Comparison of the Composition of Three *Mahonia* Plants Based on GC-MS Analysis

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Abstract. Plant material evidence inspection is *Mahonia bealei* (Fort.) Carr., *Mahonia fortunei* (Lindl.) and *Mahonia bodinieri* Gagnep. are three common medicinal plants commonly found in *Mahonia*. In this study, gas chromatography-mass spectrometry (GC-MS) was used to compare the chemical constituents of stems and leaves of these three plants. The results showed that 6 of the volatile oils of the three plant species contained the same chemical composition, which was neophytadiene, palmitic acid, n-dodecane, octacosane, erucamide, and vitamin E oil, but the percentage content was difference. The main components of the volatile oils of the three plant stems were different. Erucamide was only detected in *Mahonia fortunei* (Lindl.) Fedde, oleic acid amide was only detected in *Mahonia bealei* (Fort.) Carr., and oxidized cyclooctene, and four compounds such as triphenylphosphine oxide was detected in *Mahonia bodinieri* Gagnep. ...

1 Introduction

Mahonia plants belong to Berberidaceae shrubs or small trees. There are about 100 species in the world, mainly distributed in East Asia, Southeast Asia, North America, Central America and Western South America. There are about 35 species in China^[1]. The genus is mainly planted with roots and stems. It is called thorn berberine, thorn jasper and gongcao wood. In some areas, it is also used as a leaf for its leaves. Therefore, roots, stems and leaves of *Mahonia* plants can be used as medicine. It is used as a folk medicine and traditional medicine in various distribution areas in China. It has the functions of purging fire and detoxifying, nourishing yin and tonifying the lungs, clearing away heat and dampness, and also nourishing the liver and kidneys^[2]. It is mainly distributed in Sichuan, Guizhou, Yunnan and southeastern China. This study analyzed and compared the composition of *Mahonia fortunei* (Lindl.) Fedde, *Mahonia bealei* (Fort.) Carr. and *Mahonia bodinieri* Gagnep.

There are many reports on the chemical composition of *Mahonia* plants. For the three chemical studies of *Mahonia fortunei*, Liu Yuxiang et al.^[3] used steam distillation to extract volatile oil from *Mahonia bodinieri* Gagnep. The chemical constituents were identified by gas chromatography-mass spectrometry (GC-MS) and the chemical constituents were identified by gas chromatography. More than 50 components were separated from the volatile oil of *Mahonia bodinieri* Gagnep. 36 compounds were identified, accounting for more than 90% of the total. *Mahonia bodinieri* Gagnep.

The main components of the volatile oil of the leaves are: palmitic acid (54.49%), and the higher content is linoleic acid (5.98%), α -farnesene (5.51%), methyl linolenic acid (3.45%), methyl palmitate (3.36%) and the like.

Dong Lei et al.^[4] used steam distillation to extract volatile oil from the stem of *Mahonia bealei* (Fort.) Carr., and determined the relative percentage of each component in volatile oil by normalization method and combined it with gas chromatography-mass spectrometry (The chemical composition of the structure was identified by GC-MS. A total of 96 components were detected and 18 of them were identified, accounting for more than 80% of the total volatile oil. Dong Lei et al.^[5] also used steam distillation to extract volatile oil from *Mahonia bealei* (Fort.) Carr. leaves, and detected a total of 155 components, and identified 28 compounds, accounting for more than 50.6% of the total volatile oil. Fan Libo^[6] and others extracted ethyl acetate extracts from the stems and leaves of *Mahonia fortunei* (Lindl.) Fedde with ethyl acetate. The extracts were concentrated and purified by repeated silica gel column and gel column chromatography to obtain 5 compounds. By physical and chemical properties and TLC, ¹H NMR, ¹³C NMR, MS analysis, the structure of the compound was identified as berberine (I), jatrorrhizine (II), 5-methoxy zephyr product D (III) (Note: for the first time isolated from this genus), luteolin (IV) and β -sitosterol (V). This extraction method is cumbersome and complicated to operate, but the obtained extract has high purity.

