Some Components of the Absolute of the Flowers of *Jasminum sambac* (L.) Ait.

Luz Oliveros-Belardo
National Academy of Science and Technology
Philippines

Roger M. Smith
Reader in Analytical Chemistry
University of Technology
Loughborough, England

Milagros P. Ocampo
Former Dean
College of Pharmacy
The Philippine Women's University
Manila, Philippines

ABSTRACT

The absolute of the flowers of Jasminum sambac (L.) Ait. that were collected in San Pedro, Laguna, Philippines, showed linalool as the major volatile component. Present in lesser quantities were benzyl acetate and benzyl benzoate. A mixture of hydrocarbons was noted. Aliphatic and aromatic esters were detected.

INTRODUCTION

Jasminum sambac (L.) Ait. belongs to the family *Oleaceae*. Under the genus *Jasminum*, there are four plants that are found in the Philippines (Padilla, *et al.*, 1976). They are *Jasminum bifarium* Wall, called "sampagitang gubat"; *Jasminum grandiflorum* Linn., the well known "jasmine"; *Jasminum multiflorum* (Burm f.) Andr. or "sampagitang sunsong"; and *Jasminum sambac* (L.) Ait. the popular "sampaguita". On the basis of the limb (corolla tube) there are two kinds of *Jasminum sambac*. That with a double limb is called "kampupot", the less fragrant variety. That with a single limb is the "sampagita"

proper which is noted for its exquisite fragrance. The latter is the subject of the present study, Fig. 1.

Fig. 1. *Jasminum sambac* (L.) AIT. in bloom.

J. sambac is a native of tropical Asia. It abounds in the Philippines. It is easy to cultivate requiring only little care and attention. The popularity of sampagita flower has not waned through the ages. While the attraction of other cultivated blooms has come and gone as in a fad, the sampagita in its simplicity, fragrance and easy availability to everyone (rich or poor) remains steadfast as a beloved flower of the Filipinos.

The flowers are a source of modest income from home gardens and are a steady source of revenue for established

flower shops because the sampagita garlands, pompoms, sprays and bouquets are in demand during some festive occasions.

The annual *Flores de Mayo* gathers elegantly dressed young girls who parade to the church carrying sampagita to offer to the Virgin Mary. The traditional *Santacruzan* has the sampagita flowers as the dominant floral decor in the arch that signals the coming of Santa Elena. Even if there is no occasion, Filipino women go about their daily chores sporting a small cluster of sampagita in their hair.

The sampagita plant boosts livelihood in some localities in the countryside. It has been reported (Anonymous, 1988) that a couple in San Pedro, Laguna, earns a neat P6,000.00 monthly from their two-hectare sampagita farm.

The term sampagita had a romantic origin. It is said that lovers in a betrothal ceremony in early days exchanged sampagita garlands to seal their love with the vow ``sumpakita''. Probably, in the words of the senior author, the vow ran as follows:

> With this simple flower
> Whose charm fades never,
> Before God I swear
> I will love you forever.

The derivative, sampagita, became the symbol of mutual true love.

Sampagita fascinated writers and poets. Songs were composed, and lyrics written to glorify the flower. The top accolade came when the former Governor General of the Philippines, Frank Murphy, in February 1934, proclaimed the sampagita as the National Flower of the Philippines.

Among the products derived from the Jasminums, it is the absolute of *J. grandiflorum* that is considered one of the most precious and important ingredient in perfumery. It is obtained in various Mediterranean countries - France, Italy, Egypt, Morocco and Algeria and in a limited amount in India. More than 130 components including 17 basic compounds have been reported in the oil with benzyl acetate as the chief constituent (Cheng and Chao, 1977).

Jasmine absolute coming from countries mentioned earlier show approximately the same composition of volatile neutral components but their relative percentages depend on their geographical origin. The difference inevitably influences the quality of the odor. According to observations made by travellers, some features of *J. sambac* flowers from Egypt and China differ from those from the Philippines.

