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GC-MS PROFILING OF VOLATILE COMPOUNDS FROM FIFTEEN DIFFERENT VARIETIES OF INDONESIAN SHALLOT GROWN IN TIDAL SWAMPLAND

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ABSTRACT

In this study, fifteen commercial varieties of Indonesian shallot (*Allium cepa* L.) grown in tidal swamp land were analyzed for Gas Chromatography-Mass Spectrophotometry (GC-MS) profiling of volatile compounds. A total of 64 volatiles were identified in fifteen varieties of Indonesian shallot. The cycloartenol was identified containing a major compound in all shallot varieties. Multivariate data analysis revealed that (23S)-ethylcholest-5-en-3-β-ol, obtusifoliol, pentacosane, furfural, cholesterol, 23 S/R-methylcholesterol, 9, 17-octadecadienal, 1-nonadecene, 14-methylergost-8-en-3-ol, 14α-methyl-δ8-ergostenol, ergost-5-en-3-ol, octacosane, and docosane contributed the most to classification of different Indonesian shallot varieties. This work provides the complete map of volatiles compound in Indonesian shallot that grown in tidal swampland, with Manjung variety exhibiting the most distinct volatile compounds among studied shallot varieties. The 1-((dicyclohexylphosphorothioyl) methyl) piperidine, volatile sulfur-containing compounds, was indeed the major component of Majung variety.

Keywords: *Allium cepa*, GC-MS, Multivariate analysis, Tidal swampland, Volatiles

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INTRODUCTION

Shallot (*Allium cepa*), with name “bawang merah” in Indonesia, is the most significant commodity vegetable in Indonesian agricultural sector. From a nutritional aspect, the bulb shallots are rich in carbohydrates, protein, total fat, vitamins, electrolytes, and minerals[1]. In Indonesia, shallots have for centuries been recognized as a spice in foods[2] that are consumed raw or processed[3]. They are also rich in flavonoids[4], saponins[5], and phenolics[6] that have been observed for some pharmacological activities. In literature, the shallots are considered to possess efficacy as antidiabetic[7], antioxidant[8], antimicrobial[9], anticancer[10, 11], and antiinflammatory[12].

Several works have reported on the potentially of shallots varieties for plant-breeding purposes in tidal swampland. Ningsih and Noor[13] reported that the Bauji and Bima Brebes of shallot varieties have adapted in the tidal swampland of South Kalimantan, Indonesia. Another report showed that Biru Lancor variety of shallot which has the highest productivity of 24.5 tonnes/ha grown in the tidal swampland of South Kalimantan, Indonesia[14]. Plants produce a high diversity of secondary metabolites in response to the different location and environmental by their adaptation[15-18]. The qualities of shallot influenced by metabolite composition[19]. The volatile compounds contained in the shallot that determine the quality of the aroma and flavor of this plant[20, 21]. The metabolite composition of shallot is affected by differences in genetic varieties and cultivated regions[22]. Nevertheless, metabolite profiles of shallot varieties that grow in tidal swampland remain unexplored, and knowledge is limited. Therefore, this study evaluated the fifteen varieties of Indonesian shallot grown in tidal swampland by GC-MS profiling of volatile compounds.

EXPERIMENTAL

The bulbs of shallot varieties were collected from different sources as shown in Table 1. The fifteen of shallot varieties were planted at the tidal swampland in Mambulau Barat, Anjir Serapan Timur, Kapuas, Central Kalimantan, Indonesia in 2016. The completely randomized design with three replications used for cultivation. All shallot materials were grown under the same conditions with 20 × 15 cm spacing. Two days before planting, fertilizer cow manure, dolomite, and SP-36 were applied at the rate of 10 tonnes/ha, 5 tonnes/ha, and 650 kg/ha, respectively. Fertilizer NPK Mutiara (400 kg/ha) was applied during planting in 15 and 30 days after planting. The bulb of shallots was harvested at the sixty days after planting. The fresh bulb of shallot varieties was obtained for the sample in the GC-MS analysis.

