NRCP Research Journal
Vol. 3, No. 2, July-September, 1993

STUDIES ON THE UTILIZATION OF CITRUS WASTES

FELICIDAD E. ANZALDO and ANNABELLE V. BRIONES
Perpetual Help College of Rizal, Las Piñas, Metro Manila, Philippines
Industrial Technology Development Institute
Department of Science & Technology, Bicutan, Tagig, Metro Manila, Philippines

ABSTRACT

The volatile oil was removed from the wastes of calamansi (Citrus microcarpa Bunge), suha (Citrus grandis L.) and dalanghita (Citrus aurantium L.) by hydro-steam distillation and by expression. Hydro-steam distillation gave the highest yield. The physicochemical properties of the oils were also determined. Distilled oils have higher values of acid and ester numbers with lower values of specific gravity and refractive index than the expressed oils. Identification of the chemical constituents was done by thin-layer chromatography, gas-liquid chromatography and infra-red spectroscopy. The results showed the presence of limonene, citral, geraniol, α- pinene, β - pinene, terpineol and geraniol.

The residues after distillation of the volatile oil were utilized for the production of pectin. The results recorded a yield of 5.51% for dalanghita, 4.26% for calamansi and 1.34% for suha. The product obtained conforms with the specifications set by the United States Pharmacopeia XXII (1990) and are classified as rapid-set type.

Utilization of oil-free citrus wastes for carotenoid production was also done. The highest yield of carotenoid content was observed in calamansi as compared to suha and dalanghita.

INTRODUCTION

Citrus is one of the most popular fruits in the country. Likewise it is considered as an important crop and a top dollar-earner industry.

Citrus is chiefly utilized for its pulp and juice but the rind, pressed pulp, covering each individual segment of the edible portion, and seeds are considered as wastes. To a small extent, the rind has been made into confections. The average annual per capita consumption in the Philippines is approximately 7.0%. During peak season there is an abundant supply of these fruits. Thus, it is the aim of this project to find means of producing from these otherwise waste commodities into marketable goods such as volatile oils, pectin, and carotenoids. The commercial utilization of these wastes has aroused interest for the production of scents, flavors, jelling agents and colorants. Most of our

food and drug industries utilize these products which are usually imported. It is therefore, important to produce them locally in order to offset the cost of importation and to provide a means of utilizing products which could otherwise be disposed of as waste.

Volatile oils popularly referred to as essential oils are isolated from odoriferous plants by distillation, expression, and solvent extraction. These oils are used in three primary ways: as odorants, as flavors and as pharmaceuticals. Citrus oils are obtained from various parts of the plant. This study deals with the oils from the fruit of three Philippine species and the parts of the fruit not used as food. Citrus microcarpa Bunge contains volatile oil in the leaves and rind. These oils contain aldehydes, cyanogenetic substances, glucosides, linalool, linalyl acetate, α- pinene, sesquiterpenes and tannins (Quisumbing, 1978). The calamansi oil from leaves produces a satisfactory carminative effect similar to that of peppermint oil (Villa-Simbra, 1939). The volatile oil of the rind of Citrus aurantium L. contains 92% limonene and methyl anthranilic acid methyl ester (Quisumbing, 1978). The rind of Citrus grandis Osbeck yields a volatile oil "pompelmus" oil, containing α - pinene, 0.5 – 1.5%; D-limonene, 90-92%; linalool, 1-2%; citral, 3-5%; geraniol, 1-2%; linalyl and geranyl acetate, 25%; free alkaloid, 8.61%; and ester, 4.38%. The leaves contain volatile oil, 1.7%; dipentane, 25%; linalool, 15%; citral, 1.0%. The flowers yield a volatile oil (Quisumbing, 1978). Other researches done on volatile oils were on the rinds of Citrus hystrix DC. (Florento and Oliveros-Belardo, 1959), Citrus nobilis Lour. (Cruz & Concha, 1965), and Citrus grandis Osbeck (Rosalinda and Concha, 1972).

Pectin is a purified carbohydrate product obtained from the dilute acid extract of the inner portion of the rind of citrus fruits or from apple pomace. It consists chiefly of partially methylated polygalacturonic acid. The term pectin designates pectinic acids containing at least 7 or 8% methyl ester groups expressed as methoxyl, and capable of forming gels (jellies) with sugar (or other polyhydroxy compounds) and acid under suitable conditions. Calamansi rind contains 3.25% of pectin on a fresh weight basis. Pectin content of the seeds is 2.60% and 6.13% of the pulp (Manalo, *et al.,* 1985). Results showed that about 4.2% pectin (fresh weight basis) could be obtained from calamansi seeds (Magwili and Guzman, 1971). Hung lemon yielded 30.03% pectin and ladu mandarin, 74.20% (Rongo and Quiatson, 1940).

Matured citrus fruit rinds have distinctive and attractive colors ranging from pale yellow through orange to red (Kefford and Chandler,

1970). This is due to the group of yellow or orange water soluble, polyene carotenoids found in plants and in bacteria (Phillip, 1975). Over fifty different compounds have been isolated from the carotenoid fraction of citrus fruits, including hydrocarbons, epoxides, monols, monals, diols, diol monoepoxides, diol epoxides, polyols, aldehydes, and ketones. The peel of Citrus microcarpa Bunge has the highest carotenoid content followed by the juice and the pulp in decreasing order (Luis, *et al.,* 1976).

MATERIALS AND METHODS

I. Materials

Wastes from *Citrus microcarpa Bunge* (calamansi), *Citrus grandis L.* (suha) and *Citrus aurantium L.* (dalanghita) found in Figs. 1 to 3, were used in this study. The parts used were the rind, pulp, and seeds of calamansi, and rind of suha and dalanghita. Samples of *Citrus microcarpa Bunge* were bought from markets in Metro Manila while *Citrus grandis L.* were collected in Quezon Province. *Citrus aurantium L.* were collected in Oriental Mindoro and Batangas.

II. Obtention of Volatile Oils

The hydro-steam distillation process and cold-expression method were employed in this experiment.

Hydro-steam distillation - The fresh samples were weighed, comminuted and placed in a muslin bag suspended in a flask containing water. When the water boiled, the steam rose through the suspended bag, thus injecting heat and oil extraction took place. The oil was collected and placed in amber-colored bottles.

Expression Method - The albedo or the white portion was removed from the rind and the oil was expressed by hand. For reproducible results a mechanized press is recommended. The slurry was placed in a separatory funnel and allowed to stand. The oil was separated from the water and dried using anhydrous sodium sulfate.

III. Extraction of Pectin

The samples were comminuted and subjected to hydro-steam distillation for one hour to remove the volatile oil. After extraction, the

samples were then washed with running water to remove soluble sugars and glycosides. The next step, was to hydrolyze the protopectin to soluble pectin. This was accomplished by treating the samples with two parts of 0.2% hydrochloric acid solution for thirty minutes at 80°C –100°C. Immediately the mixture was filtered and the spent pulp was again treated with one part of 0.2% acid solution for a second extraction to maximize the yield. The pectin liquors were combined and added to two parts of alcohol for precipitation. The mixture was stirred, allowed to stand overnight, filtered through muslin cloth to separate the pectin from the alcoholic liquor. The pectin was washed two times with recovered alcohol and was given a final dehydrating wash in 95% alcohol. The pectin was dried at 60°C, pulverized, and stored.

