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Phytochemical Content of *Garcinia Mangostana* Linn Peels Methanol-Chloroform Extract and Pyrolysis Liquid

Garcinia Mangostana Linn. Kabuğunun Metanol-Kloroform Ekstraktı ve Piroliz Sıvısının Fitokimyasal İçeriği

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Abstract

Garcinia mangostana Linn. (GML), also known as mangosteen, is a tropical fruit and is called the "Queen of Fruits" and "King of Fruits" in some Southeast Asian countries. While GML fruit is used as a therapeutic supplement in traditional medicine and a food ingredient in Southeast Asian cuisine, the peel of GML plant is used as a natural dye. Although GML fruits contain many bioactive compounds, the peel of the fruit, which accumulates in the environment and becomes waste as a result of consumption and processing, becomes a factor that increases air pollution due to the foul-smelling compounds they emit. In this study, the phytochemical content of fruit peel, which has negative effects as waste, was analyzed. LC-MS/MS results showed that the main components of the fruit peel extract were vanillic acid, baicalein, and vanillin compounds. As a result of the GC-MS/MS analysis, the presence of high levels of palmitic and stearic acid in the GML peel was determined. Additionally, it was observed that the phytochemical contents changed significantly in the pyrolyzed samples of the peel. In particular, LC-MS/MS results showed that GML peel has a high commercial potential thanks to the bioactive compounds it contains.

Keywords: *Garcinia mangostana*, mangosteen, LC-MS/MS, GC-MS/MS, pyrolysis.

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Özet

Garcinia mangostana Linn. Mangostan olarak da bilinen (GML), tropik bir meyve olup bazı Güneydoğu Asya ülkelerinde "Meyvelerin Kraliçesi" ve "Meyvelerin Kralı" olarak adlandırılmaktadır. GML meyvesi geleneksel tıpta tedavi edici bir takviye ve Güneydoğu Asya mutfağında bir gıda maddesi olarak kullanılırken, GML bitkisinin kabuğu doğal bir boya olarak kullanılmaktadır. GML meyveleri birçok biyoaktif bileşik içermesine rağmen tüketim ve işlenme sonucu çevrede biriken ve atık haline gelen meyvenin kabuğu, yaydığı kötü kokulu bileşikler nedeniyle hava kirliliğini artıran bir faktör haline gelmektedir. Bu çalışmada atık olarak olumsuz etkileri olan meyve kabuğunun fitokimyasal içeriği analiz edilmiştir. LC-MS/MS sonuçlarına göre, meyve kabuğu ekstraktının ana bileşenlerinin vanilik asit, baicalein ve vanilin bileşikleri olduğu tespit edilmiştir. GC-MS/MS analizi sonucunda GML kabuğunda yüksek düzeyde palmitik ve stearik asit varlığı belirlendi. Ayrıca kabuğun piroliz örneklerinde fitokimyasal içeriklerin önemli ölçüde değiştiği gözlendi. Özellikle LC-MS/MS sonuçlarında, GML kabuğunun içerdiği biyoaktif bileşikler sayesinde yüksek bir ticari potansiyele sahip olduğunu gösterdi.

Anahtar Kelimeler: *Garcinia mangostana*, mangostan, LC-MS/MS, GC-MS/MS, piroliz.

1. Introduction

Garcinia mangostana Linn. (GML) is a tropical fruit native to the Malaya peninsula and the Sunda Islands. It belongs to the family of Guttiferae and is also called the Queen of Fruits. The mangosteen is mainly consumed for its fruit, and the pulp, which accounts for more than 60% of the fruit's total weight, is discarded, making it of little economic value. In Indonesia, the production of mangosteen in 2022 amounted to 343.000 tons (1). Mangosteen peels, which are directly discarded and accumulate in the environment, are a new cause of pollution, especially air pollution due to the bad odor they produce. Therefore, it is essential to process and recycle mangosteen peel waste from these industries to mitigate these potential problems (2). People in these countries use the pericarp (peel, rind, husk, or ripe pulp) of the GML as a traditional medicine to treat abdominal pain, diarrhea, dysentery, infected wounds, suppurations, and chronic ulcers (3,4). Experimental studies have shown that extracts of mangosteen have antioxidant, antitumor, antiallergic, anti-inflammatory, antibacterial, and antiviral effects (3). Mangosteen peels contain many secondary metabolites, especially phenolic and hydroxy-xanthones, which have antibacterial and antioxidant properties (2).

