

Table S1

Chromatographic parameters for simultaneous analysis of five marker components in *P. pubescens* leaves by HPLC

Chromatographic parameter			
Column	Gemini C ₁₈ analytical column (250 mm × 4.6 mm, 5 μm)		
Detector	DAD (310, 325, 335, and 350 nm)		
Flow rate	1.0 mL/min		
Injection volume	10.0 μL		
Column temperature	40.0 °C		
Mobile phase	A: 0.1% (v/v) aqueous formic acid		
	B: 0.1% (v/v) formic acid in acetonitrile		
Gradient elution	Time (min)	A (%)	B (%)
	0	95	5
	25	40	60
	30	60	60
	35	95	5
	45	95	5

DAD; diode array detector

Table S2

System suitability for HPLC analysis of the five marker components

Compound	k'	α	N	R_s	T_f
Chlorogenic acid	2.94	1.19	399752	14.09	1.08
Isoorientin	3.50	1.19	650618	3.46	1.10
Orientin	3.63	1.04	633528	3.46	1.08
Isovitexin	3.95	1.03	722500	2.62	1.06
<i>p</i> -Coumaric acid	4.06	1.03	529916	2.62	1.05

k' ; capacity factor, α ; relative retention, N ; theoretical plate number, R_s ; resolution, and T_f ; tailing factor

Table S3Repeatability of retention time of the five marker analytes using HPLC ($n = 6$)

No.	Retention time (min)				
	Chlorogenic acid	Isoorientin	Orientin	Isovitexin	<i>p</i> -Coumaric acid
1	12.23	13.91	14.33	15.29	15.65
2	12.24	13.92	14.34	15.31	15.66
3	12.24	13.92	14.34	15.31	15.66
4	12.24	13.92	14.34	15.30	15.66
5	12.24	13.92	14.34	15.31	15.66
6	12.25	13.93	14.34	15.31	15.66
Mean	12.24	13.92	14.34	15.30	15.66
SD	0.01	0.01	0.01	0.01	0.01
RSD (%)	0.06	0.04	0.04	0.04	0.04

