ESSENTIAL OILS

By Luz O. Belardo, Ph.D., Academician

PART I
Introduction

It is a pleasure to present a paper on a fascinating area of natural products, the essential oils. The coverage of this presentation is limited to brief discussions on the nature, production, chemistry, and uses of essential oils; hence, it is by no means complete. Occasionally, some of the results of my chemical study on some new Philippine essential oils will be touched.

Essential oils are so-called, not because they are in a way necessary to the well-being of the users,. but because they are essences. The word essential in this case was derived from the Paracelsian concept (1493-1541) of *Quinta essentia* or *quintessence*, meaning the fifth element after the alchemist's mercury, sodium chloride, sulfur and lead. It was considered the last possible and most sublime extract of the most condensed form of the plant or drug.

Since antiquity, man has been mystified by essential oils and has made great efforts to obtain them. The whims and demands of royal families for perfumed baths, luxurious boudoirs and sumptuous banquets compelled the hot search for aromatic plants. It will be recalled that the quest for spices was concomitant with the ambition of early naval expeditions to discover and conquer new lands far across the seas.

Essential oil is also called volatile oil, because it is a greasy liquid, and volatile because the spot it leaves on brown wrapping paper loses its translucency and finally disappears.

Production

Essential oils are obtained from different parts of plants, rarely from animals. The traditional methods of extracting the oil are distillation, expression, extraction with low-boiling solvents, and enfleurage, each method being chosen according to the suitability to the plant material. Distillation is the most commonly used method. Expression is limited to the obtention of the oil by piercing or rasping the oil sacs in the rinds of fruits as in the case of oil of orange. Low-boiling solvents extract components of oil in practically intact condition that can produce perfumes of very fine quality reproducing to a remarkable degree the odor of the living flowers. Ilang-ilang oil that is used in the creation of the masterpieces of French perfumery is obtained, not by distillation, but by extraction with low-boiling solvents. Enfleurage utilizes fats to capture the delicate bouquet of flowers where physiological activity of developing and giving off perfumes continue even after picking, as in jasmine. Each of the aforementioned methods has its merits and demerits.

A number of ways of extraction have been developed for special cases. Extraction with liquid carbon dioxide, vacuum-tight distillation, and warm fermentation prior to distillation are in use (1). A process that was introduced in the '70s and was found very useful in accounting for the greatest number of volatiles from plant materials is the headspace technique (2). The volatiles from a sample are trapped by a porous material. It is brought into equilibrium with a gas phase over it in a closed vessel after which a certain volume of the gas phase is injected into a GC for qualitative and quantitative purposes.

A method which is claimed to yield the genuine essential oil consists in piercing the oil sac of the plant and drawing the oil by means of a syringe-like glass capillary, and analyzing directly with GLC.

Nature of Essential Oils

Essential oil is characterized by an enormous chemical complexity. It is a commodity the chemistry of which, one might say, embodies a definition of organic chemistry, that is, chemistry of hydrocarbons and their derivatives. Almost every class of organic compounds is likely to be present (hydrocarbons, oxygenated, sulfuretted, nitrogenated and even halogenated compounds) in multiple combinations and in varying proportions. Each essential oil has its main component(s) and many minor ones. The predominant component of oil of peppermint is menthol; oil of turpentine, pinene; oil of anise, anethole.

Among the physical properties, odor and taste are preferentially looked into: odor by the perfumer, and taste by the flavorer.

The properties of each oil are imparted by the combined attributes of all its constituents. The chemical properties depend upon the functional group or groups present in each component.

Fractionation and Analysis

In the distant past, essential oil chemists depended solely on fractional distillation for the separation, and on solid derivatives formation for the identification of components of essential oils.

(1) Jenkins, G. & W. Hartung, *The Chemistry of Organic Medicinal Compounds*, John Wiley & Sons, N.Y., 1949, page 283.
(2) Sirikulvadhana, S., W.G. Jennings & G. Vogel, *International Flavors & Food Additives, 6*, 126 (1975).

With the advent of chromatography came what may be called revolution in essential oil chemistry. Some findings that were obtained by methods of long long ago are, today, in need of review and re-evaluation because some of them are found wanting in the light of modern methods of analysis. Fifteen years ago, the bilberry fruit was reported to contain no more than ten volatile constituents. Lately, its gas chromatogram revealed a total of 109 components. From 1891 to 1976, jasmine flower was known to have only fifty volatiles. In 1977, one hundred and thirty compounds were reported (3). The many attempts at reconstituting the flavor of our breakfast beverages resulted in the discovery thru GC that coffee has six hundred volatiles; cocoa, three hundred twenty; and tea, three hundred sixty (4). Such is the wonder of the gas chromatograph.

Today, column chromatography, thin layer chromatography and gas liquid chromatography, and often a simultaneous combination of them are used for the fractionation of essential oils.

Chemical means of separating groups of components of essential oils have not been done away with. In some instances when the presence of phenols, lactones, and acids are indicated, the oil and/or the absolute is treated with sodium carbonate or sodium hydroxide before applying column chromatography.

A method which this author used with success in the analysis of the oil of *Peperomia pellucida* L. (HBK) (5), is a large automated steady state counter current distribution which has 100 tubes of 25 ml. capacity each. The beauty of the set-up lies in its capacity to hold much more quantity of oil than what preparative GLC can accommodate. Moreover, it does not need much attention as it can run by itself thru the night after which the fractions are picked up from the collectors in the morning.

In industry, however, fractionation in large scale is still used, employing giant fractionating columns under pre-tested conditions that would insure stability of specific fractions desired.

Other separation techniques include gel permeation chromatography which is a form of liquid chromatography that sorts polymer molecules in a gel-packed column according to their size in solution. Also, the droplet counter current chromatography which is an all liquid separation technique that is based on the partitioning of solute between a steady stream of droplets of moving phase and column of surrounding stationary phase.

---

(3) *Proceedings of the VIIth International Congress of Essential Oils* (Kyoto, Japan, October, 1977) published March, 1979, page 473.
(4) Vitzthum, O.G. & P. Werkhoff, *Aroma Analysis of Coffee, Tea and Cocoa by Headspace Technique*, Hag, Hagstrasse, Bremen, W. Germany, Page 115. Thru *Int. Flav. & Food Additives, 10,* 79 (1979).
(5) Oliveros-Belardo, L., *Perf & Ess. Oil Record, 58,* 359 (1967).

In the search for and in the identification of new compounds of which essential oils seem to be inexhaustible sources (as the kind and number of organic compounds obtained therefrom are still on the increase) GLC is undoubtedly very useful. However, there are still a number of conservative and seasoned perfumers who are not yet completely sold to the efficacy of the gas chromatography. They say (6): —

> "It is true that the gas chromatograph has proved useful separating components of essential oils, but in dealing with trace elements that are the key factors in giving an essential oil its character, the best chromatograph is the nose with a detector far more sensitive than any detector."

It is a fact that all essential oils have numerous trace components and nuances, all of which contribute to the total aroma of the oil. Remove any of them and the odor of the oil changes. A gas chromatograph will show how many trace components there may be, but may not identify all of them, whereas a trained nose can tell if something is missing in or something is different in the usual oils that it sniffs from day to day. To this, I might say that the gas chromatograph and the nose can complement each other. The GLC is objective, the nose could be subjective. Besides there is still a lack of trained noses. It is for this reason that the art and science of olfaction are being developed and fully utilized now by big essential oil and perfumery houses because it is recognized that it is the nose that helps the perfumer envision and determine the scent that perchance would entice and satisfy the ever changing preferences of milady for varied creations in perfumery.

It has now become common practice to couple the GC with some auxillary identification apparatuses by leading part of the effluent material to other types of equipment. Thus, there is the GC-MS, GC-IR, and even GC-TLC. However, the coupling would give valid results only when an eluted peak represents just *one* compound. In the case of terpenic components where isomerism is a characteristic property, an eluted peak may consist of more than one substance. This problem has motivated the search for an innovative set-up and led to the development of what is called *Tandem Gas Chromatograph* (7). The system is actually made of two independent GC machines. The first one has the main column for survey of peaks. It has also a smelling port. The second machine has two columns, one of which is polar, and the other non-polar, The effluent from the first oven is led to the two columms of the

---

(6) From Editorial, Flavor *Industry*, *1*, 284 (1970).

(7) *Proceedings of the VIIth International Congress of Essential Oils* (Kyoto, Japan, October, 1977) published March, 1979, page 323.

second oven where any complex peak is resolved into separated peaks and finally led to an attached IR spectrophotometer. This innovation satisfies the need, not only of the flavorer and perfumer for a "sniff test" thru the smelling vent, but also of the analytical chemist for his identification interest.

Spectroscopy has triggered an immense advancement in the identification of natural products. On account of the rapidity with which it can "thumb print" an organic compound, the spectroscopes have become indispensable tools in the study of essential oils, considering the fact that many of the liquid components of essential oils are unstable and need immediate analysis as soon as they are isolated.

Conclusions that are based on the short-cut methods of GC retention time, UV, IR, NMR, MS as compared with authentic standards, have been considered valid and are acceptable. It is obvious, however, that such comparison method will work with already known compounds but not with new unknown ones. It would still be necessary to coordinate spectroscopic results with identification of solid derivatives. Accomplishing its synthesis is a sure way of establishing the absolute configuration.

Uses of Essential Oils

Essential oils are used in medicine, pharmacy, industry and agriculture. Their extensive uses, however, are as odorant and flavorant.

