CHANGES IN VOLATILES AND NUMBING COMPOUNDS OF DRIED ANDALIMAN (*Zanthoxylum acanthopodium*) UPON VARIOUS DRYING TECHNIQUES

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Bogor, January 2021

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SUMMARY

SIGIT SUHARTA. Changes in Volatiles and Numbing Compounds of Dried Andaliman (*Zanthoxylum acanthopodium*) upon Various Drying Techniques. Advised by CHRISTOFORA HANNY WIJAYA and DASE HUNAEFI.

Andaliman (*Zanthoxylum acanthopodium* DC) is an endemic plant from North Sumatera, commonly used as spices and folk medicines. Andaliman has a robust citrus aroma and numbing trigeminal sensations. Unfortunately, the research, usage, and popularity of andaliman are much behind its related species, such as *Z. piperitum* (Japanese pepper) and *Z. bungeanum* (Sichuan pepper).

The main hurdles in fresh andaliman usage are the fast rotting and rapid flavor degradation. Proper processing techniques by farmers and industries will be crucial to expand its usage. Drying could prevent andaliman from degradation by reducing the moisture content; however, its effects on volatiles, numbing compound, and aroma profile have not been fully understood.

Unsaturated alkylamides (sanshools) have been reported to be responsible for the unique numbing sensation. Analysis of sanshools is usually conducted using column chromatography or High Pressure Liquid Chromatography; however, these methods tend to be time-consuming and requires a large amount of costly solvent. On the other hand, aroma analysis is conducted using Gas Chromatography-Mass Spectrometry (GC-MS), which requires researchers to use two types of analytical methods to get the complete picture of both the aroma and taste of andaliman. However, three studies managed to analyze sanshools by GC-MS, which will shorten the research timeline and reduce research costs.

This research was composed of three main stages: drying of andaliman (sun, sunshade, shade, oven, and freeze drying), confirmation of the GC-MS parameter, analysis of the volatiles, sanshools, sensory and physical characteristics. The volatiles and sanshool analysis were conducted with GC-MS, while the sensory analysis used the Rate All That Apply-Hedonic method. Physical characteristics such as moisture, water activity, yield, bulk density, and color were analyzed. Statistical data analysis using Principal Component Analysis (PCA), one-way ANOVA, Duncan posthoc, Pearson's correlation, and Partial Least Square regression analysis were conducted to evaluate the impact of drying on volatiles, numbing, and sensory profile as well as to determine the volatiles responsible for andaliman aroma quality.

The logarithmic thin-layer drying model best-described andaliman drying kinetics. The drying process significantly altered andaliman appearance, aroma profile and physical properties. No significant difference was found in the yield of each drying method; however, shade drying resulted in the highest moisture and water activity, while sun drying and freeze drying resulted in the lowest moisture content and water activity. Freeze drying resulted in the lowest bulk density. All drying methods managed to produce andaliman with less than 17.90% moisture content and 0.6 water activity, indicating the drying targets have been achieved. Generally, drying increased the a*, indicating green color degradation, however, no significant difference was observed in the a* values of dried samples.

GC-MS analysis of all chloroform andaliman extract managed to detect total of 67 peaks while identifying 42 compounds. However, 25 unidentified peaks could

comprise of other sanshool isomers. Fresh and dried andaliman generally had similar total relative content of volatiles and chromatogram pattern, differing mostly in the individual compound quantities.

The content of limonene, (E)-2-hexenal, geranial, α-pinene, sabinene, and β-myrcene as well as the intensities of citrus and green aroma tended to decrease. In contrast, the content of geranyl acetate, citronellal, neral, α-sanshool as well as the intensities of warm and lime leaf aroma tended to increase upon drying. The more efficient extractions of volatiles with the absence of water and the hydrolyzation of volatiles from its glycosides by the native enzyme or acid and isomerization of citral could explain the increase of specific compounds in dried andaliman. The overall aroma intensities of all samples were not significantly different despite variability in each volatiles content. Oven-dried andaliman had a high liking score, similar to fresh, shade, and freeze-dried andaliman. PCA on volatiles and aroma intensities resulted in a similar separation of samples. Shade-dried and freeze-dried andaliman were clustered while the sun and sunshade-dried andaliman were clustered. Oven-dried and freeze-dried andaliman were separated from the other samples, indicating their unique qualities and that no drying process managed to produce dried andaliman with a similar aroma profile to fresh andaliman.

