

Varietal Discrimination of Pineapple (*Ananas comosus* L.) Using Chromatographic Fingerprints and Chemometrics

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Abstract: Online solid-phase extraction-liquid chromatography (online SPE-LC) with diode array detector (DAD) was used to obtain the chromatographic fingerprint of bioactive compounds of pineapple (*Ananas comosus* L.). The extracts from 40 samples of three different varieties of pineapple (Morris, MD2, and Josaphine) were obtained using pressurized liquid extraction (PLE) prior to separation using online SPE-LC. The SPE-LC method was optimized and validated and applied to 40 pineapple samples of those three varieties. Seven bioactive compounds identified include catechin, epicatechin, chlorogenic acid, ferulic acid, quercetin, myricetin, and bromelain. For varietal discrimination, the relative areas of 16 selected peaks were subjected to chemometric techniques. The three pineapple varieties were successfully discriminated using cluster analysis (CA) and principal component analysis (PCA).

Keywords: online SPE-LC; pineapple; bioactive compounds; chromatographic fingerprint; chemometrics

■ INTRODUCTION

Pineapple (*Ananas comosus* L.) is widely cultivated in tropical countries, including Malaysia [1-2]. Pineapple is known to contain a significant amount of bioactive compounds such as anthocyanins, polyphenols, and bromelain, a health-inducing enzyme. Many studies have reported on the biological properties of pineapple such as anti-oxidative [3], anti-browning [4], anti-inflammatory, and anti-platelet activities [5]. Food policies such as stated in General Food Law Regulation No.178/2002 gives the right to the consumers to obtain truthful information about the fruit they purchased, and the data includes the composition, types, grades, and origin of the food [6]. The current quality control of fruits in Malaysia is based solely on the morphological traits and with the manual inspection done by the agricultural officer [7]. This approach depends on the human's perception and judgment, which may be biased and inconsistent.

The World Health Organization (WHO) has recommended chromatographic fingerprint analysis as a

quality control strategy for foods with medicinal values [8-9]. The chromatographic fingerprint of phenolic compounds has been successfully used by researchers in the authentication of honey [10], olive oil [11-12], and herbal medicines [13]. The development of a valuable chromatographic fingerprint requires efficient extraction, cleanup, and separation methods. Pressurized liquid extraction (PLE) has been successfully applied for the extraction of thermal-sensitive bioactive compounds, including phenolic compounds from plants and fruits [14-15]. It involves extraction using solvents in a liquid state at elevated temperature and pressure to enhance the extraction process. For plant extracts, removal of interference and analyte concentration, known as the cleanup step, is usually required prior to analysis [2]. Solid-phase extraction (SPE) usually consists of 4 steps: conditioning/equilibration, loading, washing, and elution. This technique has been largely applied and proved to be a good alternative to traditional liquid-liquid extraction. Due to the laborious steps in SPE, an

online SPE-LC is getting more attention. The SPE process in both approaches follows the same steps and is governed by the same principles. However, using online SPE-LC, the eluted analytes are directly transferred into the analytical column for separation and quantitation. Thus, online SPE-LC approach has the advantages of a significant reduction in sample preparation time and less human handling.

In this study, an online SPE-LC was developed to obtain a chromatographic fingerprint of selected bioactive compounds as an alternative to traditional quality control of pineapple. The developed method was used to analyze three common varieties of pineapple in Malaysia (MD2, Morris, and Josaphine). These varieties were selected because seventy percent of the fresh pineapple fruit produced in Malaysia is from Morris variety. Josaphine pineapple is the most common variety cultivated on an annual cycle in Malaysia, while MD2 variety is listed as major export crop under Malaysia National Key Economic Agenda (NKEA). Chemometric methods such as cluster analysis (CA) and principal component analysis (PCA) were applied to the dataset of the chromatographic fingerprints to discriminate the selected pineapple varieties.