They provide the elements for making perfumes — those favorite magical concoctions that evoke people, events and emotions. Perfumes are likened to melodies. Soft music in its perfect tonal harmony, is soothing to the nerves and inspiring to one's spirit. Similar elating effects are derived from perfume which is akin to a harmony, a pleasant blending of fragrant materials extricated from plants.

The possibilities for countless creations by the perfumer is tremendous. While the musician has only eight basic notes out of which thousands of melodies have already been composed, the perfumer has today no less than 4,000 fragrance ingredients at his disposal with which he can create millions of possible combinations (8).

Flavor oils, like oils of garlic, onions, cloves, cinnamon and pepper, are the donors of the appetizing odor of roasting barbecue

(8) Lindsay, A. F., *Household and Personal Products Industry, 11,* 40 (1974).

and chicken *adobo* (9). The diner's appetite is further satisfied with a cup of ice cream the flavor of which is accented with essences from jackfruit and mango. Rounding up the elegant dinner is the brewed coffee whose enticing aroma emanates from its volatile oil.

PART II

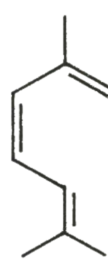
A. Types of constitutents found in essential oils, represented by selected terpenic and sesquiterpenic components.
B. Characteristic reactions illustrating the chemical properties of essential oils.
C. Gas chromatograms of some Philippine essential oils studied by L. Oliveros-Belardo.

TYPES OF CONSTITUENTS FOUND IN ESSENTIAL OILS

A. HYDROCARBONS, NON-TERPENIC AND TERPENIC.
   1. PARAFFINS. EXAMPLE, NORMAL HEPTANE found in *PITTOSPORUM RESIMFERUM* HENSL.
   2. OLEFINS.
      a. MONENES. (ONE DOUBLE BOND, F), EXAMPLE, OCTYLENE.
      b. DIENES (TWO F's), EXAMPLE, ISOPRENE.
      c. TRIENES (THREE F's), EXAMPLE, ACYCLIC TEPENES:

MYRCENE

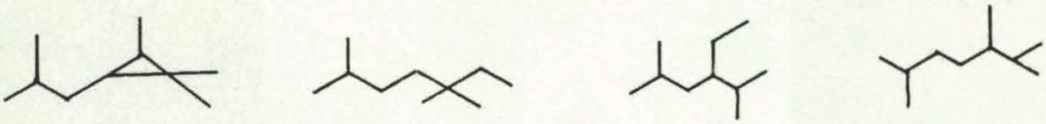
OCIMENE



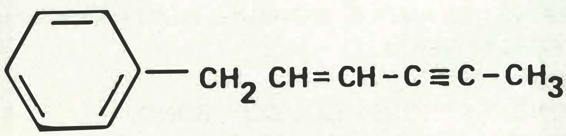
The skeleton formulas above obey Wallach's (1887) isoprene rule for terpenes.

(9) A Filipino native dish of chicken or pork cooked with salt, vinegar and spices, garlic predominating.

Some monoterpenes, like those found in *Compositae* plants, do not follow the isoprene rule. They have the following carbon skeletons:



3. CYCLIC
   a. AROMATIC
      EXAMPLES:
      p–CYMENE IN NUMEROUS VOL. OILS (turpentine, lemon, coriander, cinnamon, sage, origanum, etc.)
      STYRENE IN STYRAX AND HONDURAS BALSAM NAPHTHALENE IN OILS OF CLOVES, ORRIS ROOT AND STYRAX
      AN INTERESTING BENZENE DERIVATIVE IS AGROPYRENE, THE FIRST HYDROCARBON WITH AN ETHYLENIC AND AN ACETYLENIC LINKAGE OBSERVED IN NATURE.
      95% IN THE OIL OF *AGROPYRUM REPENS*

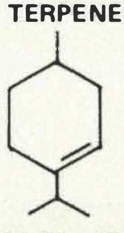


AGROPYRENE

95% in the oil of *Agropyrum Repens*

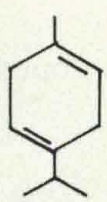
SELECTED EXAMPLES OF CYCLIC TERPENES FOUND IN ESSENTIAL OILS.

(1) MONO CYCLIC
(a) MONENES, ONE F

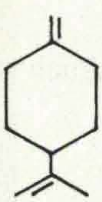


Δ^3- MENTHENE (THYME OIL)

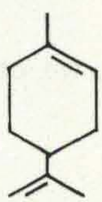
(b) DIENES, F'S BOTH INSIDE, OR OUTSIDE OR ONESIDE AND THE OTHER OUTSIDE OF THE CYCLE:



TERPINENE (OCIMUM OILS)



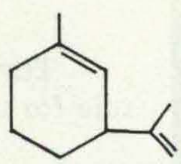
¢ LIMONENE



LIMONENE

(CITRUS OIL)

TERPINOLENE (MANILA ELEMI)



SYLVESTRENE (PINE NEEDLE)

(c) POSSIBLE ISOMERISM

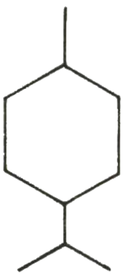
POSITION ISOMERS, DEPEND ON POSITION OF F'S.
OPTICAL (DEXTRO AND LEVO).
RACEMIC (OPTICALLY INACTIVE).
GEOMETRIC (CIS-AND TRANS-).
CONFORMATION ISOMERISM (CHAIR AND BOAT FORMS).

CHAIR CONFORMATION

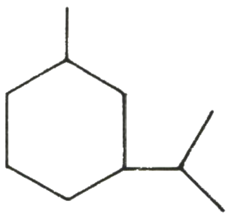
BOAT CONFORMATION

b. HYDROAROMATIC

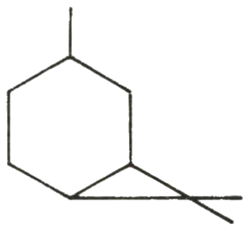
Some ring systems from which the structures of cyclic terpenes, $C_{10}H_{16}$, and their oxygenated compounds are derived:



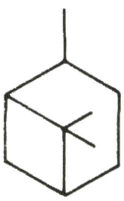
P-MENTHANE



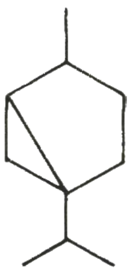
M-MENTHANE



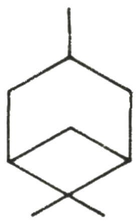
CARANE



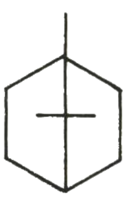
PINANE



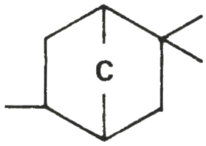
THUJANE



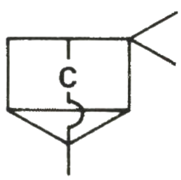
ORTHODANE



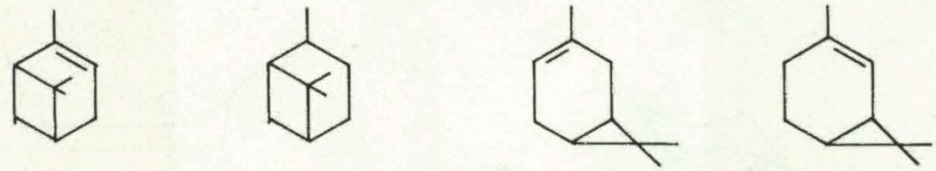
CAMPHANE



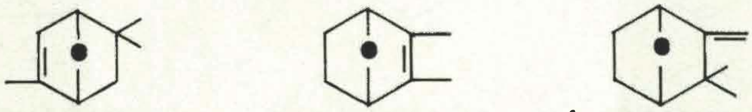
FERNCHANE



CYCLOFENCHANE

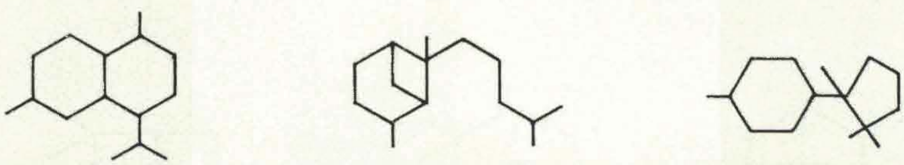


(2) BICYCLIC TERPENE HYDROCARBONS, TWO CYCLES AND ONE DOUBLE BOND.



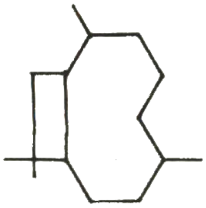
α-PINENE β-PINENE (TURPENTINE OIL) Δ^3-CARENE Δ^4-CARENE (TURPENTINE OIL)

SABINENE (JUNIPERUS SABINA L.) α-THUJENE (B. SERRATA) β-THUJENE ORTHODENE (ORTHDON OILS)

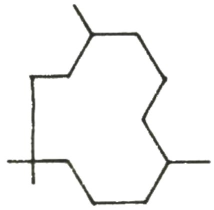


FENCHENE SANTENE (SANDALWOOD OIL) CAMPHENE (EUCALYPTUS OIL)

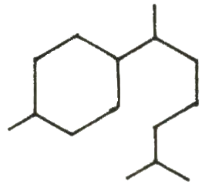
Each of these ring systems is the carbon skeleton for the Sesquiterpene Hydrocarbon or Hydrocarbons written below it.



