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Chemotaxonomic Significance of Taxifolin-3-O-arabinopyranoside in Chinese *Rhododendron* genus

Tae Hee Kim[1], Hyeon Du Jang[2], Ye Ji Kim[2], Ye Eun Kwon[1], Sun Min Park[1], Min Seok Kim[1], Chan Ho Lee[2] and Sun Eun Choi[1,2,*]

[1]*Dr. Oregonin Inc., Chuncheon 24341, Republic of Korea*
[2]*Department of Forest Biomaterials Engineering, College of Forest and Environmental Sciences, Kangwon National University, Chuncheon 24341, Republic of Korea*

Abstract

More than half of the global distribution of the *Rhododendron* genus is found in China, with over 74% being endemic species. However, there is still insufficient data to chemically classify the *Rhododendron* genus native to China. Therefore, in this study, a chemotaxonomic study was conducted to determine the presence of taxifolin-3-O-arabinopyranoside, a flavonoid compound, in the *Rhododendron* genus native to China. Forty-three species of *Rhododendron* native to China—20 from across China, 8 from Beijing, 6 from Yanbian, and 9 from Yunnan—were utilized in the experiment. Through HPLC analysis, the retention time was compared with that of taxifolin-3-O-arabinopyranoside, a standard compound, and quantitative analysis was conducted. As a result, taxifolin-3-O-arabinopyranoside was detected in 22 out of 43 the Chinese *Rhododendron* species. Afterwards, LC-MS/MS analysis was performed on the 22 species in which taxifolin-3-O-arabinopyranoside was detected to determine whether the molecular weight was consistent with the standard compound. Under negative conditions, it was confirmed that all samples exhibited the same molecular weight as taxifolin-3-O-arabinopyranoside, 435-436 m/z. The same compound was detected in more than half of the *Rhododendron* species used in the experiment, and taxifolin-3-O-arabinopyranoside was determined to be an indicator compound for *Rhododendron* species native to China. In addition, the possibility of using the above results as basic data for chemical classification of Chinese *Rhododendron* genus was confirmed.

Key Words: *Rhododendron* native to China, Taxifolin-3-O-arabinopyranoside, HPLC analysis, LC-MS/MS, chemotaxonomic significance

Introduction

Rhododendron is a plant that belongs to the Ericaceae family and is primarily found in East Asia and Southeast Asia. With over 1,000 species distributed worldwide, it is one of the largest plant resources. Approximately 571 species, more than half, are reported to be found in China (Popescu and Kopp 2013; Zeng et al. 2021). *Rhododendrons* are found in most parts of China, except for Xinjiang and Ningxia, and they are present in 60% of the country. Additionally, more than 74% of the *Rhododendron* species growing naturally in China are endemic (Yu et al. 2017).

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Corresponding author: Sun Eun Choi

Department of Forest Biomaterials Engineering, College of Forest and Environmental Sciences, Kangwon National University, Chuncheon 24341, Republic of Korea

Tel: +82-33-250-8324, Fax: +82-33-902-9990, E-mail: oregonin@kangwon.ac.kr

It has been reported that the flowers and young branches of plants in the *Rhododendron* genus have been used in folk medicine or traditional medicine in various countries since ancient times. In Chinese folk medicine, the dried stems, leaves, and flowers of *R. spinuliferum* were utilized to remove phlegm, relieve coughs, and function as an anti-asthmatic remedy. Additionally, the dried leaves of *R. dauricum*, also known as Mansan Hong, were used to treat acute and chronic bronchitis and as an expectorant (Qiang et al. 2011). *R. agglutinatum* was used to treat arthritis, and *R. anthopogonoides* was used to reduce body heat, detoxify, provide anti-inflammatory effects, and remove swelling. *R. capitatum* was used for the treatment of abdominal pain, while *R. mariae*, *R. micranthum, R. mucronatum*, and *R. mucronulatum* were utilized for treating cough and phlegm. *R. mucronulatum* and *R. tomentosum* have also been used to treat rheumatism (Popescu and Kopp 2013).

These activities were found to be the effects of various secondary metabolites of *Rhododendron* genus. The secondary metabolites of *Rhododendron* genus discovered to date include sesquiterpenoids, diterpenoids, triterpenoids, coumarins, phenols, flavonoids, and grifolin derivatives (Cao et al. 2004; Iwata et al. 2004; Peng et al. 2004; Olennikov and Tankhaeva 2010; Lou et al. 2015; Ye et al. 2020). Among them, flavonoid compounds are representative secondary metabolites of *Rhododendron* genus. Research is being conducted on various activities, such as antioxidant, anti-inflammatory, antibacterial effects, suppression of allergic inflammation, and improvement of chronic inflammatory diseases, such as atopy (Kim et al. 2008; Ahn et al. 2010; Fu et al. 2012; Liu et al. 2022).

Types of flavonoids isolated from Chinese *Rhododendron* include quercetin-3-O-β-D-galactopyranoside isolated from *R. schippenbachii*, *R. dauricum*, *R. micranthum*, and *R. capitatum* (Zhang et al. 2019; Sun et al. 2019; Hui and Sun 2012), quercetin-3-O-α-L-arabofuranoside isolated from *R. schippenbachii, R. dauricum* (Liu et al. 2022), quercetin-3-O-α-L-rhamnoside isolated from *R. schippenbachii, R. dauricum,* and *R. micanthum* (Liu et al. 2022), syzalterin, poriolin, myricetin, farrerol-7-O-β-D-glucopyranoside, azaleatin, (+)-catechin, isorhamnetin, taxifolin isolated from *R. dauricum* (Hui and Sun 2012; Zhang et al. 2019), ferrerol, kaemferol isolated from *R. dauricum* and *R. micranthum* (Hui and Sun 2012; Sun et al. 2019; Zhang et al. 2019), quercetin isolated from *R. dauricum, R. micranthum,* and *R. capitatum* (Hui and Sun 2012; Sun et al. 2019; Zhang et al. 2019), and taxifolin-3-O-α-L-arabinopyranoside, quercetin-3-O-α-L-arabinopyranoside, orcinol glucoside isolated from *R. anthopogonoides* (Gui et al. 2020), myricitrin and rutin isolated from *R. micranthum* (Zhang et al. 2019; Liu et al. 2022).

However, taxifolin-3-O-arabinopyranoside, a flavonoid compound discovered as an indicator substance for species of the *Rhododendron* genus native to Korea in our research team's previous study (Kim et al. 2022), has not been identified in many species of the *Rhododendron* genus native to China. Accordingly, in this research, we conducted a chemotaxonomic study on *Rhododendron* species native to China. Taxifolin-3-O-arabinopyranoside, an indicator substance obtained directly from Korean native *Rhododendron*, was utilized as a standard compound to confirm its presence in Chinese *Rhododendron* species through HPLC analysis and LC-MS/MS analysis. The purpose of this study was to validate the plausibility of the research results and determine whether taxifolin-3-O-arabinopyranoside can be considered as an indicator substance for Chinese *Rhododendron* species.

Materials and Methods

Extracts of Rhododendron species native to China

Extracts of 43 species of the *Rhododendron* genus native to China were purchased from the International Biological Materials Research Center of the Korea Research Institute of Bioscience and Biotechnology as materials for this study. Samples were collected from 20 areas in China, 8 in Beijing, 6 in Yanbian, and 9 in Yunnan. Identification of individual Chinese species was confirmed based on information provided by the Korea Research Institute of Bioscience and Biotechnology, and rather than being directly distinguished, purchase and identification barcodes were included in the sample list. Extracts were obtained from various plant parts, including branches, stems, leaves, and flowers. Each extract was dissolved in methanol to prepare a stock solution of 20,000 ppm, which was then diluted and used at a concentration of 1,000 ppm. For the standard compound, we utilized taxifolin-3-O-arabinopyranoside, isolated and purified from the roots of native Korean *R.*

mucronulatum Turcz., a substance obtained through previous research conducted by our research team (Fig. 1) (Kim et al. 2022). The list of samples used in the experiment is presented in Table 1.

HPLC-based quantitative analysis of Taxifolin-3-O-arabinopyranosdie in Chinese Rhododendron species

Dissolving the standard compound taxifolin-3-O-arabinopyranoside in methanol to create a 250 ppm solution, followed by dilutions to concentrations of 125, 62.5, 31.25, 20, 10, and 1 ppm, allowed the generation of a standard calibration curve for calculating the limit of detection (LOD). The equation used to calculate the detection limit is as follows. Subsequently, stock solutions of 43 samples from the Chinese *Rhododendron* genus were individually dissolved in methanol and diluted to 1,000 ppm. The equipment used for HPLC analysis was a Chrozen HPLC equipment and a Chrozen UV/Vis detector. Phenomenex KJ0-4282 was used as a guard column, and a SkyPak C18 analytical column (5 μm) was used as the analytical column. The analysis is conducted at room temperature, with a flow rate of 1 mL/min, a wavelength of 280 nm, an injection volume of 20 μL, and a run time of 40 minutes. The mobile phases used in the analysis were 1% formic acid in water (H_2O) and acetonitrile (CH_3CN). The analysis was conducted under the following conditions: 0 min, 10% acetonitrile; 20 min, 35% acetonitrile; 25 min, 100% acetonitrile; 35 min, 10% acetonitrile; 40 min, 10% acetonitrile. Following the analysis, the retention time of each sample was compared with the standard compound taxifolin-3-O-arabinopyranoside, and quantitative analysis was conducted based on the limit of detection (LOD).