■ EXPERIMENTAL SECTION

Materials

Forty samples of ripened fruits of three pineapple varieties (Moris, MD2, and Josaphine) were purchased from local traders. The fruits were peeled, cut into thin pieces, and dried for 48 h at 45 °C in an oven (Memmert UN110). The dried flesh was stored in a dark-covered container prior to extraction. The standards for selected bioactive compounds (epicatechin, catechin, quercetin, chlorogenic acid, ferulic acid, myricetin, and bromelain) were purchased from Merck (Darmstadt, Germany). Acetonitrile (HPLC grade), methanol (HPLC grade), and acetic acid were purchased from Merck Schuchardt (Hohenbrunn, Germany).

Instrumentation

Pressurized liquid extraction

PLE was performed using Dionex ASE 350 accelerated solvent extractor (Thermo Scientific Ltd.

Surrey, UK). The extracts from 40 pineapple samples were obtained using the PLE method. Dried flesh of pineapple (60 g) was accurately weighed, mixed with an equal amount of diatomaceous earth, and transferred to a 100 mL PLE stainless steel extraction cell with cellulose filter at the bottom end to eliminate particles in the extracts. The sample cell was then closed to medium tightness and placed into the carousel of the ASE 350 system. Extraction was performed using single cycle mode with 100% of methanol as the solvent. The extracted analyte was purged from the sample cell using pressurized nitrogen. The PLE parameters were: static cycle, 1; flush volume, 100%; purge time, 120 sec; and the optimized PLE parameters were: extraction temperature, 105 °C; extraction time, 20 min. After PLE, each extract was transferred into online SPE-LC vials before analysis [16].

Online SPE-LC

Analysis of bioactive compounds was done using online SPE-LC (Dionex Ultimate 3000 Liquid Chromatography system) with diode array detector (DAD) using two C18 columns, a 5 µm, 4.6 mm × 50 mm for SPE cleanup and a 5 µm, 4.6 mm × 250 mm for separation of compounds. The column temperature was maintained at 40 °C in an oven, and the injection volume was 100 µL. Eluted compounds were monitored at the optimized detection wavelength of 280 nm. Data acquisition was performed by Chromeleon software. The mobile phase consisted of ultrapure water (A), methanol (B), and acetonitrile (C). The separation done with application of gradient elution 0–19 min: 50% A: 20% B: 30% C; 20–25 min: gradient elution 15% A: 40% B: 45% C; 25–40 min: gradient elution 10% A: 80% B: 10% C. The flow rate was set at 1 mL/min throughout the analysis [17]. Fig. 1 shows the chromatogram of selected bioactive compounds obtained using the optimized online SPE-LC method.

Procedure

Calibration and linearity

The standard solution of all bioactive compounds was prepared in HPLC grade methanol. The concentration of standards of bioactive compounds was

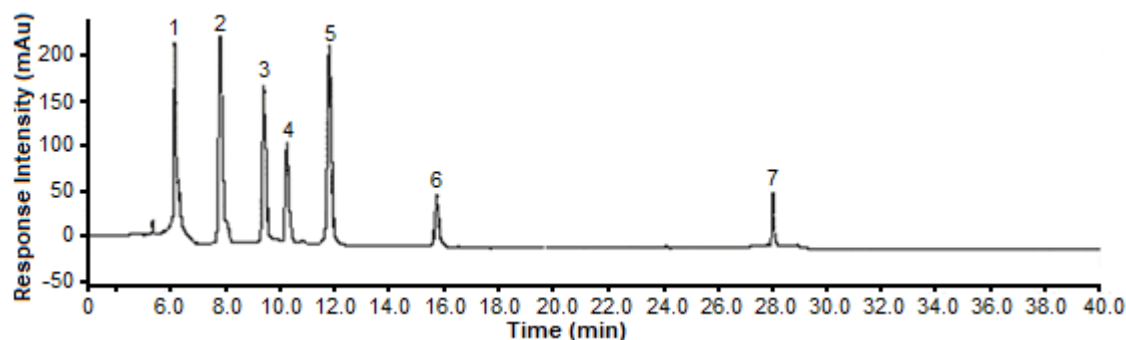


Fig 1. Chromatogram of selected bioactive compounds standards (100 mg/L), 1) catechin; 2) epicatechin; 3) chlorogenic acid; 4) ferulic acid; 5) myricetin; 6) quercetin; 7) bromelain