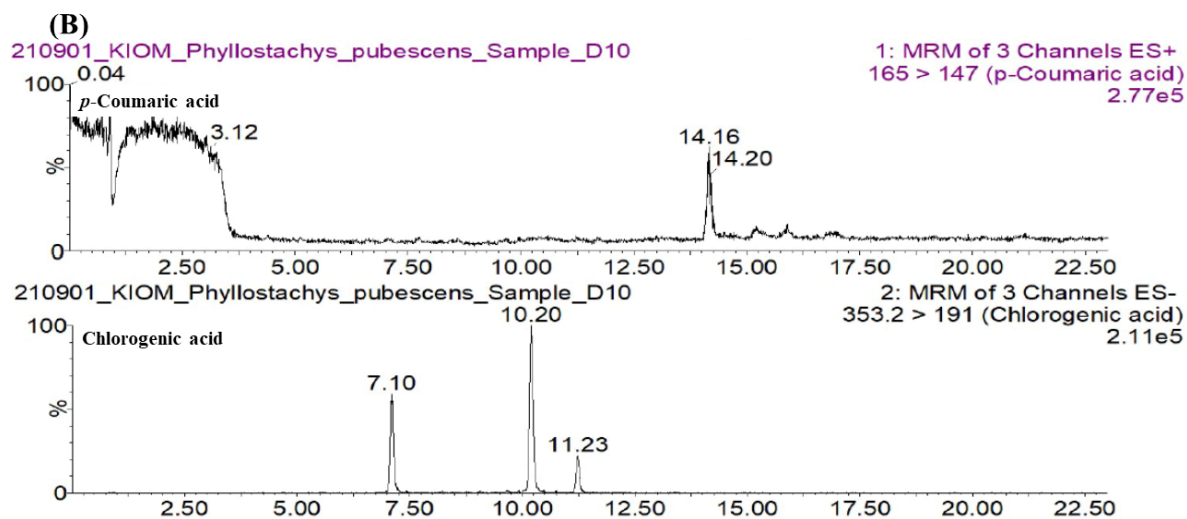
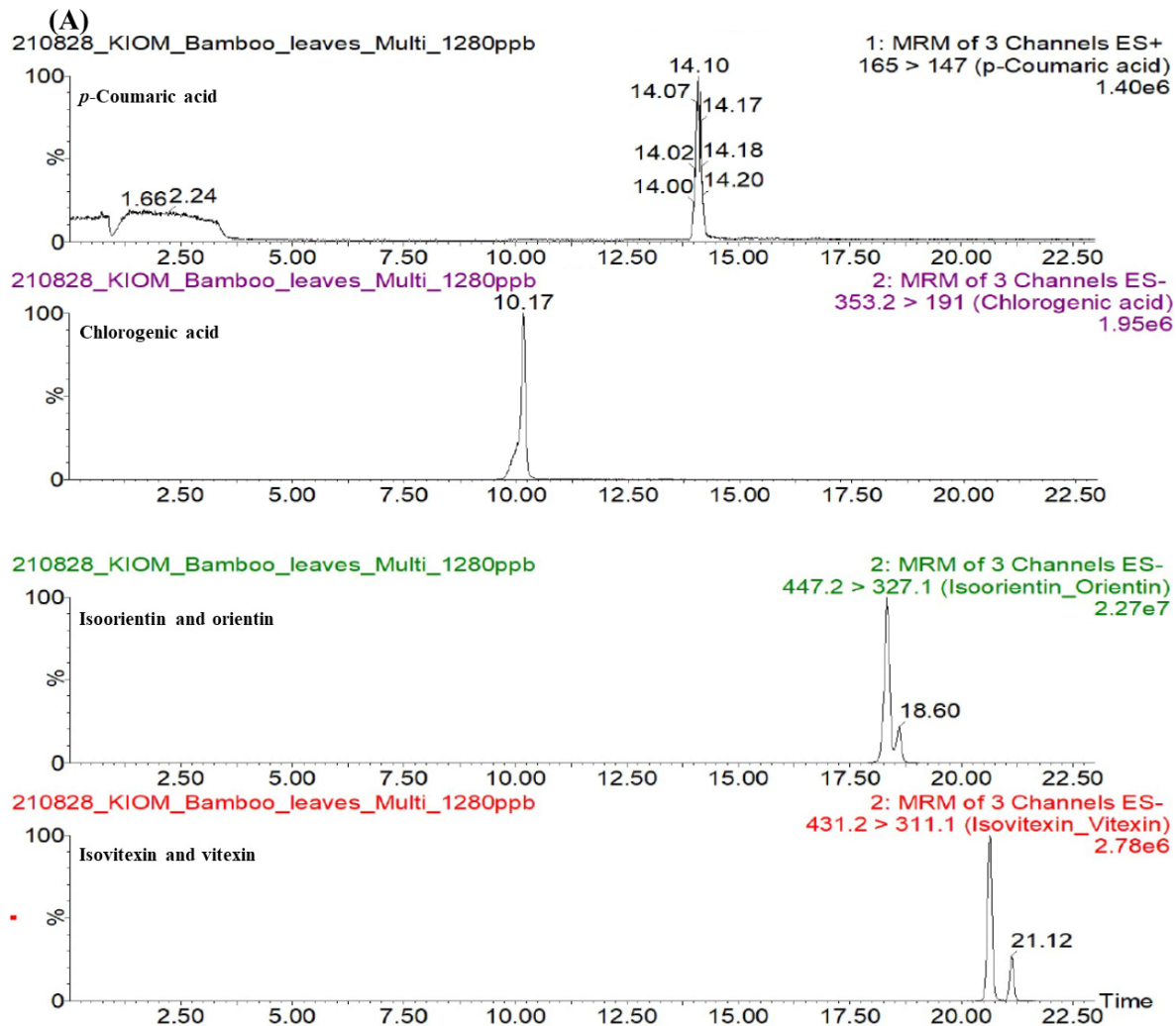
Table S4Repeatability of peak area of the five marker analytes using HPLC ($n = 6$)

