

2.1. Source of Materials

Samples of cinnamon stem bark, root-bark and leaf used for the studies have been collected from two large plantations in the southern coastal belt of Sri Lanka.[9] This area provides the bulk of the island's cinnamon. In these plantations, the cinnamon plant is regularly " coppiced " and maintained as a small bush. The oils were obtained by steam distillation in glass laboratory units as well as in commercial field stills. Bark oils obtained by distillation of the cinnamon quills of commerce were also examined.

2.2. Gas Chromatographic Methods

The freshly distilled oils were examined using temperature programmed gas liquid chromatographic procedures described previously.[8] For the analytical work, a Varian Moduline (1740—1) instrument with flame ionisation detectors was used. Four different stationary phases were employed in packed analytical columns (3 m x 3.2mm). The operating parameters are indicated in Table 1. Using these four different stationary phases, retention times for the individual components were first obtained, and compared with those of authentic samples. Peak enrichment techniques were used to obtain an idea of the identity of the constituents. In order to obtain further confirmation of the identity of the individual constituents, preparative GLC methods were employed with a Varian Aerograph Model 90 P3 with thermal conductivity detector. The columns used were 3m x 6.4 mm and stationary phase was Carbowax 20 M. The individual constituents separated by preparative GLC were collected in thin capillary tubes or bubbled into pre-cooled solvents. Sometimes it was expedient to remove the major component of each oil by chemical methods, so that the minor constituents were better separated by preparative GLC.[9]

TABLE 1. Operating parameters for analytical GC.

Instrument	: Varian Aerograph Moduline 1740—1	
Detector	: Flame ionisation	
Columns	: 1. 15% LAC—2R—446 on firebrick A.W. 2. 10% Carbowax 20M on Chromosorb W 3. 15% S.E. 30 on Chromosorb W 4. 10% FFAP on Chromosorb W Dimensions 3m x 3.2 mm.	
Column Temperature	: Initial 60 °C Final 220 °C	
Programme Rate	: 2 °/min. linear	
Injection Block temperature	: 200 °C	
Detector Oven temperature	: 260 °C	
Gas flow rates	: Carrier gas (Argon) Hydrogen Air	25 ml/min. 25 ml/min. 250 ml/min.
Recorder	: Range 1 mV Chart speed 5 mm/min.	

2.3. Infra-red Spectroscopy

Infra-red spectra were obtained on Perkin-Elmer 700 double beam spectrophotometer with grating optics. The spectra of compounds collected in capillary tubes were recorded as smears on sodium chloride plates. The spectra of most of the minor components which were obtained by trapping in pre-cooled solvents were recorded in solutions with the respective solvents in the reference beam. The identifications were confirmed by authentic spectra published by other workers or by comparison with spectra of authentic compounds obtained by us.

3. Quantitative Methods

3.1. Quantitation by Gas Chromatography

Quantities of the various components of each oil were determined from representative analytical chromatograms by measurement of peak areas. Several replicate analyses were made and the mean values were recorded (Table 2).

TABLE 2. Composition of the cinnamon oils as determined by GLC.

