Subcritical carbon dioxide and conventional extraction techniques of Sandalwood oil: an industry project.

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Abstract:

Sandalwood oil is an important export commodity in many countries and it is important for industry to have a capacity for rapid and accurate determination of oil content and quality for commercial samples. In this study we compared the effect of eight methods of oil extraction (one type of steam–distillation, two types of hydro-distillation, one type of subcritical CO_2 extraction and four types of solvent extractions) on oil yield and concentration of major components in a single commercial sample.

Oil yield was greatest for subcritical CO_2 (3.83g/L) followed by the solvent extractions (2.45-3.7g/L), hydro distillations (1.86-2.68g/L) and steam distillation (1.60g/L). The greatest combined levels of α- and β-santalol were found for subcritical-CO_2 (83%) ethyl alcohol (84%) and steam distillation (84%).

Organoleptic analysis revealed that the oil derived from the subcritical-CO_2 extraction and all three distillations (hydro, alkaline-hydro and steam) were recorded as 'pleasant'. In contrast three of the four solvent extracted sandalwood oils were recorded as 'less pleasant' indicating the generally inferior note of oil derived from these methods. Given the high relative yield, high level of santalols and superior note of the subcritical-CO_2 extracted oil it can be concluded that this is the best technology for sandalwood oil extraction used in this study.

Introduction

Sandalwood oil plays an important role as an export commodity in many countries and its trade depends on accurately quantifying yield and quality. These measures however can be influenced by the method of extracting the volatile oils from the heartwood. Steam distillation, hydro distillation, solvent extraction, supercritical fluid extraction (SC-CO_2) and liquid CO_2 extraction have been used to obtain the volatile oil from sandalwood (Moretta *et al.* 1998; Marongiu *et al.* 2006).

Moretta *et al.* (1998) found the yield of extractable material and total volatiles was highest for supercritical fluid extraction. The percentages of five sesquiterpene alcohols were highest in the steam distillate, indicating this process extracted fewer non-volatile materials than other methods.

Marongiu *et al.* (2006) evaluated yield and composition of heartwood oil extracted from *Santalum album* using supercritical carbon dioxide (SC-CO_2) and hydro distillation. Higher oil yield (4.11 %) was obtained in 1 h with SC-CO_2 compared with a 30h hydro distillation (1.86 %). Santalol levels also differed between the two methods with 46.1% and 35.0% α-santalol and 20.4% and 14.0% β-santalol for SC-CO_2 and hydro-distillation respectively.

Hettiarachchi (2008) found that hydro-distillation was a superior method for recovering oil compared with solvent extraction since it more accurately reflects the results obtained during industrial processing.

In this study we compare the extraction technologies amongst subcritical carbon dioxide, steam-distillation, hydro-distillation and solvent extraction. Subcritical carbon dioxide extraction may be brought to conditions where extractability of low masses may be good at higher pressures. Due to this, the density of fluid may be reduced with conditions to the temperature of operation. Hence subcritical carbon dioxide was employed for the high density of the sandalwood powder, as density of the fluid is higher compared to supercritical conditions due to operation at 28°C of subcritical carbon dioxide. Thus the yield obtained of sandalwood oil was higher with subcritical carbon dioxide.

Supercritical carbon dioxide extraction operated above the critical temperature of CO_2 (31.1°C) and critical pressure (73.9 bars) where as subcritical carbon dioxide extraction operated below critical temperature of CO_2 (31.1°C). The density of subcritical carbon dioxide usually is higher than supercritical carbon dioxide extraction and very useful process of extracting natural products with high mass density like sandalwood oil.

More economical and rapid methods of oil extraction are demanded by different sectors like clinical aromatherapy, perfume industries, pharmaceuticals, and spiritual use. This article is an early step in seeking the most appropriate method suited for volatile oil determination.

Materials and Methods

Whole sandalwood chips and sandalwood oil were provided by MPMC Chennai India.