IV. Extraction of Carotenoid

Each sample was subjected to hydro-steam distillation for one hour to remove the volatile oil. The residue was then soaked in 10% alcoholic solution overnight and filtered. The residue was washed again with one part of the solvent. The filtrate and washings were combined, concentrated to a syrupy mass, and washed with ether to remove the chlorophyll. The product after removal of chlorophyll was then dried under vacuum and ground to a coarse powder.

V. Physical Constants of the Volatile Oil

The specific gravity and refractive index of the oils were determined using the pycnometer method and an Abbe refractometer respectively (Jenkins, *et al.,* 1957). The method of determining the ester number was by saponification with heat while the acid number was obtained by the titration method (Guenther, 1948).

The solubility of the oil in alcohol was determined by adding 20 drops of oil in 5 mL each of 50, 60, 65, 70, 80, 90 and 95% ethanol.

VI. Identification of the Chemical Constituents of Volatile Oil

Thin-layer chromatography was carried out by using Silica Gel GF254 as coating with Benzene:Ethyl acetate (47.5 mL: 2.5 mL) as solvent system. The spots were developed by exposure to iodine vapor. The apparatus used for gas-liquid chromatography was a GC Shimadzu Model 7-A with thermal conductivity detector, using nitrogen as carrier gas. Infra-red spectra were obtained by using KBr pellets using a Perkin-Elmer 1330 IR Spectrophotometer.

VII. USP XII Analysis of Pectin

A. Identification Tests for Pectin

A sample approximately one gram in weight was heated with 9 mL of water on a steam bath until a solution was formed. A stiff gel was formed after cooling.

A 5 mL solution (1 in 100) was added with 1 mL of 2 N sodium hydroxide and allowed to stand at room temperature for 15 minutes. A gel was formed indicating the presence of pectin.

B. Measurement of Galacturonic Acid Content

The pectin was washed free of mineral acid with alcohol and titrated with 0.5 N NaOH. Each mL of alkali used in the total titration is equivalent to 97.07 mg of $C_6H_{10}O_7$.

C. Measurement of Methoxyl Content

The chloride-free pectin was moistened with alcohol, and 100 mL CO_2-free water was added then stirred vigorously to obtain an even suspension. The solution was titrated with 0.5 N NaOH and allowed to stand after the addition of 20.0 mL of 0.5 N NaOH. The pink color was discharged by adding an equal amount of 0.5 N HCl and titrated with 0.5 N NaOH to a faint pink color. Each mL of 0.5 N NaOH used in the saponification titer is equivalent to 15.52 mg of $-OCH_3$.

D. Moisture Determination

One gram of each pectin sample was weighed in a tared dish and heated at 100oC in a convection oven to constant weight.

E. Setting Time and Temperature

Sixty grams of sugar was mixed with 0.5 g pectin sample and 39.5 mL water then heated until the temperature of the mixture reached 106°C. Citric acid (0.5 g) was added and placed in a water bath at 30°C. Setting time and setting temperature of the pectin/sugar mixture were recorded.

VIII. Measurement of Total Carotenoid Content

Total carotenoid content was determined according to the Official Methods of analysis for Carotenoids (AOAC, 1990). All analytical procedures were carried under subdued light. Solvents and reagents were of analytical grade.

RESULTS AND DISCUSSIONS

Volatile oils

The extraction of volatile oil from the rinds of calamansi, dalanghita, and suha was carried out using two processes namely, hydro-steam distillation and cold expression method. The highest yield of oil was obtained by distillation process. The results are tabulated in Table 1. Among the three samples studied, dalanghita gave the highest yield of oil. Several trial runs were conducted to recover calamansi oil by hand expression of the rind with pressed pulp but negative results were obtained.

Volatile oils can still be distilled from suha and dalanghita peels after being hand-pressed since citrus peels do not yield all of their volatile oil content upon pressing. The quantity of peel oil available as cold-pressed oil varies greatly and, as noted is always less than that by the distillation method.

It was also observed that during the first hour of distillaiton, highest yield of oil can be obtained. As shown in Fig. 4, the yield of oil dropped considerably as the distillation was continued. The graph showed an inversely proportional relationship between the volume of oil obtained and distillation time exhibited by the three samples. The maximum yield of oil can be obtained during the first three hours of distillation.

The physical constants of the oils obtained were then determined. The results are shown in Table 2. Distilled oils have higher values of acid and ester numbers compared to expressed oil and lower values of specific gravity and refractive index. Distilled citrus oils showed differences in flavor and composition when compared to the corresponding cold-pressed oils. The high-boiling components in cold-pressed oils are not present in distilled oils. The latter are unstable due to the absence of anti-oxidants which is observed in cold-pressed oils.

The chemical constituents of the oils were also identified by thin-layer chromatography, infra-red spectroscopy, and gas-liquid chromatography. Pure samples of citral, geraniol, limonene, α - pinene, β - pinene, terpineol, and linalool were used as standards in the identification of compounds present in the citrus oils. The thin-layer chromatograms of all samples showed the presence of limonene, α - pinene, β - pinene, terpineol, geraniol, citral, and linalool (Figs. 5, 6 and 7). TLC results were in agreement with those from gas liquid chromatography of the oils.

Limonene is by far the largest hydrocarbon component in citrus oils. Results of IR-analysis (Figs. 8 and 9) showed the presence of limonene in all of the samples. The presence of sharp peaks at 3000 cm^{-1} to 2900 cm^{-1} and 1650 cm^{-1} to 1590 cm^{-1} indicated a monocyclic unsaturated hydrocarbon.

The gas-liquid chromatograms of the samples (Figs. 10-15) showed the presence of limonene, citral, geraniol, α - pinene, β - pinene, terpineol and linalool. Identification of the components was done following the usual method of peak enrichment using authentic samples.

Pectin

Studies were conducted to utilize citrus wastes (calamansi rind, seed, pulp; suha and dalanghita rind) for the production of pectin. The extraction was carried out three times using the same sample to get the maximum yield. The recovery of pectin from dalanghita rind was higher than calamansi wastes and suha rind (Table 3). Investigation of its chemical properties indicated high methoxyl and galacturonic acid content (Table 4). Results of the analysis are within the specifications set by the USP XII. Pectin yields not less than 6.7 % of methoxy groups ($-OCH_3$) and not less than 74.0% of galacturonic acid ($C_6H_{10}O_7$) calculated on tge dried basis. The pectins isolated from citrus wastes were all of the rapid-set type as observed in their short period of setting.

Pigment/Coloring Matter

The recovery of carotenoid from citrus rinds was carried out after the separation of essential oil. The highest yield calculated on dry weight basis was obtained from suha, followed by dalanghita and calamansi as shown in Table 5. However calamansi exhibited higher content of carotenoid as compared to suha. It has been shown that the distribution of carotenoid depends largely on species and cultivar differences (Citrus Science and Technology, 1977).

