RESOURCING POTENTIAL OF OLIVE OIL POMACE

by

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Olive oil is a kind of high-quality edible oil obtained by quick extraction from the fresh olive fruit. It has rich biological activity and positive effect on human health which leads to the increase of the demand for olive oil. Olive pomace is a by-product of olive oil during processing which is also rich in biologically active ingredients. But it is often treated as waste, not only causes environmental pollution but also a great waste of resources. In order to explore the high value utilization of olive oil by-products, the extract components of olive oil pomace by benzene, ethanol and acetone were analyzed by gas chromatography-mass spectrometry. The results showed that there were 109, 70, and 71 components which identified in benzene, ethanol and acetone extracts of olive oil pomade respectively. Many of these components can be resourced in industries of biomedicine, bioenergy, spices, and food additives.

Key words: bioactive ingredients, bioenergy, high value utilization, olive oil, pomace

Introduction

Oleaeuropaea is a world-famous fruit tree species and woody oil tree species of *oleaceae* [1]. It is an important economic forest in subtropical region. Olive oil is mainly produced in countries along the Mediterranean Sea. For example: Morocco, Spain, Greece, Italy, Tunisia, Syria, Turkey and other countries [2]. Olive oil is a kind of high-grade edible oil, which is extracted from fresh olive fruits by cold pressing. Without heating and chemical treatment, its natural nutrients can be retained [3]. The oil content of fresh olive fruits ranges from 20% to 30% [4]. The annual oil production of global olive oil fluctuates from 2.6 million to 3 million tons [5]. Olive oil is not only a high-quality edible oil, but also widely used in pharmaceutical industry and daily chemical industry [6].

Medically, Olive oil can improve the digestive system. Olive oil has a high content of oleic acid (monounsaturated fatty acid) monounsaturated pancreatic enzymes and degrade oil which help it to be absorbed by intestinal mucosa [7, 8]. Olive oil contains more than 80% unsaturated fatty acid and 70% oleic acid which makes it can reduce the incidence of cardiovascular disease [9, 10]. Olive oil can also prevent colon and brain cancer [11-13]. Moreover, Olive oil is mainly used as base oil, skin cleaning oil, skin care and massage oil in daily cosmetics [14]. Because of its high value, olive oil is increasingly popular with consumers.

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At present, the production of olive oil mainly adopts three-phase separation technology, which separates fresh fruit pulp into Pomace, waste liquid and olive oil [15]. The development and utilization of olive oil residue is mainly to extract the residue oil again and use it as fertilizer, but it has not been used efficiently [16]. In this paper, the bioactive components in olive pomace were analyzed by gas chromatography-mass spectrometry (GC-MS). It is of great significance to study the high-value utilization of olive pomace to achieve green sustainable development and efficient utilization of resources.

Materials and methods

Materials

The olive pomace used in this experiment is the pomace produced by a three-phase separation process in an olive oil processing plant in Longnan City, Gansu Province. After drying at 35 °C, the powder is prepared by a high-speed universal beater.

Extraction by three solvents

The 15 g pomace powder was weighed (weighing accuracy is 0.01 g) on the electronic balance and put into flask. The pomace was divided into three groups, adding 300 mL benzene, acetone and ethanol solution respectively [17]. Each solvent was repeated three times and compared with each other. Seal and put in ultrasonic for 5 minutes. Then the electric hot water bathing pot was heated to 80 °C, 56 °C, and 78 °C, respectively, and put into a flask to extract for 3 hours [18]. The filtrate was obtained by vacuum filtration after extraction. The filtrate after filtration is evaporated by vacuum rotary evaporation. The filtered extract was concentrated to about 20 mL and labeled in a small bottle for GC-MS detection.

Component analysis by GC-MS

The GC-MS instrument model: Thermo Fisher DSQ II. Gas chromatographic conditions were set as follows: HP-5MS column (30 cm \times 0.25 mm \times 0.25 µm), carrier gas was high purity helium, flow rate was 1.0 mL/min, split ratio was 50:1, GC program was started at 50 °C and maintained for 1 minute. At the rate of 10 °C/min, it rises to 250 °C, maintains for 5 min, then rises to 280 °C at the rate of 5 °C/min, and maintains for 24 min [19].