Subcritical carbon dioxide

Supercritical carbon dioxide pilot plant was procured from UHDE, GmbH, Germany with the grant from DST, Government of India. The carbon dioxide (99.9%) was purchased from the Indian Oxygen Limited for conducting the research. All the solvents like Toluene, Benzene, Ethyl alcohol, Diethyl ether, were purchased from the SD Fine and Qualinogens, India of GR grades.

Extraction of sandalwood powder with 60µm particle size was employed throughout the processing. The particle size was kept as such so that neither the air channelling would form in case of fine size nor the large particle size would affect the yield.

Sandalwood chips were pulverized and sieved through 60µm to ensure uniformity of the heart wood sample. Sub samples were taken from this homogenized sample and oil was extracted using one of eight methods including subcritical carbon dioxide extraction, solvent extraction (benzene, diethyl ether, ethyl alcohol, and toluene), hydro distillation and steam-distillation. The extracted oil was subsequently evaluated according to the standard methods mentioned in Guenther (1985). Physical properties of the extracted oil were also determined from quality and fragrance point of view.

Sandalwood oil extraction with Liquid (subcritical) carbon dioxide

170 g of 60µm of sandalwood powder was charged in to the extractor of Pilot plant of SC-CO_2. The extraction was conducted at pressure of 200 bars, temperature 28°C, flow rate 5 kg h-1, and batch time 4 h. Sandalwood oil obtained was 3.76 g.

Solvent extraction

The solvents benzene, diethyl ether, ethyl alcohol, and toluene were used to extract sandalwood oils from the homogenised sub samples of heartwood. Each heartwood sub sample consisted 100g of sandalwood powder with a particle size of 60µm was charged along with 600 ml of solvents. The powder was placed in the muslin cloth thimble and placed into 600mL of solvent within a Soxhlet apparatus. Contact (batch) time was 5-hours for each of benzene, diethyl ether and ethyl alcohol and 12-hours for toluene (Table 1). Post extraction solvent was concentrated under reduced pressure; the concrete recovered was dissolved in 99.9% ethyl alcohol to yield the absolute. While extracting with solvents a concrete of the sandalwood was obtained, this concrete was then hydro distilled using the methods outlined below for a period of 12 h to obtain the essential oil.

Hydro distillation

Whole sandalwood chips were immersed in cold water for 24 h. A total of 100 g of 60µm particle of sandalwood powder was charged in the Clevenger apparatus in 1:5 ratio of deionised water. Hydro distillation was carried out for a period of 30 hours.

Hydro-distillation using alkaline water

The method above was repeated with except the water used was 0.3 wt% alkalinity to keep the pH moderate for the hydro distillation. This distillation was carried out for a period of 48 hours.

Extraction Process	Batch Time (hours)
Liquid CO_2 extraction	4
Solvent (benzene)	5
Solvent (Diethyl ether)	5
Solvent (Ethyl alcohol)	5
Solvent (toluene)	12
Hydro distillation	*30
Hydro distillation, alkaline treated water	**48
Steam-distillation, pilot plant	10

Table 1: Methods of extraction used in this study including heartwood sub sample treatment and batch time (hours).
*Avoiding the artefacts formation for long distillation.
**To evaluate the yield and quality of the oil under the controlled pH conditions.