The mass composition of mangosteen peel waste contains approximately 60-70% lignocellulose. Biomass of lignocellulosic; It contains three main groups: lignin, cellulose, and hemicellulose. Organic compounds such as alcohols, phenols, furans, esters, ketones, organic acids, aldehydes, and phenols are included in this group. For this purpose, a pyrolysis technique with gradual heating and different temperature stages is applied to obtain bio-oils obtained from biomass sources (5, 6). Pyrolysis is a thermal degradation process used to break down natural or synthetic polymers into low molecular weight components in an oxygen-free environment (7). The main aim of this application is to determine different applicable parameters such as reactor type, temperature, catalyst, pressure, and amount of material to obtain economically valuable components (8).

In this study, the phytochemical content of the products obtained by two different methods such as extraction and pyrolysis of the fruit peel of the *Garcinia mangostana* Linn plant were determined by spectrometric methods such as GC-MS/MS and LC-MS/MS. Thus, the data obtained from this study provides insight into its use in different industrial areas.

2. Material and Method

2.1. Materials

The methanol, chloroform, acetone, ethyl acetate, and hexane used in this study were of analytical purity and were obtained from Sigma Aldrich.

2.2. Extraction and Pyrolysis Process

The GML peels were dried at 105°C for 12 hours and ground into powder using a grinder. The ground GML peels were washed with deionized water and dried in the oven at 60°C for 2 days. For extraction, powdered GML peels were extracted with methanol-chloroform (1:1, v/v) for 3 days. The pyrolysis process was carried out with a fixed bed pyrolysis (reactor) device in an inert nitrogen atmosphere. 100 g of solid sample was added to the feed reactor chamber. Then, Nitrogen gas was exposed to 550°C for 2 hours in an inert environment at a heating rate of 10°C min-1(8).

2.3. LC-MS/MS Analysis

The analysis was performed on an Agilent 1260 Infinity II LC system. The method flow rate was set at 0.5 mL min^{-1}, the total run time was 30 min and the oven temperature was set at 40°C. Chromatographic separation was performed on an Agilent Poroshell120 EC-C18 reversed-phase analytical column (100 mm × 3.0 mm, 2.7 µm). Eluent A (H_2O + 5 mM ammonium formate) and eluent B (MeOH + 0.1% formic acid) were used as mobile phases. Detection by mass spectrometry was performed on an Agilent 6460 Triple Quadrupole Mass Spectrometry System equipped with electrospray ionization (LC-ESI-MS/MS) (9-11).

2.4. GC-MS/MS Analysis

The GML crude extract and pyrolysis liquids content was analyzed by GC-MS/MS using an Agilent 7000 A GC/MS Triple Quad with 7890 GC, 7693 autosampler, and 7697A headspace sampler. The materials and methods used in the analysis are given in detail in our previous study (8, 12).

3. Results and Discussion

3.1. Phytochemical content of extracts and pyrolysis liquid

The phytochemical analysis results of the obtained GML crude extract and pyrolysis liquid are given in Table 1-2 and Figure 1-3.