prepared between 5–200 mg/L for quantification in pineapple samples. Linearity was determined as (R^2) of the calibration graph. The coefficient of determination showed good linearity ($R^2 > 0.997$) as shown in Table 1.

Precision

The repeatability of this method was conducted using three replicates of the standard mixture (50 mg/L) to give low percent RSD ranging between 2.1-4.6% (Table 1).

Limit of detection and limit of quantitation

The limit of detection (LOD) and quantification (LOQ) were determined based on the signal-to-noise ratio (S/N) of about 3 and 10, respectively. The LOD values were between 2.4 and 5.2 mg/L, while the LOQ values were between 8.2 and 17.1 mg/L for each standard compound (Table 1).

Data analysis

Chemometric analysis applied on the dataset of chromatographic fingerprints was done using XLSTAT 2013 software (Addinsoft, New York, NY). Peak areas of

16 selected peaks were utilized as variables to evaluate the similarities and differences in CA and PCA.

RESULTS AND DISCUSSION

Identification of selected bioactive compounds in pineapple samples was performed by comparing their retention times and UV spectra with that of the standard compounds. Fig. 2 shows the chromatograms of representative samples from the three pineapple varieties and Table 2 tabulates the amount of selected bioactive compounds in all pineapple samples. Bromelain, epicatechin and chlorogenic acid existed in all pineapple varieties. The amount of catechin was found highest in Josaphine pineapple (5.23 mg in 100 g of dried pineapple), but not detected in most MD2 samples. The presence of catechin and epicatechin was reported by a study on the Bali pineapple [18]. Catechin was also reported in grapes and teas in high amount [19]. Epicatechin, however, showed a higher amount in MD2 varieties than in other varieties.

Table 1. Coefficients of determination, precision, limit of detection (LOD) and limit of quantification (LOQ) of selected bioactive compounds

Compounds	Correlation coefficient (R^2)	LOD (mg L^{-1})	LOQ (mg L^{-1})	Precision (% RSD)
Catechin	0.997	4.2	14.1	3.2
Epicatechin	0.975	4.5	15.3	2.1
Chlorogenic acid	0.994	5.2	17.1	3.9
Ferulic acid	0.997	3.4	11.2	2.8
Quercetin	0.994	2.4	8.2	4.6
Myricetin	0.995	3.6	12.0	4.3
Bromelain	0.995	3.1	9.6	2.6

Table 2. Quantitative determination of bioactive compounds in pineapple samples (mg/100 g dried pineapples \pm RSD (n = 3), ND: not detected)