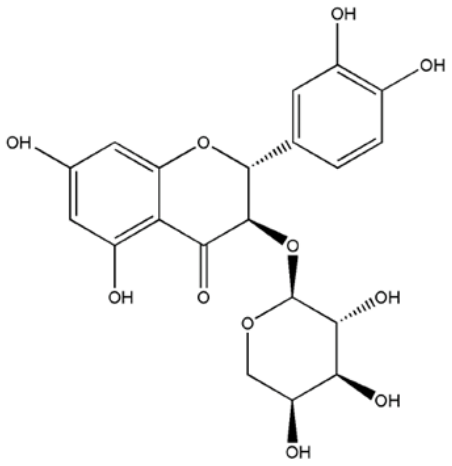

Fig. 1. Structure of Taxifolin-3-O-arabinopyranoside.

LOD (limit of detection) $=3.3\times SE/S$
(SE, standard error; S, slope of the calibration curve)

Confirmation of the molecular weight of native Chinese Rhododendron species using LC-MS/MS

Among 43 samples from the Chinese *Rhododendron* genus, LC-MS/MS analysis was performed only on samples for which standard compounds were detected in quantitative HPLC analysis. Through analysis, the molecular weight was compared to that of the standard compound to determine if they were the same. The analysis was conducted under negative conditions. The equipment used for LC-MS/MS analysis was the QTRAP 4500 (AB SCIEX, USA). Phenomenex KJ0-4282 was used as a guard column, and a SkyPak C18 analytical column (5 μm) was used as the analytical column. The analysis temperature is room temperature, with a flow rate of 1 mL/min, a wavelength of 280 nm, an injection volume of 20 μL, and a run time of 40 minutes. The mobile phases used in the analysis consisted of 1% formic acid in water (H_2O) and acetonitrile (CH_3CN). The analysis was conducted under the following conditions: 0 min, 10% acetonitrile; 20 min, 35% acetonitrile; 25 min, 100% acetonitrile; 35 min, 10% acetonitrile; 40 min, 10% acetonitrile.

Results and Discussion

To conduct HPLC analysis of 43 samples of the *Rhododendron* genus native to China, taxifolin-3-O-arabinopyranoside, a standard compound, was diluted by concentration to prepare a standard calibration curve $y=29{,}860x+16{,}982$, $R^2=0.9997$. Accordingly, the limit of detection (LOD) is 2.45 ppm, and the HPLC chromatograms of the samples in which the peak of the standard compound was detected are shown in Figs. 2-23.

As a result of HPLC analysis, taxifolin-3-O-arabinopyranoside, a standard compound, was detected in 22 out of 43 species of *Rhododendron* in China. The remaining 21

Table 1. Sample list

No.	Habitat	Species	part	Barcode no.
1	China	*Rhododendron molle* (Blume) G. Don	F.E.	PBCN12073
2	China	*Rhododendron chionanthum* Tagg & Forrest	F.E.	PBCN12649
3	China	*Rhododendron delavayi* Franch.	F.E.	PBCN12638
4	China	*Rhododendron simsii* Planch.	F.E.	PBCN12775
5	China	*Rhododendron pubescens* Balf.f. & Forrest	F.E.	PBCN12831
6	China	*Rhododendron telmateium* Balf. F. & W.W. Sm.	F.E.	PBCN13093
7	China	*Rhododendron rupicola* var. *chryseum* (Balf. F. & Kingdon-Ward) Philipson & M.N. Philipson	F.E.	PBCN13163
8	China	*Rhododendron traillianum* var. *dictyotum* (Balf. F. ex Tagg) D.F. Chamb.	F.E.	PBCN13089
9	China	*Rhododendron primuliflorum* Bureau & Franch.	F.E.	PBCN13092
10	China	*Rhododendron hippophaeoides* Balf. f. & W.W. Sm.	F.E.	PBCN13119
11	China	*Rhododendron wardii* W.W. Sm.	F.E.	PBCN13120
12	China	*Rhododendron vernicosum* Franch.	F.E.	PBCN13146
13	China	*Rhododendron vaccinioides* Hook.	F.E.	PBCN13244
14	China	*Rhododendron rupicola* W.W. Sm.	F.E.	PBCN13197
15	China	*Rhododendron cephalanthum* Franch.	F.E.	PBCN13208
16	China	*Rhododendron glischrum* Balf. f. & W.W. Sm.	F.E.	PBCN13399
17	China	*Rhododendron mucronatum* (Blume) G. Don	F.E.	PBCN13451
18	China	*Rhododendron spiciferum* Franch.	F.E.	PBCN13633
19	China	*Rhododendron simsii* Planch.	F.E.	PBCN13649
20	China	*Rhododendron ovatum* (Lindl.) Planch. ex Maxim.	F.E.	PBCN13671
21	Beijing	*Rhododendron micranthum* Turcz.	F.E.	PBCN14039
22	Beijing	*Rhododendron mucronulatum* Turcz.	F.E.	PBCN14286
23	Beijing	*Rhododendron mucronulatum* Turcz.	Leave, stem	PBCN14968
24	Beijing	*Rhododendron ovatum* (Lindl.) Planch. ex Maxim.	Leave, stem	PBCN15754
25	Beijing	*Rhododendron kwangsiense* H.H. Hu ex P.C. Tam	Leave, stem	PBCN17369
26	Beijing	*Rhododendron ovatum* (Lindl.) Planch. ex Maxim.	Leave, stem	PBCN17386
27	Beijing	*Rhododendron championiae* Hook.	Leave, branch	PBCN18846
28	Beijing	*Rhododendron rivulare* Hand.-Mazz.	Leave, branch	PBCN19363
29	Yanbian	*Rhododendron dauricum* L.	branch	PBCN13782
30	Yanbian	*Rhododendron chrysanthum* Pall.	F.E.	PBCN16145
31	Yanbian	*Rhododendron schlippenbackii* Maxim	Stem, flower	PBCN16379
32	Yanbian	*Rhododendron schlippenbackii* Maxim.	Leave, stem	PBCN16429
33	Yanbian	*Rhododendron Parvifolium* Adams.	Leave, stem	PBCN16478
34	Yanbian	*Rhododendron mucronulatum* Turcz.	Leave, branch	PBCN18417
35	Yunnan	*Rhododendron decorum* Franch.	Leave, stem	PBCN15220
36	Yunnan	*Rhododendron annae* Franch.	Leave, stem, branch, flower	PBCN18450
37	Yunnan	*Rhododendron irroratum* Franch.	Leave, stem, branch	PBCN18451
38	Yunnan	*Rhododendron strigillosum* Franch.	A.P.	PBCN18879
39	Yunnan	*Rhododendron lutescens* Franch.	A.P.	PBCN18890
40	Yunnan	*Rhododendron pumilum* Hook.f.	F.E.	PBCN18907
41	Yunnan	*Rhododendron wumingense* W.P.Fang	A.P.	PBCN18914
42	Yunnan	*Rhododendron minutiflorum* Hu	A.P.	PBCN18885
43	Yunnan	*Rhododendron microphyton* Franch.	F.E.	PBCN18934

F.E., full extract; A.P., area part.

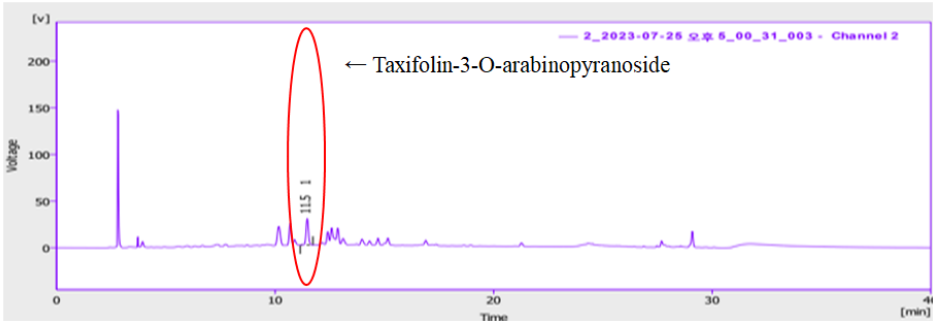

Fig. 2. HPLC chromatogram of the sample 2. Sample 2=*Rhododendron chionanthum* Tagg & Forrest (China) 1,000 ppm.

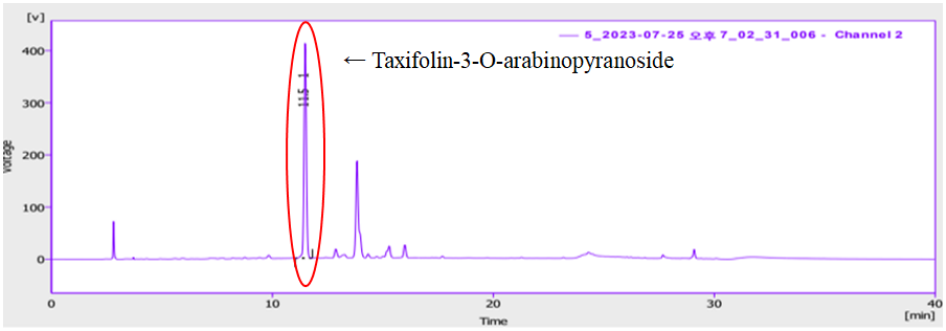

Fig. 3. HPLC chromatogram of the sample 5. Sample 5=*Rhododendron pubescens* Balf. F. & Forrest (China) 1,000 ppm.

