

# Metabolomics Reveals Discrimination of Chinese Propolis from Different Climatic Regions

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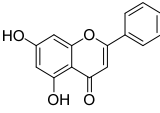
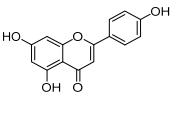
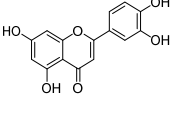
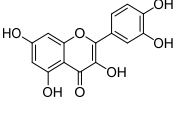
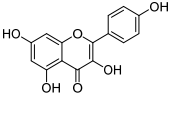
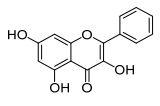
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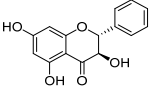
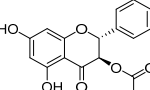
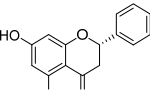
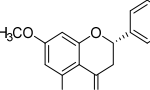
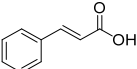
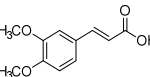
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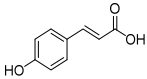
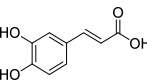
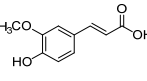
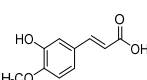
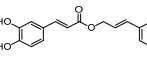
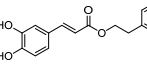
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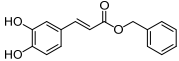
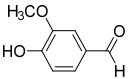
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**Table S1.** Assignment of chemical compositions in CWTP and CMTP.

No.	Types	Identified compound	Structure of compound	Characteristic $\delta^1\text{H}$ (ppm) and multiplicity	$\delta^{13}\text{C}$ (ppm)
1		Chrysin		7.86 (d, $J = 7.3$ Hz), 6.49 (d, $J = 1.8$ Hz, H-8), 6.34 (d, $J = 1.8$ Hz, H-6).	163.3 (C-2), 105.5 (C-3), 161.0 (C-5), 99.0 (C-6), 164.4 (C-7), 94.3 (C-8), 103.7 (C-10), 131.0 (C-1'), 126.4 (C-3' and 5'), 129.3 (C-2' and 6'), 132.0 (C-4').
2	Flavone	Apigenin		7.89 (d, $J = 7.0, 1.2$ Hz, H-2' and 6'), 6.53 (d, $J = 2.0$ Hz, H-8).	164.4 (C-2), 105.3 (C-3), 162.0 (C-5), 99.8 (C-6), 164.2 (C-7), 94.5 (C-8), 158.0 (C-9), 103.7 (C-10), 128.5 (C-2' and 6'), 116.0 (C-3' and 5'), 162.5 (C-4').
3		Luteolin		6.70 (s, H-3), 6.88 (d, $J = 8.4$ Hz, H-5').	164.2 (C-2), 105.5 (C-3), 162.0 (C-5), 99.0 (C-6), 164.5 (C-7), 94.3 (C-8), 158.0 (C-9), 103.7 (C-10), 113.1 (C-2'), 146.6 (C-3'), 150.1 (C-4'), 115.7 (C-5').
4		Quercetin		6.91 (d, $J = 8.0$ Hz, H-5'), 7.74 (dd, $J = 8.0, 2.0$ Hz, H-2').	146.6 (C-2), 135.1 (C-3), 161.5 (C-5), 98.4 (C-6), 163.7 (C-7), 94.5 (C-8), 156.0 (C-9), 102.9 (C-10), 122.4 (C-1'), 115.2 (C-2'), 145.1 (C-3'), 115.4 (C-5').
5	Flavonol	Kaempferol		8.09 (d, $J = 8.2$ Hz, H-2' and 6'), 6.38 (d, $J = 2.0$ Hz, H-8).	146.7 (C-2), 136.1 (C-3), 161.5 (C-5), 98.4 (C-6), 163.1 (C-7), 93.5 (C-8), 103.1 (C-10), 122.4 (C-1'), 129.5 (C-2' and C-6'), 115.4 (C-3' and C-5'), 158.0 (C-4').
6		Galangin		8.18 (d, $J = 7.6$ Hz, H-2' and 6'), 6.49 (d, $J = 1.8$ Hz, H-8), 6.28 (d, $J = 1.8$ Hz, H-6).	145.5 (C-2), 138.0 (C-3), 178.3 (C-4), 161.0 (C-5), 98.4 (C-6), 164.4 (C-7),