Samples	Catechin	Epicatechin	Chlorogenic acid	Ferulic acid	Myricetin	Quercetin	Bromelain
J1	4.483 \pm 0.002	1.799 \pm 0.002	1.343 \pm 0.032	1.077 \pm 0.001	0.222 \pm 0.021	0.635 \pm 0.011	7.345 \pm 0.003
J2	4.827 \pm 0.012	1.873 \pm 0.003	1.392 \pm 0.001	0.833 \pm 0.064	0.155 \pm 0.011	0.744 \pm 0.002	7.637 \pm 0.005
J3	4.601 \pm 0.041	1.947 \pm 0.011	1.445 \pm 0.002	1.109 \pm 0.011	0.302 \pm 0.001	0.619 \pm 0.004	7.762 \pm 0.029
J4	3.552 \pm 0.029	2.058 \pm 0.052	1.705 \pm 0.001	1.267 \pm 0.003	0.237 \pm 0.005	0.249 \pm 0.001	6.476 \pm 0.063
J5	4.459 \pm 0.011	2.080 \pm 0.033	1.004 \pm 0.031	0.956 \pm 0.022	0.329 \pm 0.006	0.674 \pm 0.083	7.707 \pm 0.041
J6	4.769 \pm 0.005	1.915 \pm 0.041	1.415 \pm 0.011	0.835 \pm 0.015	0.217 \pm 0.006	0.421 \pm 0.002	8.001 \pm 0.011
J7	4.824 \pm 0.003	2.048 \pm 0.001	1.101 \pm 0.015	1.315 \pm 0.021	0.279 \pm 0.003	0.436 \pm 0.016	8.058 \pm 0.002
J8	3.388 \pm 0.010	1.908 \pm 0.006	1.335 \pm 0.048	1.151 \pm 0.002	0.325 \pm 0.017	0.593 \pm 0.003	11.443 \pm 0.001
J9	5.166 \pm 0.001	2.085 \pm 0.008	1.419 \pm 0.001	1.242 \pm 0.001	0.270 \pm 0.002	0.625 \pm 0.002	7.002 \pm 0.004
J10	4.450 \pm 0.005	1.985 \pm 0.022	1.742 \pm 0.017	1.283 \pm 0.003	0.248 \pm 0.039	0.754 \pm 0.001	8.155 \pm 0.042
J11	4.858 \pm 0.012	1.843 \pm 0.061	1.219 \pm 0.002	1.023 \pm 0.046	0.137 \pm 0.003	0.358 \pm 0.023	9.284 \pm 0.002
J12	3.794 \pm 0.009	1.853 \pm 0.002	1.459 \pm 0.048	1.362 \pm 0.003	0.307 \pm 0.054	0.470 \pm 0.004	7.948 \pm 0.014
J13	4.883 \pm 0.018	2.077 \pm 0.002	1.536 \pm 0.033	1.402 \pm 0.021	0.218 \pm 0.012	0.828 \pm 0.024	11.590 \pm 0.013
J14	5.233 \pm 0.009	2.238 \pm 0.008	1.302 \pm 0.012	1.455 \pm 0.001	0.146 \pm 0.003	0.884 \pm 0.001	7.838 \pm 0.007
J15	3.992 \pm 0.071	1.867 \pm 0.032	1.429 \pm 0.038	1.008 \pm 0.003	0.196 \pm 0.029	0.663 \pm 0.003	10.323 \pm 0.005
M1	2.399 \pm 0.002	0.235 \pm 0.001	0.651 \pm 0.071	ND	ND	0.080 \pm 0.031	2.898 \pm 0.048
M2	2.176 \pm 0.016	0.104 \pm 0.006	0.751 \pm 0.001	ND	ND	ND	3.425 \pm 0.025