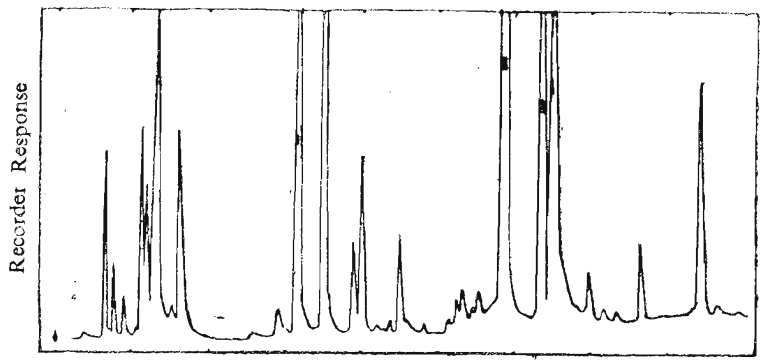
Compound	PERCENTAGE		
	Leaf Oil	Bark Oil	Root-Bark Oil
α—Pinene	0.2	0.2	1.7
Camphene	+	+	0.8
β—Pinene	+	+	1.2
Sabinene	—	+	+
Δ^3Carene	+	+	+
α—Phellandrene	+	+	+
α—Terpinene	+	+	+
Limonene	+	+	—
1 : 8 Cineole	0.15	1.65	15.2
γ—Terpinene	—	+	—
p—Cymene	0.35	0.55	1
α—Ylangene	0.25	+	trace
Camphor	—	trace	60
Linalool	1.5	2.3	1.2
β—Caryophyllene	1.85	1.35	—
4—Terpinen-l-ol	—	—	+
α—Humulene	0.2	0.2	0.2
α—Terpineol	0.15	0.4	3.8
Piperitone	0.1	+	+
Cuminaldehyde	—	0.25	—
Geraniol	+	+	+
Safrol	0.65	+	0.7
Unidentified	0.35	+	+
Cinnamaldehyde	1.3	74	3.9
Methyl cinnamate	trace	—	—
Ethyl cinnamate	trace	—	+
Cinnamyl acetate	0.8	5	0.3
Eugenol	87	8.8	5
Acetyl eugenol	1	trace	+
Cinnamyl alcohol	0.6	+	—
Benzylbenzoate	2.67	1	0.3

3.2. Determination by Infra-red Spectroscopy

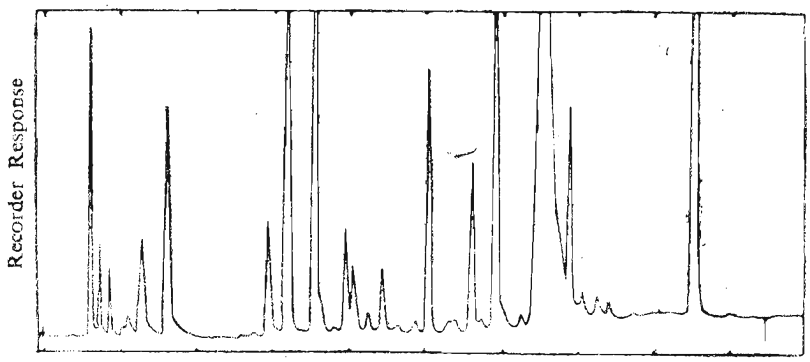
Several compounds were quantitatively estimated by measurement of an absorption peak in the IR spectra which was characteristic of the individual compound. The assignments of the peaks of the spectrum of each oil as being due to the various individual compounds present in it were made, firstly, by comparison with the characteristic peak frequencies in the individual spectra of the pure constituents themselves Then the peak enhancement caused by addition of a small amount of a particular constituent helped to verify such peaks as being due to that constituent. Estimates were further confirmed by differential spectroscopy where the addition of a small amount of the pure compounds one at a time to the solvent in the reference beam resulted in the reduction in intensity of the peaks due to that particular compound When the quantity added was made equal by suitable manipulation to the amounts present in the oil, the peaks due to this compound were completely obliterated. The choice of a suitable peak for quantitative estimation of each constituent compound was most important, as a peak which was solely due to this particular compound had to be selected. Once such peaks were suitably selected, the Beer-Lambert-Law was employed for the estimation of the different compounds. The accuracy of the estimates were checked by obtaining the differential spectrum. When the estimate was incorrect, (that is when it was too high or too low), this was indicated by the appearance of negative or residual peaks respectively. By these infra -red methods it was possible to determine eugenol, acetyl eugenol, cinnamyl acetate, benzyl benzoate and cinnamaldehyde in cinnamon leaf oil ; cinnamaldhyde, eugenol and cinnamyl acetate in cinnamon bark oil ; and camphor, 1 : 8 cineole and cinnamaldehyde in cinnamon root-bark oil.