				93.6 (C-8), 157.0 (C-9), 102.4 (C-10), 122.5 (C-1'), 127.6 (C-2' and C-6'), 128.6 (C-3' and C-5'), 130.0 (C-4').
7	Pinobanks in		5.08 (d, $J = 11.9$ Hz, H-3), 4.56 (d, $J = 11.9$ Hz, H-2).	83.3 (C-2), 72.4 (C-3), 195.9 (C-4), 163.1 (C-5), 96.0 (C-6), 163.7 (C-7), 96.8 (C-8), 167.7 (C-9), 100.6 (C-10), 136.5 (C-1'), 127.6 (C-2' and 6'), 128.7 (C-3' and 5'), 129.1 (C-4').
Flavanonol				
8	Pinobanks in-3-O- acetate		6.08 (d, $J = 2.0$ Hz, H-8), 6.03 (d, $J = 2.0$ Hz, H-6), 5.81 (d, $J = 12.0$ Hz, H-3), 2.03 (s, CH <sub>3</sub> -3).	20.3 (CH <sub>3</sub> ), 168.1 (acetyl), 81.2 (C-2), 72.4 (C-3), 191.5 (C-4), 165.5 (C-5), 96.8 (C-6), 167.7 (C-7), 95.7 (C-8), 163.0 (C-9), 101.6 (C-10), 136.1 (C-1'), 128.0 (C-2' and 6'), 128.9 (C-3' and 5'), 129.5 (C-4').
9	Pinocemb rin		2.82 (dd, $J = 17.2, 3.2$ Hz, H-3), 3.09 (dd, $J = 17.2, 13.1$ Hz, H-3), 5.41 (dd, $J = 13.1, 3.2$ Hz, H-2).	79.2 (C-2), 43.3 (C-3), 195.8 (C-4), 165.5 (C-5), 96.8 (C-6), 167.7 (C-7), 95.2 (C-8), 164.2 (C-9), 102.9 (C-10), 138.3 (C-1'), 127.4 (C-2' and 6'), 129.1 (C-3' and 5'), 129.3 (C-4').
Flavanone				
10	Pinostrobin		2.84 (dd, $J = 17.2, 3.2$ Hz, H-3), 3.11 (dd, $J = 17.2, 13.1$ Hz, H-3), 5.43 (dd, $J = 13.1, 3.2$ Hz, H-2).	55.7 (OCH <sub>3</sub> ), 79.2 (C-2), 43.2 (C-3), 195.6 (C-4), 164.2 (C-5), 95.2 (C-6), 168.1 (C-7), 94.0 (C-8), 162.8 (C-9), 103.1 (C-10), 138.3 (C-1'), 126.1 (C-2' and 6'), 128.9 (C-3' and 5'), 129.5 (C-4').
11	Phenolic acid		6.43 (d, $J = 16.0$ Hz, H-2), 7.73 (d, $J = 16.0$ Hz, H-1).	169.5 (C-1), 118.5 (C-2), 146.7 (C-3), 136.1 (C-1'), 129.5 (C-2' and 6'), 130.7 (C-3' and 5'), 131.0 (C-4').
12	3,4- Dimethox		6.34 (d, $J = 16.0$ Hz, H-2), 7.68 (d, $J = 16.0$ Hz, H-1), 3.90 (s, OCH <sub>3</sub> ),	169.5 (C-1), 115.9 (C-2), 146.7 (C-3), 127.4 (C-1'),