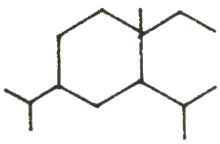
THE CARYOPHYLLENES



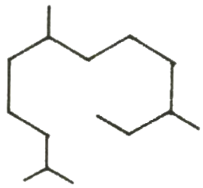
THE HUMULENES



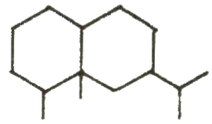
THE BISABOLENES
ZINGEBERENE
SESQUIPHELLANE
DRENES
THE CURCUMENES



THE ELEMENES



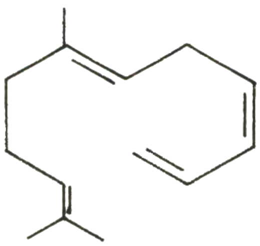
THE FARNESENES



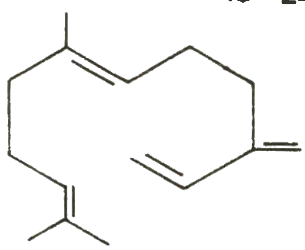
VALENCENE

SOME EXAMPLES OF SESQUITERPENE HYDROCARBONS, $C_{15}H_{24}$

1. ACYCLIC

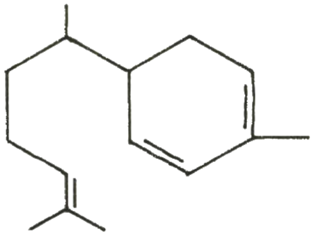


SESQUICITRONELLENE
(CITRONELLA OIL)

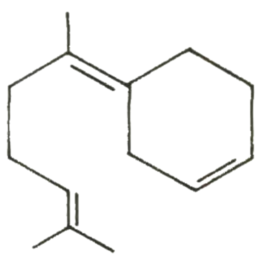


BETA FARNESENE
(YLANG YLANG)

2. MONOCYCLIC

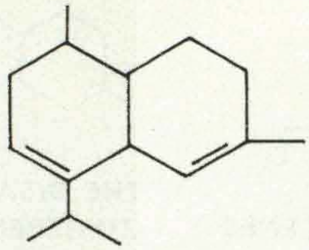


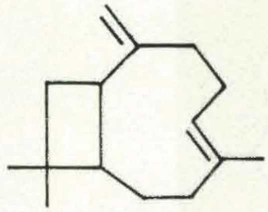
ZINGIBERENE
(OIL OF GINGER)



GAMMA BISABOLENE
(OIL OF MYRRH)

3. BICYCLIC

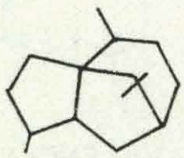




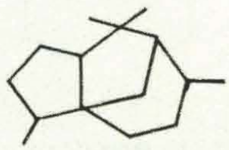
ALPHA CADINENE

CARYOPHYLLENE

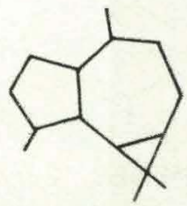
Each of the following ring systems is the skeletal structure for the Sesquiterpene Hydrocarbon or Hydrocarbons written be low it.



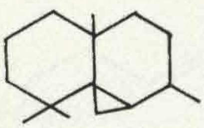
THE PATCHOULENES
CYPERENE



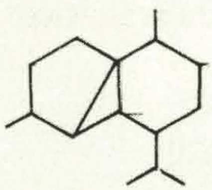
THE CEDRENES



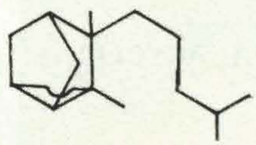
THE GURJUNENES
ALLO-AROMADENDRENE



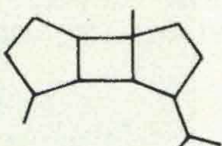
THUJOPSENE



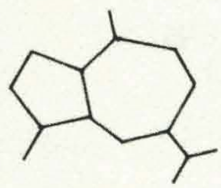
THE CUBEBENES



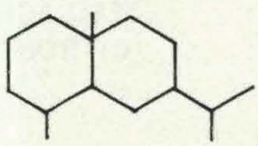
THE SANTALENES



THE BOURBONENES



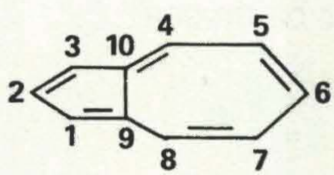
THE GUAIENES



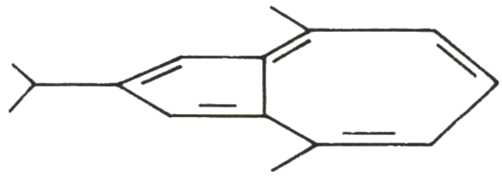
THE SELINENES

A group of Hydrocarbons, closely related to the Sesquiterpenes, are the *Azulenes.* The interesting feature of the basic compound is its pure blue color from which time the name azulene was derived. The colors of the derivative range from blue-violet, violet, red-violet or even green.

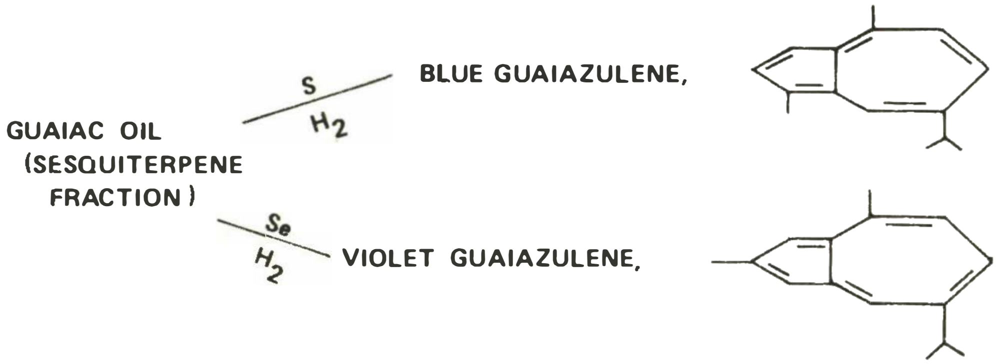
CARBON SKELETON:



EXAMPLES:

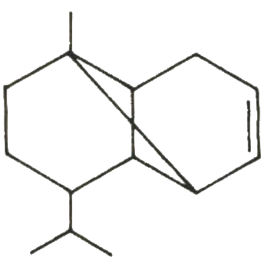


VETIVAZULENE

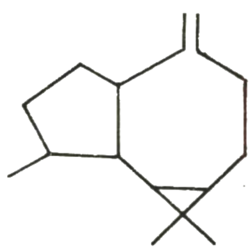


Occurence: Oils of chamomile (15%), Guaiac, Cubeb, Valerian, Galbanum, Wormwood, Eucalyptus, etc.

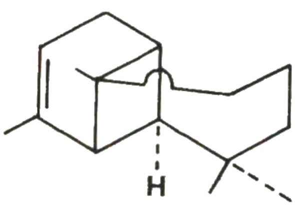
4. Examples of Tricyclic Sesquiterpene Hydrocarbons.



COPAENE
(70% IN THE OIL OF
SINDORA INERSIS FROM
DAVAO, PHILIPPINES).

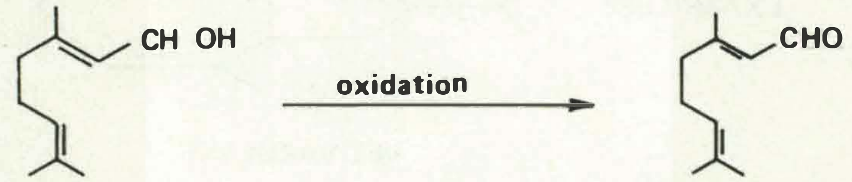


ALLO-AROMADENDRENE
(MAJOR COMPONENT OF OIL FROM
WOOD OF PHILIPPINE *SANDORICUM*
KOETJAPE (BURM. f.) M.
ISOLATED IN 1969), by L.O. BELARDO

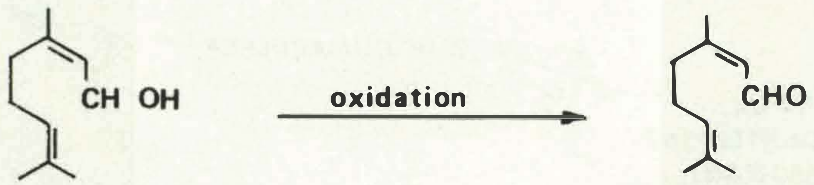


ALPHA-LONGIPINENE
(ISOLATED AS A NEW SUBSTANCE FROM SWEDISH PINE
OIL IN 1965. ISOLATED AS ONE OF THE MAIN
COMPONENTS FROM OIL OF THE WOOD OF *S.*
KOETJAPE (BURM.f.) MERR. IN 1969), by L.O. BELARDO

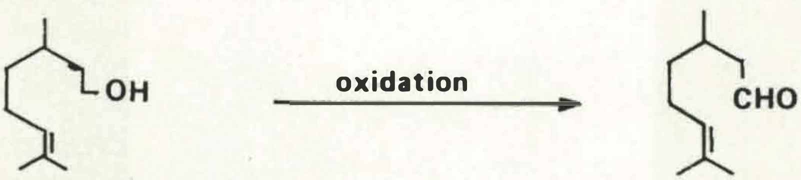
ALCOHOLS ALDEHYDES
OF CONSIDERABLE IMPORTANCE IN PERFUMERY:



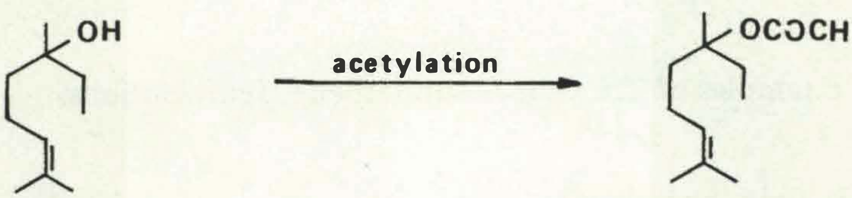
GERANIOL GERANIAL (CITRAL A)