Table-1: Sources of fifteen Indonesian shallots (*Allium cepa*) varieties used in this research

S. No.	Name of varieties	Sources
1	GH2(RM7411)	Nganjuk, West Java
2	Tajuk	Sumenep, West Java
3	Bauji	Central Java
4	Keta Monca	Tangkiling, Central Kalimantan
5	Bima Brebes	BALITSA, Central Kalimantan
6	Katumi	Central Java
7	Mentes	BALITSA, Central Kalimantan
8	Rubaru	Sumenep, West Java
9	Pancasona	BALITSA, Central Kalimantan
10	Kramat 1	Central Java
11	Pikatan	BALITSA, Central Kalimantan
12	Super Philips	Nganjuk, West Java
13	Biru Lancur	Tangkiling, Central Kalimantan
14	Maja	Central Java
15	Manjung	Sumenep, West Java

Fresh bulbs of each shallot varieties were cut into small pieces and were extracted (10 g) with methanol (50 mL) in a sealed container for 5 days at room temperature. Filtrate used as a sample in the GC-MS analysis. The analyses were performed using GC-MS system (Agilent GC seri 7890 and Agilent MS seri 5975) equipped with a HP Ultra 2 capillary column (30 m × 0.20 mm, 0.11 µm). Each metabolite components were identified by matching their recorded mass spectra of the GC-MS data system. The metabolite components were identified by a compound name, molecular formula, and molecular weight with using comparison peak spectra in NIST and PubChem databases.
Statistical analyses of the data were determined by principal component analysis (PCA) and hierarchical cluster analysis (HCA) with using the R package[23]. The PCA was performed with log data transformation and mean centering, while in HCA was applied using Euclidean distances with ward clustering algorithm.

RESULTS AND DISCUSSION

A total of 64 components of volatile compounds were detected in the bulbs of fifteen shallot varieties that grow in tidal swampland at Central Kalimantan, Indonesia. List of a compound name of these metabolites is presented in Table-2. The compound of 1-((dicyclohexylphosphorothioyl) methyl) piperidine, thiophene-

2-acetamide,N-(4-chlorophenyl), 3,3'-hexamethylenedithiophene, and pyrrolidine-2,5-dione, 1-(4-fluorophenyl)-3-(2-thyenylmethylamino)- are showed as volatile sulfur-containing compounds. The previous study reported that volatile sulfur compounds in *Allium* species are generated by the metabolism of Alk(en)yl cysteine sulfoxides[22, 24]. The ferredoxin-sulfite reductase (SiR) gene was regulated in the metabolism of sulfur assimilation and metabolism in *A. cepa*[25]. In tidal swampland, maybe the expression of SiR gene was limited. Therefore only four of volatile sulfur-containing compounds identified from 64 components of volatile compounds in fifteen shallot varieties. In this study, the cycloartenol was identified containing as a major compound in all shallot varieties. Cycloartenol was an important triterpenoid of the sterol class which was biological activities such as anti-fertility[26], anti-inflammatory, anti-tumor, antioxidant, antibiosis and anti-Alzheimer's disease[27].

Figure-1A shows the PCA plot for grouping the metabolite profiles of volatile compounds in shallots bulbs different varieties. A total of 64 volatiles compound from 15 varieties of Indonesian shallots were used in PCA plot with PC1 (15.8%) and PC2 (13.7%) accounting for 29.5% of the total variance. Shallot varieties of Manjung, Biru Lancur, Rubaru, Kramat 1, Keta Monca, Maja, Pikatan, and Bauji were separated from Super Philips, Katumi, Pancasona, GH2(RM7411), Bima Brebes, Tajuk, and Mentes along PC1 while GH2(RM7411), Katumi, Pancasona, Manjung, Biru Lancur, Rubaru, Kramat 1, Super Philips, and Pikatan were separated from Mentes, Tajuk, Bauji, Maja, Keta Monca, and Bima Brebes along PC2.