M3	2.571 \pm 0.003	0.261 \pm 0.003	0.716 \pm 0.006	ND	ND	ND	3.251 \pm 0.032
M4	2.789 \pm 0.006	0.278 \pm 0.019	0.761 \pm 0.008	ND	ND	ND	2.908 \pm 0.011
M5	2.781 \pm 0.002	0.604 \pm 0.008	0.639 \pm 0.025	ND	ND	ND	3.583 \pm 0.002
M6	2.544 \pm 0.038	0.450 \pm 0.013	0.578 \pm 0.043	ND	ND	ND	4.077 \pm 0.006
M7	2.925 \pm 0.004	0.202 \pm 0.064	0.549 \pm 0.002	ND	ND	ND	2.878 \pm 0.002
M8	2.363 \pm 0.006	0.154 \pm 0.002	0.668 \pm 0.005	ND	ND	ND	6.371 \pm 0.015
M9	2.781 \pm 0.036	0.124 \pm 0.042	0.483 \pm 0.011	ND	ND	ND	3.376 \pm 0.004
M10	2.544 \pm 0.062	0.086 \pm 0.011	0.620 \pm 0.035	ND	ND	ND	4.032 \pm 0.001
M11	2.925 \pm 0.021	0.275 \pm 0.017	0.577 \pm 0.001	ND	ND	ND	3.349 \pm 0.026
M12	2.363 \pm 0.003	0.462 \pm 0.043	0.643 \pm 0.007	ND	ND	ND	2.332 \pm 0.001
M13	2.200 \pm 0.005	0.214 \pm 0.061	0.560 \pm 0.005	ND	ND	ND	2.990 \pm 0.002
M14	1.529 \pm 0.007	0.313 \pm 0.011	0.669 \pm 0.018	ND	ND	ND	7.021 \pm 0.011
M15	1.886 \pm 0.002	0.284 \pm 0.004	0.555 \pm 0.012	ND	ND	ND	5.074 \pm 0.043
MD 1	ND	5.449 \pm 0.011	3.157 \pm 0.032	0.597 \pm 0.004	1.963 \pm 0.044	1.629 \pm 0.009	4.473 \pm 0.016
MD 2	ND	5.480 \pm 0.032	3.402 \pm 0.022	0.653 \pm 0.008	1.825 \pm 0.002	1.436 \pm 0.021	4.718 \pm 0.001
MD 3	ND	4.372 \pm 0.049	2.785 \pm 0.021	0.616 \pm 0.001	1.793 \pm 0.005	2.128 \pm 0.032	4.149 \pm 0.001
MD 4	ND	3.171 \pm 0.002	3.648 \pm 0.001	0.628 \pm 0.006	1.721 \pm 0.001	2.287 \pm 0.028	4.835 \pm 0.006
MD 5	0.047 \pm 0.001	4.239 \pm 0.049	3.675 \pm 0.071	0.504 \pm 0.012	1.695 \pm 0.011	1.921 \pm 0.025	3.575 \pm 0.019
MD 6	ND	5.579 \pm 0.024	3.717 \pm 0.001	0.661 \pm 0.008	1.639 \pm 0.025	2.061 \pm 0.066	4.915 \pm 0.022
MD 7	ND	3.603 \pm 0.052	3.429 \pm 0.003	0.531 \pm 0.005	1.969 \pm 0.039	1.655 \pm 0.004	4.568 \pm 0.001
MD 8	ND	2.456 \pm 0.011	3.406 \pm 0.004	0.637 \pm 0.001	1.731 \pm 0.041	1.373 \pm 0.011	5.590 \pm 0.021
MD 9	ND	6.547 \pm 0.002	2.995 \pm 0.012	0.709 \pm 0.011	1.687 \pm 0.032	1.672 \pm 0.031	7.210 \pm 0.004
MD 10	ND	5.517 \pm 0.038	3.151 \pm 0.019	0.651 \pm 0.024	1.7540 \pm 0.004	2.005 \pm 0.002	5.935 \pm 0.006