Mass spectrometry conditions: Programmed scanning mass ranges from 30 AMU to 600 AMU, ionization voltage is 70 eV, ionization current is 150 mu An electron ionization (EI). The temperature of ion source and quadrupole is set at 230°C and 150°C, respectively [20].

Results

Analysis of active components and functions of benzene extract from olive pomace

By GC-MS, 109 substances were identified from 146 peaks of benzene extract from olive residue. The total ion flow diagram as shown in fig. 1(a), begins to peak in about 2.5 minutes. The hydrocarbons first appear, esters, aldehydes and alcohols appear in turn in 5 to 7 minutes, carboxylic acids appear in 10 minutes, ketones appear in about 11 minutes, and phenols appear in about 17 minutes. The peak time is 2 to 37 minutes, including 86 hydrocarbons, 12 esters, 12 carboxylic acids, 10 alcohols, 9 aldehydes, 6 ketones, 3 phenols, 3 carboxylates 2 amines compounds and 3 other compounds. The functional substances found in the extracts can be divided into biomedicine, bioenergy, chemical raw materials, spices and food additives

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by GC-MS, (b) functional categories of extracted components

according to their functions. The proportion of each part is shown in fig. 1(b). Amongthem, the components used for bioenergy are n-octane, cyclohexanol, tetratetracontane, 1-tetradecene, 2, 4-hexadiyne, methyl cyclohexane, ethyl cyclopentane, 1, 2-dimethyl-cyclooctane, heptacosane and n-tetracosanol-1. Other representative substances are: in amine compounds the content of N, N-dimethyl-formamide was 13.94% of the total compound content. The N, N-dimethyl-formamide is a widely used solvent. The N, N-dimethyl-formamide is a good solvent for many kinds of macromolecule compounds, such as polyurethane, polyvinyl chloride, polyacrylonitrile, etc. It can also be used as extractant, medicine and pesticide amidine [21]. Among alcohols, the highest content of beta-sitosterol is 4% of the total quality. Betasitosterol plays an important role in reducing cholesterol, relieving cough, expectorating phlegm, inhibiting tumors and repairing tissues. It can also be used in type II hyperlipidemia, atherosclerosis and chronic tracheitis, as well as in early cervical cancer and skin ulcers [22]. In aldehydes, the highest content of trans -2- decenal is 2.75%. Trans -2- decene aldehyde can be used as spice, mainly for poultry and citrus flavors [23]. The highest content of styrene in hydrocarbon compounds is 2.4%, styrene is mainly used to produce styrene series resin and styrene butadiene rubber, and also produces ion exchange resins and pharmaceuticals. In addition, styrene can also be used in pharmaceutical, dyestuff, pesticide and mineral processing industries [24]. Trans-squalene content is 1.02%. Trans-squalene is a highly valuable nutritional medicine for the treatment of hypertension, hypotension, anemia, diabetes mellitus, cirrhosis of liver, cancer, constipation, worms and teeth; external application for tonsillitis,

asthma, bronchitis, cold, tuberculosis, rhinitis, gastric ulcer, duodenal ulcer, gallstones and bladder stones, rheumatism, neuralgia, *etc.* [25]. The content of dibutyl phthalate in esters is 8.75%. Dibutyl phthalate is mainly used as plasticizer for nitrocellulose, acetic acid fiber and polyvinyl chloride [26-28].

Analysis of active components and functions of ethanol extract from olive pomace

The 70 substances were identified by GC-MS analysis of 77 peaks in ethanol extract from olive residue, The total ion flow diagram shows in fig. 2(a), peaking from 2.6 minutes, the first is alcohols, hydrocarbons in about 3 minutes, esters and aldehydes in turn in about 6 minutes, carboxylates in about 7 minutes, ketones in about 8 minutes, carboxylic acids and amines in turn. The phenolic compounds appeared in about 10 minutes and began to appear in about 12 minutes. The peak time was 2 to 37 minutes, including 8 hydrocarbons, 11 esters, 16 carboxylic acids, 8 alcohols, 10 aldehydes, 11 ketones, 3 phenols, 1 carboxylate, 2 amines and 7 other compounds. The functional substances found in the extracts can be divided into biomedicine, bioenergy, chemical raw materials, spices and food additives according to their functions. The proportion of each part is shown in fig. 2(b). The components used for bioenergy are n-octane, oleic acid, octadecanoic acid and 17-Pentatriacontene. Other representative substances: n-octane content in hydrocarbons is up to 1.33%, which is one of the components of industrial gasoline. It can also be used as a solvent and organic synthetic raw material [29]. The highest content of esters is dibutyl phthalate, which is the same as benzene extract; the highest content