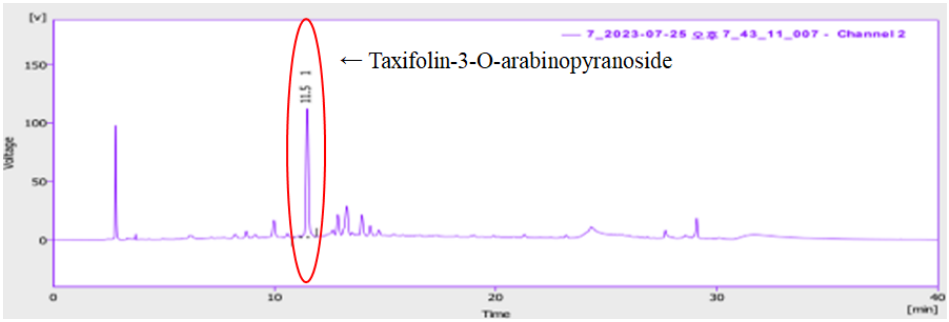

Fig. 4. HPLC chromatogram of the sample 6. Sample 6=*Rhododendron telmateium* Balf. F. & W.W. Sm. (China) 1,000 ppm.

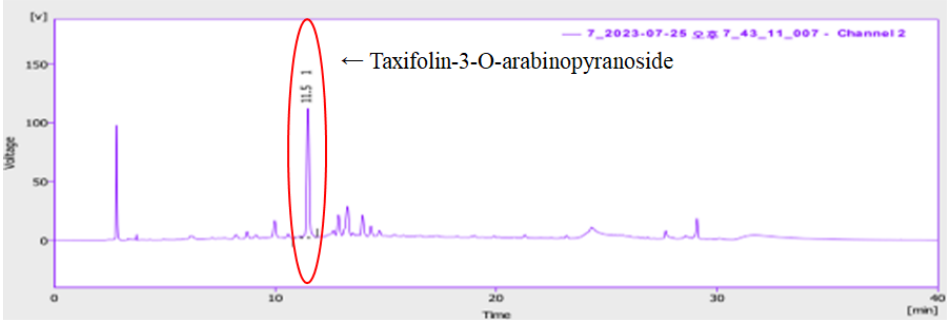

Fig. 5. HPLC chromatogram of the sample 7. Sample 7=*Rhododendron rupicola* var. *Chryseum* (Balf. F. & Kingdon-Ward) Philipson & M.N. Philipson (China) 1,000 ppm.

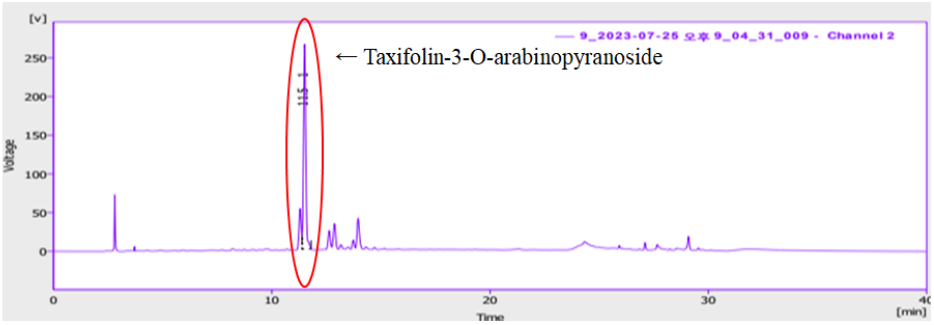

Fig. 6. HPLC chromatogram of the sample 8. Sample 8=*Rhododendron traillianum* var. *dictyotum* (Balf. F. ex Tagg) D.F. Chamb. (China) 1,000 ppm.

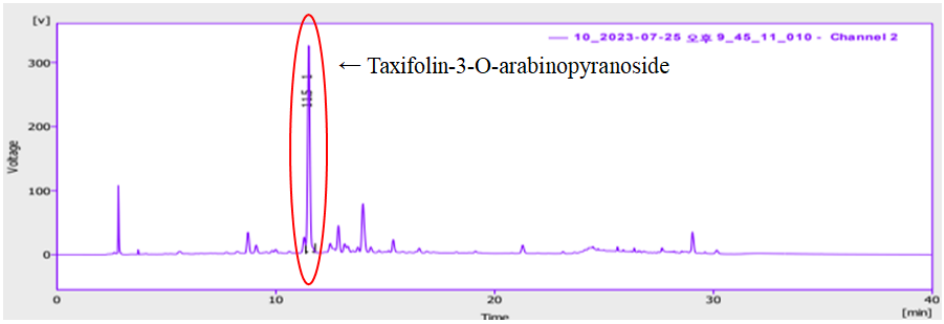

Fig. 7. HPLC chromatogram of the sample 9. Sample 9=*Rhododendron primuliflorum* Bureau & Franch. (China) 1,000 ppm.

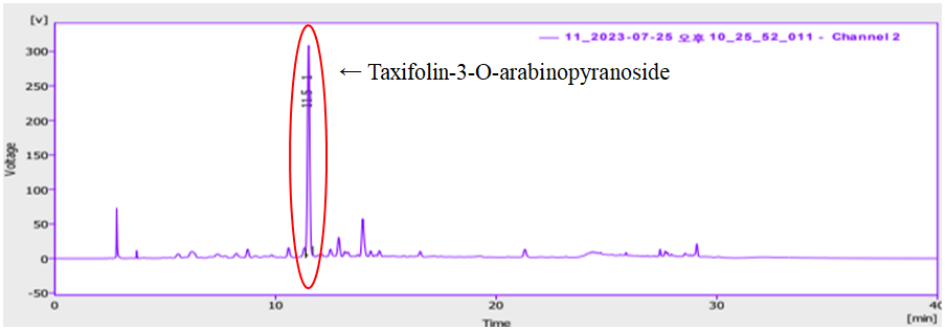

Fig. 8. HPLC chromatogram of the sample 10. Sample 10=*Rhododendron hippophaeoides* Balf. F. & W.W. Sm. (China) 1,000 ppm.

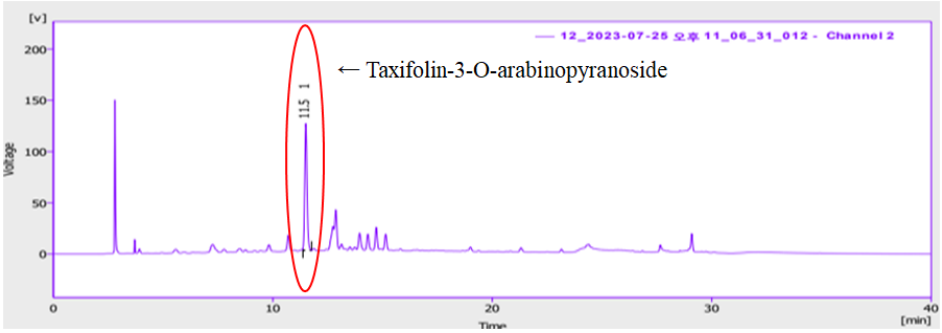

Fig. 9. HPLC chromatogram of the sample 11. Sample 11=*Rhododendron wardii* W.W. Sm. (China) 1,000 ppm.

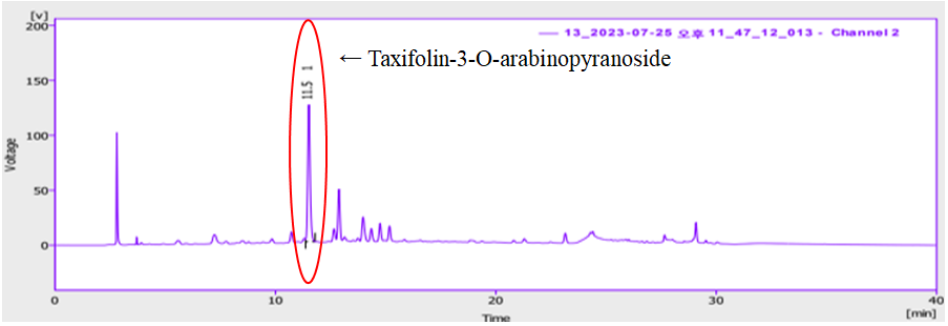

Fig. 10. HPLC chromatogram of the sample 12. Sample 12= *Rhododendron vernicosum* Franch. (China) 1,000 ppm.

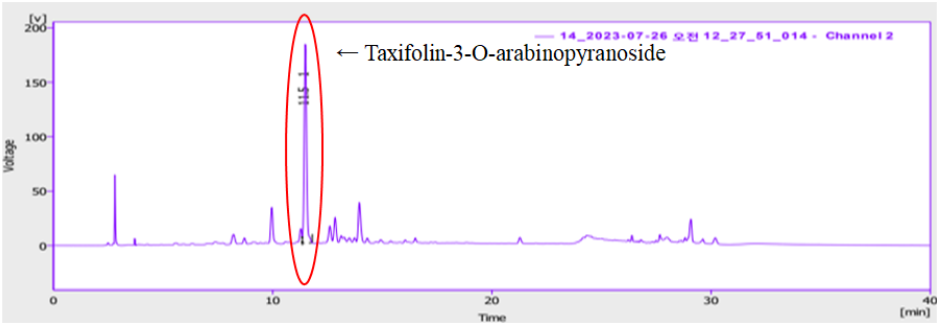

Fig. 11. HPLC chromatogram of the sample 13. Sample 13= *Rhododendron vaccinioides* Hook. (China) 1,000 ppm.