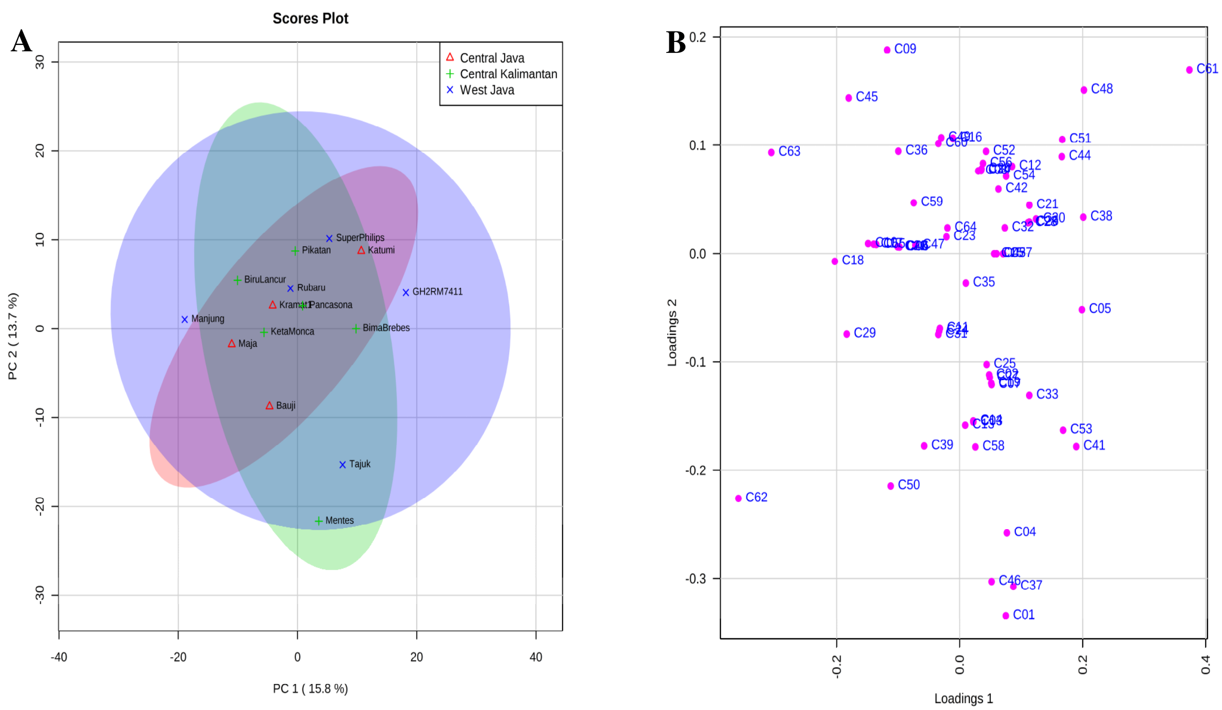

Fig.-1: PCA scores plot (A) and loading plot (B) from volatile compounds of GC-MS data sets of Indonesian shallots varieties. C01-C64: name of the volatile compounds in Table-1.

PCA loading plot was identified to determine the metabolite markers in every shallot varieties (Figure 1B). Metabolite markers for GH2 (RM7411) variety include (23S)-ethylcholest-5-en-3-β-ol. Metabolite markers for Tajuk and Mentes varieties include obtusifoliol, pentacosane, and furfural. Metabolite markers for Bauji variety include cholesterol and 23 S/R-methylcholesterol. Metabolite markers for Maja and Manjung varieties include 9, 17-octadecadienal and 1-nonadecene. The 14-methylergost-8-en-3-ol was metabolite marker for Biru Lancur variety. Metabolite markers for Katumi variety include 14α-methyl-δ8-ergostenol, ergost-5-en-3-ol, and octacosane. The metabolite of docosane was a chemical marker for Bima Brebes variety.