Liu Yuxiang^[3], Dong Lei^[4, 5] and others use steam distillation to extract volatile oil, which is only suitable

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for good volatility, can be distilled without steam, does not react with water, and is insoluble or Extraction of water-insoluble ingredients. The method has the advantages of simple equipment, simple operation, high safety, low cost, high oil yield and no pollution to the environment. However, this method also has some shortcomings. During the operation, *Mahonia fortunei* plants are susceptible to heat, easy to coke, or change the chemical composition^[7], so that the extracted volatile oil components are inaccurate, resulting in gas chromatography-mass spectrometry analysis is an error.

2 Materials and methods

2.1 Sample collection and processing

In March 2017, *Mahonia bealei* (Fort.) Carr. was collected at Nanjing Zhongshan Botanical Garden; *Mahonia fortunei* was collected at Nanjing Forest Police College; *Mahonia bodinieri* Gagnep. was collected in south eastern Guizhou. The three kinds of *Mahonia fortunei* collected were naturally air-dried, and then crushed into powders by a grinder to obtain 15 g of each powder, which was placed in a sample bag for use.

2.2 Instruments and reagents

Laboratory equipment: METTLER TTOLEdo (model: MT5), gas chromatography-mass spectrometer (Agilent Technologies 7890A GC system, 5975C inter XL MSD Agilent, USA) with autosampler, KQ-250B ultrasonic cleaning (Kunshan Ultrasonic Instrument Co., Ltd.), TG16-WS desktop high-speed centrifuge (Shanghai Luxiangyi Centrifuge Instrument Co., Ltd.), grinding machine.

2.3 Gas Chromatography-Mass Spectrometry Analysis

The method of extracting the components of volatile oil by double liquid phase: weigh 3g of stem and leaf powder of three *Mahonia fortunei*, respectively, and place them in a 10ml centrifuge tube, and add 9ml of 1:1 n-hexane/anhydrous ethanol to mix ultrasonic aid. The mixture was extracted for 30 minutes, repeated twice, and left to stand at room temperature for 30 minutes, and then centrifuged for 10 minutes by means of a centrifuge (rotation speed: 40×100 r / min), and the supernatant was extracted and used.

2.3.1 Gas chromatographic conditions

The column is HP-5MS GC column with a column length of 30m, an inner diameter of 0.25mm and a membrane thickness of 0.25 μ m. The carrier gas is high-purity nitrogen, and the carrier gas saves 20ml/min; the split ratio is 20:1; the syringe size is 10ul. Sample

volume 1 ul; pressure 8.2317 psi (1 MPa = 145 psi); flow rate 1 ml / min; after running 1 min; programmed temperature: initial temperature 60 ° C, 20 ° C / min to 320 ° C, for 5 min; solvent delay 3 min

2.3.2 Mass spectrometry conditions

Ion mode EI; ion source temperature 230 ° C, maximum 250 ° C; quadrupole temperature 150 ° C, maximum 200 ° C; transmission line temperature 230 ° C; solvent delay 3 min.

3 Results

The total ionograms of the six samples were obtained by gas chromatography-mass spectrometry. The peaks of the total ion currents were scanned by mass spectrometry to obtain the mass spectra of the components, and then the mass spectra of the six samples were identified by mass spectrometry database. The percentage of each compound in the volatile oil of 6 samples was calculated according to the peak area normalization method.

3.1 Chemical composition analysis of leaf volatile oil

Three kinds of *Mahonia* leaf volatile oil were analyzed by GC-MS and identified as chemical components, as shown in Figure 1 and Table 1. The same ingredients of the three are neophytadiene, palmitic acid, n-octadecane, octacosane, erucamide, and vitamin E oil. The total content of the six components is *Mahonia bealei* (high to low). Fort.) Carr. (85.370%), *Mahonia bodinieri* Gagnep. (65.207%), *Mahonia fortunei* (54.506%). Among them, *Mahonia fortunei* and *Mahonia bodinieri* Gagnep. contain phytosterols of 8.486% and 7.199%, respectively, but *Mahonia bealei* (Fort.) Carr. does not have this ingredient. *Mahonia fortunei* and *Mahonia bealei* (Fort.) Carr. contain linolenic acid, 3.101% and 3.079%, respectively, but *Mahonia bodinieri* Gagnep. does not have this ingredient.

