Supplementary material

Uncovering the Secrets of Agarwood Aroma with Regions and Grades using A Comprehensive Analytical Strategy

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Materials and methods

1.1 Materials

A total of 55 batches agarwood samples used in this study were obtained from different sources, including China, Vietnam, Cambodia, Myanmar, Brunei, and Indonesia. 15 batches of agarwood (Samples 1-15) were collected from China, 22 batches of agarwood (Samples 16-31, Samples 49-55) were collected from Vietnam, of which samples 49-55 were Kynam, 2 batches of agarwood (Samples 32-33) were obtained from Myanmar, 3 batches of agarwood (Samples 34-36) were obtained from Cambodia. Moreover, agarwood from the Sin-chew zone were also collected, 10 batches agarwood (Samples 37-46) were collected from Indonesia, the rest of 2 batches agarwood were obtained from Brunei. The above agarwood samples include artificial perforated and chemically induced agarwood as well as various types of wild agarwood. Agarwood samples used in this experiment were provided and authenticated by Agarwood Professional Committee of Shanghai Commercial Federation (Shanghai, China). Voucher specimens were deposited in the herbarium of the Institute of Chinese Materia Medica, Shanghai University of Traditional Chinese Medicine (Shanghai, China). All the samples are crushed into powder before use.

The SPME fiber used in this experiment was divinyl benzene/carboxen/poly-dimethylsiloxane (DVB/CAR/PDMS) (50/30 μm, 10 mm) fiber and the SPME arrow was divinyl benzene/carbon-WR/poly-dimethylsiloxane ((DVB/C-WR/PDMS) (120 μm, 20 mm) that produced from Supelco Inc. (Bellefonte, PA, USA).

1.2 Morphological identification

The morphological identification of the agarwood samples was evaluated based on the description in the Chinese Pharmacopoeia (2020 version). The quality of the samples was evaluated by observing the appearance, color, odor, texture, and the extent of the distribution of dark brown or tan resin on the wood surface. The samples were preliminarily divided into high quality and ordinary agarwood.

1.3 Establishment of MRM and SIM method

The creation of the MRM method consisted of determining the precursor ions, setting the product ions, and optimizing the collision energy steps. The Q3 Scan data file based

on the mixed solution of the standard was used to determine the precursor ions, then the product ion determination method was created. Moreover, the collision voltage range and voltage interval were entered to create the scanning method with different CE voltages. Finally, optimized ion pairs and CE voltages using standards can be used to obtain higher sensitivity data, and the detailed information of the database is listed in Table S1.

In addition, SIM method was automatically created based on the smart aroma database. First of all, there is a built-in standard curve in the database, and a calibrated standard curve is obtained based on the internal standard solution (p-Bromofluorobenzene, 1,2-Dichlorobenzene-d4, and Acenaphthene-d10). For sample determination, the concentration of the target compound can be obtained based on the peak area, and the concentration (pg/mg) in the sample is automatically calculated by inserting the weight of the sample into the software.

1.4 HS-SPME-GC-MS analysis

The agarwood samples were analyzed using a headspace preheated system (AOC-6000). 100 mg of agarwood powder was weighted and placed in a 20 mL glass vial. The vials were sealed using Teflon and placed into a headspace autosampler oven. The pretreat temperature was set to 90℃ for 30 min, the aroma compounds were enriched by SPME arrow and subsequently desorbed and transported by carrier gas to GC-MS for analysis. A sample vial without agarwood powder was also tested by the same conditions and used as a control. Correction of retention time is performed by using normal alkanes to ensure high reliability of compound identification.

The chemical constituents of odor form agarwood were identified by using TQ8050 NX Triple Quadrupole GC-MS (Shimadzu Corporation, Kyoto, Japan) operated in Full scan and multiple reaction monitoring (MRM) mode simultaneously. The GC separation was performed by using a Inertcap pure-wax column (30 m × 0.25 mm, 0.25 μm, GL Sciences). The temperature of transfer and sample lines was kept at 150℃. Ultra-high purity helium (99.99%) was used as carrier gas with a flow rate of 4 mL/min. The analytic conditions were as follows: injection port temperature of 250 ℃; split ratio of 5:1. The chromatographic conditions for GC are specified as follows: the initial

temperature was at 50 ℃ and held for 5.0 min, then increased to 250 ℃ at 10 ℃/min and held for 10.0 min. Electron ionization (EI) was used as the ionization method, and the ion source temperature was set at 200℃.