With regard to *J. sambac*, literature has not yet come up with voluminous records on an extensive chemical study even if the plant is cultivated widely in some countries like China, Egypt and India. Cited was the occurrence of 4-methyl-5-ethyl nicotinate as the major basic component (29%) of the absolute of *J. sambac* from China (Toyoda, *et al.* 1977).

In the Philippines, there were several groups that attempted to obtain the sampagita floral essence. One of the earliest was in 1956 when a volatile oil with specific gravity of 0.9285 at 30°C was obtained (Cruz, *et al,* 1956). In 1976, another group tried different methods of extracting the essence of the flower. They found out that the oil was not amenable to extraction by the three types of distillation - water distillation, hydro-steam distillation and steam distillation which seemed to be harsh to the delicate oil. Enfleurage was tried, but probably because there was no suitable fat corps available locally, the oily product was scanty. Moreover, it also smelled of fat that almost concealed the floral scent. Continuous solvent extraction in Soxhlet produced a highly impure extract with diminished fragrance. The continuous heat received by the receiver flask for prolonged periods of time could have destroyed fragrant components. Finally, maceration with organic solvents proved to be the least damaging to the floral components. The process did not use heat during the recovery of the solvent in the flash evaporator which was carried out at a low temperature under reduced pressure.

Three solvents were tried for the maceration: petroleum ether, ethyl alcohol and hexane. Petroleum ether was too volatile to maintain its constant volume because of the rapid loss through evaporation in the process of periodically opening the lid of the tightly covered maceration containers for purpose of necessary stirring, filtering and replacement of solvent. Ethyl alcohol, while least expensive and not prone to rapid evaporation, required higher temperature in its recovery. Between petroleum ether and ethyl alcohol, hexane was observed to be sort of the "happy medium" - the better maceration solvent to use in capturing the essence of the flowers. Thus, in preparing the concrete, hexane was used as the solvent.

Thin layer chromatography of the concrete showed 9 major fractions one of which gave a solid derivative wih 2,4-dinitro-phenylhydrazine indicating it to be either an aldehyde or a ketone. Two other fractions when analyzed by GC-MS and subsequently compared with known standards, showed the presence of linalool and benzyl acetate in the concrete.

Perfumers use the absolute instead of the concrete from flowers for the reason that the concrete contains considerable proportion of materials which are hardly volatile such as floral wax, glycerides, solvent residues - components that do not contribute at all to the odor desired. In preparing the absolute a greater portion of the non-volatiles are eliminated leaving a more fragrant product. This is one reason why absolute is more expensive than concrete.

The object of the present study is to prepare the absolute of the flowers of *Jasminum sambac* (L.) Ait. from local sources, identify some fragrance materials therein, and compare the results with those of the concrete.

MATERIALS AND METHODS

Preparation of the Absolute from the Flowers of *Jasminum sambac* (L.) Ait

The flowers of *J. sambac* that were used in this investigation were collected in San Pedro, Laguna, Philippines. They were plucked before sunrise in order to avoid contact of the sun's rays with dew drops that might be clinging to the petals, otherwise a sunglass effect will heat and destroy the delicate essence of the flower.

The fresh flowers were freed from dirt, leaves and stalks. After weighing, they were placed inside large wide mouth dark colored glass jars. Hexane was poured in until the flowers were completely soaked in it. The containers were tightly covered, set aside and opened only for stirring from time to time. This maceration was carried out for several days after which the hexane was filtered off and the flowers returned to the jars for a next maceration. Re-macerations were carried out until the flowers were devoid of scent. The combined hexane filtrate was concentrated in a flash evaporator into a viscous extract called the concrete. The concrete was exhaustively treated with ethyl alcohol. Insoluble substances were filtered off. The filtrate was flash evaporated into a concentrate, a thick floral oil called the absolute.