No.	Peak area				
	Chlorogenic acid	Isoorientin	Orientin	Isovitexin	<i>p</i> -Coumaric acid
1	1,770,950	1,506,998	1,292,847	1,423,144	1,897,993
2	1,767,368	1,502,200	1,288,098	1,418,291	1,890,987
3	1,794,637	1,525,428	1,306,379	1,438,257	1,918,884
4	1,768,468	1,505,733	1,287,574	1,419,711	1,893,611
5	1,780,640	1,519,401	1,298,785	1,432,187	1,909,363
6	1,791,903	1,528,323	1,309,987	1,443,697	1,924,334
Mean	1,778,994.33	1,514,680.50	1,297,278.33	1,429,214.50	1,905,862.00
SD	12,039.28	11,124.31	9430.71	10,457.87	13,829.81
RSD (%)	0.68	0.73	0.73	0.73	0.73

Table S5LC–MS/MS MRM analysis conditions for quantification of markers in *P. pubescens* leaves

UPLC conditions		MS conditions	
UPLC system	Acquity UPLC I-Class	MS system	Xevo TQ-XS
Column	Acquity UPLC BEH C ₁₈ column (2.1 mm × 100 mm, 1.7 μm)	MS software	MassLynx v4.2
Column temp.	45 °C	Ion source	ESI ⁺ or ESI ⁻
Sample temp.	5 °C	Acquisition mode	MRM
Injection volume	2.0 μL	Capillary voltage	3.0 kV
Flow rate	0.3 mL/min	Cone gas flow	50 L/h
Mobile phase A	0.1% (v/v) formic acid and 5 mM ammonium formate in distilled water	Desolvation gas flow	700 L/h
Mobile phase B	Acetonitrile	Desolvation temp.	500 °C
Gradient	Time (min)	A (%)	B (%)
	Initial	100	0
	23	85	15
	23.1	5	95
	24.9	5	95
	25.0	100	0
	28.0	100	0

ESI; electrospray ionization, MRM; multiple reaction monitoring



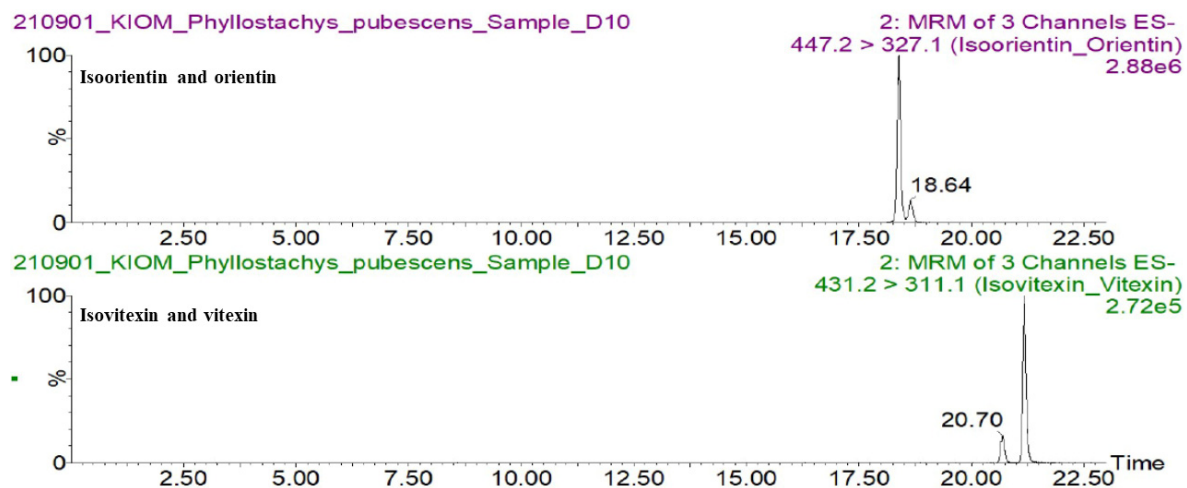


Figure S1. Extracted ion chromatograms of each standard marker (A) and marker compound in 80% ethanol extract of the microwave-dried *P. pubescens* leaves sample (B) measured by LC-MS/MS MRM mode.

