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ESSENTIAL OIL OF *DIPTEROCARPUS GRANDIFLORUS* BLANCO: CHEMISTRY AND POSSIBLE SOURCE OF ENERGY*

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Introduction

The genus *Dipterocarpus* is of interest commercially because gurjun balsam oil is obtained from one or more of the following species: *Dipterocarpus jourdainii* Pierre; *Dipterocarpus tuberculatus* Roxb.; *Dipterocarpus costalus* Roxb.; *Dipterocarpus intricatus* Dyer; and *Dipterocarpus turbinatus* Gaertn. *D. tuberculatus* is the most common source of the oil.

The subject of this present study is *Dipterocarpus grandiflorus* Blanco. This tree, which is known locally in the Philippines as *apitong,* is reputed to be the most abundant (ca. 20%) in the commercial Philippine forests (1), Figure 1. The resin of *D. grandiflorus* is known locally as *balau.* Until now, no extensive commercial use for the oil of *D. grandiflorus* has been found. There is, however, some local use of *balau* oleoresin as an illuminant, for varnishing, and caulking boats. The wood of *D. grandiflorus* is moderately hard so it has found some use in construction and in the manufacture of medium grade furniture (2).

The object of this current study is to identify the chemical composition of the essential oil which was obtained from the water distillation of the oleoresin of *D. grandiflorus* Blanco. In addition, the use of the oil as a source of energy will be examined. The origin of the oleoresin in this study was from the wild trees found in the deep forests of the province of Leyte in the Philippines.

The oil was extracted by water distillation, the distillation method that was found to give the highest yield of oil from the oleoresin:-38-40% from the freshly collected oleoresin. It possessed a similar aroma to gurjun balsam. The color was light yellow, turning a bit dark on standing. It was insoluble in water, very soluble in common organic solvents except ethyl alcohol, very miscible with gasoline, kerosene, and diesel oil. Some physical and chemical constants of the oil were determined and are shown in Table 1. The oil was subjected to analysis using procedures that have been described in detail elsewhere (3), (4).

Chemical Composition of the Oil

As an initial infrared spectra of the oil of *D. grandiflorus* Blanco indicated that it was mainly sesquiterpene hydrocarbon in nature, the oil was first separated into oxygenated constituents (1%) and hydrocarbons (99%) by chromatographing it over Al_2O_3 (Activity II). The hydrocarbon fraction was then concentrated to

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[1] RJR Technical Co., Avoca Division, Winston-Salem, NC., USA

Figure 1. *Dipterocarpus grandiflorus* Blanco (actually 40 meters high) with coconut trees in the foreground.

1.5 Gm. and this was re-chromatographed over 115 Gm. of 15% $AgNO_3/Al_2O_3$ using gradient elution (hexane-diethyl ether-methanol). Individual fractions were concentrated on a water bath and subjected to preparative gas chromatography on a 12ft. x 0.25 in. column, packed with 10% Carbowax 20M coated on 60-80 mesh neutral and silanized Chromosorb W. All components were characterized by carefully comparing their infrared spectra with standard infrared spectra in one of the

Table 1. Physical and Chemical Constants of the Essential Oil of *Dipterocarpus Grandiflorus* Blanco

Specific gravity, d_{30}^{30}	0.9228
Refractive index, n_D^{30}	1.4930
Congealing point	–3°C
Acid value	0.7819
Saponification value	16.35
Ester value	15.5681
Iodine value	200.45

Table 2. Constitutents Previously Identified in *Dipterocarpus* Resin Oils

α – Gurjunene	γ – Gurjunene
β – Gurjene (Calarene or $\Delta^{1,\,10}$ – Aristolene)	
Caryophyllene	α – Humulene
β – Elemene	Allo-Aromadendrene
Valencene	Cyperene
Farnesene	Capaene

author's (BML) spectral library and with previously published spectra. In addition, the whole oil was subjected to a GC-MS analysis. The results obtained from this analysis confirmed the findings of the analysis described above. Because of the quantities involved, only the hydrocarbon fraction was examined.