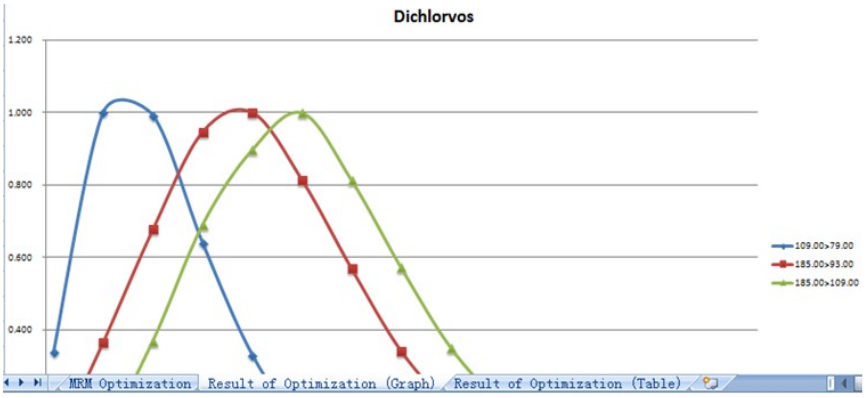
1.5 GC-MS Data processing

The acquired data were identified based on two databases. Firstly, the peaks obtained in SCAN mode were identified qualitatively based on the National Institute of Standards and Technology (NIST) MS Library, NIST 17. The collected mass spectral data were compared with the standards from database, in which the similarity greater than 85% could be considered as the same compound. Besides, the data obtained in MRM mode were compared with the retention time and characteristic ion pairs from the smart aroma database, enabling rapid screening of trace aroma compositions in samples.

1.6 Chemometrics analysis

Before performing the chemometric analysis, raw GC–MS data (.qgd file) were formatted into a NetCDF file by LabSolutions software (version 4.5, Shimadzu Corp., Kyoto, Japan). The NetCDF file was then loaded into MSDIAL online platform (http://prime.psc.riken.jp/compms/msdial/main.html) to perform deconvolution and alignment and generate a normalized dataset. After that, the normalized dataset was further subjected to principal component analysis (PCA), partial least squares discriminant analysis (PLS-DA), orthogonal projection to latent structures discriminant analysis (OPLS-DA) and hierarchical cluster analysis (HCA) by SIMCA 14.0 software (Umetrics, Umeå, Sweden), which aimed to identify differences between various origin and different quality agarwood and highlight components that make prominent contribution to the grouping (VIP > 1). Heat map analysis was conducted by using Origin software (Northampton, Massachusetts, USA). One-way ANOVA was performed using Statistical Product and Service Solutions (SPSS) software (Armonk, New York, USA).

(A)



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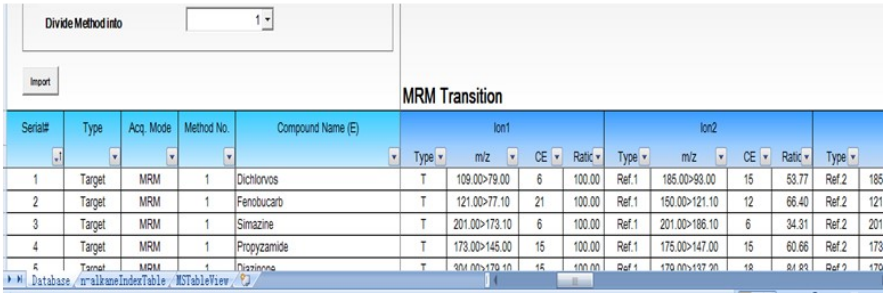


Serial#	Type	Acq. Mode	Method No.	Compound Name (E)	Ion1 Type	Ion1 m/z	Ion1 CE	Ion1 Ratio	Ion2 Type	Ion2 m/z	Ion2 CE	Ion2 Ratio	Type
1	Target	MRM	1	Dichlorvos	T	109.00>79.00	6	100.00	Ref.1	185.00>93.00	15	53.77	Ref.2
2	Target	MRM	1	Fenobucarb	T	121.00>77.10	21	100.00	Ref.1	150.00>121.10	12	66.40	Ref.2
3	Target	MRM	1	Simazine	T	201.00>173.10	6	100.00	Ref.1	201.00>186.10	6	34.31	Ref.2
4	Target	MRM	1	Propyzamide	T	173.00>145.00	15	100.00	Ref.1	175.00>147.00	15	60.66	Ref.2

Fig. S1 Establishment of MRM method. (A) Optimization of collision voltage; (B) Diagram of Smart Database.