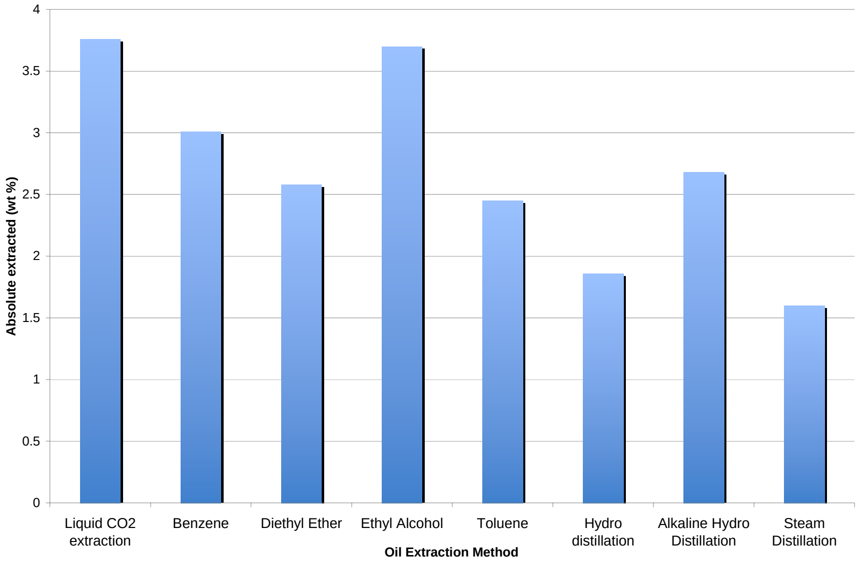

Figure 1. Oil content across eight extraction methods from an homogenized sample of *Santalum album* powder

Pilot steam distillation plant

1 kg of pulverized 60µm sandalwood powder was charged in the steam distillation of 50 litre capacity in the ratio of 1:5. Steam distillation was carried out for 10 h. Steam pressure of 1kg/h-was used throughout the process of distillation (Moretta et al. 1998).

Analysis of the sandalwood oil

The oil extracted by each of the techniques was analyzed by gas chromatography (Perkin-Elmer-8500). Column specification and temperature programme are described as: column SE30(10%) on chromosorb W, column material S.S, column length 4 m, internal diameter 1/8 inch, injector temperature 300^{o}C, FID temperature 300^{o}C, Flow rate of N_2 38 ml/min., temperature programming 100-250^{o}C with 6^{o}C/min.

Organoleptic Characterisation

Sandalwood oil samples obtained using the methods in this study were evaluated for their organoleptic properties, by commercial perfumer R. Harlalka of Nishant Aromas in Mumbai, India.

Results and Discussion

Oil Yield

Oil yield differed substantially among the eight different extraction methods used in this study. Given the homogenised powdered heartwood sample in which all methods were based the differences observed in this study would be due largely to heartwood preparation and extraction method. The subcritical-CO_2 and ethyl alcohol extraction methods were found to have an equivalent yield (2.8 and 3.7% respectively), which were substantially greater than all remaining methods (Figure 1). The hydro and steam distillation methods resulted in the lowest percentage oil extracted (1.9 and 1.6% respectively) and each was substantially lower than all other methods used in this study. Interestingly the hydro distillation using 0.3% alkaline distilled water in the charge yielded a substantially greater oil yield (2.7%) than the standard hydro and steam distillations. Furthermore the 'alkaline' distillation yielded equivalent oil yield to the benzene, diethyl ether, and toluene solvent extracts (Figure 1). The oil yield in the standard hydro distillation was less than the steam distillation since the former had poorer diffusion as the oil sacs were less exposed in the coarser textured heartwood charge (Table 1).

Oil Composition

Oil composition was also found to differ substantially among the eight different extraction methods used in this study. We propose that heartwood preparation and extraction method largely contributed to the differences observed in the levels of α- and β-santalol. The subcritical-CO_2 (83%) ethyl alcohol (84%) and steam distillation (84%) were found to have the greatest combined levels of α- and β-santalol (Figure 2). Among the remaining methods the α-santalol content in the diethyl ether solvent extraction (49%) was found to be greater than the two hydro distillation methods (hydro 40% and alkaline hydro 42%). In contrast the toluene (37%) and benzene (31%) extracted oils had lower α-santalol content compared with the two hydro distillation methods (Figure 2).