Table-2: The concentration of volatile components in the 15 varieties of Indonesian shallots

No	RT	Peak area (%) of Shallot varieties														
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	2.64		1.26					53.00								
2	11.46		2.95													
3	11.52							2.64								
4	28.83	1.37	3.15	2.59				1.55	1.19	1.47					1.43	
5	30.09	1.16	9.73	6.00	9.85	6.98	7.75	6.34		6.27	5.45	3.98	7.16	4.88		
6	30.22															1.02
7	30.41		4.72													
8	30.41					6.87							11.53		8.69	
9	30.41								10.46		7.30	10.42		8.16		
10	30.42															11.54
11	30.42			4.63												
12	30.44						12.77									
13	30.58		1.09	3.43												
14	30.59							2.55								
15	30.60					1.68										
16	30.60								5.98			4.65				
17	30.60															7.50
18	30.63														6.51	3.43
19	30.63		4.42													
20	30.64												3.97			
21	31.08	2.12								1.42						
22	31.09															1.17
23	31.09										1.00					
24	31.42			5.71												
25	31.42		1.82													
26	31.43	2.67														
27	31.53		3.32													
28	31.53	2.42														
29	32.35		2.19						6.83						6.62	7.81
30	32.36	4.58														
31	32.38			7.45												
32	32.57	1.58			1.06											
33	32.79	1.34	1.36	1.97												
34	34.87												3.54			
35	34.87		2.19		4.54					2.70		2.78				
36	34.87								3.62		3.02			3.40		
37	34.87		2.75	2.07		1.00		3.53	1.05							
38	34.91	6.36				6.06										
39	35.29			1.70				2.39						1.09		
40	35.39															1.11
41	35.82		1.38			3.10	2.27	1.65								
42	35.96						1.98									
43	35.97					2.39										
44	35.98	1.26					2.98									
45	36.62												6.71	12.34		7.35
46	36.63		6.21					12.31			7.48					
47	36.63			7.39	5.90	11.72				10.79		9.30			5.98	
48	36.65	4.64					13.63		6.09							

49	37.20												1.90	2.33		
50	37.22		1.82		1.61	2.80		2.25	1.59		2.05				2.26	1.78
51	37.23	1.15					2.36			2.78						
52	37.46												13.64			
53	37.51	9.83						12.60								
54	38.13						5.66									
55	38.13															6.16
56	38.15												5.90			
57	38.17					6.36										
58	38.17							6.08								
59	38.17													7.78		
60	38.19										9.02	10.73				
61	38.55	6.28	11.01			9.73	8.14		8.37			5.42	8.50			
62	38.57			9.28	9.62			7.87						8.29	9.81	10.81
63	38.59		4.11	14.65	12.61		13.72		12.30	11.34	14.38	16.24		13.78	13.06	13.05
64	39.95	19.56	13.97	20.61	32.71	24.37	24.54	22.88	32.61	23.70	30.51	30.30	34.71	30.71	33.59	28.81