A survey of the literature reveals that a number of hydrocarbons have already been isolated from oils of *Dipterocarpus* species by Bisset *et al.* (5). A list of these constituents can be seen in Table 2. They also reported that two *Dipterocarpus* balsam oils of Philippine origin have been found to contain mainly sesquiterpene hydrocarbons, shown in Table 3. These same authors also compared the composition of the Philippine oil of *Dipterocarpus grandiflorus* Blanco with two further oils of Sabah origin. These results along with our findings can be seen in Table 4. As can

Table 3. Comparative Chemical Composition of Philippine *Dipterocarpus* Oils

D. granicilis Bl.:	β – Caryophyllene (75%) & α – Humulene (25%)
D. grandiflorus Blanco:	α – Gurjunene (20%), Allo-Aromandendrene (50%) Caryophyllene (4%) & α – Humulene (20%)
Acc. to Bisset (1966)	

be seen, the composition of our oil is very similar to the previously published information with the exception that we have identified copaene, β-elemene, germacrene D, and γ-gurjunene in the oil of *D. grandiflorus* for the first time. The gas chromatogram of the oil is shown in Figure 2.

Preliminary Energy-Related Experiments

In the present age when the cost of petroleum-based fuels is continually on the rise, there has been a frantic search for substitutes for these fuels. A source of substitutes that has been in focus for the last couple of years is the plant kingdom. It has fascinated the scientists, agronomists, and industrialists because certain plants not only serve as an alternative source of energy but also ensure the renewable and, therefore, inexhaustible supply of that source.

A plant that caught our interest is *Dipterocarpus grandiflorus* Blanco the oleoresin of which might be a possible source of energy. In the Philippine hinterlands, the oleoresin is extensively used for lighting purposes. It is tightly packed at the end of a handy bamboo pole, ignited and used in the form of a torch (6). This observation was suggestive of the presence of easily combustible components in the oleoresin and gave us the notion that it might be worth examining its essential oil to find out if this oil or its constituents could serve as liquid fuels.

Among the properties that are sought for in liquid fuels, the following take precedence:

a. *Specific gravity.* A lighter fuel will have a smaller growth of penetration in the air charge but will have greater dispersion and wider cone angle. These parameters will determine the degree of efficiency of combustion of the fuel.

b. *Distilling range.* Most fuels are not pure compounds but a mixture of a large number of components, each having its own different boiling point. Hence, a fuel may start to boil at a low temperature, the lower boiling components gradually boiling away, but the temperature must be raised to keep the higher boiling components in the vapor state. For services involving rapidly fluctuating loads and speeds the more volatile fuels may provide better performance. However, best fuel economy is generally achieved from heavier types of fuels because of their higher heat content.

Table 4. Comparative Chemical Composition of the Oil of *Dipterocarpus Grandiflorus* Blanco

		Percentage Composition	
Compound	*2 Sabah Oils**	*Philippine Oil**	*Our Results*
Copaene	–	–	0.14
α – Gurjunene	3 – 10	20	6.28
β – Gurjunene	0 – 10	–	–
β – Elemene	–	–	0.34
Caryophyllene	? – Trace	4	1.83
Allo-Aromadendrene	80 – 95	50	77.85
α – Humulene	? – Trace	20	2.58
Germacrene D	–	–	0.67
γ – Gurjunene	–	–	0.43

*Acc. to Bisset (1966)

c. *Percent volatility or evaporation rate.* Generally, in higher-speed engines, the lower the volatility, the better, since too volatile a fuel is liable to cause detonation and give rise to gassing or vaporlock problems in the fuel injection system. On the other hand, if volatility is too low a further delay period will be introduced because of the greater time taken to form a gas envelope on the outside of the sprayed droplets.

d. *Flammability.* The basic reaction involved in fuel burning is the chemical union of oxygen in the combustion air with the major fuel elements, carbon and hydrogen. When sufficient air is present, the combustion liberates large quantities of heat. Thus, fuels are hazards when subjected to ignition in locations other than the engine combustion.

e. *Viscosity.* Viscosity is an important characteristic in a diesel fuel since it affects the power to operate the pump. It has also an influence on the size of the fuel particles sprayed through the injection nozzle.

f. *Flash point.* Flash point is defined as the temperature at which vapors arising from the oil sample will ignite momentarily, or flash, on the application of a flame under specified conditions. The lower the flash point of a fuel the greater the danger of explosion and fires resulting from the ignition of the lower boiling components. Hence, the flash point is significant in determining the volatility of a combustible liquid. It can also estimate the temperature at which a fuel can be safely stored.