SUMMARY AND CONCLUSION

Volatile oils can be recovered from citrus wastes using two processes namely: hydro-steam distillation and hand expression. The latter process is not applicable to calamansi , unless a special type of mechanical press is utilized. Among the three samples studied dalanghita rind gave the highest yield of oil, 1.33% by distillation process and 0.60% by hand expression. Suha rind yielded 0.75% by hydro-steam distillation 0.21% by hand expression. The yield of oil from calamansi rind with pulp using the hydro-steam distillation process is 0.71% and 0.705 from the rind alone. The distillation process requires three hours of distillation to obtain the maximum yield of oil from the three samples. The physicochemical properties of the citrus oils showed that distilled oils have higher values of acid and ester numbers with lower values of specific gravity and refractive index as compared to expressed oils. Identification of the chemical constituents of the oils was done by thin-layer chromatography, gas-liquid chromatography, and infra-red spectroscopy. The results showed the presence of limonene, citral, geraniol, α- pinene, β- pinene, terpineol, and linalool.

Citrus wastes were found to be good source of pectin. Dalanghita gave the highest yield of pectin (5.51%, dry weight basis), followed by calamansi, with a yield of 4.26% (dry weight basis) then suha (1.34%, dry weight basis). The method adapted in the extraction process of pectin yielded a product that conforms to the specifications set by United States Pharmacopeia XXII (1990) and classified as rapid-set type based on its shorter time for setting.

Carotenoid can also be recovered from citrus wastes after being extracted with volatile oil. The highest yield of carotenoid was obtained from suha with a yield of 3.96% as compared with dalanghita, 3.23%. Calamansi gave a lowest yield of 1.87%. The percentage composition of carotenoid was determined and calamansi gave the highest carotenoid content of 6.28 mg/g followed by suha with a yield of 3.55 mg/g. Dalanghita contained 3.30 mg/g of carotenoid.

The studies on the utilization of citrus wastes for volatile oils, pectin, and pigment showed the viability of producing locally citrus oils, pectin, and carotenoids in commercial scale.

LITERATURE CITED

Association of Official Agricultural Chemists. 1990.

Brown, W.H. 1941. Useful plants of the Philippines, Vol. 2 Bureau of Printing, Manila

Citrus Science and Technology 1977. Vols. 1 & 2 AVI Publishing Company, Inc. Westport, Connecticut.

Cruz, F.P., and J.A. Concha. 1965. The Essential Oils from the Rind of *Citrus nobilis Lour. var. Ladu. Journal of Philippine Pharmaceutical Assoc.,* 5 (5):215

Florento, C.D., and L.O. Belardo. 1959. A Study on the Volatile oil of the rind of *Citrus hystrix D.C.* var. Miciantha. *Journal of Philippine Pharmaceutical Assoc.,* 46: 55

Gibbs, A.D., and F. Agcaoili. 1912. Philippine citrus Fruits: Their Commercial Possibilities and Chemical Study of a Few of the Most Important Varieties., Philippine *Journal of Science,* Sect. A 7 pp. 403-415, plates 1-5

Guenther, E. 1948. The Essential Oils, Vols. 1 & 3 D.V. Nostrand Co., Inc., Toronto, New York and London.

Jenkins, G.L. *et al.* 1957. Quantitative Pharmaceutical Chemistry. McGraw-Hill Book Co., Inc., New York.

Kefford, J.F., and B.V. Chandler. 1970. The Chemical Constituents of citrus Fruits. New York, Academic Press.

Luis, E.S. *et al.* 1976. The Chemical Constituents of Kalamansi *(Citrus microcarpa Bunge)* and Dayap *(Citrus aurantifolia Swingle). Phil. Journal of Food and Science Technology* 7 (1): pp 87- 91.

Magwili, T.H., and M.P. Guzman 1971. Pectin Preparation from Calamansi Seeds and Watermelon Rind, BSHE Thesis, University of the Philippines. College of Home Economics.

Manalo, J.B. *et al.* 1985. Pectin: A Product of Calamansi (Citrus microcarpa Bunge) Fruit Waste. *National Institute of Science and Technology Journal* 2 (1): 19.

Philippine National Formulary 1980: Kalamansi, National Science Development Board, 1st Ed. p. 45.

Philipp, T. 1975. Carotenoid Esters in Plant Products. Food Technology, 29. no. 5 pp. 50-54.

Quisumbing, E. 1978. Medicinal Plants of the Philippines. pp. 454-455.

Quisumbing, E. 1981. *Citrus microcarpa Bunge. Journal of Philippine Pharmaceutical Association* 34:1-12.

Rongo, V. , and S.L. Quiatson. 1940. Determination and Extraction of Pectin from Citrus and Othe Fruits . Philippine Agriculture 29: 1-19.

Rosalinas, Z.A., and J.A. Concha. 1972. A Chemical Study of the Essential Oil of *Citrus grandis Osbeck* (Family Rutaceae). *Journal of Philippine Pharmaceutical Association* 58 (1-4):36-37.

United States Pharmacopeia 1990. XXII Revision.

Villa-Simbra, E., and Luz B. Oliveros. 1939. *C. mitis* 'Kalamansi', MS Thesis, Philippine Women's University.

Table 1. Yield of oil from citrus fruits.

	Method	Part Used	Yield of oil with respect to the fresh or dried weight of the whole fruit % W/W	Yield of oil with respect to the fresh or dried weight of the rind and pulp % W/W	Total Hours Consumed
Calamansi	Hydro-steam distillation	rind with pulp	0.20%	0.71%	12 h
	Hydro-steam distillation	rind	0.20%	0.70%	12 h
Suha	Hydro-steam distillation	rind	0.10%	0.75%	12 h
	Expression	rind	0.04%	0.21%	12 h
Dalanghita	Hydro-steam distillation	rind	0.24%	1.33%	12 h
	Expression	rind	0.13%	0.60%	12 h

Table 2. Physicochemical Properties of Citrus Oils.

	SAMPLES						STANDARD		
	CALAMANSI OIL		SUHA OIL		DALANGHITA OIL		BITTER ORANGE OIL	LEMON OIL	SWEET ORANGE OIL
	Hydro-steam distillation		Hand Expression	Hydro-steam distillation	Hand Expression	Hydro-steam distillation	Cold Expression		
	Rind	Rind with Pulp							
Specific gravity (25 C)	0.8382	0.8365	0.8779	0.8250	0.8440	0.8487	0.8420 - 0.8480	0.8490 - 0.8550	0.8420 - 0.8460
Refractive Index	1.4690	1.4683	1.4788	1.4677	1.4700	1.4685	1.4742 - 1.4755	—	1.4723 - 1.4737
Acid No.	1.1200	1.1200	0.8415	0.8915	0.8415	1.1220	—	—	—
Ester No.	8.35	8.42	2.81	5.61	2.80	5.61	—	—	—
Color	Colorless to pale yellow		Lemon yellow	Color-less	Lemon yellow	Color-less	Pale Yellow	Pale yellow or greenish liquid	Yellow to deep orange
Solubility	Soluble at 90% to 95% alcohol						soluble in 4 vols. alcohol	soluble in 3 vols. alcohol	soluble in 2 vols. 90% alcohol
Odor	Pleasant fruit odor		Sweet fruit odor	Pleasant fruit odor	Sweet fruit odor	Pleasant fruit odor	Characteristic orange odor		

Table 3. Percentage yield of pectin from citrus wastes (dry weight basis).