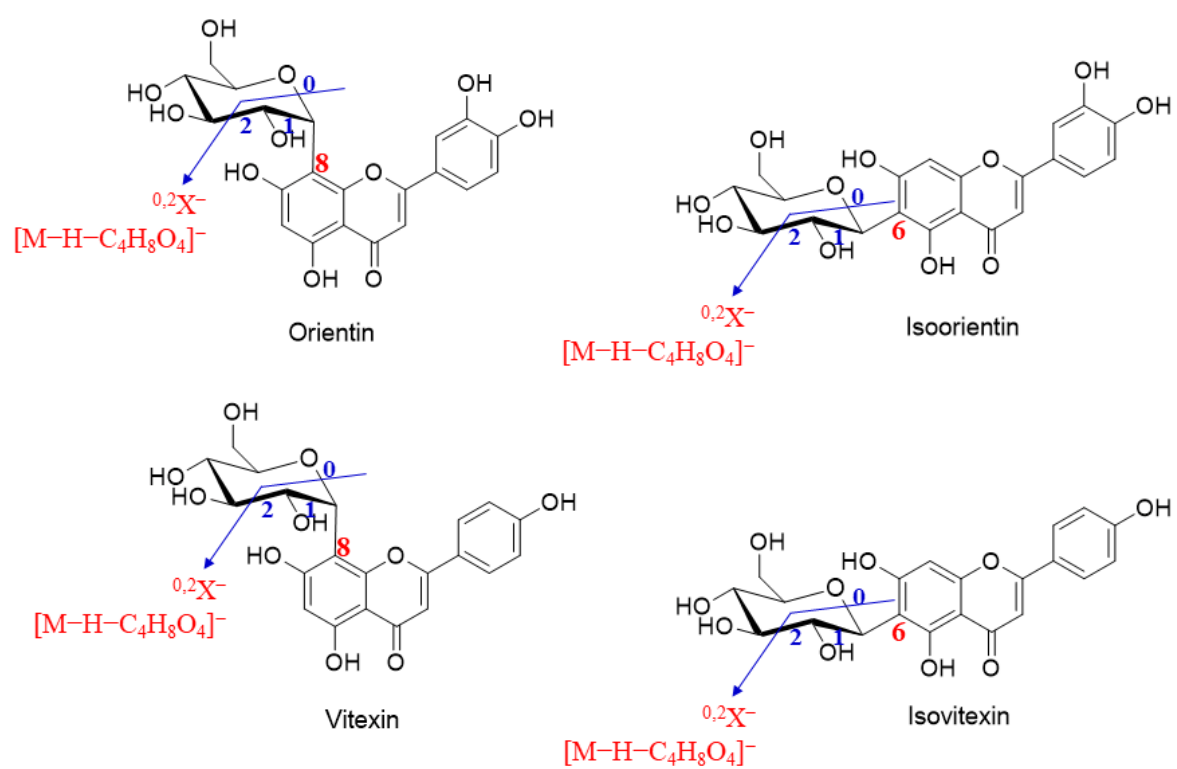


Figure S2. Fragmentation of the C-glycosides

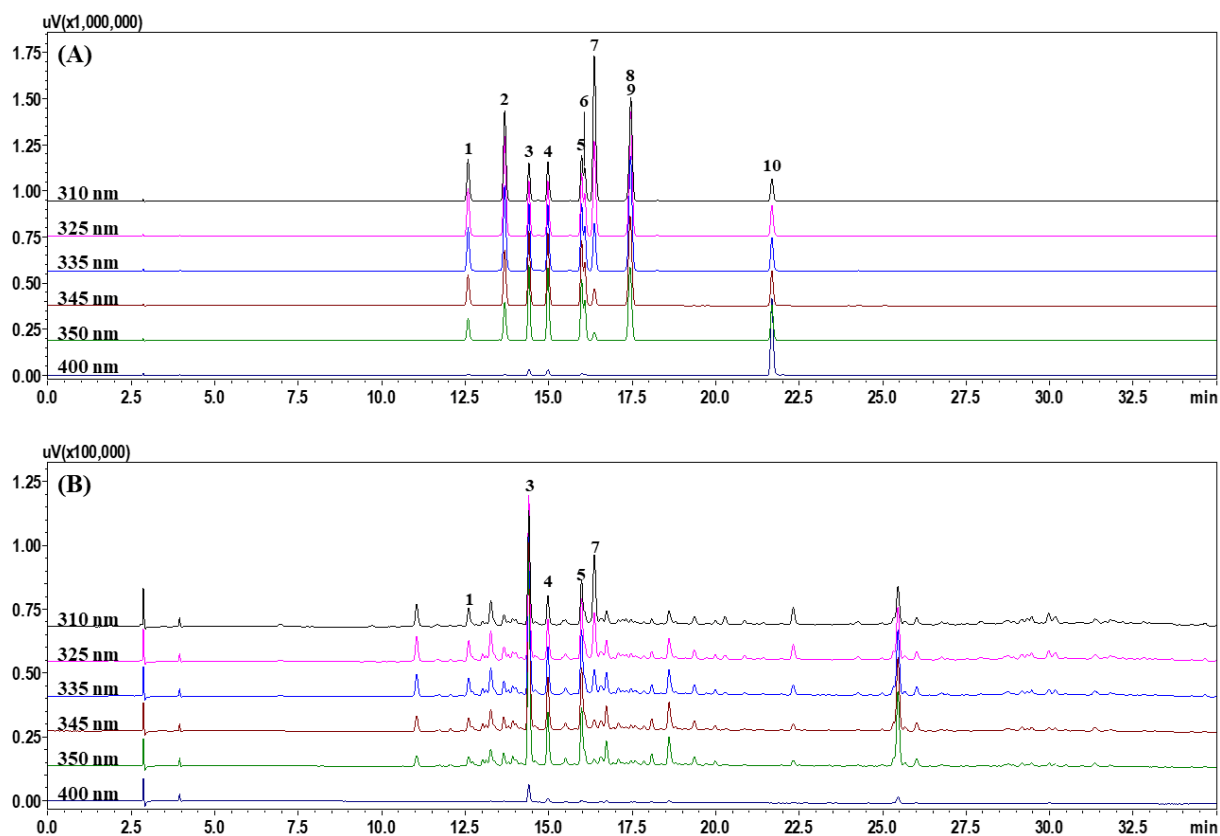


Figure S3. Chromatogram standard solution (A), *P. pubescens* leaves sample (B) for selecting marker components of *P. pubescens* leaves by HPLC–DAD analysis system. Chlorogenic acid (1), caffeic acid (2), isoorientin (3), orientin (4), isovitexin (5), vitexin (6), *p*-coumaric acid (7), ferulic acid (8), scopoletin (9), and triclin (10).