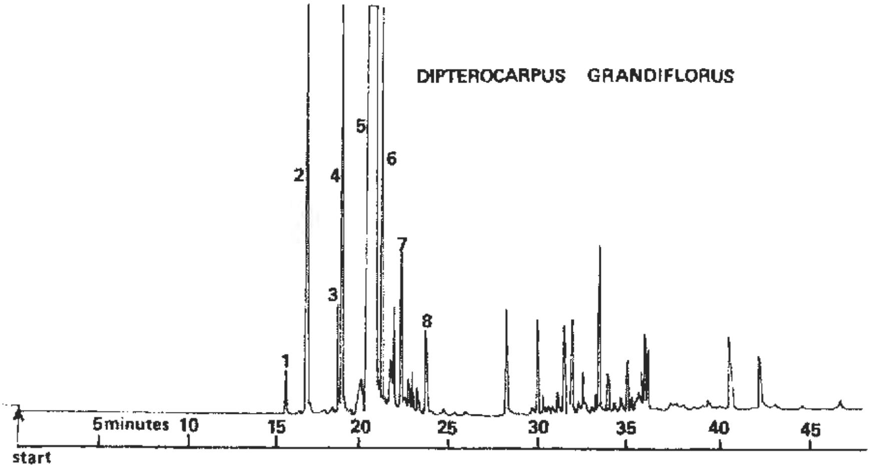

Figure 2. Gas chromatogram of the essential oil of *Diptercarpus grandiflorus* Blanco.

g. *Corrosion.* This is measured by the amount of discoloration on a mechanically cleaned strip of copper sheet when a strip of copper sheet is immersed in the fuel sample and heated under specified conditions. This will indicate if sulfur is present in a fuel. The formation of sulfur compounds during combustion can result in service corrosion of engine parts. Also, the presence of free water in the fuel is generally considered conducive to corrosion particularly of the ferrous parts of the engine.

h. *Heating value.* The heat of combustion is important as an indication of the amount of potential energy present in the fuel. It is of interest in determining the engine performance with regard to specific fuel consumption. This is measured in a bomb calorimeter and is expressed either in calories per gram Cal/Gm. or in British Thermal Unit per pound (BTU/lb).

For purpose of comparison, the oil of *D. grandiflorus*, kerosene, and a sample of commercial crude oil were examined for the afore-mentioned criteria. The results indicated that the value for *D. grandiflorus* oil compared favorably with most of the typical values for kerosene and the crude oil. The comparison is shown in Table 5.

Comparative Energy Contents

The energy content of the essential oil of *D. grandiflorus* was measured in a Parr adiabatic automatic calorimeter. Average of the results obtained was compared with the heating values recorded in literature for a number of crude oils abroad (7). It showed that while the heating value of *D. grandiflorus* oil was a bit below those of Texas, Oklahoma, Pennsylvania, and Wyoming crude oils, it was higher than the crude oils of Kansas, Mexico, and California, as can be seen in Table 6.

Table 5. Comparative Properties of Oil of *D. Grandiflorus* Blanco, Crude Petroleum Oil, and Kerosene

	Oil of D. grandiflorus	*Crude Oil*	*Kerosene*
Distilling range	175-261°C	120-600°C	175-275°C
Percent volatility	19.0	17.93	99.8
Flammability (seconds) 1.5 cc.	47.6	–	45
Viscosity	4	1.3	2.4
Flash Point	110°C	66°C	42°C
Corrosion (Cu strip)	No. 1	–	No. 1
Heating Value Cal./Gm.	10,640	10,628	11.006

Table 6. Comparative Energy Contents

Fuel (Crude Oil)	*Cal/Gm.*	*BTU/lb.*
Mexico	10,419	18,755
California	10,506	18,910
Kansas	10,628	19,130
D. GRANDIFLORUS	10,640	19,148.4
Texas	10,811	19,460
Oklahoma	10,834	19,502
Pennsylvania	10,836	19,505
Wyoming	10,839	19,510

Fractionation of the Oil

In order to have an idea which portion(s) of the essential oil of *Dipterocarpus grandiflorus* Blanco, would be of practical importance with respect to the percentage in which it is available and the heat of combustion it can generate, the oil was fractionally distilled under a reduced pressure of 67 mm. There were five fractions obtained, as shown in Table 7, all of which were mixtures as indicated by gas chromatography. Three of the fractions gave heating values that were higher than that of the whole oil. Since the oil is predominantly sesquiterpene in nature, it was

Table 7. Fractionation of the Essential Oil of *D. Grandiflorus* Blanco

Fraction	*Volume (ml.)*	*Distilling range °C*	*Percent*	*Pressure (mm. Hg)*	*Cal./Gm.*	*BTU/lb.*
1	10.8	122-144	10.8%	67	10,774	19,393
2	5.0	148-168	5.0%	67	10,347	18,624.6
3	17.4	170-180	17.4%	67	10,796	19,432.8
4	19.3	182-186	19.3%	67	10,322	18,579.6
5	27.0	187-190	27.0%	67	10,723	19,301
Residue	12.0					
Total	91.5					
				Whole Oil . . .	10,640	19,148.4

likely that the high energy fractions contained the $C_{15}H_{24}$ hydrocarbons. This formula is within the range of the molecular weights of the components comprising the hydrocarbons in the diesel fuel.