Figure 2. (a) Total ion flow diagram of ethanol extract from olive residue by GC-MS, (b) functional categories of extracted components

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of oleic acid in carboxylic acid compounds is the total. Oleic acid is an organic chemical raw material, can be used as processing aid, defoamer, spices, adhesives and lubricants. It is used for precision polishing and electroplating polishing of precious metals (such as gold, silver) and non-metals, as analytical reagents, solvents, lubricants and flotation agents, and also in sugar industry. Biochemical studies, gas chromatography comparison of samples, determination of ammonia, calcium and copper, determination of calcium, magnesium and sulfur. Activity of protein kinase C in hepatocytes [30], the highest content of alcohols is beta-sitosterol, the highest content of aldehydes is trans-2-decenoaldehyde.

Analysis of active components and functions of acetone extract from olive pomace

A total of 88 peaks of acetone extract from olive pomace were identified by gas chromatography-mass spectrometry.71 substances were identified, the total ion flow diagram shows in fig. 3(a) peaks begin in 2.5 minutes. The first peaks are carboxylic acids, esters and hydrocarbons in about 3 minutes, alcohols in about 3.6 minutes, aldehydes in about 6 minutes, carboxylates in about 7 minutes, ketones in about 7 minutes. Compounds appeared in about 10 minutes, phenolic compounds began to appear in about 12 minutes, and the peak time was 2 to 37 minutes. Including 22 hydrocarbons, 9 esters, 18 carboxylic acids, 10 alcohols, 10 aldehydes, 6 ketones, 4 phenols, 1 carboxylate, and 8 other compounds. The functional substances found in the extracts can be divided into biomedicine, bioenergy, chemical raw materials, spices and food additives according to their functions. The proportion of each part is shown



Figure 3. (a) Total ion flow diagram of acetone extract from olive residue by GC-MS, (b) functional categories of extracted components

in fig. 3(b), the components used for bioenergy are sec-butyl acetate, o-xylene, (1-methylethyl)-benzene, tetratetracontane, palmitoleic acid, oleic acid, and octadecanoic acid. Other representative substances: the most abundant hydrocarbons are 2, 4-dimethylhexane, which accounts for 2.16% of the total compounds, and 2,4-dimethylhexane can be used as chemical raw materials. The content of trans squalene is 1.02%. The largest content of ester compounds is menthyl acetate. It can be used as an edible flavor, and is mainly used for making flavors of peppermint, fruit and berries [31]. The highest contents of acids were oleic acid 30.07% and hexadecanoic acid 9.31%. Sixteen alkanic acids can be used as precipitating agents, chemical reagents and waterproofing agents, and can be used to prepare colorless chloramphenicol and various metal palmitates, which can be used as emulsifiers in emulsion polymerization. Alcohols contain 3.70% beta-sitosterol. The most abundant aldehyde compound is trans-2-nonaneldehyde.

Conclusions

The olive pomace was extracted with three solvents, and the extract was identified by GC-MS. It was found that olive pomace contained a large number of reusable substances. The most active ingredient was benzene, and 109 substances were detected in the extract. Of these substances, 86 are hydrocarbons, 12 esters, 12 carboxylic acids, 10 alcohols, 9 aldehydes, 6 ketones, 3 phenols, 3 carboxylates, 2 amines and 3 other compounds. Nonanal, trans-2-decenoal-dehyde, 2-undecene aldehyde, 3-methyl-2-cyclohexene-1-one, trans-2-nonyl acid, palmitoleic acid, hexadecanoic acid, stearic acid, 2, 2'-methylene bis-(4-methyl-6-tert-butylphenol), trans-squalene and beta-sitosterol were detected in the three solvent extracts. Among them, trans-2-decenoaldehyde, 2-undecanonaldehyde, nonanal and trans-2-nonanelic acid can be used as food spices; trans-squalene; bioenergy and beta-sitosterol are important biomedical components. These substances are the key components for high value utilization of olive pomace in the future.