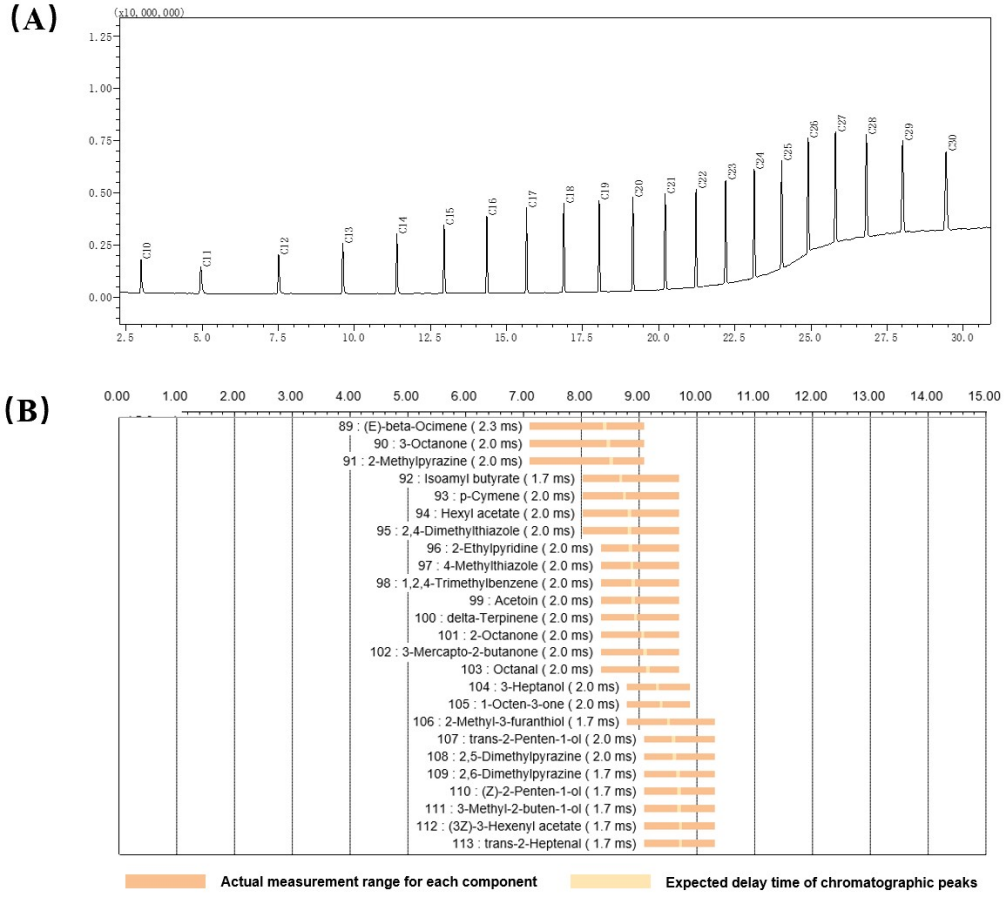
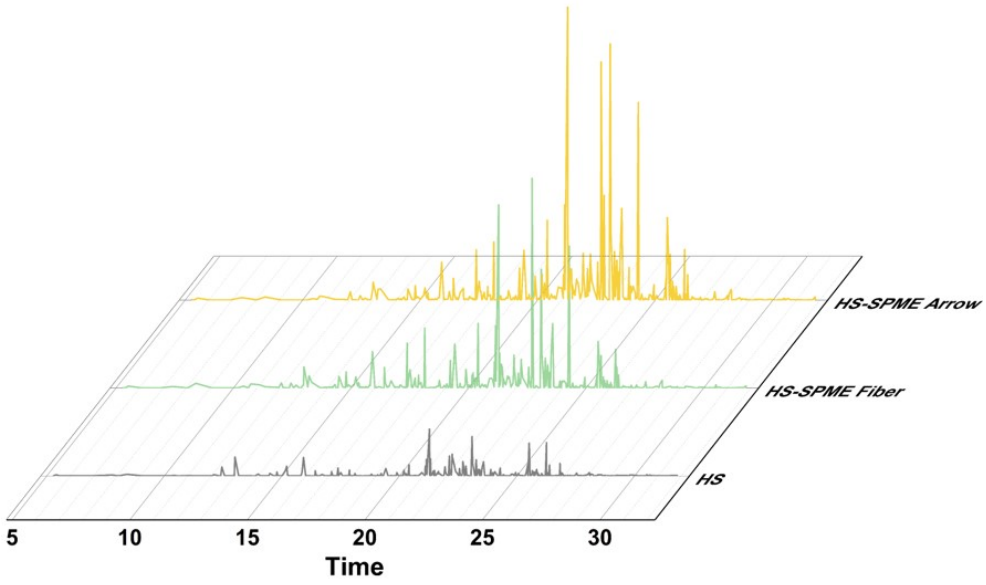