Fig. 1. Total ion flow diagram of leaf volatile oil of *Mahonia fortunei*, *Mahonia bealei* (Fort.) Carr. And *Mahonia bodinieri* Gagnep.

Table 1. Volatile oil composition of *Mahonia fortunei*, *Mahonia bealei* (Fort.) Carr. And *Mahonia bodinieri* Gagnep

Component name	structural formula	<i>Mahonia fortunei</i> content (%)	<i>Mahonia bealei</i> (Fort.) Carr. content (%)	<i>Mahonia bodinieri</i> Gagnep. content (%)
3-Tetradecanone	C ₁₄ H ₂₈ O	7.226	0	0
Neophytadiene	C ₂₀ H ₃₈	8.859	9.771	9.857
3,7,11,15-Tetramethylhexadec-2-en-1-yl acetate	C ₂₂ H ₄₂ O ₂	3.261	0	0
n-Hexadecanoic acid	C ₁₆ H ₃₂ O ₂	3.695	4.697	1.498
Octacosane	C ₂₈ H ₅₈	1.234	17.327	8.154
Nonacosane	C ₂₉ H ₆₀	5.106	16.254	7.598
13-Docosenamide,	C ₂₂ H ₄₃ NO	13.071	28.608	24.408
Vitamin E	C ₂₉ H ₅₀ O ₂	22.541	8.713	13.692
9,12-Octadecadienoic acid (Z,Z)	C ₁₈ H ₃₀ O ₂	3.079	3.101	0
.beta.-Sitosterol	C ₂₉ H ₅₀ O	8.486	0	7.199
Tetracosane	C ₂₄ H ₅₀	8.709	0	0
1,2,5-Oxadiazol-3-amine,4-(4-methoxyphenoxy)	C ₉ H ₉ N ₃ OS	3.411	0	0
13-Hexacosyne	C ₂₆ H ₅₀	3.763	0	0
17-Pentatriacontene	C ₃₅ H ₇₀	6.669	0	0
1,4-Benzenediol,2,5-bis(1,1-dimethylethyl) - 2,5-	C ₁₄ H ₂₂ O ₂	0	5.539	0
9,12,15-Octadecatrien-1-ol, (Z,Z,Z) -	C ₁₈ H ₃₂ O	0	5.990	0
Bicyclo[4.1.0]heptane, 3-methyl	C ₆ H ₁₀ O ₂	0	0	2.121
1-Hexadecyne 1	C ₁₆ H ₃₀	0	0	30.145
Octacosanal	C ₂₈ H ₅₆ O	0	0	4.281
1,1'-Biphenyl,3,3',4,4',5,5'-hexamethoxy-	C ₁₈ H ₂₂ O ₆	0	0	5.304
Benzenepropanenitrile,.beta.-phenyl- 3, 3	C ₁₅ H ₁₃ N	0	0	4.872
Eicosane	C ₂₀ H ₄₂	0	0	3.431
Berbine, 13,13a-didehydro-9,10-dimethoxy-2,3-(methylenedioxy)	C ₂₀ H ₁₉ NO ₄	0	0	7.442

The specific chemical composition of *Mahonia fortunei* is from tetradecane (8.709%) and 3-tetradecanone (7.226%), and the specific chemical composition of *Mahonia bealei* (Fort.) Carr. is 2,5 - Di-tert-butyl hydroquinone (5.539%); *Mahonia bodinieri* Gagnep. The specific chemical composition percentages from high to low are 1-hexadecane (30.145%), 3,3-diphenylpropionitrile (4.872%), dihydroberberine (7.442%), analytical pure n-icosane (3.431%).