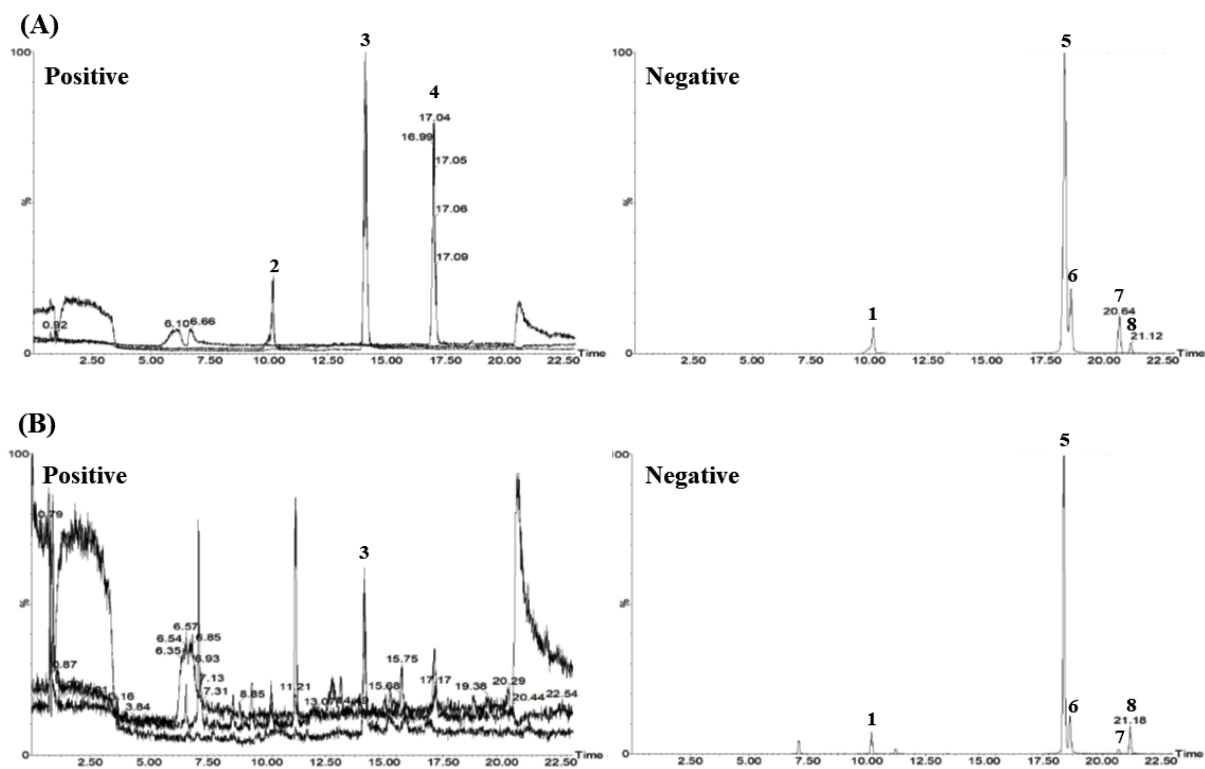


Figure S4. Total ion chromatogram standard solution (A), *P. pubescens* leaves sample (B) for selecting marker components of *P. pubescens* leaves by LC-MS/MS MRM analysis system in positive and negative ion modes. Chlorogenic acid (1), caffeic acid (2), *p*-coumaric acid (3), ferulic acid (4), isorientin (5), orientin (6), vitexin (7), and isovitexin (8).

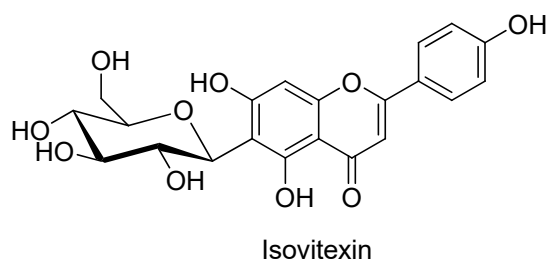
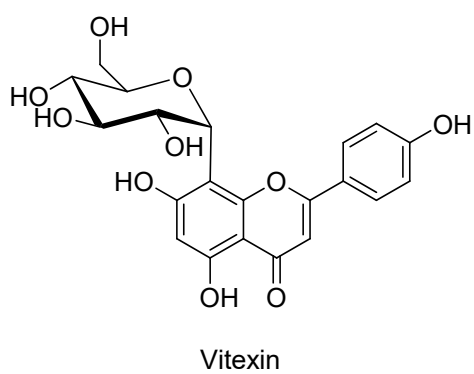
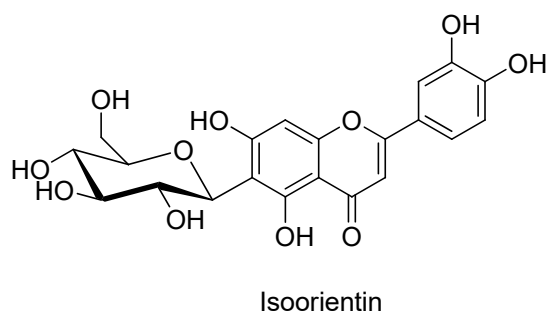
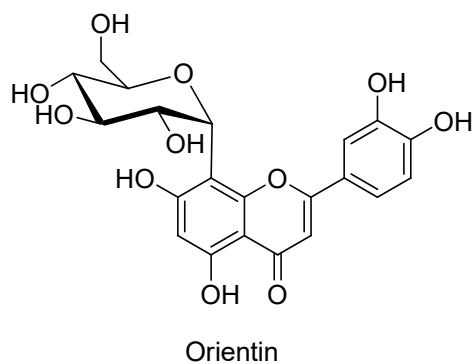
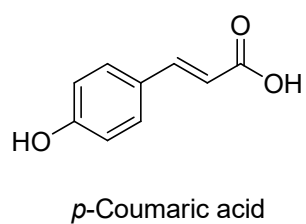
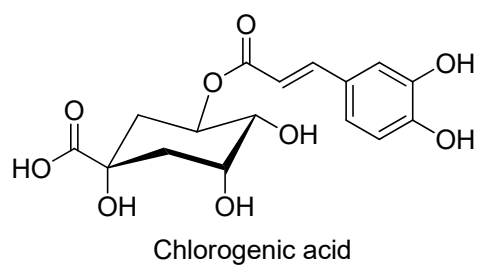


Figure S5. Chemical structures of the six marker components in *P. pubescens* leaves