	1st Extraction	2nd Extraction	3rd Extraction	Total	Total Hours
Calamansi Wastes (rind, seed, pulp)	2.30	1.63	0.33	4.26	12 hrs.
Suha rind	0.49	0.44	0.41	1.34	12 hrs.
Dalanghita rind	2.55	2.08	0.88	5.51	12 hrs.

Table 4. Percentage yield and properties of pectin from citrus wastes

	% Yield	% Moisture (oven-dried)	% Ash	Color	Methoxyl Content %	Galacturonic Acid %	Setting Time (min)	Setting Temperature
Calamansi Wastes	4.26	8.10	4.95	Off-white	11.42	80.17	5	90°C-60°C
Suha Rind	1.34	9.45	3.04	Off-white	9.30	80.19	10	85°C-60°C
Dalanghita Rind	5.51	8.63	2.11	Off-white	7.32	78.40	15	80°C-60°C

Table 5. Percentage yield of pigment and carotenoid content.

	% Yield (dry weight basis)	Appearance	Color	Carotenoid Content Mg/g
Calamansi with 1 hour distillation	1.87	powder	rusty yellow	6.28
Dalanghita with 1 hour distillation	3.23	powder	rusty yellow	3.30
Suha with 1 hour distillation	3.96	powder	rusty yellow	3.55

Figure 1. *Citrus microcarpa* Bunge.

A - Habit with branched fruits
B - Fruits with branch
C - Flower
D - Section of Flower
E - Fruit
F - Transection of Fruit

Ref.: Brown, W.H. 1941. Useful Plants of the Philippines, Vol. 2

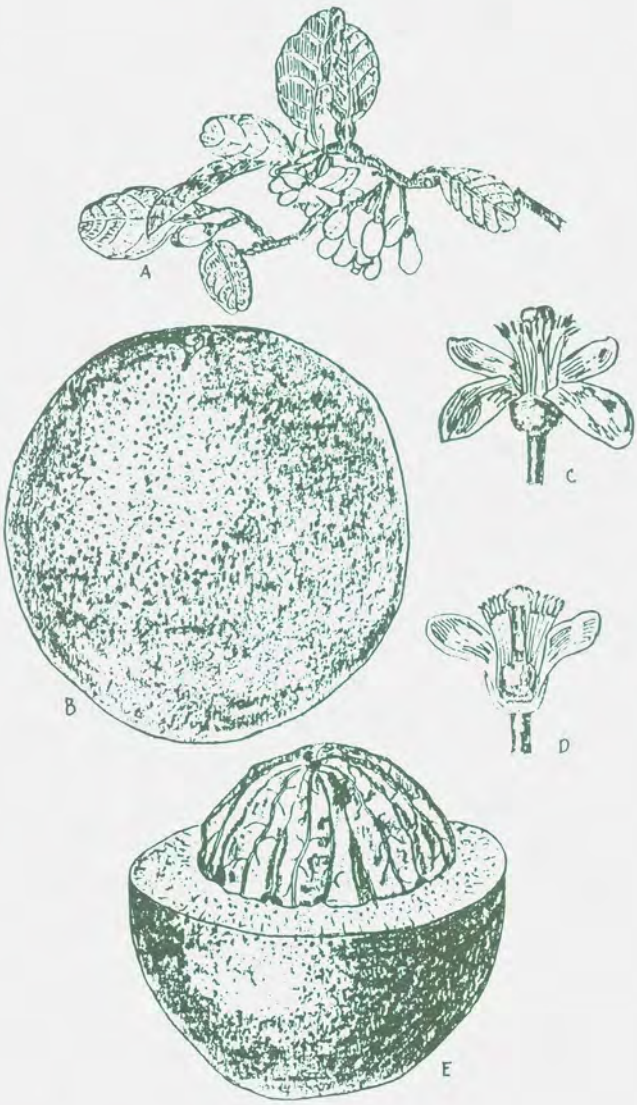

Figure 2. *Citrus grandis* L.

A - Flowering branch
B - Fruit
C - Flower
D - Section of Flower
E - Section of Fruit

Ref.: Brown, W.H. 1941. Useful Plants of the Philippines, Vol. 2

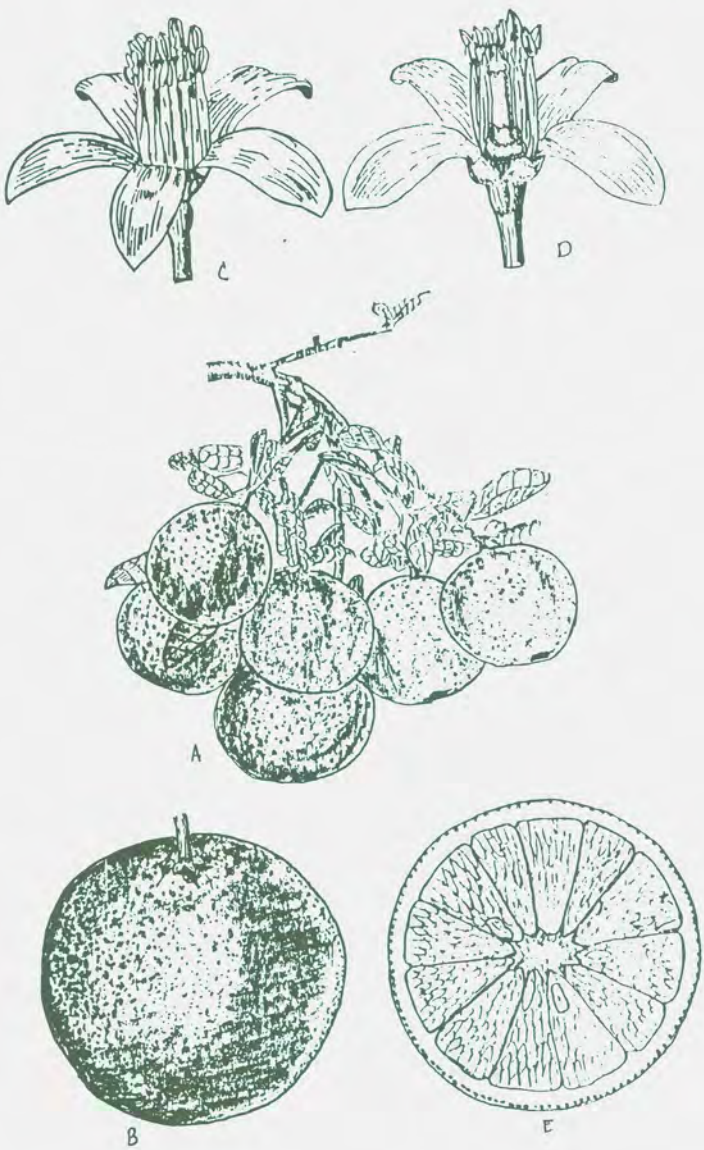

Figure 3. *Citrus aurantium* L.