Quercetin was present in MD2 and Josaphine samples except in Morris samples. This may be due to MD2 as a hybrid or genetically modified seedlings derived from Josaphine by the Malaysian Agriculture Research and Development Institute (MARDI) [20]. Even though the similarities and differences among the three varieties of

pineapple can be observed in the chromatographic fingerprints obtained, a more systematic approach in varietal discrimination was further evaluated using chemometric techniques as this approach will help to discriminate even the slightest variation of bioactive compounds [21].

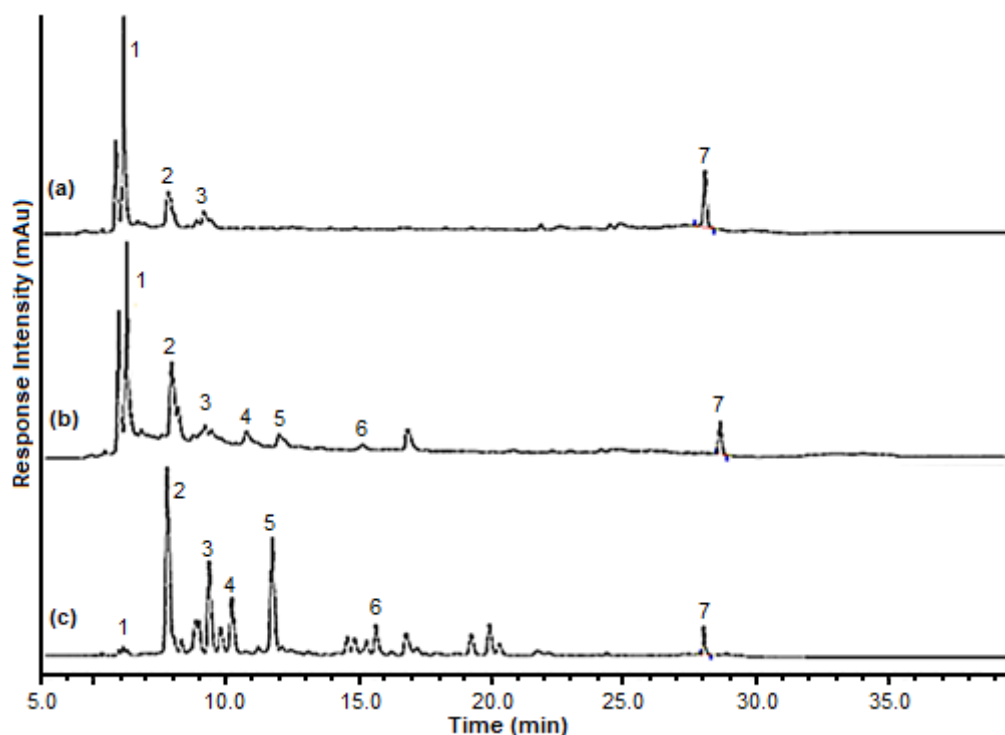


Fig 2. Representative chromatographic fingerprints of three different varieties of pineapples obtained at 280 nm (a) Morris (b) Josaphine (c) MD2. 1) catechin; 2) epicatechin; 3) chlorogenic acid; 4) ferulic acid; 5) myricetin; 6) quercetin; 7) bromelain

Chemometric Analysis

For chemometric analysis, relative peak areas of 16 peaks were selected inclusive of 7 identified bioactive compounds and 9 unknown compounds. A larger number of variables were needed to perform thorough varietal discrimination.

Cluster Analysis (CA)

Cluster analysis is a multivariate method that aims to classify a sample of subjects (or objects) on the basis of a set of measured variables into a number of different groups such that similar subjects are placed in the same group [22]. The dataset was grouped using Ward's linkage with squared Euclidean distance as a measure of similarity [23]. Fig. 3 shows the dendrogram obtained. The three pineapple varieties were clearly grouped in individual clusters. However, within each cluster, subgroups could be observed due to the origin (location) and maturity of samples. Maturity can affect significantly the different composition of bioactive compounds in fruits [24].

Principle Component Analysis (PCA)

PCA has been implemented in many recent studies for authentication and classification in food [25-28]. It was also used in a recent study to determine the seasonal and regional variation in food authentication based on chromatographic fingerprinting [29]. The variation in the chromatographic fingerprints of each pineapple varieties analyzed by PCA (Fig. 4) yielded 3 principal components (PCs) also known as varimax factors analyzed with some of them consist of strong factor loading as shown in Table 3.