List of chemical compounds: 1=Furfural; 2=2-Furancarboxaldehyde, 5-(hydroxymethyl); 3=5 (Hydroxymethyl)-2-furaldehyde; 4=Hexadecanoic acid; 5=Octadeca-9,12-dienoic acid; 6=Cyclopentadecanone, 2-hydroxy; 7=Isoindole-1,3,5-trione, perhydro-2-[2-(1-piperidyl)ethyl]-; 8=16,28-Secosolanid-5-en-3-ol, (3.beta.); 9=2-Ethyl-5-(12-tridecenyl)pyrrolidine; 10=1-((Dicyclohexylphosphorothioyl) methyl) piperidine; 11=1,2-Dihydro-3-methoxy-2-oxo-1-piperidinomethylpyridine; 12=Cyclohexanone, 2,2'-methylenebis; 13=1-Eicosene; 14=Cis-13-docosenoyl chloride; 15=Thiophene-2-acetamide,N-(4-chlorophenyl); 16=3,3'-Hexamethylenedithiophene; 17=Pyrrolidine-2,5-dione, 1-(4-fluorophenyl)-3-(2-thyenylmethylamino)-; 18=1-Nonadecene; 19=2-Allylcyclododecanone; 20=Cyclopentanol, 1-cyclopropyl; 21=Trans-13-octadecenoic acid; 22=Henicosane; 23=Heptacosane, 1-chloro; 24=(2-Tert-butyl-6-methylphenyl) 2,2-dimethylpropanoate; 25=BIS (2-ethylhexyl)phthalate; 26=Octadecanoic acid, 2-hydroxy-1-(hydroxymethyl)ethyl ester; 27=15-Hydroxypentadecanoic acid; 28=(9E)-9-Octadecenoic acid; 29=9, 17-octadecadienal; 30=9-oxabicyclo[6.1.0]nonane; 31=E,Z-1,3,12-nonadecatriene; 32=7-pentadecyne; 33=Squalene; 34=Celidoniol, deoxy; 35=Icosane; 36=Octadecane; 37=Pentacosane; 38=Docosane; 39=Cholesterol; 40=Stigmastan-3,5-diene; 41=Cholest-5-en-3-ol; 42=26-Nor-5-cholesten-3.beta.-ol-25-one; 43=3-Methylhenicosane; 44=Octacosane; 45=14-Methylergost-8-en-3-ol; 46=Obtusifoliol; 47=Cholest-14-en-3-ol, (3β,5α)-; 48=14α-Methyl-δ8-ergostenol; 49=Campesterol; 50=23 S/R-Methylcholesterol; 51=Ergost-5-en-3-ol; 52=(22E)-Ergosta-4,6,22-trien-3-ol; 53=peri-Xanthenoxanthene-4,10-dione, 2,8-bis(1-methylethyl)-; 54=3-(Propan-2-ylidene)cholestane; 55=(22E)-Stigmasta-7,22-dien-3-ol; 56=4.alpha.,5-cyclo-A-homo-5.alpha.-cholestan-6-one; 57=2,2,4,4,6,6,8,8-Octaethyl-[1,3,5,7,2,4,6,8] tetroxatetasilocane; 58=4,4-Dimethylcholesta-5,7-dien-3-ol; 59=8-Androsten-3-ol, 17-(2-methylallyl)-4,4,14-trimethyl; 60=1H-Isoindole-1,3(2H)-dione, 4,5,6,7-tetrahydro-2-(4-methylphenyl)-; 61=(23S)-Ethylcholest-5-en-3-β-ol; 62=Clionasterol; 63=β-Sitosterol; and 64=Cycloartenol.

HCA was applied to assess the relationship between the shallot varieties. The heat map analysis (Fig.-2) was obtained after HCA of the volatile GC-MS profiles of shallot varieties. Heatmap analysis showed four clear clusters: groups A (3 varieties), B (Manjung), C (7 varieties), and D (4 varieties). The results extracted using PCA and heat map analyses were comparable, suggesting that Manjung varieties are distinct from the other 14 varieties. The 1-((dicyclohexylphosphorothioyl) methyl) piperidine, volatile sulfur-containing compounds, was indeed the primary component of Majung volatiles (11.54%) with the highest percentile among all the shallot varieties. This information will be useful for further investigation in cultivation shallot varieties in tidal swampland.