Three categories for the ratio of α: β santalol was identified with the lowest in the subcritical-CO_2, ethyl alcohol and steam distillations (combined ratio of 1.9:1) the middle in the diethyl ether, toluene and benzene solvent extracted (2.3:1) and the highest in the two hydro distillations (3.0:1) This results shows that the hydro-distillation methods were comparatively less efficient than other methods at liberating the β-santalol compared with the α-santalol volatile content from the heartwood.

Organoleptic Characterisation

While the organoleptic characteristics are highly influenced by the levels of α- and β-santalol, other extracted compounds can also affect this measure of quality. For instance the highest combined santalol levels were found in subcritical-CO_2, ethyl alcohol and steam distillation methods, but the aroma of ethyl alcohol extracted oil was determined to be 'less pleasant', which was in contrast to the 'pleasant' aroma of the subcritical-CO_2 extraction and steam distillation (Figure 2). Furthermore oil derived from both the hydro- and alkaline-hydro distillations were deemed to be 'pleasant' despite having less α- and β-santalol than the 'less pleasant' aroma of the diethyl ether and ethyl alcohol extracted oils. These results suggest that three of the four solvent extractions (diethyl ether, ethyl alcohol and toluene) may have extracted other volatiles from the heartwood, which influenced the aroma. The benzene-extracted oil contained the lowest α- and β-santalol, however the aroma was determined as 'pleasant'. This result indicates that while the benzene solvent extraction method may be good at determining the organoleptic characteristics of oil it may not reflect the true extend of its α- and β-santalol content. Sandalwood oil extracted by subcritical CO_2 was found to be highly tenacious and with strong 'camphorous' note. Other techniques yielded an oil requiring a 'maturity' period of one week to retain an equivalent tenacity to that extracted by subcritical CO_2.

Commercial Extraction

Of the current conventional techniques employed for commercial oil extraction steam distillation produced an oil of superior quality (84.3% of santalol) compared with hydro distillation (52.6%) (Figure 2). The steam distillation method is being practiced commercially but requires considerable time and energy. The advantages of subcritical CO_2 technology is the reduced time and energy with 40-45% less energy used relative to steam distillation.

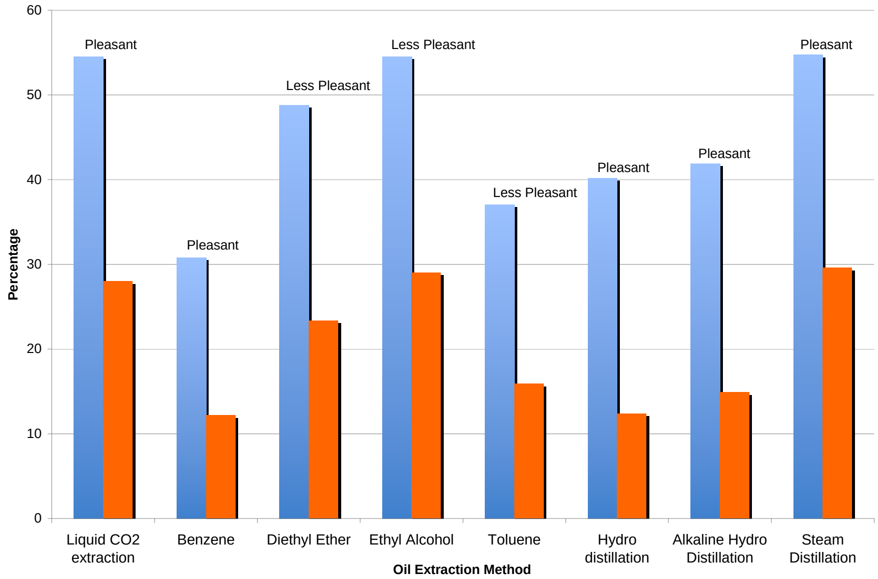

Figure 2. Oil composition and aroma quality across eight extraction methods from an homogenized sample of *Santalum album* powder.

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