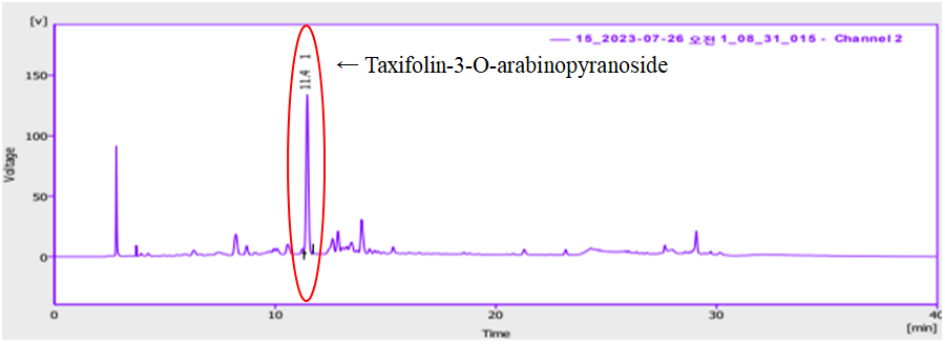

Fig. 12. HPLC chromatogram of the sample 14. Sample 14= *Rhododendron rupicola* W.W. Sm. (China) 1,000 ppm.

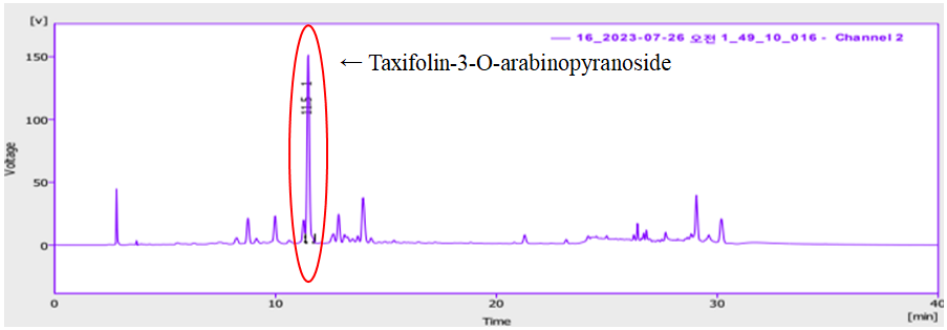

Fig. 13. HPLC chromatogram of the sample 15. Sample 15= *Rhododendron cephalanthum* Franch. (China) 1,000 ppm.

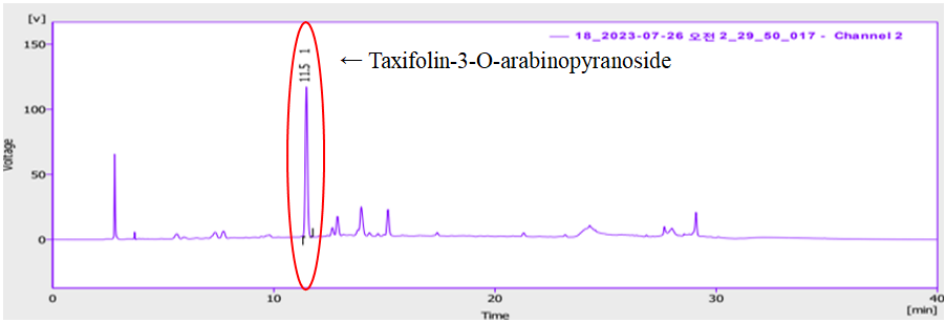

Fig. 14. HPLC chromatogram of the sample 16. Sample 16= *Rhododendron glischrum* Balf. F. & W.W. Sm. (China) 1,000 ppm.

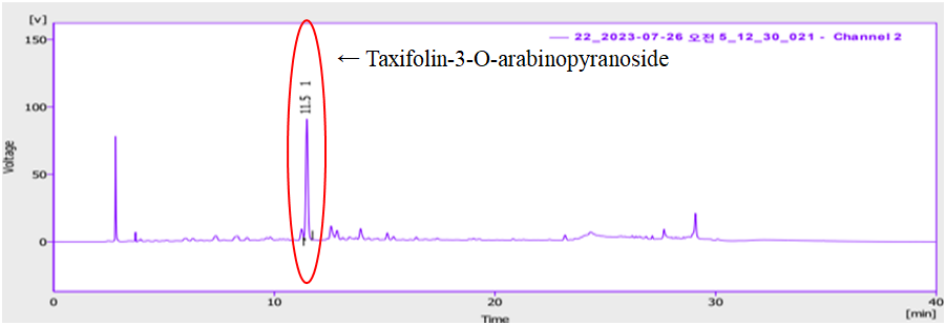

Fig. 15. HPLC chromatogram of the sample 20. Sample 20= *Rhododendron ovatum* (Lindl.) Planch. Ex Maxim. (China) 1,000 ppm.

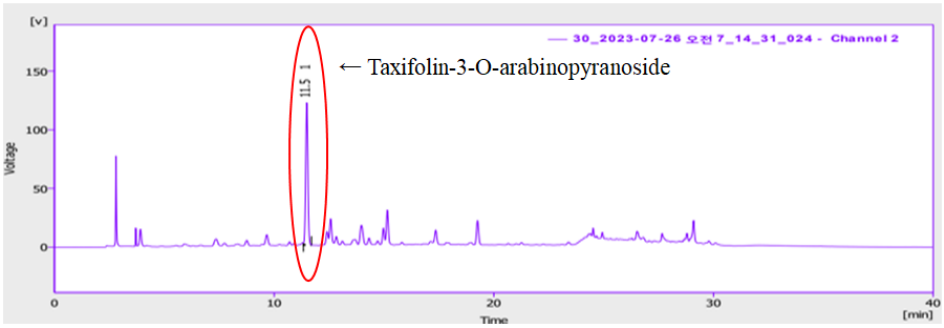

Fig. 16. HPLC chromatogram of the sample 23. Sample 23= *Rhododendron mucronulatum* Turcz. (Beijing, China) 1,000 ppm.

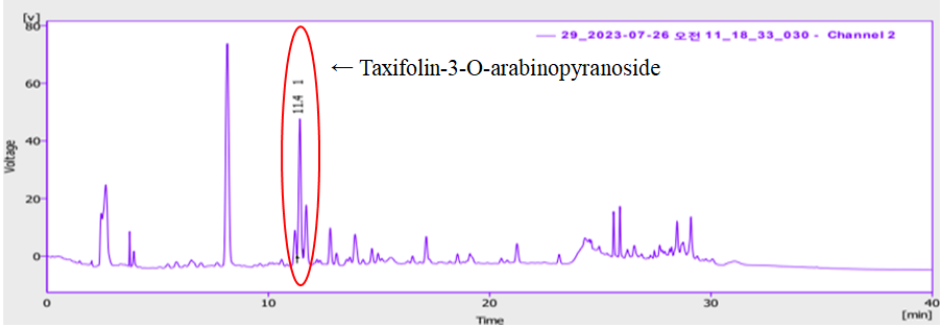

Fig. 17. HPLC chromatogram of the sample 29. Sample 29= *Rhododendron dauricum* L. (Yanbian, China) 1,000 ppm.

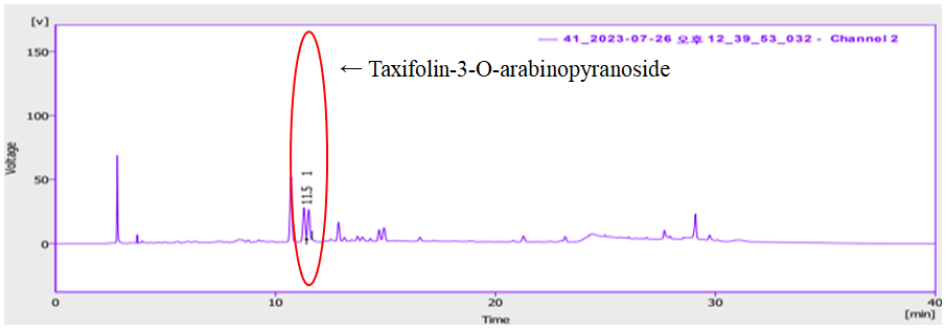

Fig. 18. HPLC chromatogram of the sample 30. Sample 30= *Rhododendron chrysanthum* Pall. (Yanbian, China) 1,000 ppm.

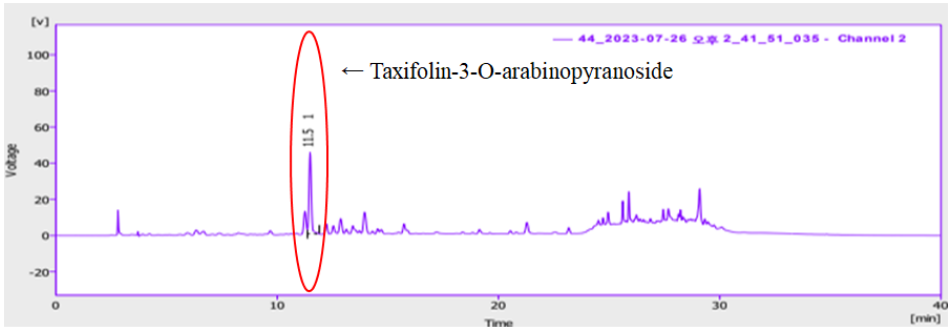

Fig. 19. HPLC chromatogram of the sample 33. Sample 33= *Rhododendron parvifolium* Adams. (Yanbian, China) 1,000 ppm.