	ycinnamic acid		3.92 (s, OCH <sub>3</sub> ).	110.5 (C-2'), 147.0 (C-3'), 156.7 (C-4'), 115.3 (C-5'), 124.1 (C-6'), 56.0 (OCH <sub>3</sub> ), 55.7 (OCH <sub>3</sub> ).
13	<i>p</i> -Coumaric acid		6.33 (d, <i>J</i> = 16.0 Hz, H-2), 6.85 (d, <i>J</i> = 8.0 Hz, H-3' and 5').	118.5 (C-2), 147.1 (C-3), 134.0 (C-1'), 128.4 (C-2' and 6'), 129.0 (C-3' and 5'), 130.8 (C-4').
14	Caffeic acid		7.06 (d, <i>J</i> = 2.0 Hz, H-2'), 6.98 (dd, <i>J</i> = 8.0, 2.0 Hz, H-6'), 6.30 (d, <i>J</i> = 16.0 Hz, H-5').	115.4 (C-2), 147.0 (C-3), 127.7 (C-1'), 115.1 (C-2'), 149.4 (C-3'), 146.7 (C-4'), 116.5 (C-5'), 122.8 (C-6').
15	Ferulic acid		7.61 (d, <i>J</i> = 16.0 Hz, H-1), 6.33 (d, <i>J</i> = 16.0 Hz, H-2), 7.07 (dd, <i>J</i> = 8.0, 2.0 Hz, H-6'), 3.84 (s, OCH <sub>3</sub> -3').	56.4 (OCH <sub>3</sub> ), 111.7 (C-2), 149.4 (C-3), 127.6 (C-1'), 116.6 (C-2'), 150.5 (C-3'), 147.1 (C-4'), 115.9 (C-5'), 124.1 (C-6').
16	<i>iso</i> Ferulic acid		6.24 (d, <i>J</i> = 16.0 Hz, H-2), 7.07 (dd, <i>J</i> = 8.0, 2.0 Hz, H-6'), 3.93 (s, OCH <sub>3</sub> -4').	55.7 (OCH <sub>3</sub> ), 167.7 (C-1), 122.4 (C-2), 144.1 (C-3), 127.3 (C-1'), 114.2 (C-2'), 146.6 (C-3'), 149.9 (C-4'), 113.0 (C-5'), 115.9 (C-6').
17	Phenolic acid ester Cinnamyl caffeate		4.71 (t, <i>J</i> = 6.0 Hz, CH <sub>2</sub> -1'), 6.71 (dt, <i>J</i> = 15.8, 2.1 Hz, H-3'), 6.40 (dt, <i>J</i> = 15.8, 6.0 Hz, H-2').	169.0 (C-1), 116.5 (C-2), 147.1 (C-3), 129.0 (C-1'), 114.9 (C-2'), 146.7 (C-3'), 149.6 (C-4'), 115.1 (C-5'), 123.0 (C-6' and 8''), 137.8 (C-1''), 127.7 (C-2'' and 6''), 129.6 (C-3'' and 5''), 124.6 (C-4''), 135.0 (C-7''), 66.0 (C-9'').
18	Phenethyl caffeate (CAPE)		4.32 (t, <i>J</i> = 6.6 Hz, CH <sub>2</sub> -1'), 3.02 (t, <i>J</i> = 7.0 Hz, CH <sub>2</sub> -2').	167.7 (C-1), 114.2 (C-2), 145.2 (C-3), 127.6 (C-1'), 115.5 (C-2' and 5'), 146.5 (C-3'), 144.0 (C-4'), 126.6

			(C-6'), 138.3 (C-1''), 128.5 (C-2'' and 6''), 128.9 (C-3'' and 5''), 122.5 (C-4''), 36.3 (C-7''), 65.2 (C-8'').
19	Benzyl caffeate		5.23 (s, CH <sub>2</sub> -1').
			167.7 (C-1), 122.4 (C-2), 144.1 (C-3), 126.4 (C-1'), 114.2 (C-2'), 145.4 (C-4'), 114.2 (C-5'), 115.3 (C-6'), 136.0 (C-1''), 128.3 (C-2'' and 6''), 127.7 (C-3'' and 5''), 121.6 (C-4''), 65.3 (C-7'').
20	Aliphatic acid	-	1.26 (brs, CH <sub>2</sub> ), 0.89 (t, <i>J</i> = 7.2 Hz, CH <sub>3</sub> ).
21	Other compounds Vanillin		9.82 (s, CHO).
			191.5 (CHO), 56.0 (CH <sub>3</sub> O), 129.5 (C-1), 114.2 (C-2), 146.6 (C-3), 151.6 (C-4), 127.5 (C-6).

s, single; d, doublet; t, triplet; q, quartet; m, multiplet; dd, doublet of doublet; dt, doublet of triplet; brs, broad single.

**Table S2.** OPLS-DA correlation coefficients p(corr) and VIP values of the discriminating compositions towards classification.

No.	Component	Resonance (ppm)	p(corr)	VIP
1	Chrysin	7.86	+0.70	2.6
2	Apigenin	7.89	+0.75	1.3
5	Kaempferol	8.09	+0.81	1.2
6	Galangin	8.18	+0.63	2.2
9	Pinocembrin	2.82	-0.80	1.6
11	Cinnamic acid	6.43	+0.64	1.2
12	3,4-Dimethoxycinnamic acid	6.34	+0.72	2.6
13	<i>p</i> -Coumaric acid	6.85	+0.81	2.4
14	Caffeic acid	6.30	+0.70	1.2
15	Ferulic acid	6.33	+0.71	1.8
16	<i>iso</i> Ferulic acid	6.24	+0.65	1.5
17	Cinnamyl caffeate	6.71	+0.72	1.6