4. Results and Discussion

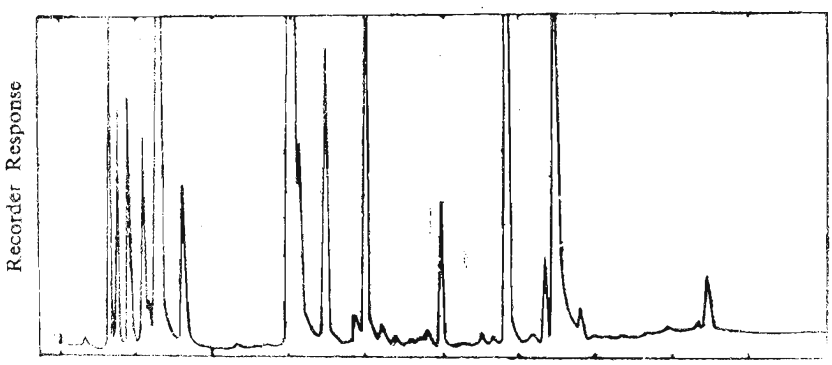
The representative gas chromatographic profiles of the three oils presented in figure (1) reveal both the qualitative and quantitative differences in the individual constituents in them. All three oils possessed the same array of monoterpene hydrocarbons (Table 2). The root-bark oil was rich in α — and β-pinene and possessed also the greater proportion of camphene in comparison to the other two. The main hydrocarbon in the root-bark oil was 1 : 8 cineole (15%). There was not much significance in the difference between leaf and bark oil with respect to their monoterpene hydrocarbons. The leaf oil contained a massive amount of the phenolic constituent eugenol. It also contained linalool, β — caryophyllene, cinnamaldehyde and benzyl benzoate in quantities of over one per cent. β—caryophyllene was the predominant sesquiterpene hydrocarbon in both leaf and bark oils. But, it was not present in root-oil. All three oils contained small amounts of α —humulene and α—ylangene. The bark oil besides cinnamaldehyde contained eugenol, cinnamyl acetate, linalool and three sesquiterpene hydrocarbons mentioned. The leaf oil contained benzyl benzoate as a major ester with traces of cinnamyl acetate, ethyl cinnamate, acetyl



Cinnamon Bark Oil



Cinnamon Leaf Oil



Cinnamon Root Bark Oil

eugenol and methyl cinnamate. The methods based on infra-red spectroscopy gave reproduceable estimates for the relative amounts of eugenol, acetyl eugenol, cinnamaldehyde, cinnamyl acetate, benzyl benzoate, camphor and 1 : 8 cineole present. Comparison of these results with those obtained by quantitative GLC are represented in Table 3. The estimation of eugenol and cinnamaldehyde agreed very closely with those obtained by GLC results, but,in the case of the esters, the GLC values were somewhat lower than the corresponding values obtained by the infra-red methods. This was consistently so and may be due to the operation of some kind of subtractive effect occuring in the GLC columns. It has been noted[4] that FFAP columns tend to absorb and abstract aldehydes. But this was not apparent in the columns used in our study. One of the advantages of the infra-red technique is that a rapid estimation could be obtained of the relative extent to which the main compounds are present using a small volume of the oil for each analysis. The cinnamon oils are of particular interest from the biogenetic standpoint. It has been recorded that the phenylpropanoids present in plants such as cinnamaldehyde and eugenol arise by way of the shikimic acid pathway and the scheme followed is most likely, similar to that proposed for the biosynthesis of lignins.[4] On the other hand, biosynthesis of terpenes occur by way of geranyl or neryl pyrophosphate and compounds like camphor arise from a carbonium ion of the bornane type.[2] The occurrence of both phenylpropanoids and terpenoids as the major constituents of three different parts of the same plant makes the biosynthetic mechanism of these compounds in cinnamon uniquely interesting. The question arises as to whether these compounds are synthesised at site or whether they are transported to the various sites of the plant in which they occur. This will have to await the results of tracer studies now in progress.*

TABLE 3. Comparison of results by IR and GLC methods.

		Percentage	
		IR	GLC
Eugenol	in leaf oil	79.9	80.0
	in bark oil	8.0	10.0
	in root-bark oil	5.0	5.0
Cinnamaldehyde	in leaf oil	2.0	2.4
	in bark oil	65.5	63.0
	in root-bark oil	3.3	3.9
Cinnamyl acetate	in leaf oil	3.2	2.1
	in bark oil	13.0	5.0
Benzylbenzoate	in leaf oil	4.5	3.4
Acetyl eugenol	in leaf oil	3.7	2.1
Camphor	in root-bark oil	52.5	59.9
1 : 8 Cineole	in root-bark oil	12.0	19.0

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