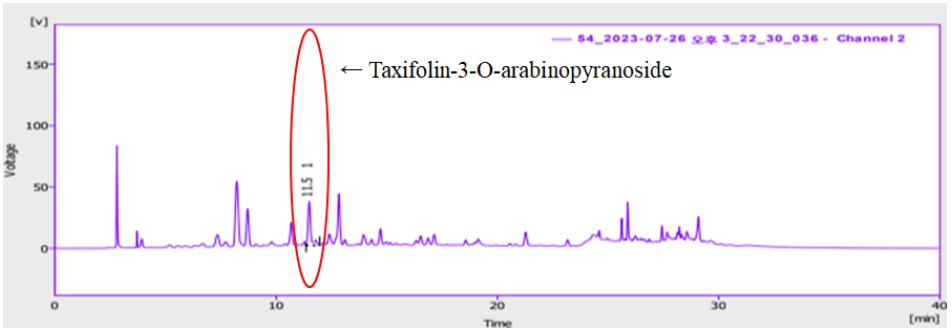

Fig. 20. HPLC chromatogram of the sample 34. Sample 34= *Rhododendron mucronulatum* Turcz. (Yanbian, China) 1,000 ppm.

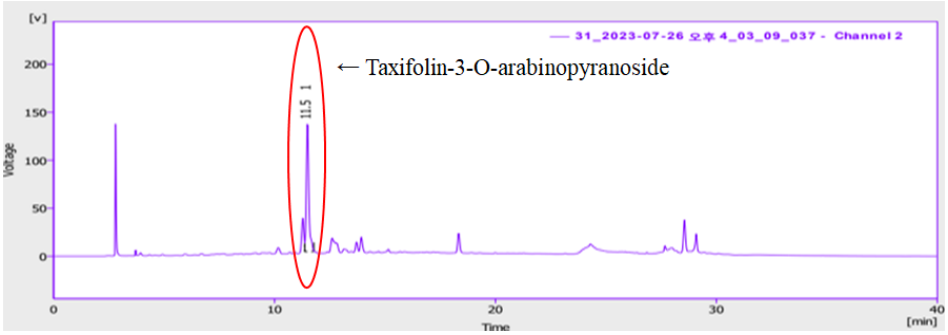

Fig. 21. HPLC chromatogram of the sample 35. Sample 35= *Rhododendron decorum* Franch. (Yunnan, China) 1,000 ppm.

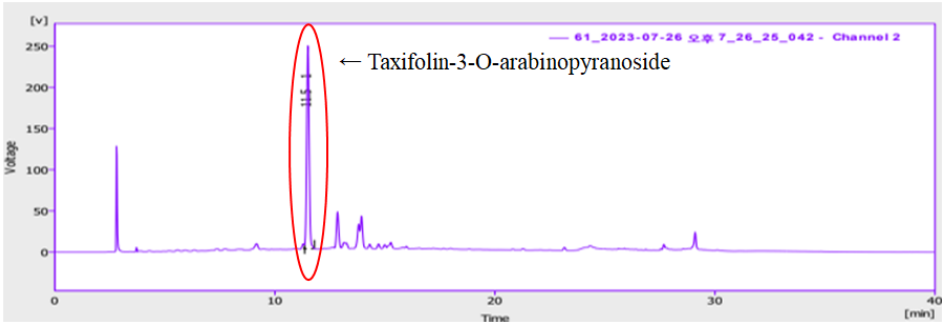

Fig. 22. HPLC chromatogram of the sample 40. Sample 40= *Rhododendron pumilum* Hook.f. (Yunnan, China) 1,000 ppm.

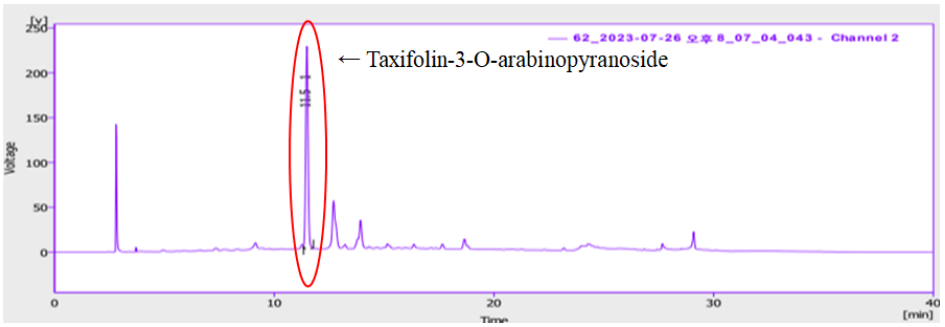

Fig. 23. HPLC chromatogram of the smple 41. Sample 41= *Rhododendron wumingens* W.P.Fang (Yunnan, China) 1,000 ppm.

species were not detected or did not meet the limit of detection (LOD), so they were treated as N.D. (Not Detected). When checked by region, standard compound was detected in 14 out of 20 species in China, 1 out of 8 species in Beijing, 4 out of 6 species in Yanbian, and 3 out of 9 species in Yunnan (Table 2).

LC-MS/MS analysis was performed on 22 species of the Chinese *Rhododendron* genus in which taxifolin-3-O-arabinopyranoside, a standard compound, was detected in HPLC analysis, and the molecular weight was compared with the standard compound. The molecular weight of the standard compound is 435-436 m/z under negative conditions, and the molecular weights of 22 Chinese *Rhododendron* species were analyzed under the same conditions. The data is shown in Figs. 24-45.

As a result of LC-MS/MS analysis, 14 species from China, 1 species from Beijing, 4 species from Yanbian, and 3 species from Yunnan all exhibited a molecular weight of 435-436 m/z, which is the same as the molecular weight of the standard compound (Table 3). Furthermore, the integration of HPLC and LC-MS/MS analysis results confirmed the presence of taxifolin-3-O-arabinopyranoside in a total of 22 out of 43 native *Rhododendron* species in China. This information is organized and presented in Table 4.

When checking the previously conducted chemotaxonomy research, there was research showing that taxifolin-3-O-arabinopyranoside was already present in some of the *Rhododendron* species tested (Ye et al. 2020; Zeng et al. 2021). In another study, HPLC and LC-MS/MS analysis confirmed that peaks with identical retention times and molecular weights were the same compound (Kim et al., 2022). Accordingly, since the same compound was found in more than half of the 43 samples conducted in this study, it can be said that taxifolin-3-O-arabinopyranoside is a common compound in Chinese *Rhododendron* species.

Conclusion

In this study, we conducted a chemotaxonomy study using taxifolin-3-O-arabinopyranoside, a flavonoid compound whose structure was directly isolated and purified from the root extract of the Korean native *R. mucronulatum* in previous research conducted by our research team. This compound can be considered an indicator substance for *Rhododendron* species native to China. Following HPLC quantitative analysis, taxifolin-3-O-arabinopyranoside was detected in 22 out of 43 species of the *Rhododendron* genus

Table 2. Data of HPLC analysis of *Rhododendron* genus native to China

No.	Habitat	Species	Retention time (min.)	Content (ppm)
1	China	*Rhododendron molle* (Blume) G. Don	N.D.	N.D.
2	China	*Rhododendron chionanthum* Tagg & Forrest	11.528±0.05	7.42±0.51
3	China	*Rhododendron delavayi* Franch.	N.D.	N.D.
4	China	*Rhododendron simsii* Planch.	N.D.	N.D.
5	China	*Rhododendron pubescens* Balf.f. & Forrest	11.528±0.04	120.23±16.24
6	China	*Rhododendron telmateium* Balf. F. & W.W. Sm.	11.500±0.02	28.81±0.96
7	China	*Rhododendron rupicola* var. *chryseum* (Balf. F. & Kingdon-Ward) Philipson & M.N. Philipson	11.489±0.01	44.86±5.40
8	China	*Rhododendron traillianum* var. *dictyotum* (Balf. F. ex Tagg) D.F. Chamb.	11.500±0.00	82.63±17.53
9	China	*Rhododendron primuliflorum* Bureau & Franch.	11.533±0.04	95.28±14.59
10	China	*Rhododendron hippophaeoides* Balf. f. & W.W. Sm.	11.533±0.03	96.47±22.34
11	China	*Rhododendron wardii* W.W. Sm.	11.517±0.03	33.90±3.34
12	China	*Rhododendron vernicosum* Franch.	11.522±0.01	37.01±4.83
13	China	*Rhododendron vaccinioides* Hook.	11.506±0.02	46.55±1.06
14	China	*Rhododendron rupicola* W.W. Sm.	11.483±0.04	36.59±5.00
15	China	*Rhododendron cephalanthum* Franch.	11.489±0.01	41.65±3.74
16	China	*Rhododendron glischrum* Balf. f. & W.W. Sm.	11.495±0.03	31.46±3.67
17	China	*Rhododendron mucronatum* (Blume) G. Don	N.D.	N.D.
18	China	*Rhododendron spiciferum* Franch.	N.D.	N.D.
19	China	*Rhododendron simsii* Planch.	N.D.	N.D.
20	China	*Rhododendron ovatum* (Lindl.) Planch. ex Maxim.	11.506±0.02	22.47±2.08
21	Beijing	*Rhododendron micranthum* Turcz.	N.D.	N.D.
22	Beijing	*Rhododendron mucronulatum* Turcz.	N.D.	N.D.
23	Beijing	*Rhododendron mucronulatum* Turcz.	11.483±0.02	28.94±0.84
24	Beijing	*Rhododendron ovatum* (Lindl.) Planch. ex Maxim.	N.D.	N.D.
25	Beijing	*Rhododendron kwangsiense* H.H. Hu ex P.C. Tam	N.D.	N.D.
26	Beijing	*Rhododendron ovatum* (Lindl.) Planch. ex Maxim.	N.D.	N.D.
27	Beijing	*Rhododendron championiae* Hook.	N.D.	N.D.
28	Beijing	*Rhododendron rivulare* Hand.-Mazz.	N.D.	N.D.
29	Yanbian	*Rhododendron dauricum* L.	11.472±0.05	12.79±1.76
30	Yanbian	*Rhododendron chrysanthum* Pall.	11.489±0.02	5.66±0.68
31	Yanbian	*Rhododendron schlippenbackii* Maxim	N.D.	N.D.
32	Yanbian	*Rhododendron schlippenbackii* Maxim.	N.D.	N.D.
33	Yanbian	*Rhododendron Parvifolium* Adams.	11.489±0.01	12.47±1.57
34	Yanbian	*Rhododendron mucronulatum* Turcz.	11.506±0.02	11.72±1.48
35	Yunnan	*Rhododendron decorum* Franch.	11.489±0.01	40.04±4.15
36	Yunnan	*Rhododendron annae* Franch.	N.D.	N.D.
37	Yunnan	*Rhododendron irroratum* Franch.	N.D.	N.D.
38	Yunnan	*Rhododendron strigillosum* Franch.	N.D.	N.D.
39	Yunnan	*Rhododendron lutescens* Franch.	N.D.	N.D.
40	Yunnan	*Rhododendron pumilum* Hook.f.	11.506±0.01	70.17±6.08
41	Yunnan	*Rhododendron wumingense* W.P.Fang	11.489±0.01	62.61±6.35
42	Yunnan	*Rhododendron minutiflorum* Hu	N.D.	N.D.
43	Yunnan	*Rhododendron microphyton* Franch.	N.D.	N.D.