NEROL NERAL (CITRAL B)

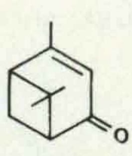


CITRONELLOL CITRONELLAL

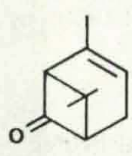


LINALOOL LINALYL ACCETATE

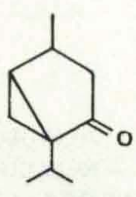
KETONES



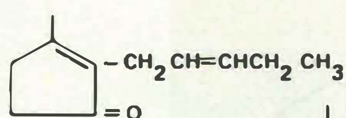
VERBENONE



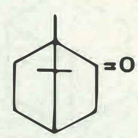
CHYSANTHENONE



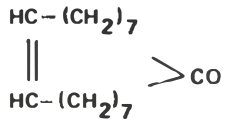
UMBELLULONE



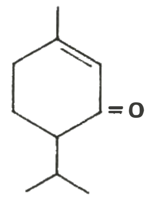
JASMONE



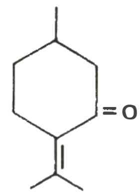
CAMPHOR



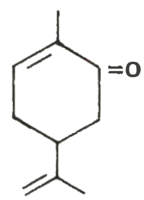
CIVETONE



PIPERITONE

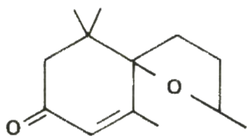


PULEGONE

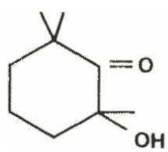


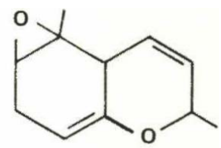
CARVONE

SOME KETONIC COMPONENTS OF BLACK TEA AROMA:



TEASPIRONE
(ALREADY SYNTHESIZED)





ESTERS

Esters are usually responsible for the fragrant odors of essential oils even if they are present in small quantities.

Some examples are:

Benzyl Acetate — in the flower oils of gardenia, jasmine and sampaguita.

Benzyl Benzoate — in ilang-ilang floral oil.

Cinnamyl Cinnamate — in cinnamon spice.

Geranyl Acetate — in oils of citionella, lemongrass, geranium, lavender, coriander, eucalyptus, etc.

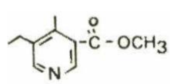
Linalyl Acetate — 70% in lavender floral oil.

Menthyl Acetate — in peppermint oil.

Methyl Anthranilate — in jasmine, tuberose, gardenia, ilang-ilang, champaca

Methyl Salicylate — in gaultheria and birch trees.

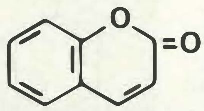
Methyl 4 — Methyl-5-ethylnicotinate, was found to be the Majór basic component (29%) of *Jasminum sambac* from China.



LACTONES

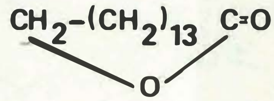
SOME EXAMPLES

1. COUMARIN



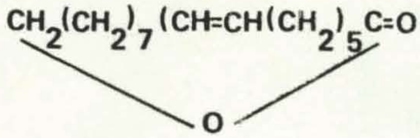
widely distributed in plants.
widely used in perfumes.

2. EXALTOLIDE



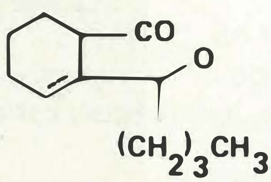
from angelica root
used in high grade perfumes.

3. AMBRETTOLIDE



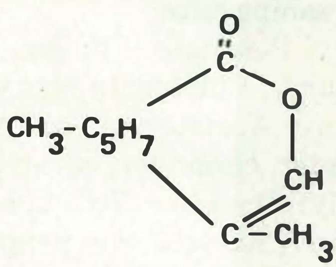
from ambrette seed.
Has the odor of musk.

4. SEDANOLITE



An odoriferous compound in
oil of celery seed.

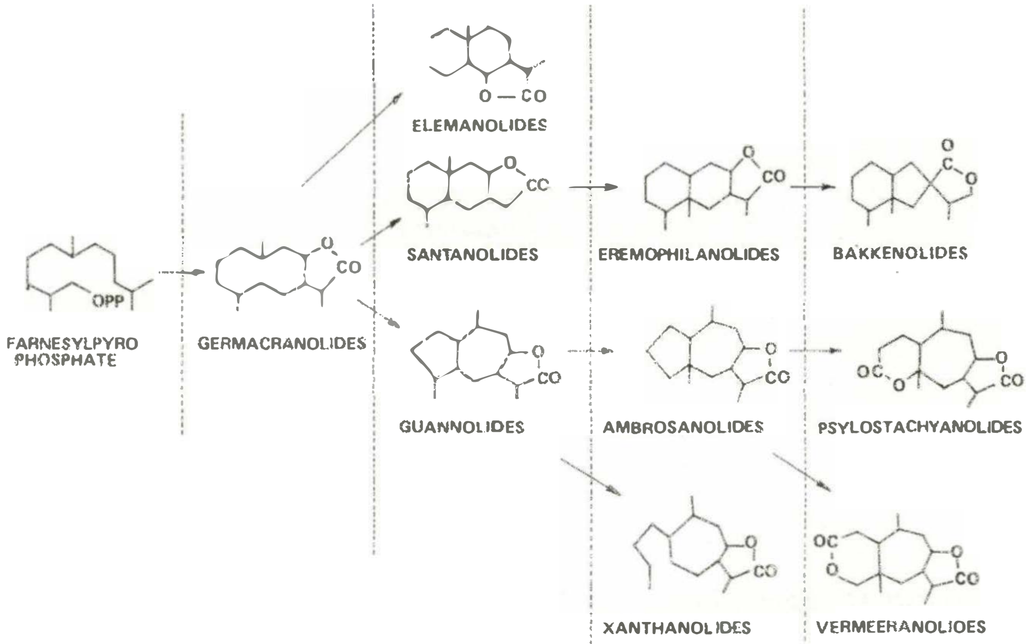
5. NEPETALACTONE



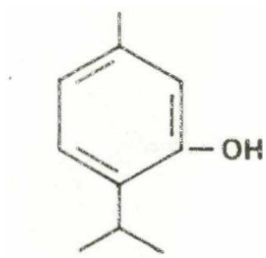
From oil of catnip plant
Attracts some species of cats
and makes them playfully excited.

SESQUITERPENIC LACTONES

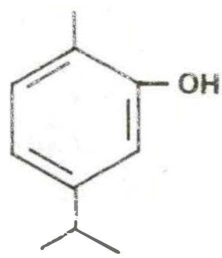
Scheme of the supposed biosynthesis of sesquiterpene lactones, each of which is derived from any of the Carbon skeletons below. Family *compositae* alone has 500 of these compounds of various types.