Data variance was explained in the first two PCs with a cumulative variability of 75.28%. Chlorogenic acid and ferulic acid possessed a strong loading in PC1. Other significant variables in PC1 could not be identified. In PC2, epicatechin and bromelain gave strong loadings. Fig. 5 shows the PCA score plot of the pineapple samples. The groupings in the score plot were in good agreement with the result obtained from CA whereby the three varieties existed in different axes. Our

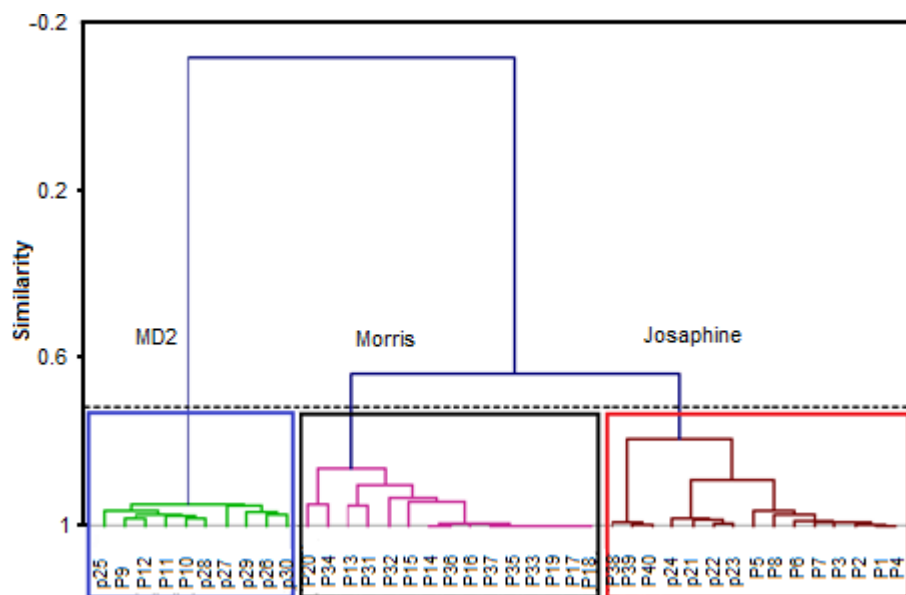


Fig 3. Dendrogram of three varieties of pineapple

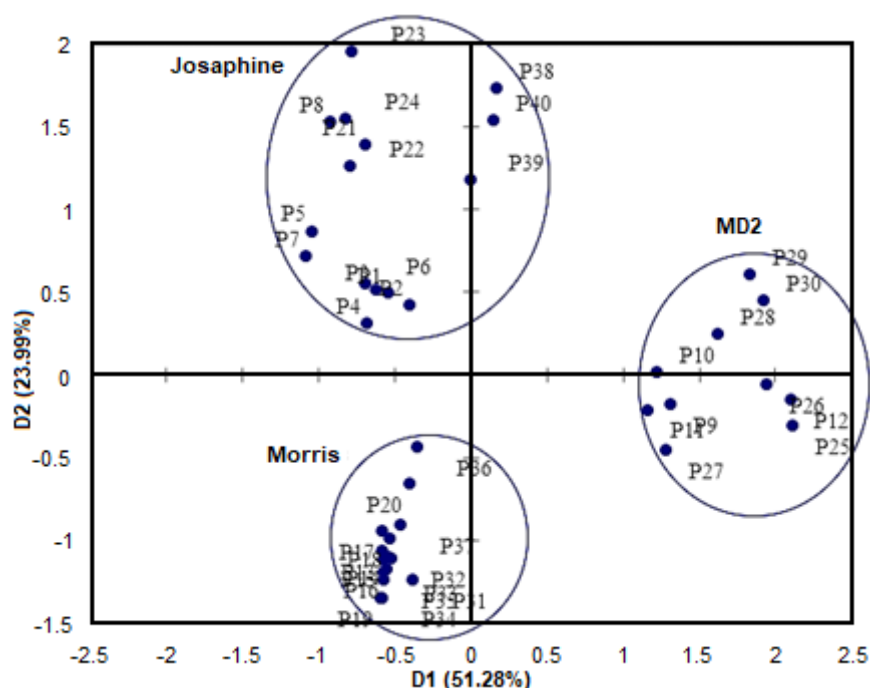


Fig 4. PCA score plot of pineapple samples. Observation was done after varimax rotation

previous studies had successfully applied CA and PCA on the authentication of Harumanis mango [30] and the clustering of Tongkat Ali roots [17].