3.1.1. GC-MS/MS analysis results

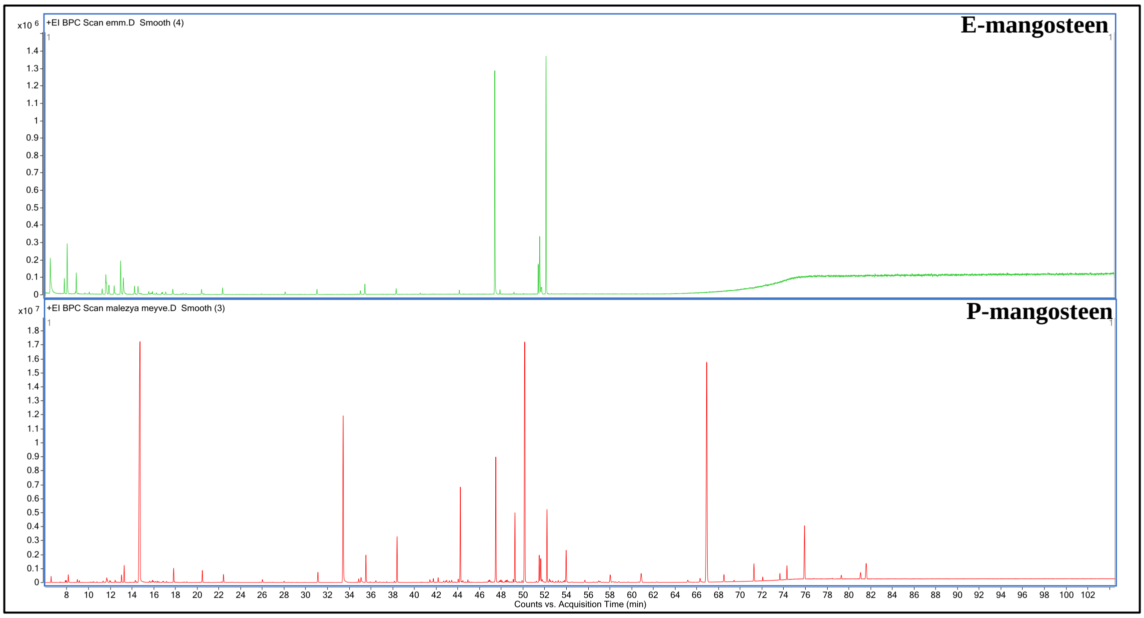

Figure 1. GC-MS/MS chromatogram of GML extract and pyrolysis liquid

Table 1. GC-MS/MS analysis result of GML extract and pyrolysis liquid

No	RT* (min.)	Compound	E-mangosteen %	P-mangosteen %
1	7.82	*m*-Xylene	1.75	0.63
2	8.08	*o*-Xylene	6.95	-
3	8.92	Unknown-1	2.62	-
4	11.31	Unknown-2	0.69	-
5	11.64	*m*-Ethyltoluene	4.09	-
6	11.93	Mesitylene	1.19	-
7	12.42	Pseudocumol	1.29	-
8	13.04	*o*-Ethyltoluene	4.80	0.65
9	13.28	Decane	-	1.32
10	14.29	Hemimellitene	1.09	-
11	14.74	2-Ethylhexanol	1.35	37.75
12	17.83	Undecane	0.74	1.21
13	22.43	Dodecane	0.94	0.69
14	31.12	Tetradecane	0.74	0.96
15	38.41	Hexadecane	0.73	3.80
16	42.19	Myristic acid methyl ester	-	0.40
17	44.24	Octadecane	-	7.73
18	47.50	Palmitic acid methyl ester	28.51	10.19
19	49.26	Eicosane	-	5.68
20	51.46	Linoleic acid, methyl ester	3.27	2.18
21	51.56	Linolenic acid, methyl ester	-	2.22
22	51.59	Oleic acid, methyl ester	8.09	-
23	51.74	12,15-Octadecadienoic acid methyl ester	1.45	-
24	52.21	Stearic acid methyl ester	29.73	5.91
25	53.97	Docosane	-	3.11
26	58.03	Arachidic acid methyl ester	-	0.98
27	60.88	Tetracosane	-	1.45
28	66.30	Behenic acid methyl ester	-	0.47
29	71.26	Hexacosane	-	1.70
30	73.65	Octacosane	-	0.53
31	74.30	Pentacosanoic acid methyl ester	-	1.14
32	75.92	Nonacosane	-	5.50
33	81.08	*β*-Sitosterol acetate	-	0.75
34	81.60	Triacontane	-	2.21

*** RT:** Retention time

Fatty acid and volatile oil contents of crude extract and pyrolysis liquid were analyzed by GC MS/MS. According to the analysis results, in the crude extract, stearic acid methyl ester (29.73%), palmitic acid methyl ester (28.51%), oleic acid methyl ester (8.09%), *o*-xylene (6.95%), *o*-ethyltoluene (4.80%), *m*-ethyltoluene (4.09%); in the pyrolysis liquid, 2-ethylhexanol (37.75%), palmitic acid methyl ester (10.19%), octadecane (7.73%), stearic acid methyl ester (5.91%), eicosane (5.68%), nonacosane (5.50%) compounds were detected in high amounts. The components and oils in fruit seeds or peels are extracted by the slow pyrolysis method, allowing them to be used for different medicinal purposes. Pyrolysis is a method generally defined as the thermal decomposition of organic components into liquid products (13). Therefore, different components were identified in the GC-MS/MS analysis of the extraction and pyrolysis liquid.