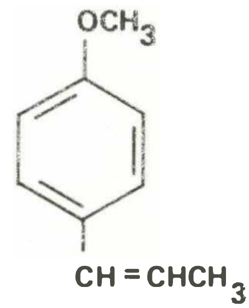
PHENOLS AND PHENOL ETHERS



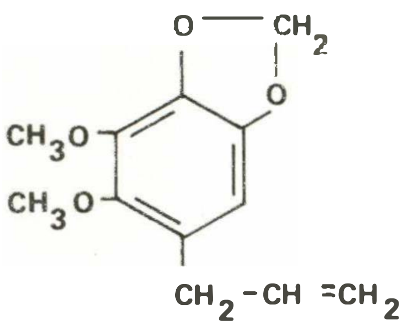
THYMOL



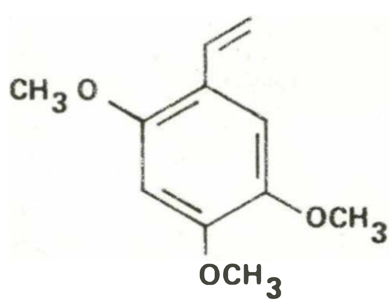
CARVACROL



ANETHOLE

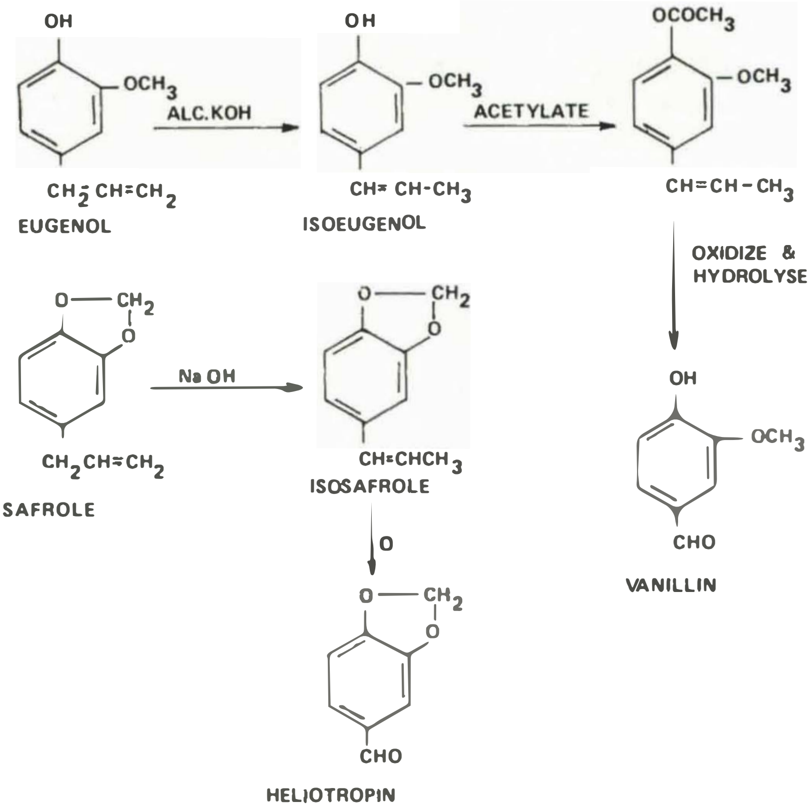


DILLAPIOLE



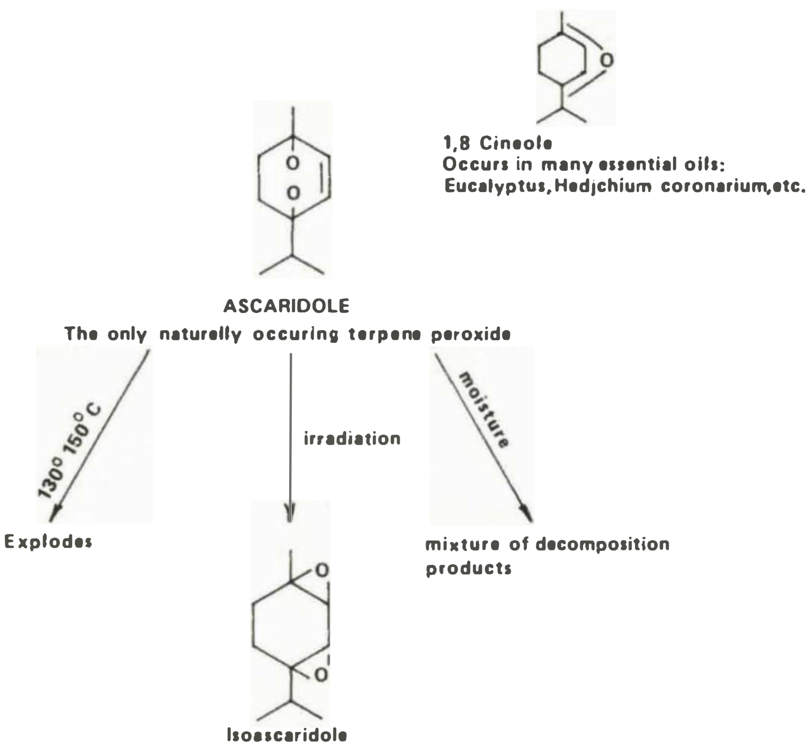
TRIMETHOXYSTYRENE

PHENOLS AND PHENOL ETHERS Continued



OXIDES IN ESSENTIAL OILS:

Ascaridole is used as anthelmintic. (It occurs in the oil of chenopodium.



On account of the above reactions, there are oils of chenopodium with zero ascaridole content.

SULFURETTED PUNGENT COMPOUNDS
ISOTHIOCYANATES and DISULFIDES
OBTAINED BY ENZYMIC ACTION ON GLYCOSIDES

1. ISOTHIOCYANATES

$R\text{-}C(\text{-}S\text{-}C_6H_{11}O_5) = N - O - SO_3^- K^+$ *enzyme,*

glucosinolate (thioglucoside)

$R - CN + [S] + \text{glucose} + SO_4$

$R - NCS$

$R - OH + CNS^-$

R = allyl (sinigrin), in black mustard, cabbage, horse-radish
= p- hydroxybenzyl (sinalbin), in white mustard
= bensyl (glucotropaeolin), in garden cress
= phenethyl (gluconasturliin), in watercress, horse radish
= 4- methylthio-trans-3-butenyl, in radish

Thus:

$$CH_2 = CH\text{-}CH_2 - N = \underset{\displaystyle O.\ SO_2OK}{\underset{|}{C}} - S - C_6H_{11}O_5$$

sinigrin

enzyme

HoH

2. DISULFIDES

FROM ALLIIN, an amino acid in garlic *(Allium sativum)*

$$2\ CH_2 = CHCH_2\ SOCH_2\ CH(NH_2)\ COOH \quad \text{(Alliin)}$$

allinase

$$CH_2 = CH\text{-}CH_2\ SO - S - CH_2\ CH = CH_2 + 2NH_3$$

allicin (a thiosulfinate)

$$+\ 2CH_3COCOOH$$

pyruvic acid.

(responsible for the typical, but not repulsive, odor of garlic)

disproportionation

$$(H_2 = CH - CH_2\ (O\leftarrow)\ S\ (\rightarrow O) - S - CH_2 = CH_2 +$$

$$CH_2 = CH - CH_2 - S - S - CH_2 - CH = CH_2$$

diallyl disulfide

(source of unpleasant smell of garlic)

+ other products

SOME SULFUR COMPOUNDS
IN ONION (*Allium cepa)*

1. FLAVORS:

   a. FRESHLY CUT, due mainly to propylpropanethiosulfonate.
   b. BOILED, due to propyl and 1-propenyl di-and trisulfides.
   c. FRIED, due to dimethylthiophenes.

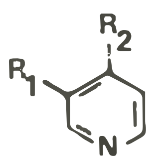
2. The LACHRYMATOR (Tear producer) is either

Propenylsulfenic acid, $CH_3\ CH = CH -- S \rightarrow O)$
H

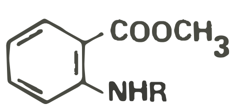
or (Swian, 1963)

Thiopropanal S — oxide, $CH_3\ CH_2\ CH\ =\ S\ (\rightarrow o)$
(Nursten 1975)

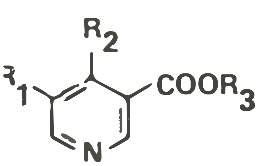
SOME NITROGENATED COMPOUNDS IN ESSENTIAL OILS METHYL ANTHRANILATE (in jasmines, gardenia, ilang-ilang, etc.); INDOLE (jasmine, champaca, night bloomers); SKATOLE (civet cat). From 1965-73, only 6 basic components were known in the jasmines. In 1977-79, fourteen new bases and 3 known anthranilates were reported. The following bases were found in *Jasminum grandiflorum & J. sambac:* —



COMPOUND NO.	R	R_1	R_2	R_3	
1		C_2H_5	H		
2		$CH = CH_2$	H		
3		$C_2\ H_5$	CH_3		
4		$CN = CH_2$	CH_3		

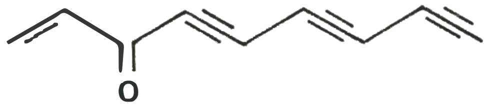


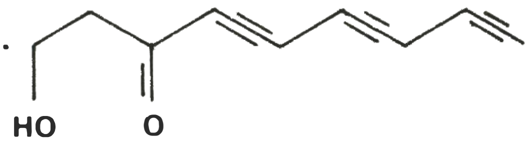
COMPOUND NO.	R	R_1	R_2	R_3	
5	H				72-86% in J. grandiflorum
6	CH_3				
7	$COCH_3$				

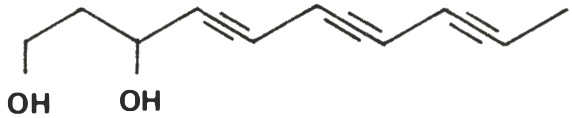


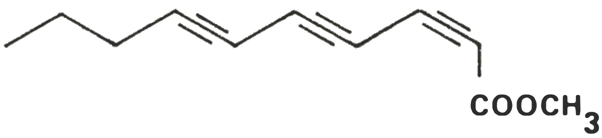
COMPOUND NO.	R	R_1	R_2	R_3	
8		H	H	H	10% in J. sambac
9		H	H	C_2H_5	
10		H	CH_3	CH_3	
11		C_2H_5	H	CH_3	
12		C_2H_5	H	C_2H_5	
13		$CH = CH_2$	H	CH_3	
14		$CH = CH_2$	H	C_2H_5	
15		$C_2\ H_5$	CH_3	CH_3	29% in J. sambac
16		$CH = CH_2$	CH_3	CH_3	
17		C_2H_5	CH_3	C_2H_5	

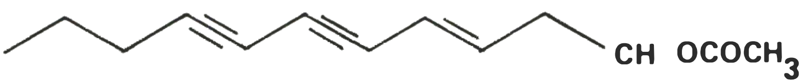
CURIOUS COMPOUNDS, UNUSUAL STRUCTURES, AND NOVEL RING SYSTEMS, (REPORTED IN LITERATURE FROM 1969).

1. 

2. 

3. 

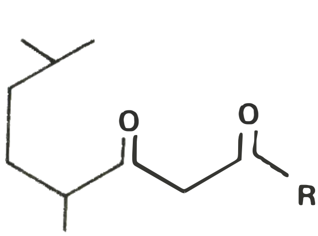
4. 

5. 

Aliphatic acetylenic compounds have, few years ago, been reported in nature. Compounds 1, 2, and 3 were isolated from the oil of garden lettuce. Compounds 4 and 5, from the oil of *Asterae* plants.

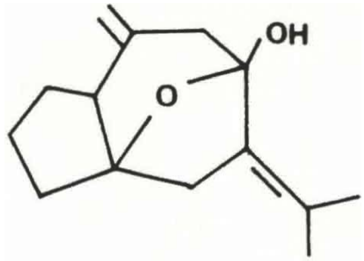
6. 

ODOROUS CONSTITUENT FROM GENUS DICTYOPTERIS.

7. 

