

Supplementary Materials:

Table S1. Details of samples of Acanthopanax Cortex and Periplocae Cortex.

No.	Sample Name	Batch Code	Origin	Collection place
W-01	Acanthopanax Cortex	20201001	Jilin Province	Drug store, Jingmen, Hubei
W-02	Acanthopanax Cortex	201907001	Hebei Province	Drug store, Xiangyang, Hubei
W-03	Acanthopanax Cortex	180101	Hubei Province	Drug store, Xiangyang, Hubei
W-04	Acanthopanax Cortex	2020903100200	Hubei Province	Drug store, Xiangyang, Hubei
W-05	Acanthopanax Cortex	Not marked	Not marked	Drug store, Xiangyang, Hubei
W-06	Acanthopanax Cortex	202101001	Hunan Province	Drug store, Xiangyang, Hubei
W-07	Acanthopanax Cortex	Not marked	Hubei Province	Drug store, Xiangyang, Hubei
W-08	Acanthopanax Cortex	2110210011	Hubei Province	Hospital, Xiangyang, Hubei
W-09	Acanthopanax Cortex	20200601	Hubei Province	CHMs company, xiangyang, Hubei
W-10	Acanthopanax Cortex	Not marked	Not marked	Drug store, Xiangyang, Hubei
W-11	Acanthopanax Cortex	210801	Shanxi Province	Medicine Market, Bozhou, Anhui
W-12	Acanthopanax Cortex	210101	Shannxi Province	Medicine Market, Bozhou, Anhui
W-13	Acanthopanax Cortex	200801	Shanxi Province	Medicine Market, Bozhou, Anhui
W-14	Acanthopanax Cortex	201102	Shannxi Province	Medicine Market, Bozhou, Anhui
W-15	Acanthopanax Cortex	201101	Shannxi Province	Medicine Market, Bozhou, Anhui
W-16	Acanthopanax Cortex	160405	Anhui Province	Drug store, Xiangyang, Hubei
X-01	Periplocae Cortex	202004001	Hebei Province	Drug store, Xiangyang, Hubei
X-02	Periplocae Cortex	Not marked	Henan Province	Drug store, Xiangyang, Hubei
X-03	Periplocae Cortex	Not marked	Not marked	Hospital, Xiangyang, Hubei
X-04	Periplocae Cortex	Not marked	Not marked	Drug store, Xiangyang, Hubei
X-05	Periplocae Cortex	210501	Shannxi Province	Medicine Market, Bozhou, Anhui
X-06	Periplocae Cortex	210401	Shannxi Province	Medicine Market, Bozhou, Anhui
X-07	Periplocae Cortex	200901	Shanxi Province	Medicine Market, Bozhou, Anhui
X-08	Periplocae Cortex	200801	Shannxi Province	Medicine Market, Bozhou, Anhui
X-09	Periplocae Cortex	201101	Not marked	Medicine Market, Bozhou, Anhui
X-10	Periplocae Cortex ^a	20160501	Hubei Province	CHM company, xiangyang, Hubei ^a
X-11	Periplocae Cortex ^b	170625	Anhui Province	Clinic, Xiangyang, Hubei ^b
X-12	Periplocae Cortex ^b	171203	Anhui Province	Drug store, Xiangyang, Hubei ^b
X-13	Periplocae Cortex ^c	Not marked	Hubei Province	Drug store, Xiangyang, Hubei ^c

^a Retention samples of the supervision and inspection samples in 2019 (Sample name marked Acanthopanax Cortex);

^b Retention samples of the supervision and inspection samples in 2018 (Sample name marked Acanthopanax Cortex);

^c Samples for supervision and inspection in 2021 (Sample name marked Acanthopanax Cortex).

Table S2. Sensors used and their main applications in PEN3 E-nose.

Sensor number	Sensor name	General description
1	W ₁ C	Aromatic compounds
2	W ₅ S	Very sensitive, broad range of sensitivity, reacts to nitrogen oxides, very sensitive with negative signals
3	W ₃ C	Ammonia, used as sensor for aromatic compounds
4	W ₆ S	Mainly hydrogen
5	W ₅ C	Alkanes, aromatic compounds, less polar compounds
6	W ₁ S	Sensitive to methane. Broad range
7	W ₁ W	Reacts on sulfur compounds, H ₂ S. Otherwise sensitive to many terpenes and sulphur organic compounds
8	W ₂ S	Detects alcohol's, partially aromatic compounds, broad range
9	W ₂ W	Aromatic compounds, sulphur organic compounds
10	W ₃ S	Reacts on high concentrations (> 100 ppm) of methane-aliphatic compounds

Table S3. *P* value of volatile organic compounds (VOCs) with VIP > 1 in OPLS-DA model analysis.