Blends With Diesel Oil

The essential oil of *D. grandiflorus* was found to blend thoroughly with diesel oil. For the purpose of exploring whether or not the oil can be used as supplemental to diesel oil, mixtures were prepared using varying proportions of the oil and diesel oil. The mixtures were used in preliminary tests with diesel engine. However, on account of the large volumes of blends that the engine performance tests require, this phase of our study, although ongoing and encouraging, has not yet proceeded far enough to warrant conclusive results.

Summary

The essential oil that was obtained by water distillation of the oleoresin of *Dipterocarpus grandiflorus* Blanco from Leyte province, Philippines, was found to contain 1% oxygenated fraction and 99% hydrocarbons, the latter mainly sesquiterpene in nature.

Aside from the sesquiterpenes that were reported by previous workers on the chemistry of Philippine *D. grandiflorus,* we have identified copaene, β-elemene, germacrene D, and γ-gurjunene in the essential oil of *D. grandiflorus* for the first time.

There were indications that the essential oil of *D. grandiflorus* might be used as a source of energy. The properties of the oil compared favorably with most of the typical values for kerosene and a commercial crude oil. The energy content, expressed in Cal./Gm., while a bit below those of crude oils from four states of USA, was higher than those of crude oils from three other places abroad. Fractionation of the oil gave 5 fractions which were mixtures. Three of the fractions gave heating values higher than that of the whole oil. The oil blended completely with diesel oil. Engine performance tests using blends containing varying proportions of our oil and diesel oil are in progress.

Considering that the yield of oil from the oleoresin is 38-40%, and taking into account West's observation (8) that one tree produces 1 Kg. of oleoresin per day, or the equivalent of 400 cc. of oil obtainable from one tree a day, one is tempted to speculate that *D. grandiflorus* Blanco would be a promising natural source to tap for liquid fuel. In addition, this source has the advantage of surviving for a long period of time and continues its resin-producing function indefinitely.

Acknowledgements

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Magdalena C. Cantoria, Discussant

Many of the dipterocarps are large trees that are familiar to us as sources of lumber. Oleoresins are characteristic of the family. Some genera belonging to the family which have attracted the attention of plant chemists are *Dipterocarpus, Shorea, Dryobalanops,* and *Hopea.* Products include gurjun balsam from *Dipterocarpus turbinatus;* varnish resins from species of *Shorea, Hopea,* and *Dryobalanops;* and edible fat, which can be used instead of cocoa butter in chocolate manufacture, from the nuts of *Shorea macrophylla;* and Borneo camphor from *Dryobalanops aromatica.* It is interesting to note that some of our own dipterocarps have become the objects of investigation for their volatile oil content.

Dr. Norman G. Bisset, now at the Chelsea College, London, Department of Pharmacy, visited our country and other Asian countries in the 60's and eventually published the results on the investigation by his group of the volatile oils of some species of *Dipterocarpus* and their isolation and identification of several hydrocarbons. It may be gathered from the paper of Dr. Belardo that this work of his group provided the background for their own investigation of apitong. Now, 17 years later, Dr. Belardo and her co-workers have added four hydrocarbons to the list identified by Dr. Bisset and his group. This is a distinct contribution to basic science.

Dr. Belardo and her co-workers have extended their basic research studies into the properties of the volatile oil of apitong relevant to its utilization as an energy source as suggested by the presence of a large fraction of hydrocarbons in the oil. Their results show that the properties of the oil are comparable to those of kerosene and a commercial crude oil. Its energy content of 10,640 cal/g is also comparable to that of other crude oils of American origin which range from 10,419 to 10,839 cal/g.