As a kind of high-quality edible oil, olive oil market demand is increasing, and the scale of olive oil processing industry is also expanding. The utilization of by-product pomace in the production process has been paid attention to. In our research and analysis, we found that olive pomace is rich in a large number of reusable ingredients. At present, most of the research on olive pomace is still in the laboratory stage, as long as we continue to study, the utilization of olive pomace will become more and more sufficient. Finally, the olive pomace would become a treasure and play an important role in realizing utilization of bio-energy.

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References

- Sebastiani, L., *et al.*, Physiological and Productive Parameters of Olive Trees (Oleaeuropaea L.) under Different Irrigation Scheduling in Central-South Italy, *Acta Horticulturae*, 949 (2012), May, pp. 115-121
- [2] Alkhatib, A., *et al.*, Olive Oil Nutraceuticals in the Prevention and Management of Diabetes: From Molecules to Lifestyle, *International Journal of Molecular Sciences*, *19* (2018), 7, 2024
- [3] Ferreirogonzalez, M, et al., Authentication of Virgin Olive Oil by a Novel Curve Resolution Approach Combined with Visible Spectroscopy, Food Chemistry, 220 (2017), Apr., pp. 331-336
- [4] Bajoub, A., et al., Assessing the Varietal Origin of Extra-Virgin Olive Oil Using Liquid Chromatography Fingerprints of Phenolic Compound, Data Fusion and Chemometrics, Food Chemistry, 215 (2017), Jan., pp. 245-255