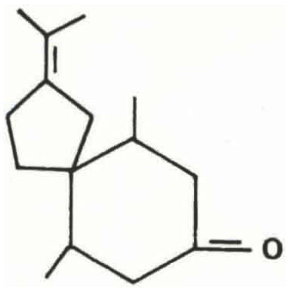
A BETA DIKETONE FROM THE OIL OF HELICHRYSUM ITALICUM.

8.



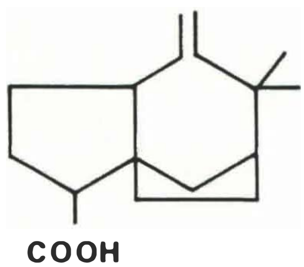
CURCUMENOL FROM
OIL OF
<u>CURCUMA</u> <u>ZEDOARIA</u>.

9.



VETIVONE

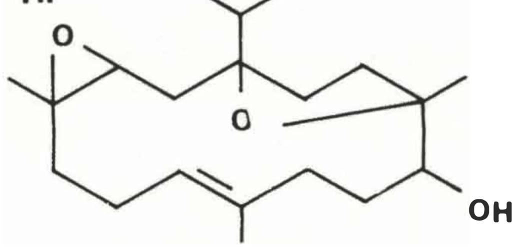
10.



(A NEW ACID)

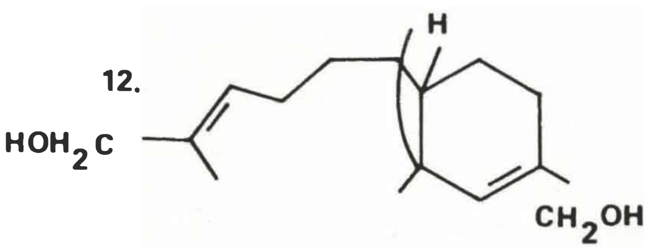
BOTH FROM VETIVER OIL

11.



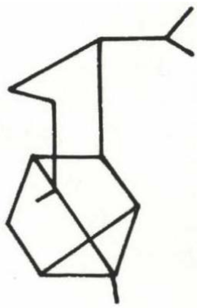
INCENSOLE OXIDE
FROM
FRANKINCENSE

12.



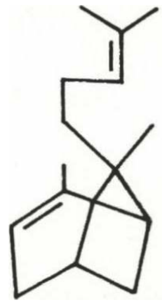
SIRENIN

13.



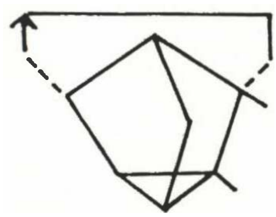
CYCLOSATIVENE
(OIL OF *ABIES MAGNIFICA*)

14.



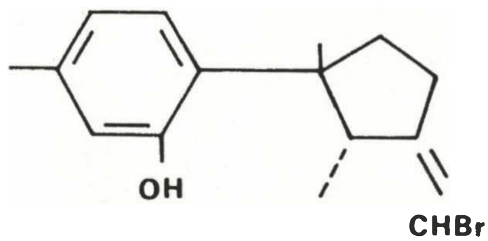
ALPHA CIS BERGAMOTENE

15.



LONGICYCLENE
THE FIRST TETRACYCLIC
SESQUITERPENE ISOLATED
FROM ESSENTIAL OIL.
(*PINUS LONGIFOLIA*)

16.

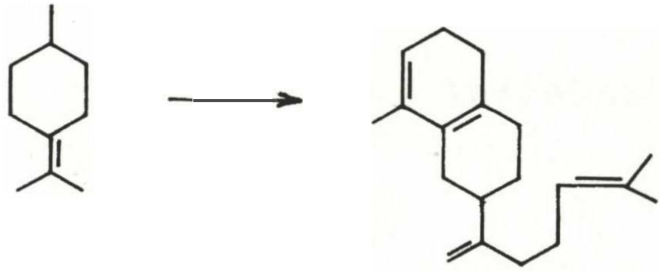


A BROMO SESQUITERPENOID.
(OIL OF *LAURENCIA NIPPONICA*)

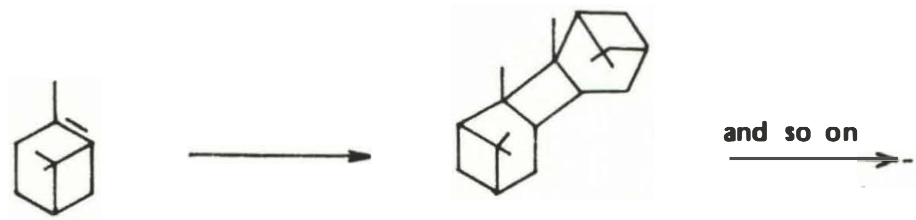
CHEMICAL PROPERTIES OF ESSENTIAL OILS

THE CHEMICAL PROPERTIES ARE SPECIFIC FOR CERTAIN OILS AND DEPEND UPON THE TYPE OF COMPONENT(S) OF THE OIL.
EXAMPLES GIVEN HERE ARE SIMPLE CASES.

1. *POLYMERIZATION:* This is shown by oils that are rich in terpene hydrocarbons where the hydrocarbon reacts by itself any number of times under certain conditions. Examples:



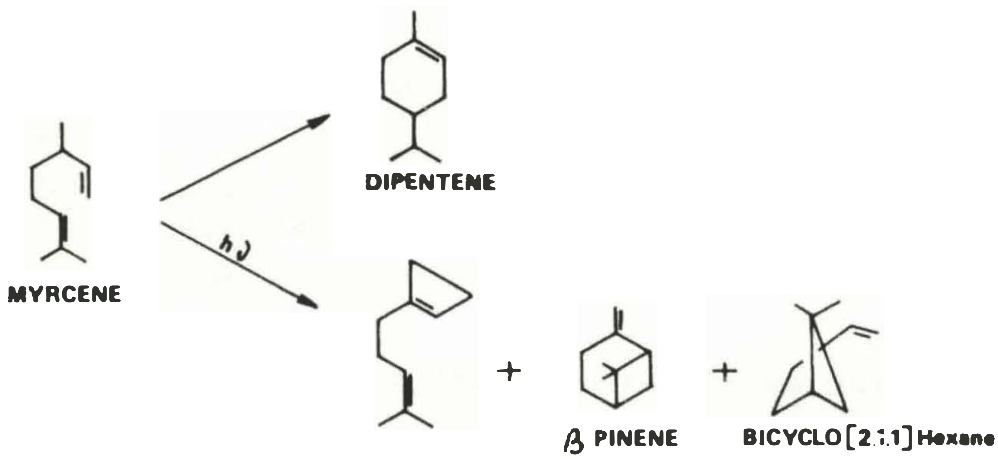
MYRCENE α-CAMPHORENE

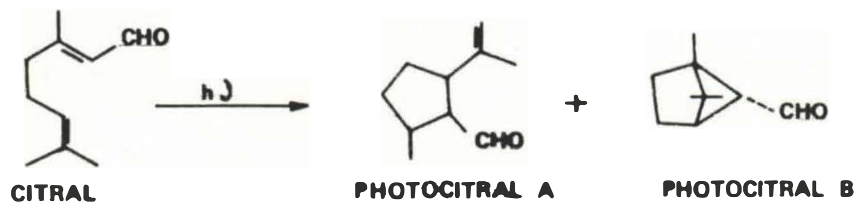


α-PINENE DIPINENE

As a whole, polymerization products in essential oils are undesirable because they come down as alcohol-insoluble residues with terebenthinate, unpleasant odor. Thus, terpeneless essential oils demand higher price than the whole oil.

2. *CYCLIZATION*





3. *REARRANGEMENT*

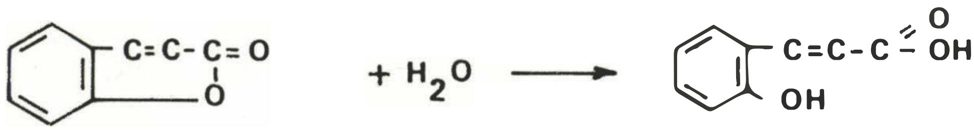
α-PINENE CAMPHENE

4. *CONDENSATION*

a. Ester formation from acid & alcohol; cinnamyl cinnamale in cinnamon oil.
b. Acetal formation
c. Ketal formation
d. Cannizaro's reaction

5. *HYDROLYSIS*

a. Indication of hydrolysis of methyl salicylate in oil of Wintergreen is its increase in acid value.
b. Indication of hydrolysis of linalyl acetate in Oil of Lavender is its lessened fragrance.
c. Lactones

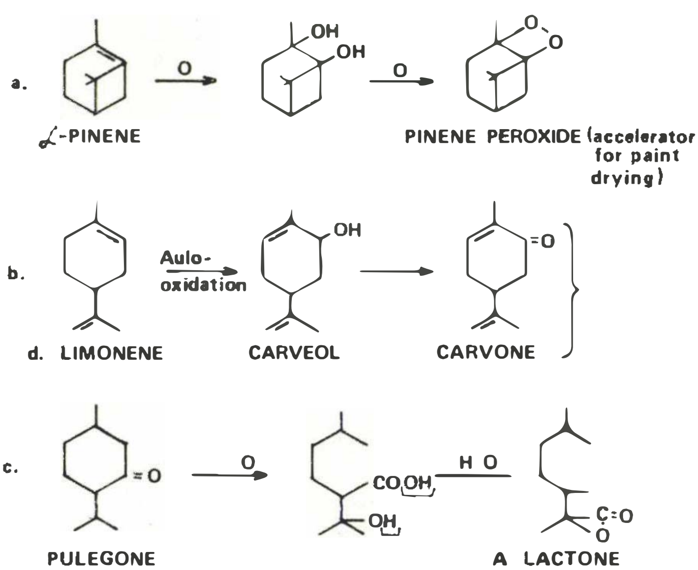


COUMARIN **O-Hydroxy Cinnamic Acid (Feebly odored)**

Coumarin odor is highly noticeable during cool evenings or early morning, but as T rises with the sunshine, the odor becomes faint or imperceptible due to hydrolysis. As twilight sets in and evening comes once more, the odor of coumarin returns.