N.D., not detected.

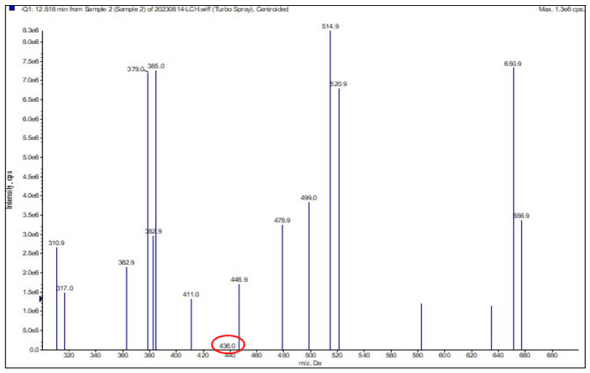

Fig. 24. Molecular weight of the sample 2. Sample 2=*Rhododendron chionanthum* Tagg & Forrest (436.0 m/z).

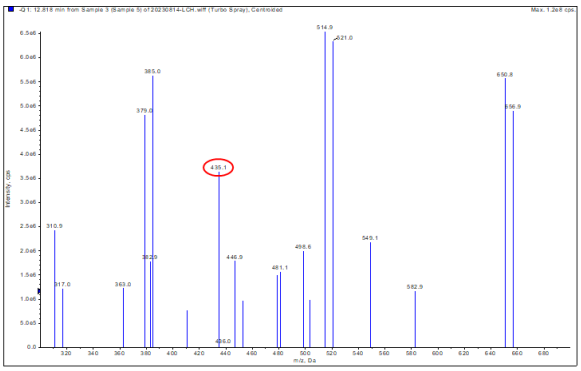

Fig. 25. Molecular weight of the sample 5. Sample 5=*Rhododendron pubescens* Balf. F. & Forrest (435.1 m/z).

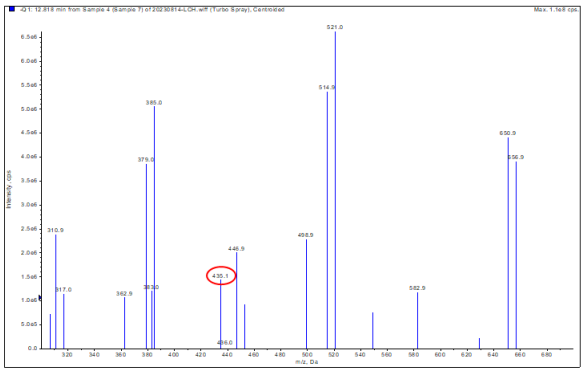

Fig. 26. Molecular weight of the sample 6. Sample 6=*Rhododendron telmateium* Balf. F. & W.W. Sm. (435.1 m/z).

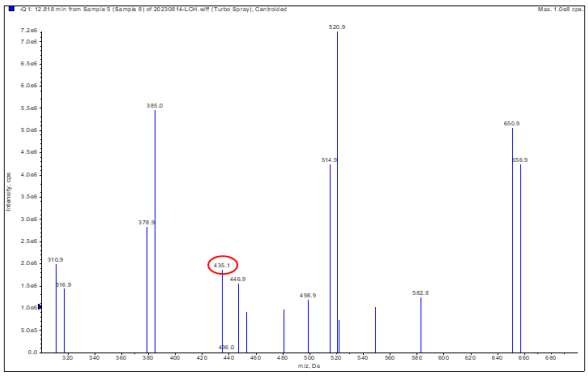

Fig. 27. Molecular weight of the sample 7. Sample 7=*Rhododendron rupicola* var. *chryseum* (Balf. F. & Kingdon-Ward) Philipson & M.N. Philipson (435.1 m/z).

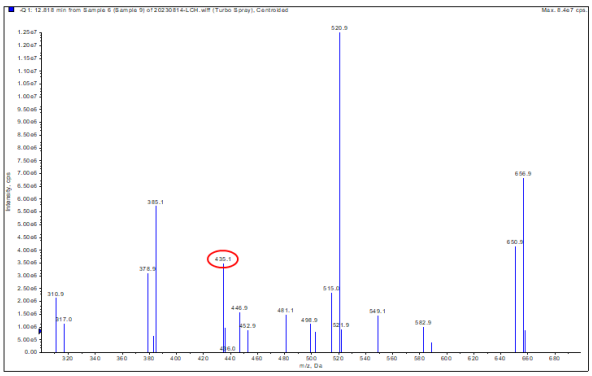

Fig. 28. Molecular weight of the sample 8. Sample 8=*Rhododendron traillianum* var. *dictyotum* (Balf. F. ex Tagg) D.F. Chamb. (435.1 m/z).

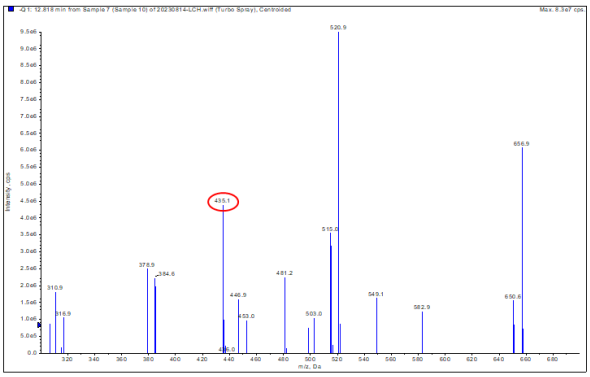

Fig. 29. Molecular weight of the sample 9. Sample 9=*Rhododendron primuliflorum* Bureau & Franch. (435.1 m/z).

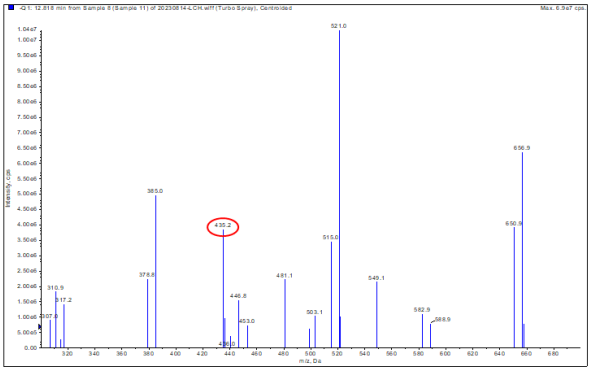

Fig. 30. Molecular weight of the sample 10. Sample 10=*Rhododendron hippophaeoides* Balf. f. & W.W. Sm. (435.2 m/z).

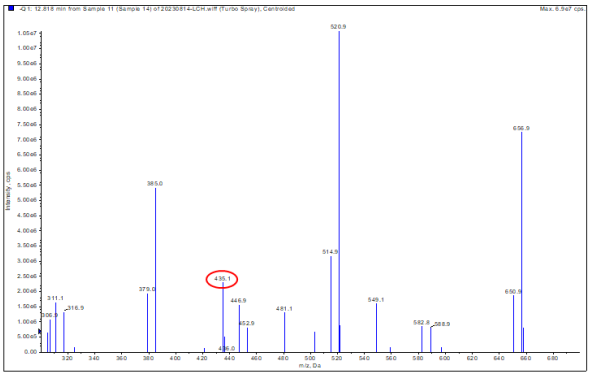

Fig. 33. Molecular weight of the sample 13. Sample 13=*Rhododendron vaccinioides* Hook. (435.1 m/z).