Fig. 2. Total ion flow diagram of stem volatile oil of *Mahonia fortunei*, *Mahonia bealei* (Fort.) Carr. And *Mahonia bodinieri* Gagnep

Table 2. Composition of essential oil from stem of *Mahonia fortunei*, *Mahonia bealei* (Fort.) Carr. And *Mahonia bodinieri* Gagnep

Component name	structural formula	<i>Mahonia fortunei</i> content (%)	<i>Mahonia bealei</i> (Fort.) Carr. content (%)	<i>Mahonia bodinieri</i> Gagnep. content (%)
9-Octadecenamide, (Z)	C ₁₈ H ₃₅ NO	0	100	0
13-Docosenamide, (Z)	C ₂₂ H ₄₃ NO	100	0	23.399
9-Oxabicyclo[6.1.0]nonane	C ₈ H ₁₄ O	0	0	27.756
Cyclodecasiloxane, eicosamethyl	C ₂₀ H ₆₀ O ₁₀ Si ₁₀	0	0	4.589
Triphenylphosphine oxide	C ₇ H ₃ D ₃ O ₄	0	0	9.87
2,5-Dihydroxybenzoic acid, 3TMS derivative	C ₁₈ H ₁₅ OP	0	0	11.191
(E) -2- bromobutyloxychalcone	C ₁₆ H ₅₀ O ₇ Si ₈	0	0	10.385
Pyridine-3-carboxamide, oxime,N- (2- trifluoromethylphenyl) - 3, 3	C ₁₅ H ₁₃ N	0	0	12.810

3.2 Chemical analysis of volatile oil from stem

Three kinds of *Mahonia fortunei* stem volatile oil were analyzed by GC-MS and identified as chemical components, as shown in Figure 2 and Table 2. *Mahonia fortunei* contains only erucamide; *Mahonia bealei* (Fort.) Carr. contains only oleic acid amide; *Mahonia bodinieri* Gagnep. contains more chemical components, the percentages from high to low are erucamide (23.399%) Cyclooctene oxide (27.756%), triphenylphosphine oxide (11.191%), 3,3-diphenylpropionitrile (12.810%), accounting for 75.156% of the total content.

4 Discussion

4.1 Comparison of chemical components between stem and leaf parts

In this study, gas chromatography-mass spectrometry was used to analyze the volatile oil samples of stems and leaves of *Mahonia fortunei*, *Mahonia bealei* (Fort.) Carr. and *Mahonia bodinieri* Gagnep. 10 chemical components, such as 3-tetradecanone, neophytadiene, erucic acid amide, palmitic acid, phytosterols, etc., were isolated from the leaves of *Mahonia fortunei*, accounting for 82.896% of the total volatile oil. Only erucamide was isolated and identified, and its stem and leaves contained erucamide, which were 100% and 13.071%, respectively. Separation and identification of 9 chemical components from the leaves of *Mahonia bealei* (Fort.) Carr., such as di-tert-butyl hydroquinone, linolenic acid, erucamide, n-dodecane, octacosane, palmitic acid, etc. The main component accounts for 94.01% of the total volatile oil. Only the oleic acid amide is isolated and identified from the stem, and its stem and leaves contain different components. 11 chemical components were isolated from the leaves of *Mahonia bealei* (Fort.) Carr., such as dihydroberberine, analytical pure n-icosane, 3,3-diphenylpropionitrile, 1-hexadecane, plant Alcohol, neophytadiene, erucamide, vitamin E oil and other main components accounted for 88.294% of the total volatile oil. Four chemical components were isolated from the stem and identified as erucamide, cyclooctene oxide and

triphenyl oxide. Phosphine and 3,3-diphenylpropionitrile accounted for 75.156% of the total volatile oil, and the stem and leaves contained erucamide and 3,3-diphenylpropionitrile, respectively, 34.59% and 29.28%.