A - Fruiting branch
B - Fruit
C - Flower
D - Section of Flower
E - Section of Fruit

Ref.: Brown, W.H. 1941. Useful Plants of the Philippines, Vol. 2

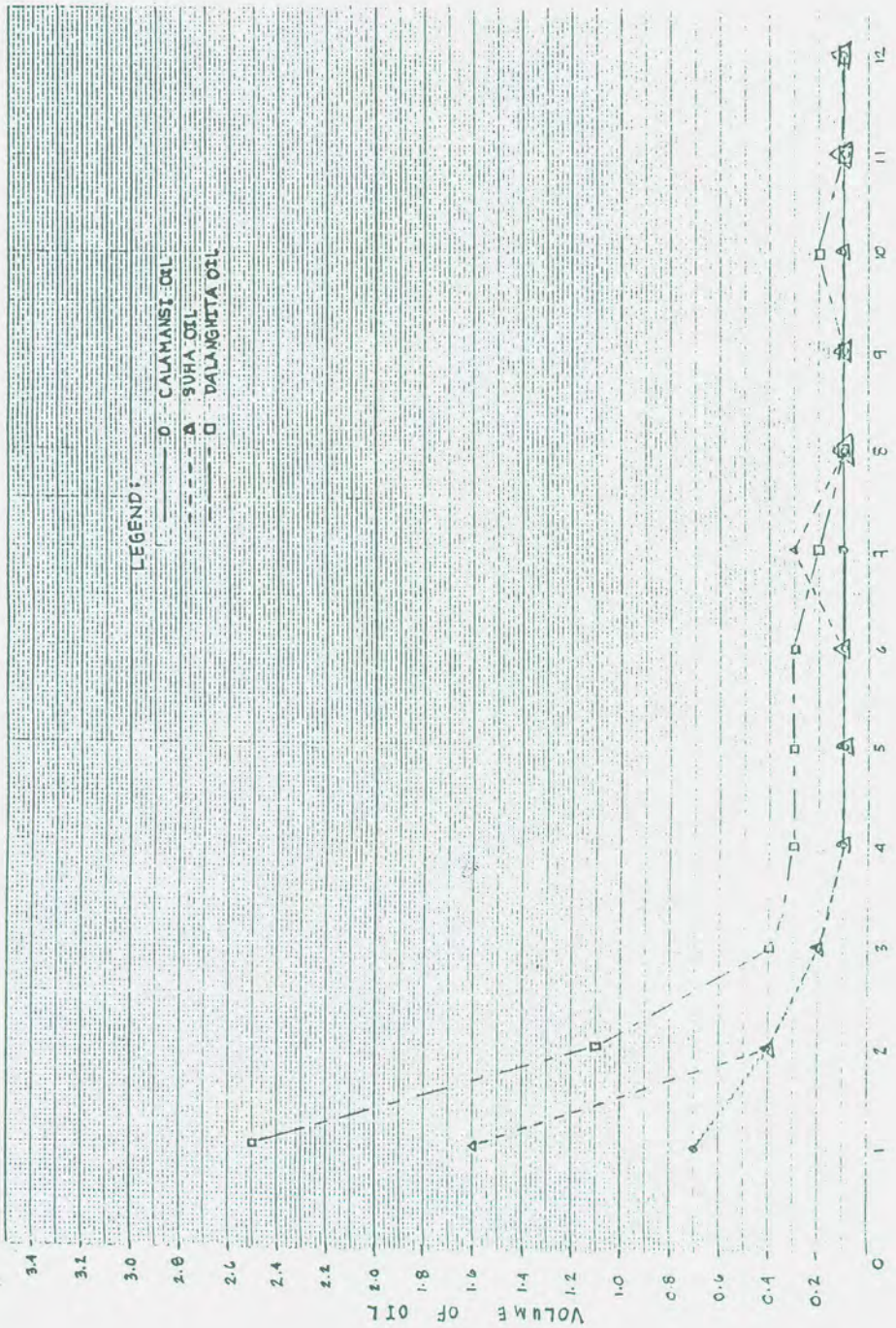

Figure 4. Effect of Distillation Time on the Yield of Citrus Oils.

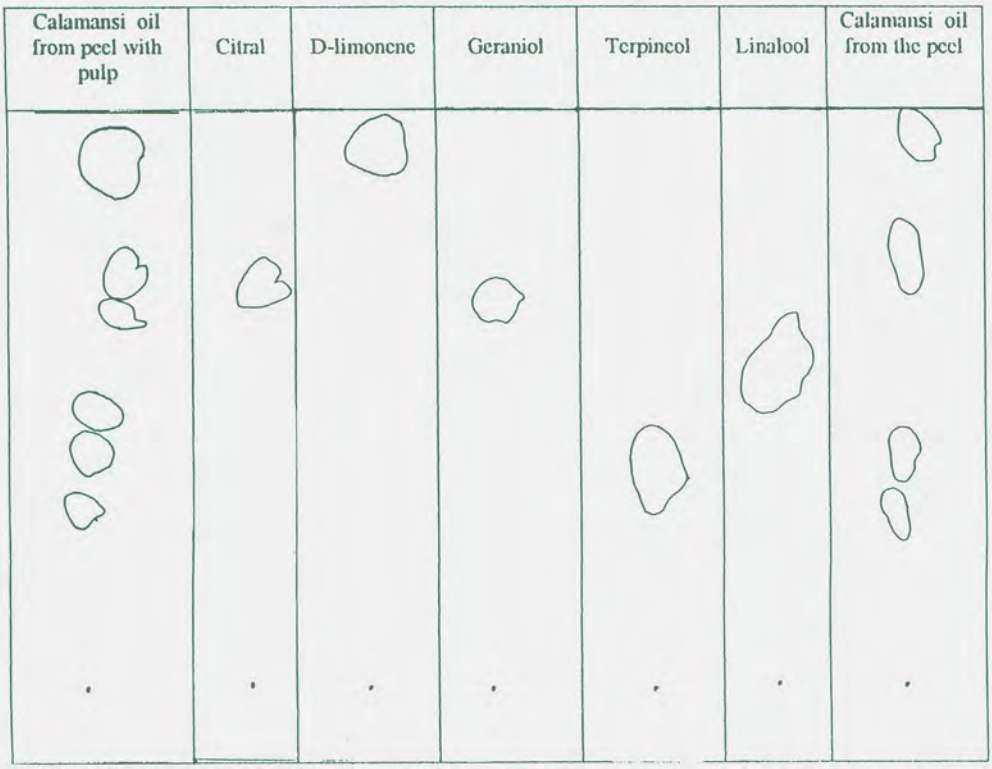

Figure 5. Thin-layer chromatogram of calamansi oil and standards.