Citrus, orange peel, and acidic aroma were the favorable attributes based on their positive correlation with the overall liking. These favorable attributes were found to be the dominant aroma in oven-dried andaliman. Partial Least Square Regression and Pearson correlation analysis of volatiles and aroma attributes showed that the citrus aroma was correlated with sabinene, limonene, (Z)-β-ocimene, β-citronellol, and geranial. Orange peel aroma was correlated with (E)-β-ocimene and citronellal, while acidic aroma was correlated with (E-)-β-ocimene, (Z-)-β-ocimene, and citronellal. This correlation indicated that these compounds played significant roles in andaliman sensory acceptability and the future screening of andaliman could be based on targeted analysis on that seven volatiles.

Even though no drying method could produce dried andaliman with a similar volatile and sensory profile to a fresh one, oven drying could be proposed as the ideal drying method because of its short duration and low water activity as well as high liking score, aroma intensity, and volatiles content.

Keywords: *Zanthoxylum*, andaliman, drying, aroma, sanshool

RINGKASAN

SIGIT SUHARTA. Perubahan Senyawa Volatil dan Mati Rasa Andaliman (*Zanthoxylum acanthopodium*) oleh Berbagai Teknik Pengeringan. Dibimbing oleh CHRISTOFORA HANNY WIJAYA dan DASE HUNAEFI.

Andaliman (*Zanthoxylum acanthopodium* DC) merupakan tanaman endemik Sumatera Utara, Indonesia yang banyak digunakan sebagai rempah makanan dan obat tradisional serta memiliki aroma *citrus* yang kuat dan sensasi trigeminal mati rasa. Kendala utama dari pemanfaatan andaliman segar adalah pembusukan yang cepat. Oleh karena itu, teknik pengolahaan yang baik sangat penting untuk memperluas pemanfaatannya. Pengeringan dapat mencegah kerusakan pada andaliman, akan tetapi, pengaruhnya terhadap komponen volatil dan mati rasa serta profil aroma andaliman belum dipahami seutuhnya.

Alkilamida tidak jenuh (sanshool) telah dilaporkan sebagai kelompok senyawa yang bertanggung jawab terhadap sensasi trigeminal ini. Analisis senyawa sanshool pada umumnya menggunakan kromatografi kolom atau *High Pressure Liquid Chromatography*; namun, metode ini cenderung membutuhkan waktu dan pelarut mahal dalam jumlah yang banyak. Selain itu, analisis aroma umumnya menggunakan *Gas Chromatography-Mass Spectrometry* (GC-MS), yang mengharuskan peneliti untuk menggunakan dua jenis metode untuk mendapatkan gambaran lengkap tentang aroma dan rasa andaliman. Namun, tiga penelitian berhasil menganalisis senyawa sanshool oleh GC-MS sehingga dapat mengurangi waktu dan biaya penelitian.

Penelitian ini terdiri dari tiga tahap, yaitu pengeringan andaliman (*sun, sunshade, shade, oven,* dan *freeze drying*), konfirmasi parameter GC-MS, dan analisis komponen volatil, sanshool, sensori, dan karakteristik fisik andaliman. Komponen volatil dan sanshool dianalisis dengan GC-MS sedangkan anlisis sensori menggunakan metode *Rate All That Apply*-hedonik. Karakteristik fisik yang dianalisis adalah kadar air, aktivitas air, rendemen, densitas kamba, dan warna. Analisis statistik menggunakan *Principal Component Analysis* (PCA), *one-way* ANOVA, analsis lanjut Duncan, korelasi Pearson, dan regresi *Partial Least Square* dilakukan untuk mengevaluasi pengaruh pengeringan terhadap senyawa volatil, *sanshools,* dan profil aroma sekaligus menentukan komponen volatil yang bertanggung jawab terhadap kualitas aroma andaliman.