6. *OXIDATION*

After storage at ordinary room conditions, none of the volatile oils is completely volatile anymore due to oxidation and/or polymerization products that form as residues.



This explains why citrus oils that are rich in limonene develop a spearmint-like odor due to the carvone formed.

d. The white residue that collects at the bottom of a bottle of Oil of Bitter Almond is benzoic acid formed by the oxidation of benzaldehyde, the latter from hydrolysis of amygdalin.

e. Geraniol $\xrightarrow{o}$ citral A

THE NEXT PICTURES WILL SHOW GAS CHROMATOGRAMS OF SOME PHILIPPINE ESSENTIAL OILS STUDIED BY L. OLIVEROS-BELARDO:

ESSENTIAL OIL OF *PEPEROMIA PELLUCIDA* (L.) HBK.

ESSENTIAL OIL OF WOOD OF *SANDORICUM KOETJAPE* (Burm. f.) MERR.

ESSENTIAL OIL OF FRUIT PEELING OF *ANONA SQUAMOSA* L.

ESSENTIAL OIL OF LEAVES OF *PSIDIUM GUAJAVA* L.

ESSENTIAL OIL OF LEAVES OF *CYMBOPOGON CITRATUS* (DC.) STAPF

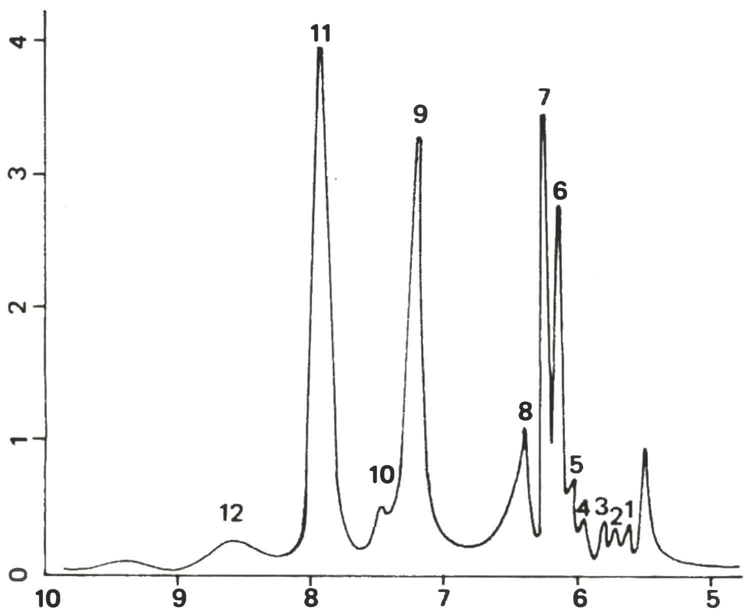


Fig. 2. Gas-liquid chromatogram of the volatile oil of Peperomia pellucida *(L.) HBK (6 ft. column of 15% polypropylene glycol, 140°—190°C., (at 5° per minute)*
Peaks studied:
(6) a sesquiterpene hydrocarbon, $C_{15}H_{24}$
7, caryophyllene
9, sesquiterpene alcohol, $C_{15}H_{25}OH$
10, a solid trimethoxystyrene
11, allyldioxymethylenedimethoxybenzene

Natividad Feliciano-de Castro, Ph. D., Discussant

The field of studies on essential oils is so far-ranging and the volume of research work that has been accomplished is so extensive that for such a limited time allotted, one has the choice to either skim the surface in a very general manner or concentrate on one small segment of the whole. It is not surprising therefore, to note that one treatise on essential oils consists of six volumes.

This brief discussion, therefore, will focus on the further expansion of certain aspects of essential oils which, hopefully, will prove interesting to all.

Essential oils (volatile oils, ethereal oils) are regarded as odorous, more or less lipophilic, complex mixtures of substances which evaporate when exposed to air at ordinary temperatures and are stored by plants in secretory cells, cavities or canals, or excreted through glandular hairs. They are found distributed in the plant kingdom in some brown and red algae and fungi and in the following main groups of green land plants (1):

— mosses and moss allies (Bryophyta)

— vascular cryptogams (Pteridophyta, ferns)

— seed plants (Spermatophyta). Essential oils are unusually abundant in several unrelated plant families such as the Labiatae, Rutaceae, Geraniaceae, Umbelliferae, Compositae, Lauraceae, Myrtaceae, Graminae, and Leguminosae.

Occurence in the plant itself can vary greatly, some plants may contain volatile oils in all of the tissues (Conifers) in others, they are found in appreciable quantities only in specific plant parts such as: the flowers (jasmin, rose) flowers and leaves (lavender, peppermint), leaves and stems (patchouli, geranium), barks (cinnamon, sweet birch), woods (cedar, sandalwood), roots (vetiver, spikenard), rhizomes (calamus, ginger) fruit rinds (bergamot, lemon) seeds (fennel, anise) and oleoresinous exudations (myrrh, storax).

Composition and Qualitative Variation

With very few exceptions, the essential oils are generally mixtures of hydrocarbons and oxygenated compounds which differ greatly in chemical composition. The odor and flavor of these oils is mainly determined by the oxygenated constituents which are usually appreciably soluble in water.

In recent years, the perfume world's interest in the organic acids which are very minor constituents of essential oils has specifically and markedly increased. Even at very low concentrations, these acids were found to determine or shade, perfume notes. Separation and identification after the transformation into the methyl esters or methyl ethers in the case of phenols, follows the procedures already discussed in Dr. Belardo's paper.

The qualitative variation in essential oils may be considered on the level of individual plants. In most cases, the composition of the oil depends on the age of the plant and of the organ that stores the oil. The example is caraway where the oil obtained from the ripe fruits used as spice, varies pronouncedly in composition from that obtained from young unripe fruits. Another important factor is that, in many species, the various parts of the plant such as roots, stalks, leaves, flowers and fruits sythesize and store their own characteristic oils. In the cinnamon tree, the main constituents vary according to the source of the oil, thus; from the bark of the branch - 65 to 76 per cent cinnamaldehyde, from the leaves — 70 to 90 per cent eugenol, and from the root bark — mainly camphor. In the citrus family, the oil from the flowers is very different from that in the fruit rind or other plant parts, e.g. orange oil (fruit rind) should not be confused with oil of neroli (orange blossom oil) nor with petitgrain (from leaves and twigs).

Environmental factors may also have a marked qualitative effect on the essential oils. Grahle and Holtzel (2) showed that for *Mentha piperita*, menthol and methyl acetate were major constituents of the oil under long day conditions only. Under short-day conditions, menthofuran was preferentially formed and stored.

Other variation levels to be considered are local populations, species and taxa of higher or different rank (3).

Essential Oils in Medicine and in Industry

Many crude drugs are used in medicine because of their essential oil content but in many cases, the oils are used as drugs in themselves. Among the therapeutic properties or uses on record are (4, 5, 6, 7, 8).

Carminative — almost all the essential oils

Anthelmintic — chenopodium oil, santonin oil, rectified turpentine oil

Antimalarial — oil of wormwood

Antirheumatic — oil of dwarf pine needles, gaultheria oil, savin oil

Antipruritic — oil of bitter almond, menthol, camphor

Antispasmodic — thyme oil

Antiseptic and germicidal — oils of oregano, cinnamon, clove, bay, juniper, sassafras, tea tree, thyme

Diaphoretic — oils of sambong, eucalyptus, cajeput
Diuretic — cubeh oil, jumper oil
Counterirritant — oil of perppermint, thyme, turpentene, wintergreen
Expectorant — oils from anise, dwarf pine needles, eucalyptus, fennel, niaouli, thyme, lagundi
Emetic — oil of chamomile
Fungicidal — clove oil, mustard oil, thyme oil
Galactagogue —fennel oil
Local anesthetic — clove oil (for teeth) peppermint oil (for pharyngitis)
Insectifuge — citronella oil
Rubefacient — oils of garlic, camphor, cajeput, mustard, rosemary
Sedative — oil of valerian
Stimulant — oils of *Hyptis suaveolens*, buchu, cajeput, clove, dwarf pine needles
Stomachic — oils of anise, cardamom, copaiba, coriander, galanga, ginger,
Sudorific — oil of yarrow, oil of *Premna odorata*, artemisia, lantana
Parasiticide — rectified pine tar and birch tar oils, cajeput oil
Vermifuge — oils of niaouli, savin

A recent report from the PROC (9) is the clinical treatment of ringworm using a 15 per cent tincture of cloves in 70 per cent alcohol. Patients with at least 2-year old ringworm of the body and feet, unsuccessfully treated with other drugs, responded after 2 - 3 days treatment, i.e., the symptoms began to subside. In general, healing was accomplished in 3 - 5 days. The active principle was considered to be the volatile oil. The essential oil of celery, especially that from the seed was reported to have sedative properties in experimental animals.

The essential oil of *Vitex negundo* L. and two other varieties have been extensively studied in the Institute of Chinese Traditional Drugs, and found very effective for coughs. Marketed in soft elastic capsules, this volatile oil is extracted by steam distillation in communes, collected by the pharmaceutical "factory" and manufactured into dosage forms (10).