Coating : Silica Gel 60 g
Solvent System : Benzene : Ethyl Acetate
Visualizing Agent : Iodine vapor

Rf Values

Calamansi Oil from peel with pulp	Citral	Limonene	Geraniol	Terpineol	Linalool	Calamansi Oil from the peel
0.35						0.34
0.43				0.40		0.42
0.50					0.53	
0.62			0.61			
0.68	0.65					0.68
0.84		0.84				0.85

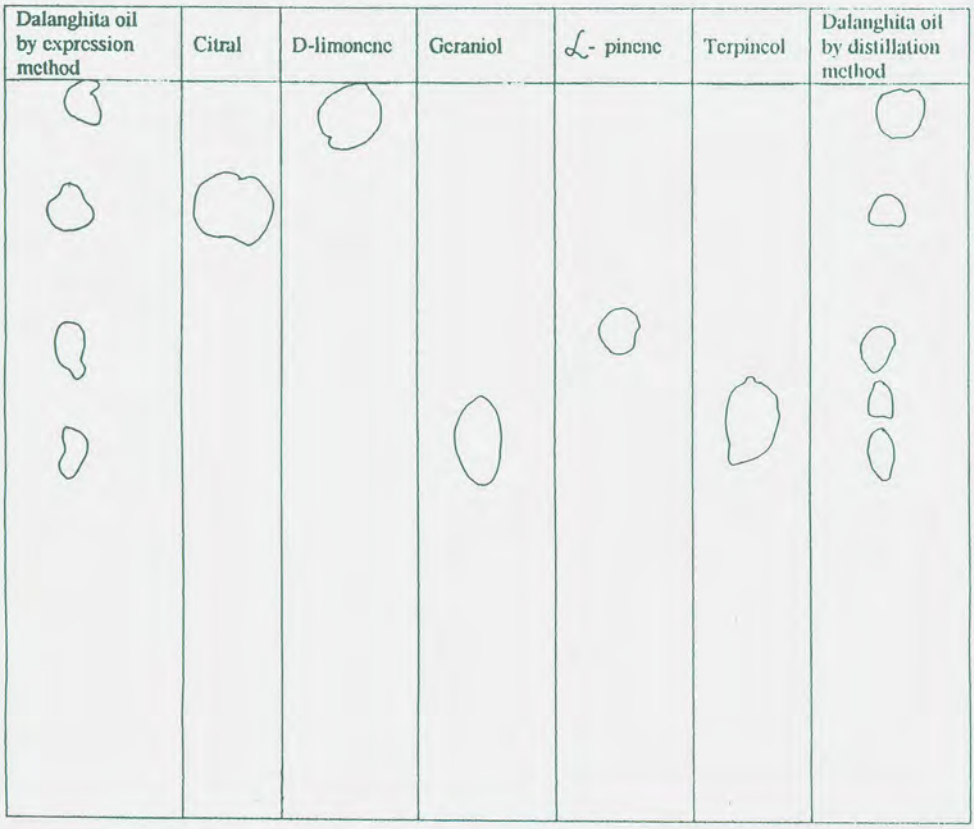

Figure 6. Thin-layer chromatogram of dalanghita oil and standards.

Coating : Silica Gel 60 g
Solvent System : Benzene : Ethyl Acetate
Visualizing Agent : Iodine vapor

Rf Values

Dalanghita Oil from peel with pulp	Citral	Limonene	Geraniol	α-Pinene	Terpineol	Dalanghita Oil from the peel
0.36			0.39			0.37
					0.43	0.45
0.51				0.54		0.52
0.72	0.72					0.72
0.86		0.84				0.86

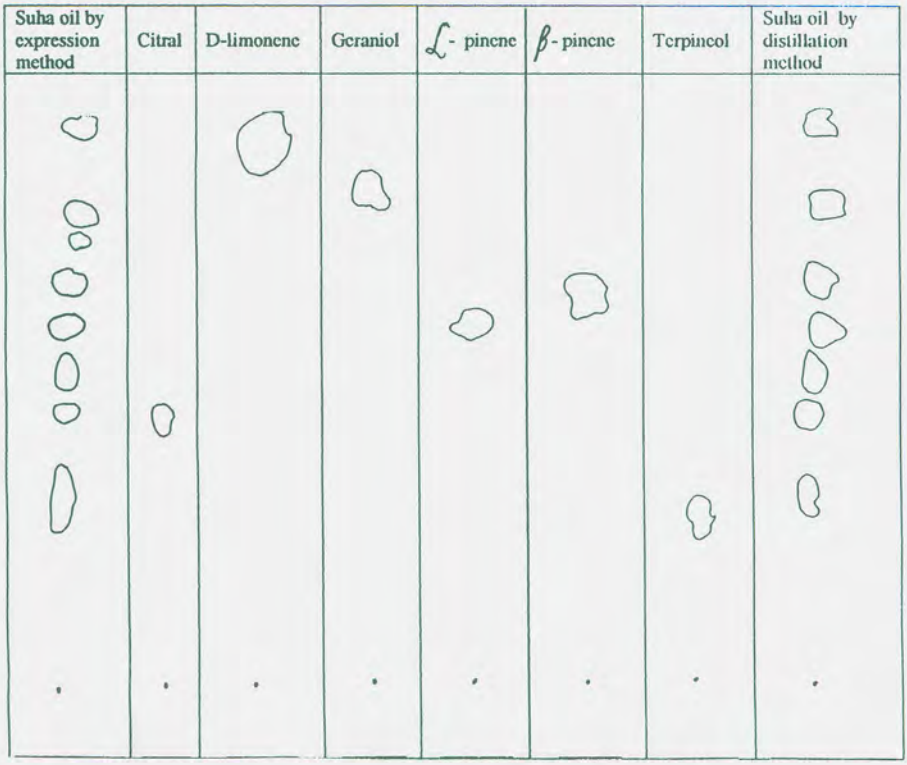

Figure 7. Thin-layer chromatogram of suha oil and standards.

Coating : Silica Gel 60 g
Solvent System : Benzene : Ethyl Acetate
Visualizing Agent : Iodine vapor

Rf Values

Suha Oil by Expression Method	Citral	Limonene	Geraniol	α Pinene	β Pinene	Terpineol	Suha Oil by Distillation Method
0.29						0.26	0.37
0.43	0.41						0.45
0.57				0.56			0.52
0.63					0.60		0.72
0.74			0.75				0.73
0.87		0.84					0.82