3.1.2. LC-MS/MS analysis results

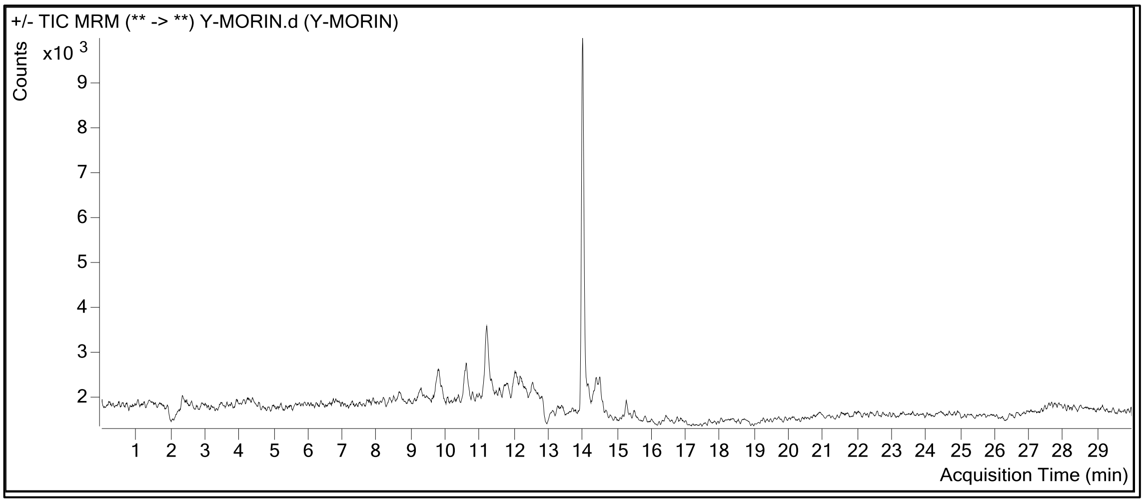

Figure 2. LC-MS/MS chromatogram of GML extract

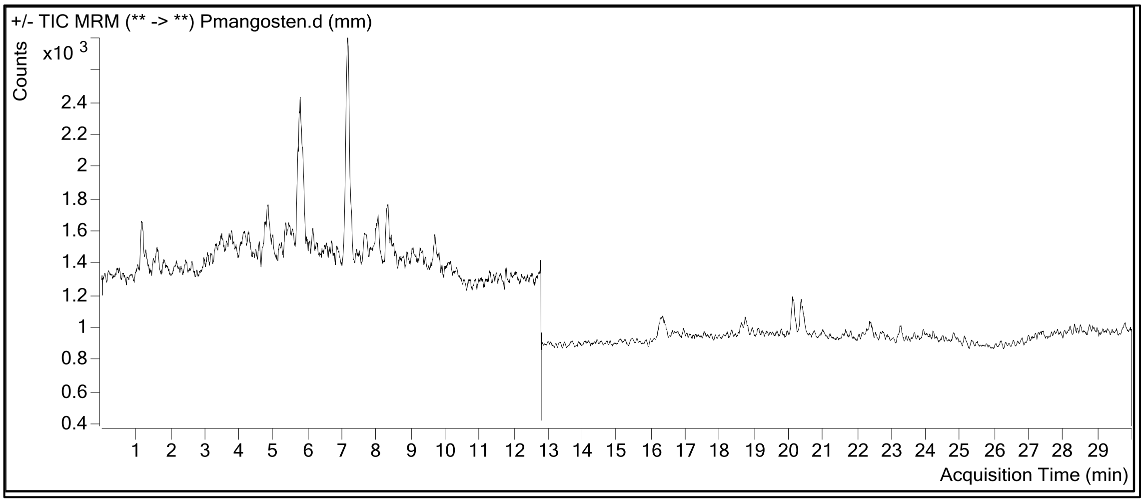

Figure 3. LC-MS/MS chromatogram of GML pyrolysis liquid

The phenolic content of the GML peels, methanol-chloroform (1:1 v/v) extract, and pyrolyzed liquid was analyzed by LC-MS/MS. According to the analysis results, 6 phenolic compounds were detected in the crude extract, while no phenolic compounds were detected in the pyrolyzed liquid. It is well-known that the structure of some phenolic compounds is damaged by temperature and cannot be detected as a result of analysis. It is for this reason that phenolic compounds cannot be determined in the pyrolyzed liquid. Vanillic acid (386.84 µg g^{-1} extract), baicalein (13.30 µg g^{-1} extract), vanillin (6.89 µg g^{-1} extract), hesperidin (6.39 µg g^{-1} extract), hydroxybenzaldeyde (4.96 µg g^{-1} extract) and isoquercitrin (4.47 µg g^{-1} extract) compounds were identified in the crude extract. In a similar study, the main compound in *Garcinia mangostana* peels was determined to be *m*-hydroxybenzoic acid (14).

Table 1. Phenolic content analysis of GML extract and pyrolysis liquid

No	Compound	RT	Pyrolysis GML Peel (µg g^{-1} extract)	Extract GML Peel (µg g^{-1} extract)
1	Hydroxybenzaldeyde	9.79	-	4.96
2	Vanillin	10.61	-	6.89
3	Vanillic acid	11.21	-	386.84
4	Isoquercitrin	12.08	-	4.47
5	Hesperidin	12.21	-	6.39
6	Baicalein	14.06	-	13.30

4. Conclusion

In this study, the phytochemical content of fruit peel, which has negative effects as waste, was analyzed. LC-MS/MS results showed that the main components of the fruit peel extract were vanillic acid, baicalein, and vanillin compounds, which have high biological activity. As a result of the GC-MS/MS analysis, the presence of high levels of palmitic and stearic acid in the GML peels was determined. Additionally, it was observed that the phytochemical contents changed significantly in the pyrolysis samples of the peel (especially in LC-MS/MS analysis). As a result, utilizing the peel of the fruit without throwing it into the environment will provide commercial gain by using the compounds they contain, and will also make significant contributions to reducing air pollution, which causes serious environmental problems.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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