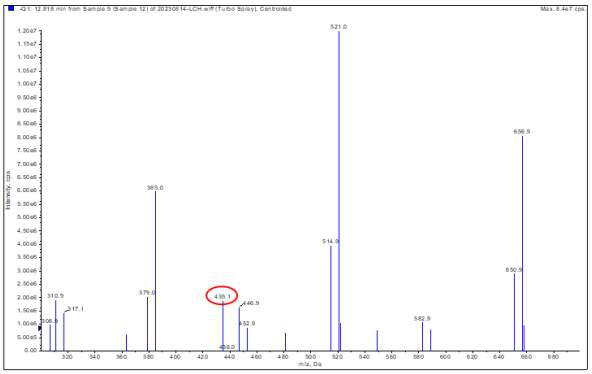

Fig. 31. Molecular weight of the sample 11. Sample 11=*Rhododendron wardii* W.W. Sm. (435.1 m/z).

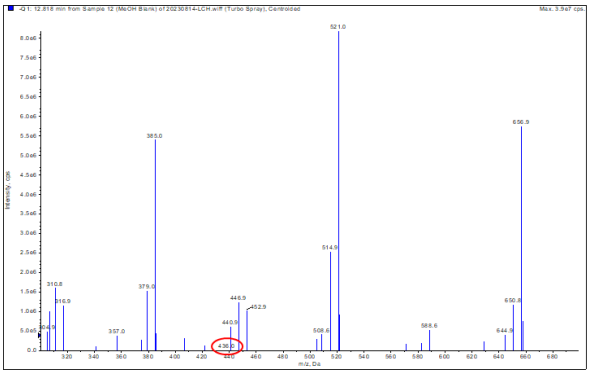

Fig. 34. Molecular weight of the sample 14. Sample 14=*Rhododendron rupicola* W.W. Sm. (436.0 m/z).

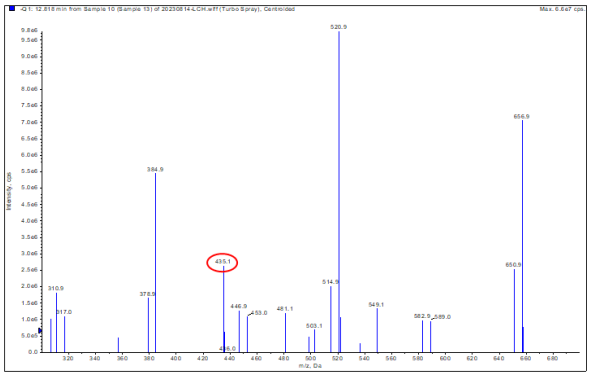

Fig. 32. Molecular weight of the sample 12. Sample 12=*Rhododendron vernicosum* Franch. (435.1 m/z).

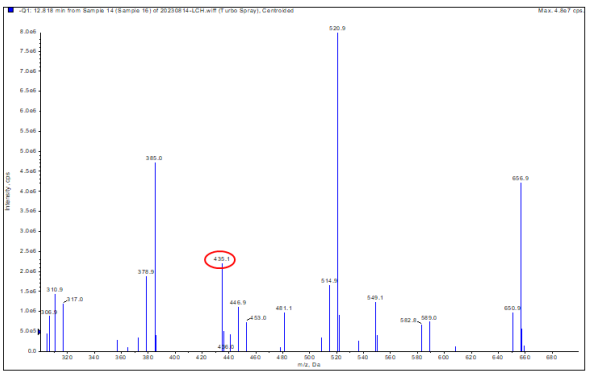

Fig. 35. Molecular weight of the sample 15. Sample 15=*Rhododendron cephalanthum* Franch. (435.1 m/z).

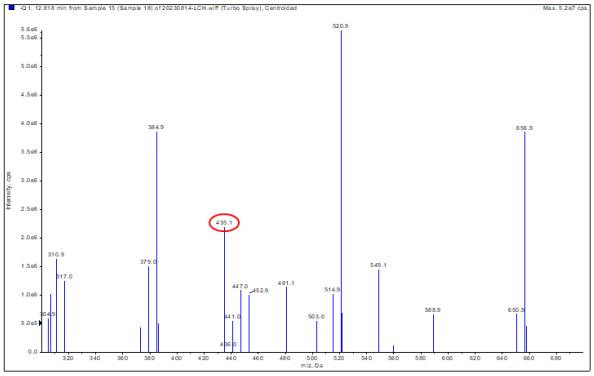

Fig. 36. Molecular weight of the sample 16. Sample 16=*Rhododendron glischrum* Balf. f. & W.W. Sm. (435.1 m/z).

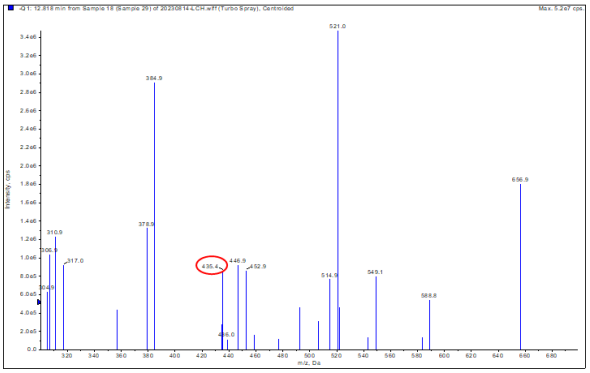

Fig. 39. Molecular weight of the sample 29. Sample 29=*Rhododendron dauricum* L. (435.4 m/z).

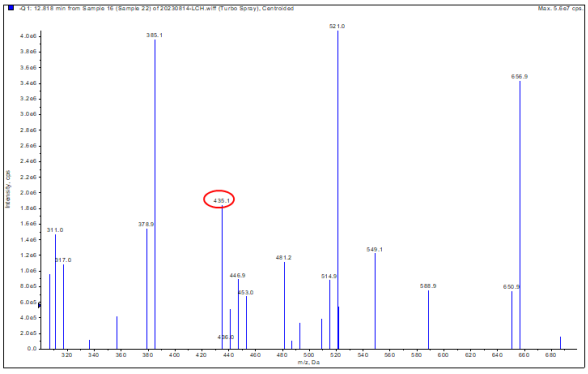

Fig. 37. Molecular weight of the sample 20. Sample 20=*Rhododendron ovatum* (Lindl.) Planch. ex Maxim. (435.1 m/z).

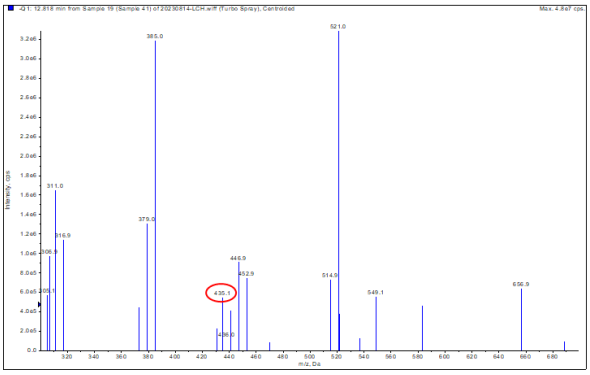

Fig. 40. Molecular weight of the sample 30. Sample 30=*Rhododendron chrysanthum* Pall. (435.1 m/z).

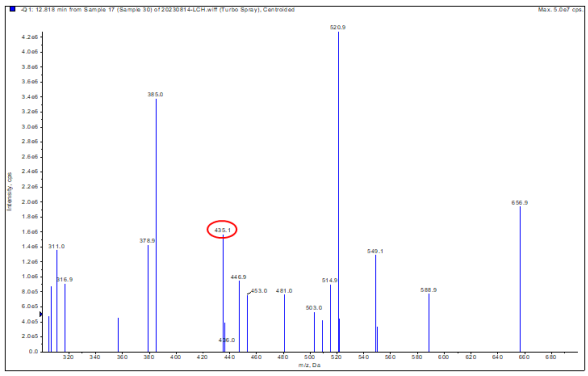

Fig. 38. Molecular weight of the sample 23. Sample 23=*Rhododendron mucronulatum* Turcz. (435.1 m/z).

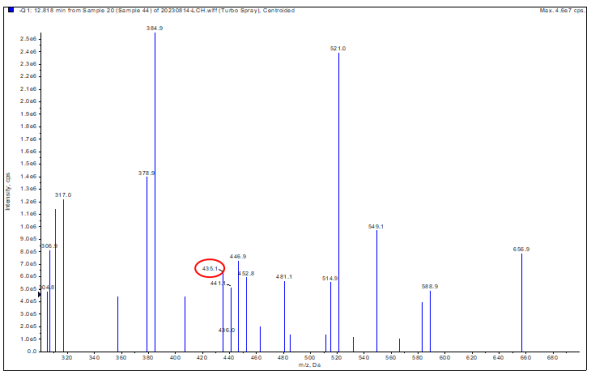

Fig. 41. Molecular weight of the sample 33. Sample 33=*Rhododendron Parvifolium* Adams. (435.1 m/z).