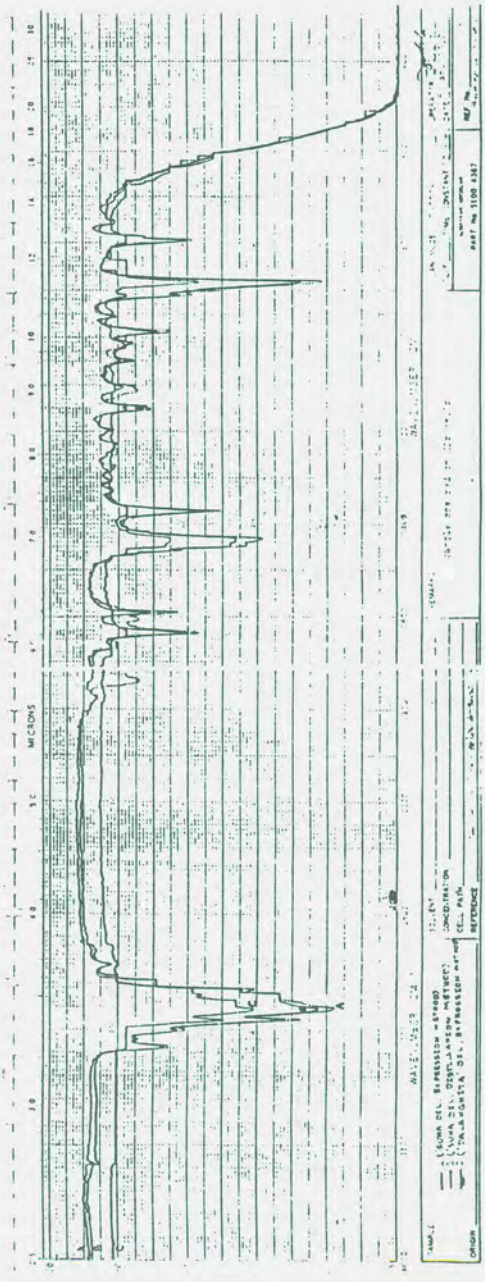

Figure 8. IR spectra of *citrus* oils.

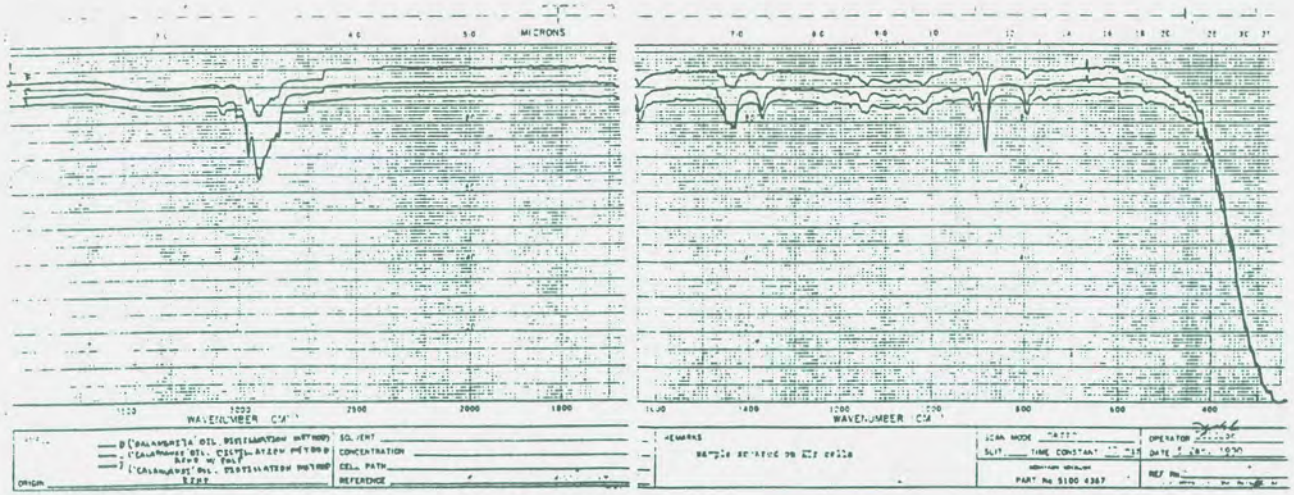

Figure 9. IR spectra of *citrus* oils.

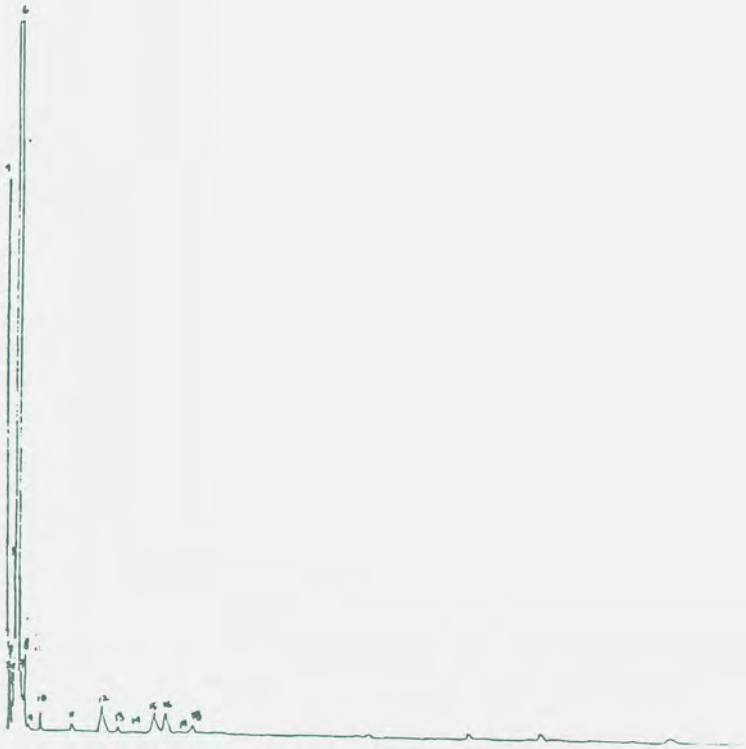

Figure 10. Gas chromatogram of the volatile oil from the rind of *Citrus microcarpa* Bunge (Distillation Method).

Conditions : Column, PEG 20m; FID detector; carrier, nitrogen gas

Peaks : 3 = α-Pinene; 5 = β-Pinene; 6 = citral; 7 = D-limonene; 12 = linalool; 15 = terpineol; 18 = Geraniol

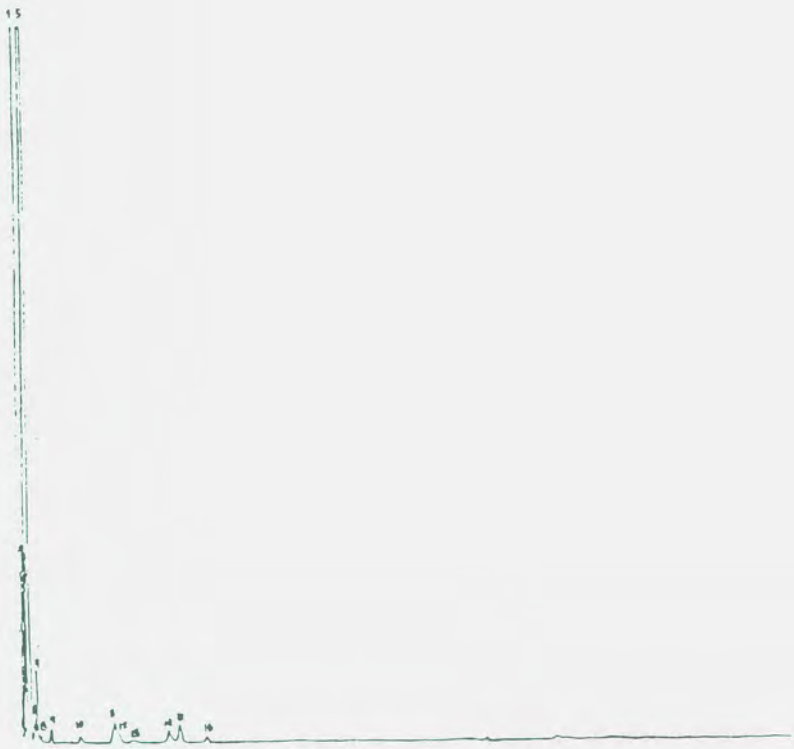

Figure 11. Gas chromatogram of the volatile oil from the rind of *Citrus microcarpa* Bunge (Distillation Method).