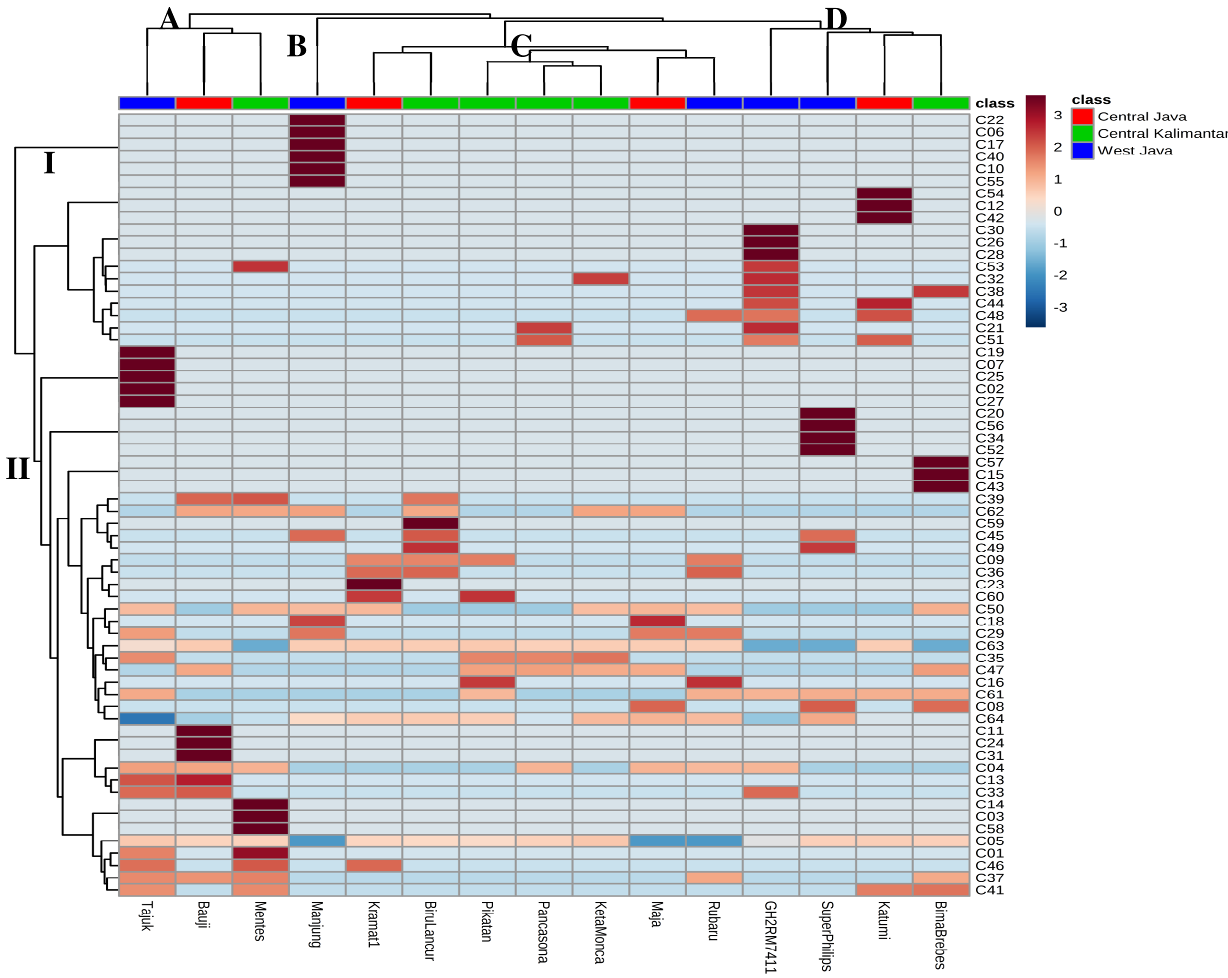

Fig.-2: The hierarchical cluster analysis (HCA) of the metabolite profiles of Indonesian shallots varieties. The graph indicated the grouping of metabolite and shallot varieties of the legend on the left and bottom, respectively. C01-C64: name of the volatile compounds in Table-1.

CONCLUSION

In tidal swampland, a total of 64 volatiles were identified with cycloartenol representing a major source of volatile components of fifteen shallot varieties. Majung variety was unique owing to their richness in 1-((dicyclohexylphosphorothioyl) methyl) piperidine of volatile sulfur-containing compounds.

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