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- [5] Hocaoglu, S. M., et al., Assessment of Technology Modification for Olive Oil Sector Through Mass Balance: A Case Study for Turkey, Journal of Cleaner Production, 188 (2018), July, pp. 786-795
- [6] Crespo, M., et al., Pharma-Nutritional Properties of Olive Oil Phenols. Transfer of New Findings to Human Nutrition, Foods, 7 (2018), 6, pp. 90
- [7] Nocella, C., et al., Extra Virgin Olive Oil and Cardiovascular Diseases: Benefits for Human Health, Endocrine Metabolic & Immune Disorders Drug Targets, 18 (2017), 1, pp. 4
- [8] Smolka, A., Schubert, M. L., Helicobacter pylori-Induced Changes in Gastric Acid Secretion and Upper Gastrointestinal Disease, *Current Topics in Microbiology & Immunology*, 400 (2017), Jan., pp. 227-252
- [9] Wickens, K. L., *et al.*, Early Pregnancy Probiotic Supplementation with Lactobacillus Rhamnosus HN001 May Reduce the Prevalence of Gestational Diabetes Mellitus: A Randomised Controlled Trial, *British Journal of Nutrition*, 117 (2017), 6, pp. 804-813
- [10] Tutino, V., et al., Tissue Fatty Acid Profile Is Differently Modulated from Olive Oil and Omega-3 Polyunsaturated Fatty Acids in ApcMin/+ Mice, Endocrine Metabolic & Immune Disorders Drug Targets, 17 (2017), 4, pp. 303-308
- [11] Alkhatib, A., et al., Olive Oil Nutraceuticals in the Prevention and Management of Diabetes: From Molecules to Lifestyle, International Journal of Molecular Sciences, 19 (2018), 7, pp. 2024-2039
- [12] Bassani, B., et al., Abstract 5272: Chemopreventive Activities of a Polyphenol Rich Purified Extract from Olive Oil Processing on Colon Cancer Cells, *Cancer Research*, 77 (2017), 13, pp. 5272-5272
- [13] Battino, M., et al., Relevance of Functional Foods in the Mediterranean Diet: The Role of Olive Oil, Berries and Honey in the Prevention of Cancer and Cardiovascular Diseases, Critical Reviews in Food Science and Nutrition, 59 (2018), 6, pp. 893-920
- [14] Clodoveo, M. L., et al., In the Ancient World, Virgin Olive Oil Was Called "Liquid Gold" by Homer and "the Great Healer" by Hippocrates, Why Has this Mythic Image Been Forgotten?, Food Research International, 62 (2014), 62, pp. 1062-1068
- [15] Di, G. L., et al., Natural Antioxidants and Volatile Compounds of Virgin Olive Oils Obtained by Two or Three-Phases Centrifugal Decanters, European Journal of Lipid Science & Technology, 103 (2015), 5, pp. 279-285
- [16] Chanioti, et al., Optimization of Ultrasound-Assisted Extraction of Oil from Olive Pomace Using Response Surface Technology: Oil Recovery, Unsaponifiable Matter, Total Phenol Content And Antioxidant Activity, LWT - Food Science and Technology, 79 (2017), June, pp. 178-189
- [17] Xu, K., et al., High-Efficient Extraction of Principal Medicinal Components from Fresh Phellodendron Bark (Cortex Phellodendri), Saudi Journal of Biological Sciences, 25 (2018), 4, pp. 811-815
- [18] Liu, L., et al., Systematic Characterization of Volatile Organic Components and Pyrolyzates from Camellia oleifera Seed Cake for Developing High Value-added Products, Arabian Journal of Chemistry, 11 (2018), 6, pp. 802-814
- [19] Heydari, R., Hosseini, M., Determination of the Fatty Acid Composition of Amygdalus Scoparia Kernels from Iran Using Gas Chromatography-Mass Spectrometry, *Chemistry of Natural Compounds*, 53 (2017), 3, pp. 538-539
- [20] Wu, C., et al., Mass Spectrometry Imaging under Ambient Conditions, Mass Spectrometry Reviews, 32 (2013), 3, pp. 218-243
- [21] Radhika, V., Ion-Solvation Behavior of Pyridinium Dichromate in Water-N, N-Dimethyl Formamide Solvent Mixtures, *Journal of Solution Chemistry*, 41 (2012), 2, pp. 261-270
- [22] Wang, X., et al., BAMBI Overexpression Together with β-Sitosterol Ameliorates NSCLC Via Inhibiting Autophagy and Inactivating TGF-β/Smad2/3 Pathway, Oncology Reports, 37 (2017), 5, 3046
- [23] Mayer, F., et al., Studies on the Aroma of Five Fresh Tomato Cultivars and the Precursors of Cis- and Trans-4,5-Epoxy-(E)-2-Decenals and Methional, J. Agric. Food Chem., 56 (2008), 10, pp. 3749-3757
- [24] Yingchun, L., et al., Reparation of Recycled Acrylonitrile- Butadiene-Styrene by Pyromelliticdianhydride: Reparation Performance Evaluation and Property Analysis, *Polymer, 124* (2017), Aug., pp. 41-47
- [25] Kotelevets, L., et al., A Squalene-Based Nanomedicine for Oral Treatment of Colon Cancer, Cancer Research, 77 (2017), 11, 2964
- [26] Han, X. M., Liu, D. C., Detection of the Toxic Substance Dibutyl Phthalate in Antarctic Krill, Antarctic Science, 29 (2017), 6, pp. 1-6
- [27] Ammar, M. K., et al., Design of Gravity Assist Trajectory from Earth to Jupiter, Applied Mathematics & Nonlinear Sciences, 3 (2018), 1, pp. 151-160
- [28] Sardar, M. S., et al., Computing Topological Indices of the Line Graphs of Banana Tree Graph and Firecracker Graph, Applied Mathematics & Nonlinear Sciences, 2 (2017), 1, pp. 83-92

- [29] Pak, K. Y., et al., Efficacy of the Perfluoro-N-Octane-Assisted Single-Layered Inverted Internal Limiting Membrane Flap Technique for Large Macular Holes, Ophthalmologica, 238 (2017), 3, pp. 133-138
- [30] Lim, G. H., *et al.*, Fatty Acid and Lipid-Mediated Signaling in Plant Defense, *Annual Review of Phytopathology*, *55* (2017), 1, 505
 [31] Liang, Y. R., *et al.*, A Highly Sensitive Signal-Amplified Gold Nanoparticle-Based Electrochemical Im-
- [31] Liang, Y. R., et al., A Highly Sensitive Signal-Amplified Gold Nanoparticle-Based Electrochemical Immunosensor for Dibutyl Phthalate Detection, Biosensors & Bioelectronics, 91 (2017), May, pp. 199-202