Conditions : Column, PEG 20m; FID detector; carrier, nitrogen gas

Peaks : 2 = α-Pinene; 3 = β-Pinene; 4 = citral; 5 = D-limonene; 11 = linalool; 14 = Terpineol; 15 = Geraniol

Figure 12. Gas chromatogram of the volatile essential oil from the rind of *Citrus aurantium* L. (Expression Method).

Conditions : Column, PEG 20m; FID detector; carrier, nitrogen gas

Peaks : 2 = α-Pinene; 3 = β-Pinene; 4 = citral; 5 = D-limonene; 11 = Linalool; 16 = terpineol; 18 = Geraniol

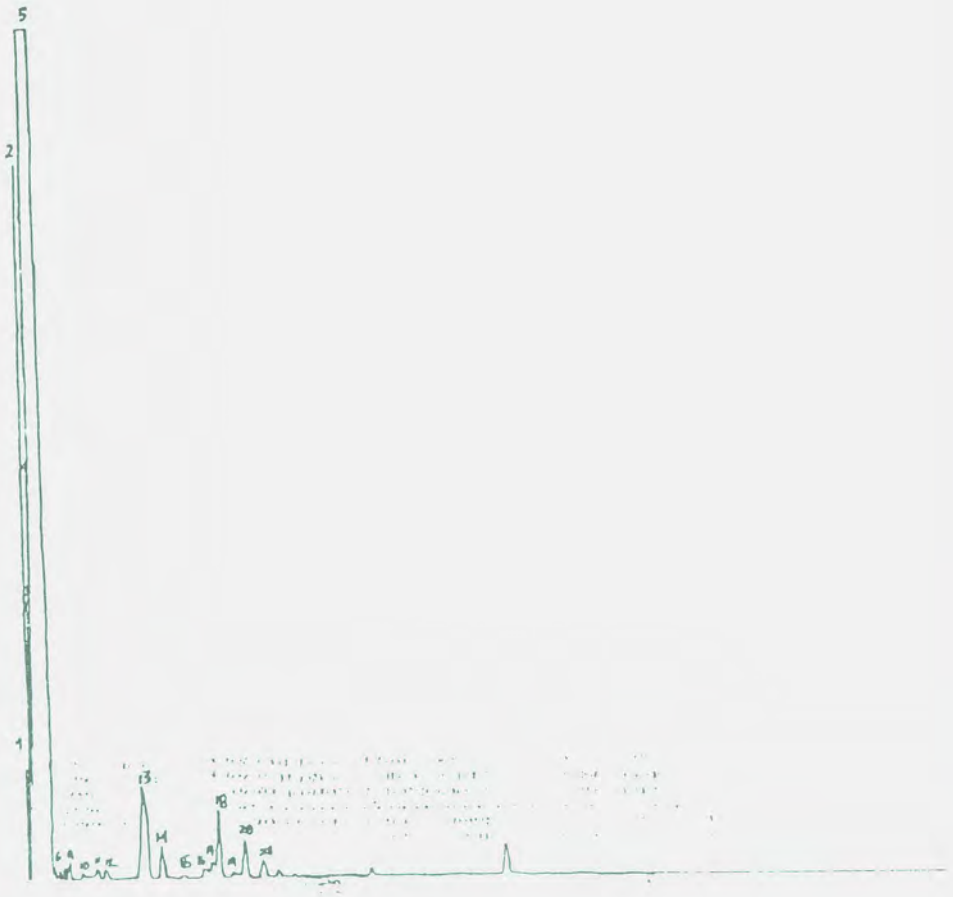

Figure 13. Gas chromatogram of the volatile essential oil from the rind of *Citrus aurantium* L. (Distillation Method).

Conditions : column, PEG 20m; FID detector; carrier, nitrogen gas

Peaks : 2 = ∝-Pinene; 3 = β-Pinene; 4 = Citral; 5 = D-Limonene; 14 = Linalool; 18 = Terpineol; 20 = Geraniol

Figure 14. Gas chromatogram of the volatile essential oil from the rind of *Citrus grandis* L. (Expression Method).

Conditions : Column, PEG 20m; FID Detector; carrier, nitrogen gas

Peaks : 3 = ∝-Pinene; 4 = β-Pinene; 5 = citral; 6 = D-limonene; 12 = Linalool; 16 = terpineol; 19 = Geraniol

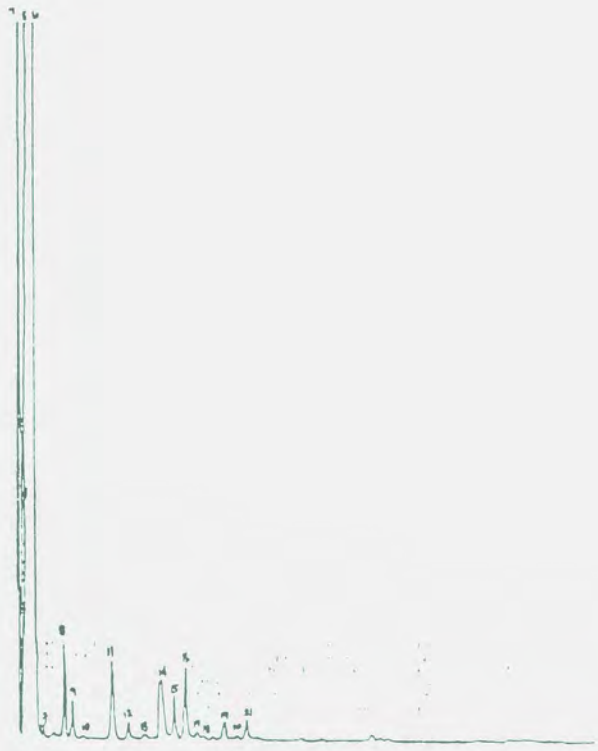

Figure 15. Gas chromatogram of the volatile essential oil from the rind of *Citrus grandis* L. (Distillation Method).

Conditions : Column, PEG 20m; FID detector; carrier, nitrogen gas

Peaks : 3 = ∝-Pinene; 4 = β-Pinene; 5 = citral; 6 = D-limonene; 12 = Linalool; 16 = terpineol; 19 = Geraniol