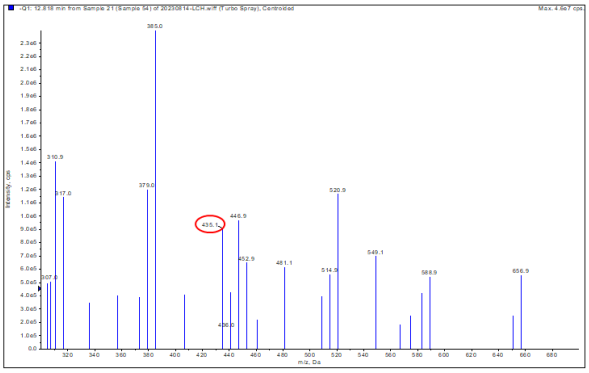

Fig. 42. Molecular weight of sample 34. Sample 34=*Rhododendron mucronulatum* Turcz. (435.1 m/z).

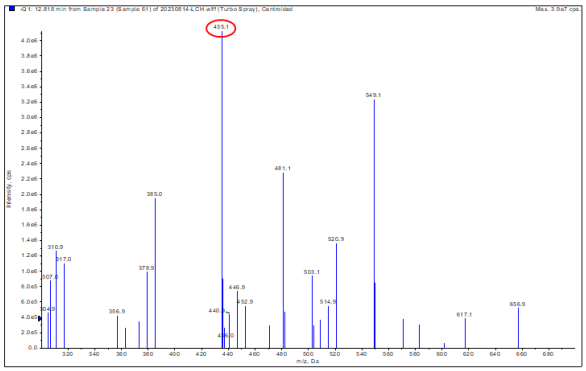

Fig. 44. Molecular weight of sample 40. Sample 40=*Rhododendron pumilum* Hook.f. (435.1 m/z).

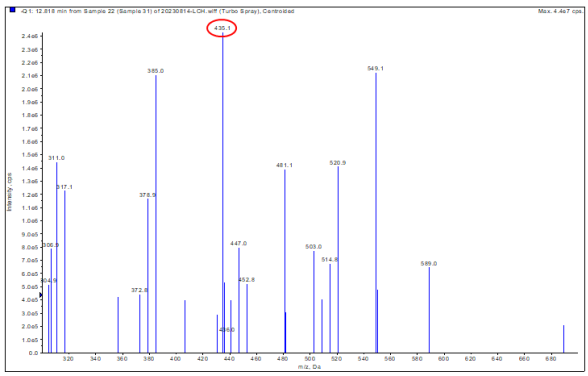

Fig. 43. Molecular weight of sample 35. Sample 35=*Rhododendron decorum* Franch. (435.1 m/z).

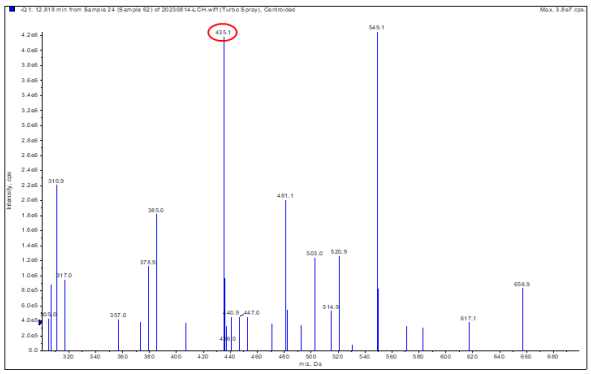

Fig. 45. Molecular weight of sample 41. Sample 41=*Rhododendron wumingense* W.P.Fang (435.1 m/z).

Table 3. LC-MS/MS data of *Rhododendron* genus native to China

No.	Habitat	Species	Molecular weight (m/z)
2	China	*Rhododendron chionanthum* Tagg & Forrest	436.0
5	China	*Rhododendron pubescens* Balf.f. & Forrest	435.1
6	China	*Rhododendron telmateium* Balf. F. & W.W. Sm.	435.1
7	China	*Rhododendron rupicola* var. *chryseum* (Balf. F. & Kingdon-Ward) Philipson & M.N. Philipson	435.1
8	China	*Rhododendron traillianum* var. *dictyotum* (Balf. F. ex Tagg) D.F. Chamb.	435.1
9	China	*Rhododendron primuliflorum* Bureau & Franch.	435.1
10	China	*Rhododendron hippophaeoides* Balf. f. & W.W. Sm.	435.2
11	China	*Rhododendron wardii* W.W. Sm.	435.1
12	China	*Rhododendron vernicosum* Franch.	435.1
13	China	*Rhododendron vaccinioides* Hook.	435.1
14	China	*Rhododendron rupicola* W.W. Sm.	436.0
15	China	*Rhododendron cephalanthum* Franch.	435.1
16	China	*Rhododendron glischrum* Balf. f. & W.W. Sm.	435.1
20	China	*Rhododendron ovatum* (Lindl.) Planch. ex Maxim.	435.1
23	Beijing	*Rhododendron mucronulatum* Turcz.	435.1
29	Yanbian	*Rhododendron dauricum* L.	435.4
30	Yanbian	*Rhododendron chrysanthum* Pall.	435.1
33	Yanbian	*Rhododendron Parvifolium* Adams.	435.1
34	Yanbian	*Rhododendron mucronulatum* Turcz.	435.1
35	Yunnan	*Rhododendron decorum* Franch.	435.1
40	Yunnan	*Rhododendron pumilum* Hook.f.	435.1
41	Yunnan	*Rhododendron wumingense* W.P.Fang	435.1

Table 4. Existence of Taxifolin-3-O-arabinopyranoside in *Rhododendron* genus native to China

No.	Habitat	Species	Taxifolin-3-O-arabinopyranoside
1	China	*Rhododendron molle* (Blume) G. Don	X
2	China	*Rhododendron chionanthum* Tagg & Forrest	O
3	China	*Rhododendron delavayi* Franch.	X
4	China	*Rhododendron simsii* Planch.	X
5	China	*Rhododendron pubescens* Balf.f. & Forrest	O
6	China	*Rhododendron telmateium* Balf. F. & W.W. Sm.	O
7	China	*Rhododendron rupicola* var. *chryseum* (Balf. F. & Kingdon-Ward) Philipson & M.N. Philipson	O
8	China	*Rhododendron traillianum* var. *dictyotum* (Balf. F. ex Tagg) D.F. Chamb.	O
9	China	*Rhododendron primuliflorum* Bureau & Franch.	O
10	China	*Rhododendron hippophaeoides* Balf. f. & W.W. Sm.	O
11	China	*Rhododendron wardii* W.W. Sm.	O
12	China	*Rhododendron vernicosum* Franch.	O
13	China	*Rhododendron vaccinioides* Hook.	O
14	China	*Rhododendron rupicola* W.W. Sm.	O
15	China	*Rhododendron cephalanthum* Franch.	O
16	China	*Rhododendron glischrum* Balf. f. & W.W. Sm.	O
17	China	*Rhododendron mucronatum* (Blume) G. Don	X
18	China	*Rhododendron spiciferum* Franch.	X
19	China	*Rhododendron simsii* Planch.	X
20	China	*Rhododendron ovatum* (Lindl.) Planch. ex Maxim.	O
21	Beijing	*Rhododendron micranthum* Turcz.	X
22	Beijing	*Rhododendron mucronulatum* Turcz.	X
23	Beijing	*Rhododendron mucronulatum* Turcz.	O
24	Beijing	*Rhododendron ovatum* (Lindl.) Planch. ex Maxim.	X
25	Beijing	*Rhododendron kwangsiense* H.H. Hu ex P.C. Tam	X
26	Beijing	*Rhododendron ovatum* (Lindl.) Planch. ex Maxim.	X
27	Beijing	*Rhododendron championiae* Hook.	X
28	Beijing	*Rhododendron rivulare* Hand.-Mazz.	X
29	Yanbian	*Rhododendron dauricum* L.	O
30	Yanbian	*Rhododendron chrysanthum* Pall.	O
31	Yanbian	*Rhododendron schlippenbackii* Maxim	X
32	Yanbian	*Rhododendron schlippenbackii* Maxim.	X
33	Yanbian	*Rhododendron Parvifolium* Adams.	O
34	Yanbian	*Rhododendron mucronulatum* Turcz.	O
35	Yunnan	*Rhododendron decorum* Franch.	O
36	Yunnan	*Rhododendron annae* Franch.	X
37	Yunnan	*Rhododendron irroratum* Franch.	X
38	Yunnan	*Rhododendron strigillosum* Franch.	X
39	Yunnan	*Rhododendron lutescens* Franch.	X
40	Yunnan	*Rhododendron pumilum* Hook.f.	O
41	Yunnan	*Rhododendron wumingense* W.P.Fang	O
42	Yunnan	*Rhododendron minutiflorum* Hu	X
43	Yunnan	*Rhododendron microphyton* Franch.	X

native to China. Subsequent LC-MS/MS analysis confirmed that these 22 species exhibited the same molecular weight (435-436 m/z) as the standard compound under identical negative conditions.

Building upon our research team's prior study, which established taxifolin-3-O-arabinopyranoside as an indicator substance in Korean *Rhododendron* species (Kim et al. 2022), the current study detected taxifolin-3-O-arabinopyranoside in over half of the *Rhododendron* species in China. This reinforces the role of taxifolin-3-O-arabinopyranoside as an indicator substance not only for *Rhododendron* species native to Korea but also for those native to China. Furthermore, these results provide essential data for the chemical classification of Chinese native *Rhododendron* species.

In addition, this suggests that taxifolin-3-O-arabinopyranoside is an indicator substance for a variety of *Rhododendron* genus in China and other countries, making it a fundamental research result for preparing chemical classification data for *Rhododendron* species around the world. Furthermore, the possibility of developing a new functional material was confirmed by discovering plants species of the *Rhododendron* genus that are valuable as useful resources.

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