The importance of essential oils on the industrial front cannot be overlooked. One of the first plastics, celluloid, was compounded of camphor. Many products with disagreeable odors became acceptable after treatment with essential oils. Some products in which they are incorporated are — synthetic rubbers, glues and other adhesives, animal feeds, automobile finishing supplies, insecticides and repellents, furniture polishes, janitor supplies, paints, paper and printing inks, petroleum and chemical products, textile processing materials and many other accompaniments of modern living (6).

Various industrial oils, for example, are obtained from citrus residues after juice extraction. "Citrus stripper oil" a by-product from processing orange and grapefruit peel and "Citrus peel oil" recovered from cannery refuse are used as sources of D-limonene a raw material for organic chemicals, and L-carvone which is used in paints, varnishes. plastics and soap perfumes. Cedarwood oil finds extensive use as insect repellent, clearing agent in microscopy, deodorant, and component of polishes while tea tree oil from Australia, is used in medicated soaps, dentrifices and certain medicinals. Fennel oil is useful in toothpastes and mouthwashes in pharmaceuticals and cough lozenges, liqueurs and confectionery and ginger oil in mouthwashes, ginger beverages and liqueurs.

One of the latest developments in essential oil utilization is the discovery of a perfume constituent which has deodorizing action. Thus, with the use of these perfumes, effective deodorants can be prepared without employing any of the customary active materials. This constitutent is reported to possess the following properties:

1. Natural occurence in a wide range of essential oils
2. A chemical structure which is in no way related to that of the usual deodorant agents
3. Experimentally demonstrated bacteriostatic effectiveness
4. A high degree of skin compatibility
5. A pleasant, rather neutral odor

Essential oils may be used as derived from nature as a fragrance ingredient or as raw material for the production of a wide range of aroma chemicals. A burgeoning industry in China, (11) the main products are natural methol crystals, USP and a fine quality dementholized peppermint oil (cornmint oil) from a particular variety of *Mentha arvensis*, *Litsea cubea* oil as source of citral and a whole range of ionones, and geranium oil. These products are readily accepted by American users in the toothpaste, mouthwash, cosmetics and toiletries industry.

Bibliography

1. Hegnauer, R. The Importance of Essential Oils in Plant Classification. Dragoco Report v 25: 204, 1978.

2. Grahle, A. and Ch. Holtzel. Photoperiodische Abhangigkeit der Bildung des Atherischen Oles bei *Mentha piperita* Naturewissenschaften 50: 552 1963.

3. Warnecke, H. M. Constituents of the Essential Oil of *Cistus ladaniferus* (Acids and Phenols) Dragoco Report v 25: 192 1978.

4. Kraus, A. and F.J. Hammerschmidt. An Investigation of Fennel Oils Dragaco Report v. 27: 31 1980.

5. Tyler, V. E. Brady, L. R. and J. E. Robbers. Pharmacognosy. Lea and Febiger. 1976

6. Schery, R. W. Plants for Man. Prentice-Hall, Inc. 1972.

7. Valenzuela, P. and J. A. Concha. Philippine Medical Plants Yielding Volatile Oil. Journal of the Philippine Pharmaceutical Association. v. 35: 385 1948.

8. Stecher, P. G., Ed. The Merck Index. Merck and Co., Inc. 1968.

9. Leung, A. L. Chinese Medicine — Potential Source for New Drugs. Drug and Cosmetic Industry, v. 125: 49 1979.

10. Personal Observation, 1979, during a study misssion on herbal medicine to the People's Republic of China.

11. Chaukin, W. China Looms as a Source of Essential Oils. Drugs and Cosmetic Industry v 126: 50 1980.

Alice A. **Buenconsejo, M.S., Discussant**

Dr. Belardo is to be commended on her work on essential oils, considering that prior to the advent of gas liquid chromatography, techniques on fractionation and characterization by physical and chemical means were resorted to by her. The use of large automated steady state counter current distribution with 100 tubes of 25 ml capacity each cited in her report, in fact made it possible for her to collect fractions which she was able to characterize and identify. With the advent of GLC, progress on essential oil chemistry has increased to a great degree. This has been of benefit to the Food and Fragrance Industry aside from the field of Pharmacy and Medicine.

On the application of essential oils, local industry today is in great need of perfumes for detergent and toilet preparations as well as flavors for a variety of foods. The work of Dr. Belardo on essential oils has revealed that the Philippines has a variety of sources for each oils, which can be used to advantage for concocting/compounding perfumes and flavors. It is just a matter of being able to produce these essential oils locally on commercial scale, such that they can be compounded into perfurmes and flavors.

In the field of perfumes for industrial products, the industrialist or Marketing man merely describes the characteristics of the scent he desires in layman's terms. It is the task of the perfumer to put together the various components, based on his knowledge of the chemistry of each of these components of essential oils, to arrive at what the industrialist desires. The industrialist or Marketing man then uses his nose to verify/judge if the perfumer's choice of components suits his needs/meets his requirements. Thus scientific techniques such as GLC to identify and obtain essential oil fractions, followed by the meticulous compounding by perfumers of components of essential oils obtained, go hand in hand with the olfactory assessment in order to arrive at the most suitable perfume for a particular use.

Persistence and zeal in the identification of the essential oils present in various local plants that have not yet been studied are still required, as there are still a lot of plants that are potential sources of essential oils. Once identified however, there is the even greater need for the commercialization of the extraction and isolation of these essential oils and their components, for only then can the knowledge gained by the zealous experimentation of researchers like Dr. Belardo be of use to the local manufacturers and in turn to the ultimate consumer. The present day cost of perfumes and fragrance imported from foreign countries is very high, due to a 100% duty levied on fragrances. As a result, the ultimate cost of a perfumed product to the consumer is correspondingly high and this can certainly be reduced if fragrances resulting from the use of essential oils derived locally can be used as alternative to the presently procured foreign perfumes.

In the field of foods, delicate flavors like mango, calamansi, guava, passion fruit and those of other local fruits are in demand and to-date not a single flavour house has succeeded in duplicating the flavour of the local mango nor the calamansi. As mentioned by Dr. Belardo, the guava fruit peel oil is presently being characterized and may shed light on the components required to arrive at a desired guava flavour. Similarly, work on the characterization of oil from the peel or pulp of local fruits will still have to be pursued, if flavors from local fruits are to be a commercial possibility in the future.

Essential Oils are indeed a "must" in day to day living, being utilized in medicines, as expounded on by Dr. de Castro, in Detergents and Toilet Preparations which would be unappealing without the variety of scents available today and which are made possible by the various essential oil components and finally in the field of Food, where the variety of foods are made interesting and distinguishable from one another by the addition of spices, flavors, aromatic-giving substances that are all either derived or in some way linked to essential oils.

Alicia O. Lustre, Ph.D., Discussant

I consider it an honor to be allowed to participate in this program as a discussant. May I take this opportunity to bring out the significant aspects of the research that was just presented to us this morning.

First of all, I would like to congratulate the researcher for her work. At the outset, it shows that it is possible for dedicated and capable scientists to conduct essential oil research in this country and to achieve recognition at par with those of other investigators abroad, inspite of the fact that locally the gas-chromatograph and the mass-spectrometer are not yet ordinary laboratory tools.

The work contributes very significantly to our store of basic information on the fascinating constituents of our local fruits, flavors and natural plants. This contribution can go a long way in making the teaching of science and chemistry in our schools more interesting to the students and more rewarding to the teachers.

I know that, well at least, in food chemistry it can be very difficult to have to demonstrate food technology principles, using apples and pears as examples. With investigations of this nature, the day will come when we can have our own local books demonstrating scientific principles using examples more familiar to us, as guavas and our own sampaguita.

As far as the economic aspects are concerned, it is reported that there are at present 1,400 flavors being used in the food industry, both natural and artificial. As food additives, these compounds have had their share of questioning from the public. There are, however, two types of food products where the use of flavors will continue to be a consequence. These are the stimulated meat products and the fruit drinks. Stimulated meat products are what we now get as the meatless bacon. the meatless hamburgers, and fruit drinks. The paper read indicates that we have the resources to contribute in part of the world's need for natural flavors particularly fruit flavors. In this regard, one significant aspect worth investigating is our utilization of fruit processing wastes particularly peels as sources of local flavorants. Thank you.

Q — Torralballa: Calvin of California went to Brazil and found plants there from which he aptly isolated petro-

	leum-like products, not volatile oils but petroleum-like products. Have you heard about this?
A — Belardo:	Yes, Dr. Torralballa. In fact it was announced here but just for lack of time, I omitted it. It says here, in 7 months a plantation at the south coast field station in California has produced more than 10 barrels of oil per acre and production is still on an output gross acre.
Torralballa:	That's right, he actually showed samples in which the oil is like crude oil.
Belardo:	Yes.
Torralballa:	And apparently, the main components then of that product are the straight hydrocarbons, instead of the turpenes.
Belardo:	Yes. This is precisely the purpose of that project announced wherein . . . .
Torralballa:	Yes. That's what I brought perhaps. Do you know the particular species then?
Belardo:	There are several . . . There are several species and these are all found in the Philippines also.
Torralballa:	Also?
Belardo:	Yes.
Torralballa:	Oh! it's wonderful.
Belardo:	And it is very easy to grow.
Torralballa:	And I knew that he went to Brazil and that was where he first found those plants.
Belardo:	Yes, because Brazil and the Philippines are tropical countries.
Torralballa:	of the same climate. . . Yes, thank you very much.
Belardo:	You are welcome.