The Composition of Manila Elemi Oil

Article *in* Flavour and Fragrance Journal · June 2006

DOI: 10.1002/ffj.2730080107

5 authors, including:

K. Husnu Can Baser
Near East University
1,106 PUBLICATIONS **11,976** CITATIONS
SEE PROFILE

Temel Ozek
Medicinal Plants, Drugs and Scientific Research Center, Eskisehir, Turkey
259 PUBLICATIONS **2,441** CITATIONS
SEE PROFILE

FLAVOUR AND FRAGRANCE JOURNAL, VOL. 8, 35–37 (1993)

The Composition of Manila Elemi Oil

Merle A. Villanueva and Rosalinda C. Torres

Industrial Technology Development Institute, Bicutan, Metro Manila, Philippines

Kemal Hüsnü Can Başer*, Temel Özek and Mine Kürkçüoğlu

Medicinal Plants Research Centre, Anadolu University, 26470 Eskişehir, Turkey

Manila elemi oil, hydrodistilled from Manila elemi gum was analysed by GC and GC–MS. Thirty-nine compounds constituting together 99.2% of the oil were identified, limonene being the most abundant (56%). The occurrence of α-phellandrene-$\Delta^{5,6}$-dimer and its implication is discussed.

KEY WORDS Manila elemi oil, *Canarium luzonicum* (Miq). Asa Gray Limonene α-Phellandrene-$\Delta^{5,6}$-dimer

INTRODUCTION

'Elemi'—derived from the Arabic 'Al-lami'—is a collective term applied to several oleoresins obtained from different plants of the family Burseraceae.[1,2] The most important and widely known of these oleoresins is Manila Gum Elemi.[2,3] This oleoresin is obtained by tapping the trunk of *Canarium luzonicum* (Miq.) Asa Gray (local name = Pili), a tree native to the Philippine archipelago.[4] The oleoresin is also known by its Spanish name 'brea blanca' (white pitch) and by its Philippine name 'sahing'. It consists of resin and 12–30% essential oil which is the subject of this study.[5,6]

Manila elemi oil is obtained by distillation from Manila elemi gum,[7–9] A number of papers have been previously published on the composition of Manila elemi oil.[10–14]

EXPERIMENTAL

Manila elemi gum was obtained from trees growing in Alabat island, Quezon province, Philippines, on 27 December 1990. The oil was water distilled from the Manila elemi gum 45 days after collection using a Clevenger-type apparatus. After 4 h of distillation, the yield of oil was 18.54%. The oil was a clear liquid, colourless to light yellow with a strong pleasant fennel-like odour, and the physical characteristics d^{20} 0.8515, n_D^{20} 1.4775, α_D^{20} + 93°, and was analysed immediately by GC and GC–MS.

The oil was kept in two different containers for one year. Sample I was kept in a brown glass and sample II in a colourless glass bottles. Both of them were kept in the refrigerator. They were subjected to analysis after one year. The results are given in Table 2. Sample II gave the following physical properties: d^2 0.8614, n_D^{20} 1.4820, α_D^{20} + 75°.

The samples used for gas chromatography (GC) and gas chromatography–mass spectrometry (GC–MS) analysis were dissolved in 1 ml of *n*-hexane (Merck), dried over anhydrous sodium sulphate, and immediately analysed.

GC Analysis

Capillary GC was carried out using a Shimadzu GC 9A chromatograph with a polar Thermon 600T fused-silica capillary column (50 m × 0.25 mm i.d.), flame ionization detector (FID) and nitrogen as carrier gas. Temperature programming was performed from 70°C isothermal for 10 min, then 70–180°C at 2°C/min and finally isothermal at 180°C for 30 min. Injector temperature 250°C; split ratio 60:1. Peak areas were computed by a Shimadzu Chromatopac integrator (CR4A).

GC–MS Analysis

A Shimadzu GC 14A was interphased with a quadrupole mass spectrometer (MS) Shimadzu

*Author to whom correspondence should be addressed.