The work of Dr. Belardo and her group now indicates studies on the physiology of the plant. Research problems that come readily to mind are the following:

1. Occurrence and distribution of the plant in the country – A proper survey will reveal the natural habitat of the plant and this will serve as a guide to the best areas where it may be grown successfully as a crop. If more trees now growing wild may be located, it will be possible to collect more samples of the oleoresin for further intensive studies.
2. Type of oleoresin-bearing structures and their location in the plant – A study of the anatomy of the tree will provide information on the type of oleoresin-bearing structures and their location in the plant. This will be helpful in devising effective methods of obtaining the oleoresin from the plant.
3. Propagation of the plant – The fastest and most efficient method of propagating the plant will have to be sought if the plant is to be developed as a crop. Generally, trees are propagated by seed, and, if this is true for apitong, then germination studies are in order.

4. Environment factors affecting the oil yield of the plant – Such factors as temperature, rainfall, altitude, and soil (physical, chemical, and microbiological properties) affect oil yield. Inorganic nutrition is also included here as part of the chemical properties of the soil. Knowledge of the extent to which the plant responds to these factors will be useful in the large-scale cultivation of the plant. It will be possible to meet the requirements of the plant for optimal growth.

5. Variation, quantitatively and qualitatively, in the oil yield with ontogenetic changes in the plant – Physiological changes in the plant as it grows and develops will result in quantitative and qualitative changes in the volatile oil yield.* Data on these changes that occur with ontogeny will be valuable in the utilization of the volatile oil as a source of energy. The quality of the oil as an energy source may be at its peak at a particular stage of growth and development of the plant. This will determine the time of collection of the oleoresin.

6. Method of collecting the oleoresin – Trees which yield oleoresins as exudates, either naturally or as a result of injury, may be continuously tapped provided the physiology of the trees is well understood. Various methods of increasing the exudate by treatment with acids, hormones, or microorganisms will have to be tried out to determine the best method. If the tree is to be grown commercially, a continuous supply of the oleoresin has to be assured.

7. Breeding and selection for improvement of the plant as a crop – The most important factors determining yield are genetic and therefore the plants with maximum yield which are hardy, disease- and pest-resistant, and which possess other desirable characteristics will have to be selected by careful breeding and hybridization studies.

In addition to studies on the biology of the plant, other related studies may be conducted such as:

1. Feasibility studies – An insight into the cost of growing the plant and collecting the oleoresin, the quantity of oil yielded, the amount of energy generated, the cost of separating the volatile oil from the oleoresin, the performance of the oil in operating diesel engines, and other relevant details will indicate the feasibility of the actual utilization of the volatile oil of apitong as an energy source.

2. Properties and possible uses of the resin – After distilling off the volatile oil from the oleoresin, the resin is left as a residue. The physical and chemical properties of the resin may be determined and the results will be original contributions to basic science. Possible uses of the resin may be found and maximum utilization of the oleoresin will be effected.

Sufficient information on the physiology of the plant and other related aspects will provide a basis for the proper science authorities of government to recommend and support the development of our Philippine dipterocarps, starting

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*Variations in composition of the oils as reported by Dr. Bisset and his co-workers and by Dr. Belardo's group in Table 4 could possibly be due to changes in the physiology of the plants or to the genetic make-up of the plants studied.

with apitong, as alternative sources of energy in the country. Here lies the significance of the research work of Dr. Belardo and her co-workers and for this their work may be justifiably commended.

Julian A. Banzon, Discussant

The sudden increase in price of petroleum oil had posed a very serious problem to us who have very little of this commodity. Petroleum is the source of liquid motor fuel; what is affected is the motor transport industry; this means the movement of food supplies, construction materials, of trade in general, of people who have to reach their stations of work and return late to their home. Liquid petroleum fuels are needed in mechanizing agriculture; plowing and tilling, applying fertilizer and pesticides, weeding, harvesting, etc.

As is well-known alcohol (ethanol) is a good substitute as liquid motor fuel especially for gasoline engines but alcohol is expensive to produce, so far. Our raw materials for its production is not only inadequate: they are needed for food use. Hence the need to locate other sources of liquid fuels: adequate in supply and where its use will not deprive us of a food material.

Here is where the study presented by Dr. Luz Oliveros-Belardo and associates becomes of special significance. The authors find that the oil derived from the oleoresin of *D. grandiflorus*, approximates the fuel characteristics of diesel fuel as reported in Tables 5 & 6. They also find this oil to be thoroughly miscible with kerosene, gasoline and diesel fuel, which means that blends are possible. It is to be noted that complete replacement of petroleum-denied fuel may not be achieved in the near future; mixtures or blends or "extenders" (to borrow a food tech term) is all that we can hope for in the meantime. The authors of this paper as well as financial supplies are to be commended for this contribution to solve the Philippine liquid fuel problem.