4.2 Comparison of chemical composition of three *Mahonia fortunei*

In this study, gas chromatography-mass spectrometry was used to analyze the volatile oil samples of *Mahonia fortunei*, *Mahonia bealei* (Fort.) Carr. and *Mahonia bodinieri* Gagnep. stems and leaves, and 14 components were isolated from the volatile oil of *Mahonia fortunei* stem and leaf. 10 chemical constituents; 10 components were isolated from the volatile oil of *Mahonia bealei* (Fort.) Carr. stems and leaves, and 9 chemical components were identified; 20 components were isolated from the volatile oil of *Mahonia bodinieri* Gagnep. stems and leaves, identified 15 chemical components. The leaves of three species of *Mahonia fortunei* contain six chemical components, including neophytadiene, palmitic acid, n-octadecane, octacosane, erucamide, and vitamin E oil, which fully exemplify these three *Mahonia fortunei* in chemistry. The same nature of the ingredients. But the unique 4-butanone of *Mahonia fortunei*, the unique 2,5-di-tert-butyl hydroquinone, oleic acid amide, *Mahonia bodinieri* Gagnep, unique dihydroberberine, *Mahonia bealei* (Fort.) Carr. Analysis of pure eicosane, 1-hexadecane, 3,3-diphenylpropionitrile, oxidized cyclooctene and other chemical components, also visually reflects their compositional differences.

Fan Libo et al [6] extracted the ethanol extracts from the stems and leaves of *Mahonia fortunei* with ethyl acetate. The extracts were concentrated and separated and purified by repeated silica gel column and gel column chromatography. Five compounds were identified. This study did not detect; Dong Lei et al [4] extracted the volatile oil from the stems and leaves of *Mahonia bealei* (Fort.) Carr. by steam distillation, and analyzed by gas chromatography-mass spectrometry. The 32 chemical components were not detected in this study; Liu Yuxiang et al [3] used steam distillation to extract volatile oil from the stems and leaves of *Mahonia*

bodinieri Gagnep. After gas chromatography-mass spectrometry analysis, it was identified. 36 chemical components were obtained, of which palmitic acid was also detected in this study, but the content was different. The results of this study were 4.697%, and Dong Lei et al^[4] showed 54.49%, and the other components were not detected.

This difference should be caused by the extraction method. In this study, the extraction method of the two liquid phase with n-hexane and absolute ethanol as the extractant is used. The difference of the extraction reagent will directly affect the detection result. The separation and identification of this experiment are identified. No ingredients have been reported except for palmitic acid.

5 Conclusion

In this study, the chemical constituents of the stem and leaf samples of *Mahonia fortunei*, *Mahonia bealei* (Fort.) Carr. and *Mahonia bodinieri* Gagnep. were analyzed and summarized. The results show that the method of extracting volatile oil components in two liquid phase is feasible and effective.

The three-liquid phase extraction method of three species of *Mahonia fortunei* volatile oil from stems and leaves, using anhydrous ethanol and n-hexane as extractants, can be reflected by gas chromatography-mass spectrometry (GC-MS) analysis. The same chemical composition is 6 kinds of neophytadiene, palmitic acid, n-octadecane, octacosane, erucamide and vitamin E oil. The difference in chemical composition is reflected in both quantity and type. In terms of quantity, *Mahonia fortunei* has identified 10 chemical components, *Mahonia bealei* (Fort.) Carr. has identified 9 chemical components, and *Mahonia bodinieri* Gagnep. has identified 15 chemical components. Chemical composition; species differences are reflected in the unique chemical composition of these three *Mahonia fortunei*, *Mahonia fortunei* contains 3-tetradecanone, *Mahonia bealei* (Fort.) Carr. contains 2,5-di-tert-butyl hydroquinone, oil Acid amide, *Mahonia bodinieri* Gagnep. contains dihydroberberine, analytical pure n-icosane, 1-hexadecane, 3,3-diphenylpropionitrile, oxidized cyclooctene.

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