Model logaritmik pengeringan lapisan tipis paling baik menggambarkan kinetika pengeringan andaliman. Proses pengeringan secara signifikan mengubah penampilan, profil aroma, dan sifat fisik andaliman. Walau tidak ada perbedaan signifikan dalam rendemen setiap metode, namun *shade drying* menghasilkan kelembaban dan aktivitas air tertinggi sedangkan s*un-drying* dan *freeze drying* menghasilkan kadar air dan aktivitas air terendah. Semua metode pengeringan berhasil menghasilkan andaliman dengan kadar air dan aktivitas air kurang dari 17.90% dan 0.6 yang menunjukan tujuan pengeringan telah tercapai. Secara umum, pengeringan meningkatkan nilai a* yang menunjukkan kerusakan warna hijau, akan tetapi tidak ada perbedaan signifikan dalam nilai a* semua sampel kering.

Analisis GC-MS dari semua ekstrak kloroform andaliman berhasil mendeteksi 67 puncak dan mengidentifikasi 42 komponen. Akan tetapi, ada 25

puncak yang tidak dapat teridentifikasi yang dapat terdiri dari isomer-isomer sanshool lainnya. Andaliman segar dan kering secara umum memiliki jumlah relatif komponen volatil yang serupa, namun terdapat variasi jumlah relatif masing-masing komponen pada setiap metode pengeringan.

Konsentrasi senyawa *limonene*, (E)-2-*hexenal*, *geranial*, α-*pinene*, *sabinene*, dan β-*myrcene* serta intensitas aroma *citrus* dan *green* cenderung mengalami penurunan, tetapi konsentrasi senyawa *geranyl acetate*, *citronellal*, *neral*, α-*sanshool* serta aroma *warm* dan *lime leaf* cenderung meningkat ketika andaliman telah dikeringkan. Ekstraksi volatil yang lebih efisien dengan tidak adanya air, hidrolisasi volatil dari glikosida oleh enzim atau asam, dan isomerisasi sitral dapat menjelaskan peningkatan beberapa senyawa dalam andaliman kering. Intensitas aroma keseluruhan dari semua sampel tidak berbeda nyata meskipun terdapat variabilitas pada kandungan volatil. Andaliman kering oven memiliki skor kesukaan yang tinggi, serupa dengan andaliman segar, *shade*, dan *freeze-dried*. PCA pada volatil dan intensitas aroma menghasilkan pemisahan sampel yang serupa. Andaliman yang dikeringkan dengan *shade drying* dan *freeze drying* dikelompokkan, sementara andaliman yang dikeringkan dengan *sun drying* serta *sunshade drying* juga dikelompokkan. Andaliman segar dan yang dikeringkan dengan oven dipisahkan dari sampel lainnya, menunjukkan kualitas uniknya serta ketidakmampuan pengeringan untuk menghasilkan profil aroma andaliman kering yang serupa dengan andaliman segar.

Citrus, *orange peel*, dan *acidic* merupakan atribut yang disukai berdasarkan korelasi positifnya dengan tingkat kesukaan secara keseluruhan. Atribut yang disukai ini ditemukan sebagai aroma dominan dalam andaliman kering oven. Regresi *Partial Least Square* dan analisis korelasi *Pearson* terhadap konsentrasi atribut volatil dan intensitas aroma menunjukkan bahwa aroma *citrus* berkorelasi dengan *sabinene, limonene, (Z)-β-ocimene, β-citronellol*, dan *geranial*. Aroma *orange peel* berkorelasi dengan *(E)-β-ocimene* dan *citronellal*, sedangkan aroma *acidic* berkorelasi dengan *(E)-β-ocimene*, *(Z)-β-ocimene, dan citronellal*. Korelasi ini menunjukkan bahwa senyawa-senyawa tersebut berperan penting dalam penerimaan aroma andaliman secara sensori sehingga ke depannya, skrining aroma andaliman dapat difokuskan terhadap analisis tertarget tujuh senyawa tersebut.

Meskipun tidak ada metode pengeringan yang dapat menghasilkan andaliman kering dengan profil volatil dan sensoris yang mirip dengan yang segar, pengeringan oven dapat diusulkan sebagai metode pengeringan yang ideal karena rendahnya durasi dan aktivitas air serta tingginya skor kesukaan, intensitas aroma, dan konsentrasi senyawa volatil.

Kata kunci: *Zanthoxylum*, andaliman, pengeringan, aroma, sanshool

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Bogor, January 2021

Sigit Suharta

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