Examination of the Absolute

Thin layer chromatography (TLC). A sample of the absolute was separated by TLC on silica gel with chloroform as solvent system. The bands were scraped off and extracted. The extracts were re-examined by GLC at 170° and 100°C. Infrared (IR) spectra and GC-MS were run on any extract that

contained a major component. Comparisons were made with known authentic samples.

Gas liquid chromatography (GLC). The absolute was examined on an 8% MS200/12500 GC on 3% XE60 column at 170°C using a Pye Unicam 104 gas chromatograph fitted with FID detector. Identification of the peaks in the gas chromatogram was aided by comparison of retention times, and by gas chromatograph-mass spectrometry coupling (GS-MS) on either SP2100 or FFAP capillary Scot columns. Comparisons were made with a number of compounds reported to be present in Jasminum oils.

RESULTS

Concrete

The flowers *J. sambac* (L.) Ait. gave a yield of 0.28% concrete after maceration with hexane. The concrete appeared to be a heterogenous brownish yellow mass that carried some floral wax.

Absolute

The absolute was prepared from the concrete by exhaustive treatment with ethyl alcohol. The alcoholic solution was concentrated under reduced pressure and temperature into a viscous, yellowish liquid, the absolute. It possessed the delicate fragrant odor of the fresh flowers. The yield was 50% of the concrete.

Thin Layer Chromatography of the Absolute

A 153 mg sample of the absolute upon separation by TLC on silica gel (chloroform as solvent) showed 8 bands. They were labelled Bands A,B,C,D,E,F,G,& H. IR of the first two bands (A & B) showed significant amounts of hydrocarbons, and a mixture of aliphatic esters, one of which was indicative of linalyl acetate (unconfirmed). GLC resolved the 4th band (Band D) into four major peaks one of which was identified by IR as benzyl benzoate, and others as aromatic esters. GLC and IR of the 7th Band (Band F) revealed the presence of benzyl acetate. GLC of the last Band (Band H) showed that it was a complex mixture of linalool as the major volatile component and some non-volatile compounds, Table 1.

Gas Liquid Chromatography of the Absolute

From the GLC analysis of the absolute, only one peak was clearly visible among several others. It corresponded to linalool,

Table 1. Thin layer chromatography of the absolute of the flowers of *Jasminum sambac* (L.) Ait. from the Philippines.

BANDS	Rf	MAJOR COMPONENTS	IDENTIFIED BY
A	1.0	hydrocarbons	IR
B	0.73	aliphatic esters	IR
C	0.7	(too small)	-
D	0.65	benzyl benxoate	GLC, IR
		aromatic esters	IR
E	0.5	(too small)	-
F	0.4	(too small)	-
G	0.3	benzyl acetate	IR
H	0.29	linalool	GLC, IR

the major component in 9.5% occurrence. This assignment was confirmed on a XE60 column. At a higher sensitivity the mixture could be seen to be much more complex. In particular, there was a large number of high boiling constituents. In a low temperature run a smaller peak appeared corresponding to benzyl acetate. Farther on was an irregularly contoured peak which, on rechromatography, was resolved into benzyl benzoate and some unidentified minor components.

GC-MS of the peaks of linalool and benzyl acetate from the absolute were the same as those found for linalool and benzyl acetate in the concrete. The mass spectra of linalool, benzyl acetate and benzyl benzoate from the absolute are shown in Figs. 2, 3, and 4. They agree with respective mass spectra that are published earlier, i.e., Masada (1972), Smith and Belardo (?), and Von Sydow (1963).

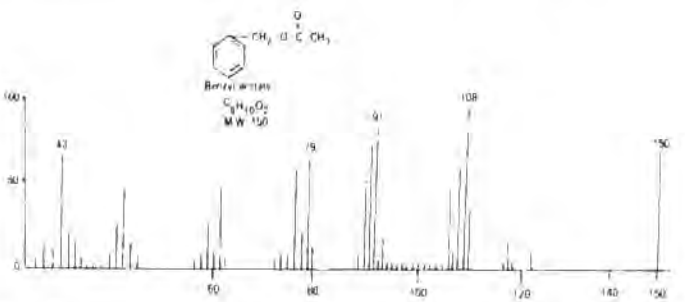


Fig. 2. Mass spectrum of linalool from the absolute of the flowers of *Jasminum sambac* (L.) Ait. from the Philippines.