0882–5734/93/010035—03$06.50

Received 4 March 1992
Accepted 22 August 1992

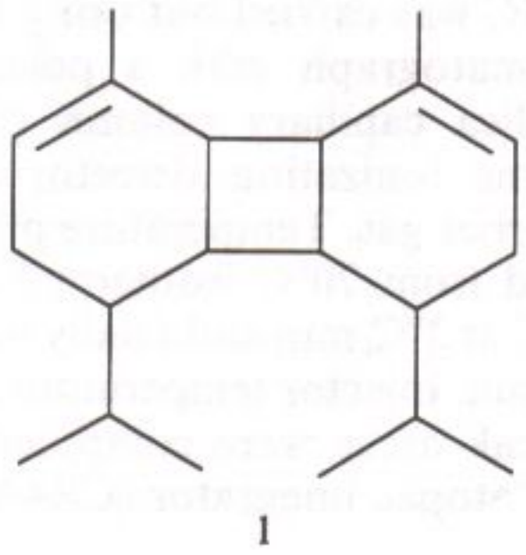
QP2000A. A fused-silica capillary column (Thermon 600T, 50 × 0.25 mm i.d.) was used with helium as carrier gas. The temperature was programmed as in the GC analysis. MS operating parameters were: ionization voltage 70 eV, scan interval 2 s and ion source temperature 250°C. A data processing system and LSS-30 library search software were used.

Identification was carried out by comparing retention times with those of reference compounds, peak-matching library search using the built-in NBS/NIH/EPA library, and comparison of MS data with those published in reference works.[15–20]

RESULTS AND DISCUSSION

Table 1 gives the analysis of the essential oil. Thirty-nine compounds identified in the oil constitute 99.2%. The occurrence of thirteen compounds in Manila elemi oil is reported for the first time. Variation in relative percentages of the components identified in GC analysis of the same oil kept for one year under different conditions is also indicated in Table 1.

The main component of the oil is limonene. According to the previously published literature, its content in the oil was reported as 23.5% to 54.1% and was stated to go up to 80%.[11–14] In the present study, it was found to be 56%. The other main components identified were α-phellandrene (17.6%), elemol (6.3%), sabinene (5.7%), α-terpinolene (2.8%), elemicin (2.4%), and β-phellandrene (2.3%). An interesting feature of this oil is the occurrence of α-phellandrene dimers. These dimers were first detected in Manila elemi oil by Brieskorn and Krauss in 1983.[12,14] This is the second report of the occurrence of an α-phellandrene dimer (**1**) in



1

the oil. In this molecule, the dimerization of two α-phellandrene molecules occurs at $\Delta^{5,6}$ to form a symmetrical cyclobutane derivative.[12] *trans* and *cis* $\Delta^{1,2}$ Dimers of α-phellandrene were not detected in this study. These dimers are believed to be photosensitization products of α-phellandrene and can also be artificially produced.[12] Therefore, they can be regarded as artefacts.

It was interesting to note that, although almost no change was observed in the oil kept in the brown container for one year, the oil kept in the colourless container during the same period showed some significant changes. The relative percentages of limonene remained more or less the same in both

Table 1. Chemical composition of Manila elemi oil

Compound[a]	Fresh oil (%)	Sample I (%)	Sample II (%)
α-Pinene	0.45	0.45	0.30
Camphene	0.03	0.02	0.02
β-Pinene	0.13	0.13	0.08
Sabinene	5.73	5.67	3.35
Myrcene	0.05	0.05	0.03
α-Phellandrene	17.56	17.25	8.75
α-Terpinene	0.15	0.13	0.08
Limonene	56.02	55.20	54.60
β-Phellandrene	2.27	2.22	1.76
(*Z*)-β-Ocimene	0.04	0.04	0.02
γ-Terpinene	0.25	0.25	0.16
(*E*)-β-Ocimene	0.03	0.04	0.03
p-Cymene	1.10	1.10	1.77
α-Terpinolene	2.82	2.76	2.47
(*E*)-Sabinene hydrate[b]	0.47	0.47	0.35
α-Copaene[b]	0.06	0.06	0.09
Camphor[b]	0.04	0.05	0.04
(*Z*)-Sabinene hydrate[b]	0.12	0.12	0.12
Linalol[b]	0.02	0.02	0.04
β-Elemene[b]	0.19	0.18	0.28
Terpinen-4-ol	0.49	0.48	0.50
α-Humulene	0.07	0.09	0.21
α-Terpineol	1.14	1.13	2.68
Germacrene-D	0.10	0.10	0.11
Piperitone[b]	0.06	0.07	0.08
Carvone	0.08	0.05	0.17
δ-Cadinene	0.02	0.06	0.04
(*Z*)-Sabinol[b]	0.10	0.12	0.18
(*E*)-Carveol[b]	0.03	0.03	0.08
p-Cymen-8-ol[b]	0.17	0.19	0.40
(*Z*)-Carveol[b]	0.02	0.02	0.06
α-Phellandrene-$\Delta^{5,6}$-dimer (**1**)	0.05	0.05	0.10
Methyl eugenol	0.18	0.18	0.31
Elemol	6.28	6.64	13.68
Guaiol	0.10	0.11	0.24
Bulnesol[b]	0.02	0.15	0.04
Eudesmol[b,c]	0.12	0.28	0.24
β-Eudesmol	0.19	0.28	0.41
Elemicin	2.40	2.53	4.65