With the aids of chemometric techniques such as PCA and CA, significant parameters, chlorogenic acid and ferulic acid concentration in each pineapple variety were further analyzed. Fig. 5 shows a graph of the ratio of

the two major bioactive compounds. The ratio of these two compounds in the three varieties of pineapple differed from each other. In Josaphine variety, the ratio of chlorogenic acid and ferulic acid concentration in the samples has only small differences where the concentration of chlorogenic acid is higher than ferulic acid. However, in MD2 variety, large differences can be

Table 3. Factor loadings for bioactive compounds detected in pineapple samples. (Strong loadings > 0.75 are shown in bold)

Parameters	PC1	PC2	PC3
X1	0.165	0.294	0.038
Catechin	0.655	0.196	0.009
Epicatechin	0.020	0.805	0.077
X4	0.102	0.737	0.074
Chlorogenic acid	0.816	0.074	0.053
X6	0.088	0.542	0.030
Ferulic acid	0.899	0.004	0.043
X8	0.854	0.009	0.095
X9	0.824	0.037	0.062
X10	0.337	0.109	0.470
X11	0.910	0.000	0.037
Quercetin	0.209	0.136	0.603
X13	0.845	0.023	0.028
Myricetin	0.564	0.044	0.342
X15	0.890	0.000	0.024
Bromelain	0.027	0.831	0.000
Eigenvalue	9.838	4.132	0.693
Variability (%)	51.28	23.99	12.41
Cumulative (%)	51.28	75.28	87.69

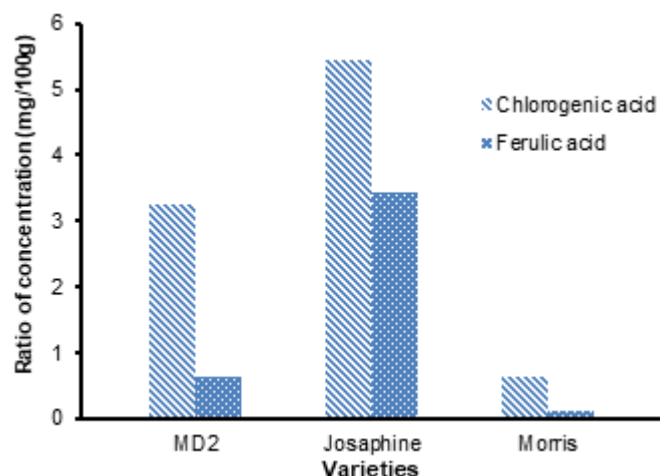


Fig 5. Ratio of concentration (mg/100 g) of chlorogenic acid and ferulic acid for three varieties of pineapples

observed in the ratio of the two compounds whereby, the concentration of chlorogenic acid is almost six times higher than that of ferulic acid. Similar to MD2 variety, chlorogenic acid in Morris variety is higher than ferulic acid. However, the total amount of these two compounds was very much lower than those in Josaphine variety. Due

to the differences in the ratio of these two compounds, the amount of chlorogenic acid and ferulic acid could be promising marker compounds to distinguish these three varieties.

■ CONCLUSION

A comprehensive and reliable chromatographic fingerprint of pineapple was obtained using PLE followed by the online SPE-LC method. The complex data of 16 compounds from 40 samples were interpreted using multivariate data analyses (CA and PCA) which successfully discriminated the three pineapple varieties. This study suggested that chromatographic fingerprints with chemometric evaluation can provide a systematic approach in quality control and authentication of fruit varieties.

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