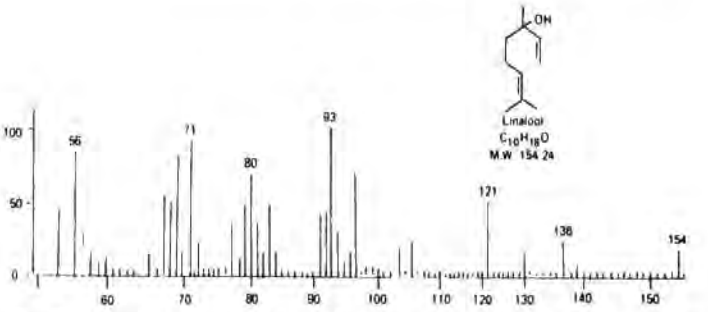


Fig. 3. Mass spectrum of benzyl acetate from the absolute of the flowers of *Jasminum sambac* (L.) Ait . from the Philippines.

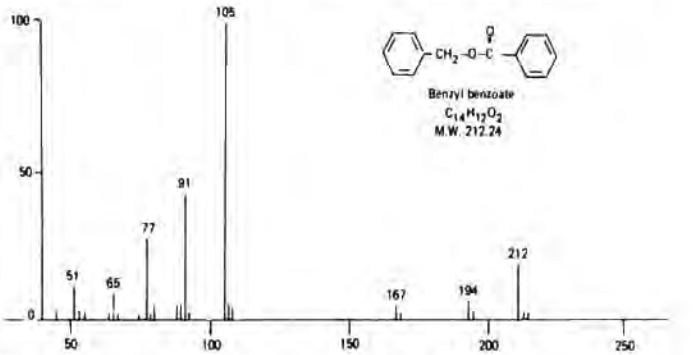


Fig. 4. Mass spectrum of benzyl benzoate from the absolute of the flowers of *Jasminum sambac* (L.) Ait. from the Philippines.

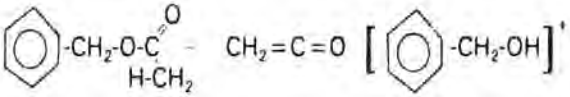
DISCUSSION

The mass spectrum of a compound with appreciable volatility shows the mass of the molecule and the masses of the fragments that are formed from the spectral decomposition.

The mass spectrum of linalool shows several significant peaks. Strong peaks at m/e 71 and m/e 80 are characteristics of monoterpene alcohols. Peak at m/e 154 corresponds to the theoretical molecular weight of 154.24. Dehydration which is one of the changes that occur upon sample volatilization 2 is reflected by m/e 136 (m.w. of terpene hydrocarbons) which was formed by the favored loss of water from the molecular ion. Alcohols containing branched methyl groups, as for example terpene alcohols, frequently show a fairly strong peak at M-33 or at m/e 121 which was brought about by loss of water and a methyl group (Silvestein, *et al,* 1974). Peak at m/e 93 is

the fragment that resulted from loss of methyl groups and water.

In the mass spectrum of benzyl acetate, the peak at m/e 150 represents the molecular weight. Base peak at m/e 108 is a re-arrangement peak representing cleavage of the acetyl group (m/e 43) and re-arrangement of a single hydrogen atom, eliminating the neutral molecule ketene frequently to form the base peak as shown as follows (Silverstein, *et al.* 1974):



The m/e 43 peak ($CH_3C{=}O^+$) and m/e 91 ($C_7H_7^+$) peaks are characteristics for benzyl acetate.