No.	VOCs	Formula	VIP	P
33	2-Hydroxy-4-methoxybenzaldehyde	C ₈ H ₈ O ₃	1.62062	< 0.05
16	(1R,5S)-6,6-dimethyl-bicyclo[3.3.1]hept-2-en-2-carbaldehyde	C ₁₀ H ₁₄ O	1.49172	< 0.05
68	methyl 2-hydroxy-4-methoxybenzoate	C ₉ H ₁₀ O ₄	1.48045	< 0.05
8	(1S,5S)-7,7-dimethyl-4-methylidenebicyclo[3.1.1]heptan-3-ol	C ₁₀ H ₁₆ O	1.44243	< 0.05
20	(1R,5S)-2-methyl-5-prop-1-en-2-ylcyclohex-2-en-1-ol	C ₁₀ H ₁₆ O	1.43818	< 0.05
25	2,7,7-trimethylbicyclo[3.1.1]hept-2-en-4-one	C ₁₀ H ₁₄ O	1.43137	< 0.05
12	2-(4-methyl-1-cyclohexa-2,4-dienyl)propan-2-ol	C ₁₂ H ₂₀ O ₃	1.3873	< 0.05
7	1-(2,2,3-trimethyl-1-cyclopent-3-enyl)ethanone	C ₁₀ H ₁₆ O	1.37597	< 0.05
15	2-[(1R)-4-methyl-1-cyclohex-3-enyl]propan-2-ol	C ₁₀ H ₁₈ O	1.35918	< 0.05
19	(1S,5S)-2,7,7-trimethylbicyclo[3.1.1]hept-2-en-4-one	C ₁₀ H ₁₄ O	1.34432	< 0.05
10	2-(4-methylidene-1-cyclohex-2-enyl)propan-2-ol	C ₁₂ H ₂₀ O ₃	1.3365	< 0.05
66	5-formyl-2-methoxyphenyl acetate	C ₁₀ H ₁₀ O ₄	1.29551	< 0.05
24	(5S)-2-methyl-5-prop-1-en-2-ylcyclohex-2-en-1-one	C ₁₀ H ₁₄ O	1.27463	< 0.05
62	3,4,5-trimethyloxolan-2-one	C ₇ H ₁₂ O ₂	1.27007	< 0.05
11	7,7-dimethyl-4-methylidenebicyclo[3.1.1]heptan-3-one	C ₁₀ H ₁₄ O	1.25103	< 0.05
13	(1R)-4-methyl-1-propan-2-ylcyclohex-3-en-1-ol	C ₁₀ H ₁₈ O	1.23982	< 0.05
14	2-(4-methylphenyl)propan-2-ol	C ₁₀ H ₁₄ O	1.23523	< 0.05
17	Dodecane	C ₁₂ H ₂₆	1.21744	< 0.05
51	(1aR,4aR,7S,7aR,7bR)-1,1,7-Trimethyl-4-methylenedecahydro-1H-cyclopropa[e]azulen-7-ol	C ₁₅ H ₂₄ O	1.21026	< 0.05
58	5-(5,5,8a-trimethyl-2-methylidene-3,4,4a,6,7,8-hexahydro-1H-naphthalen-1-yl)-3-methylpent-1-en-3-ol	C ₂₀ H ₃₄ O	1.19979	< 0.05

71	2,4-ditert-butylphenol	C ₁₄ H ₂₂ O	1.16325	< 0.05
52	(1R,4R,6R,10S)-4,12,12-Trimethyl-9-methylene-5-oxatricyclo[8.2.0.0]dodecane	C ₁₅ H ₂₄ O	1.14638	< 0.05
29	[(4S)-4-prop-1-en-2-yl-1-cyclohexenyl]methanol	C ₁₀ H ₁₆ O	1.13892	< 0.05
64	3-Hydroxy-4-methoxybenzaldehyde	C ₈ H ₈ O ₃	1.05977	< 0.05