[a]Order of elution on Thermon 600T.
[b]Compound reported for the first time in Manila elemi oil.
[c]Correct isomer not identified.

sample I and sample II. While the relative amounts of α-phellandrene and sabinene decreased almost by half, there was an approximately two-fold increase in the percentage amounts of elemol, elemicin, α-terpineol and a number of minor compounds such as α-phellandrene-$\Delta^{5,6}$-dimer in sample II. This is also supportive of an earlier proposition that α-phellandrene dimers are artefacts due to exposure to light. Furthermore, higher elemol contents reported by Lawrence as 15% and 17.3% may suggest that aged oils were used in the analysis.[11,13] Although such criteria may be used to determine the age and keeping conditions of Manila elemi oil, these findings should only be regarded as preliminary observations and more detailed studies are necessary to prove the points made above.

Acknowledgements—The authors thank Mr C. G. Ostani, C. G. Ostani Trading, Paco, Manila, for the supply of manila elemi gum.

REFERENCES

1. A. L. Tugacun, *Manila Elemi*, Forest Products Research and Industries Development Commission Technical Note No. 122 (1972).
2. *Manila Gum Elemi*, Technical Note, Philippine Bureau of Plant Industry (1988).
3. W. Brown, *Philippine Resins, Gums and Oils, Minor Products of Philippine Forests*, Vol 2. p. 42 (1921).
4. E. Quisumbing, *Medicinal Plants of the Philippines*, p. 475, Katha Publishing, (1978).
5. A. M. Clover, *Phil. J. Sci.* **2**, 1 (1907).
6. R. F. Bacon, *Phil. J. Sci.*, **4**, 100 (1909).
7. G. D. Manalo and A. P. West, *Phil, J. Sci.*, 111 (1949).
8. E. Guenther, *The Essential Oils*, Vol. 4, p. 357, D Van Nostrand, London (1965).
9. L. Oliveroz-Belardo, Z. B. Galpa and J. P. Abadiano, *Trans. Nat. Acad. Sci. and Tech. (Phil.)*, **7**, 219 (1985).
10. A. F. Summa, Ph.D. Thesis, University of Connecticut (1960).
11. B. M. Lawrence, *Perfum. Flavor.*, **5**, 55 (1980).
12. C. H. Brieskorn and G. Krauss, *Proceedings of the 9th International Essential Oil Congress*, Singapore, p. 97 (1983).
13. B. M. Lawrence, *Perfum. Flavor.*, **9**, 35 (1984).
14. C. H. Brieskorn and G. Krauss, *Planta Med.*, (4), 305 (1986).
15. Y. Masada, *Analysis of Essential Oils by GC/MS*, Hirokawa Publishing, Tokyo (1975).
16. W. Jennings and T. Shibamoto, *Qualitative Analysis of Flavour and Fragrance Volatiles by Glass Capillary Gas Chromatography*, Academic Press, London (1980).
17. A. A. Swigar and R. M. Silverstein, *Monoterpenes: Infrared, Mass, ^1H NHR and ^{13}C NMR Spectra and Kovats Indices*, Aldrich Chemical Co. Inc., Wisconsin (1981).
18. R. E. Ardrey, C. Brown, A. R. Allan, T. S. Bal and A. C . Moffat, *An Eight Peak Index of Mass Spectra of Compounds of Forensic Interest*, Scottish Academic Press, Edinburgh (1983).
19. *Eight Peak Index of Mass Spectra*, 3rd edn, 1–7, The Royal Society of Chemistry, London (1986).
20. F. W. McLafferty and D. B. Stauffer, *The Wiley/NBS Registry of Mass Spectral Data*, 1–7, Wiley, New York 1(1988).