Benzyl benzoate has the molecular formula $C_{14}H_{12}O_2$ and a molecular weight of 212.24. Its mass spectrum shows the parent peak to be 212. Two abundant ions, m/e 77 corresponding to a phenyl group, and the base peak at m/e 105 corresponding to bezoyl $(Ar\text{-}C{=}O)^+$ strongly suggest that the compound is a benzoate (Mchafferty, 1973). Fragments observed reflect Ar,

ArC, ArC-O, 2H and R or R-H, 3.

The present work showed that among the fragrance materials in the absolute of *Jasminum sambac* (L.) Ait., linalool was the major component followed by benzyl benzoate and benzyl acetate. While an earlier work on the concrete reported only linalool and benzyl acetate as principal components, the absolute in the present investigation had, in addition, benzyl benzoate, hyrocarbons and esters (aliphatic and aromatic). The absolute carried faithfully the exquisite fragrance of the fresh flowers.

In the analysis of floral extracts, there are instances when some components escape detection by GLC. They are the high boiling natural products which some investigators (Togano, *et.* al., 1977) called "residual components". In their work on Jasmine absolute they identified these residual components to be squalene, phytyl stearate, phytyl oleate, phytyl linolenate and phytyl palmitate. They are almost colorless and transparent liquids. It was observed that this group of components gives the "body" to natural jasmine oil which synthetic jasmine lacks.

In our work on *J. sambac* absolute, the gas chromatogram had less number of components than the number indicated on TLC. Band H on TLC had a large portion of non-volatile long chain components. It is likely that what did not show up in the gas chromatogram may not have eluded TLC analysis, and that Band H could have some "residual components" admixed with linalool. Those were the non-volatile or sparingly volatile components which hexane extracted during maceration, left behind as a residue on the recovery of hexane, and was partly carried over from concrete to absolute. This type of residue usually makes the TLC separation complicated, and will necessitate further special procedures for their isolation and purification.

SUMMARY, CONCLUSION AND RECOMMENDATIONS

Absolute was prepared from the flowers of *Jasminum sambac* (L.) Ait. that were collected in San Pedro, Laguna, Philippines. In the preparation of the absolute, maceration of the flowers with hexane was found to be the most suitable method of extraction, giving a 50% yield from the concrete. It was a viscous, clear, yellowish liquid which duplicated the delicate fragrant odor of the fresh flowers in contrast to the concrete which had a much lesser fragrance. GLC, TLC, IR and GC-MS of the absolute identified linalool as the major volatile component. Benzyl acetate and benzyl benzoate in lesser amounts were present. In addition, there were groups of unidentified hydrocarbons, esters and some residual components. This was another difference from the concrete. A copious amount of floral wax separated during the treatment of the concrete with ethyl alcohol.

The results of this preliminary work on the absolute of *J. sambac* gave a distinction to sampagita as having its own identity. It can now pride itself as having its major contribution to fragrance identified. Thus, while *Jasminum grandiflorum* has benzyl acetate as its chief volatile compound and *Jasminum odoratissimum* gives benzyl benzoate as its main constituent, *Jasminum sambac* from the Philippines offers linalool as its predominant volatile component.

Linalool is a valuable commodity in the world market of essences. It is an important fragrant isolate, and is widely used in perfumes, cosmetics, soap and flavor industries (Guenther and Althausen, 1974).

The study of the unidentified esters is worth pursuing. Esters are usually pleasant smelling components. No doubt

esters even in trace amounts contribute to the over-all odor of fragrant flowers. Their identification will help unravel the source of the unique fragrance of sampagita.

It is only after the other components of the absolute shall have been identified and their percentages determined may one get an indication as to whether or not *Jasminum sambac* (L.) Ait. from the Philippines would be at par or even a close runner-up to its famous cousin, Jasmine, in the latter's role as a big contributor to a country's economy through the perfumery and cosmetic industry.

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