Fig. S2 (A) Mass spectra of n-alkanes (C9-C30); (B) Schematic diagram of the AART function.

Fig. S3 Representative photogram of different agarwood samples in this study.

(A)



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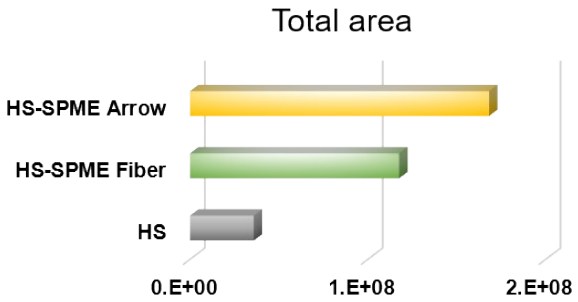


Fig. S4 Total GC–MS ion chromatograms (A) and Histogram of the sum of peak areas (B) detected by HS, HS-SPME Fiber and HS-SPME arrow methods.

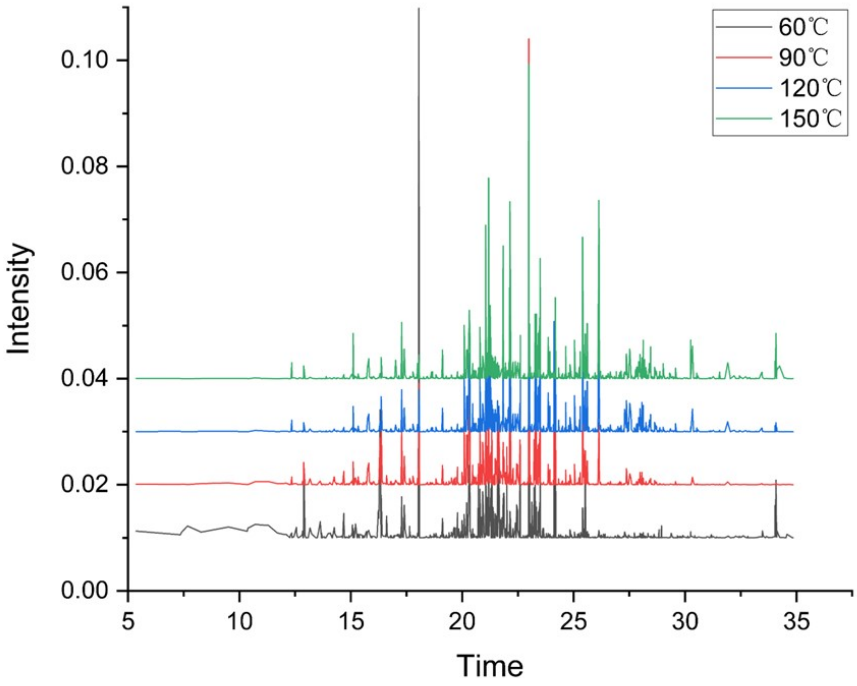


Fig. S5 Total GC–MS ion chromatograms of different extraction temperatures.

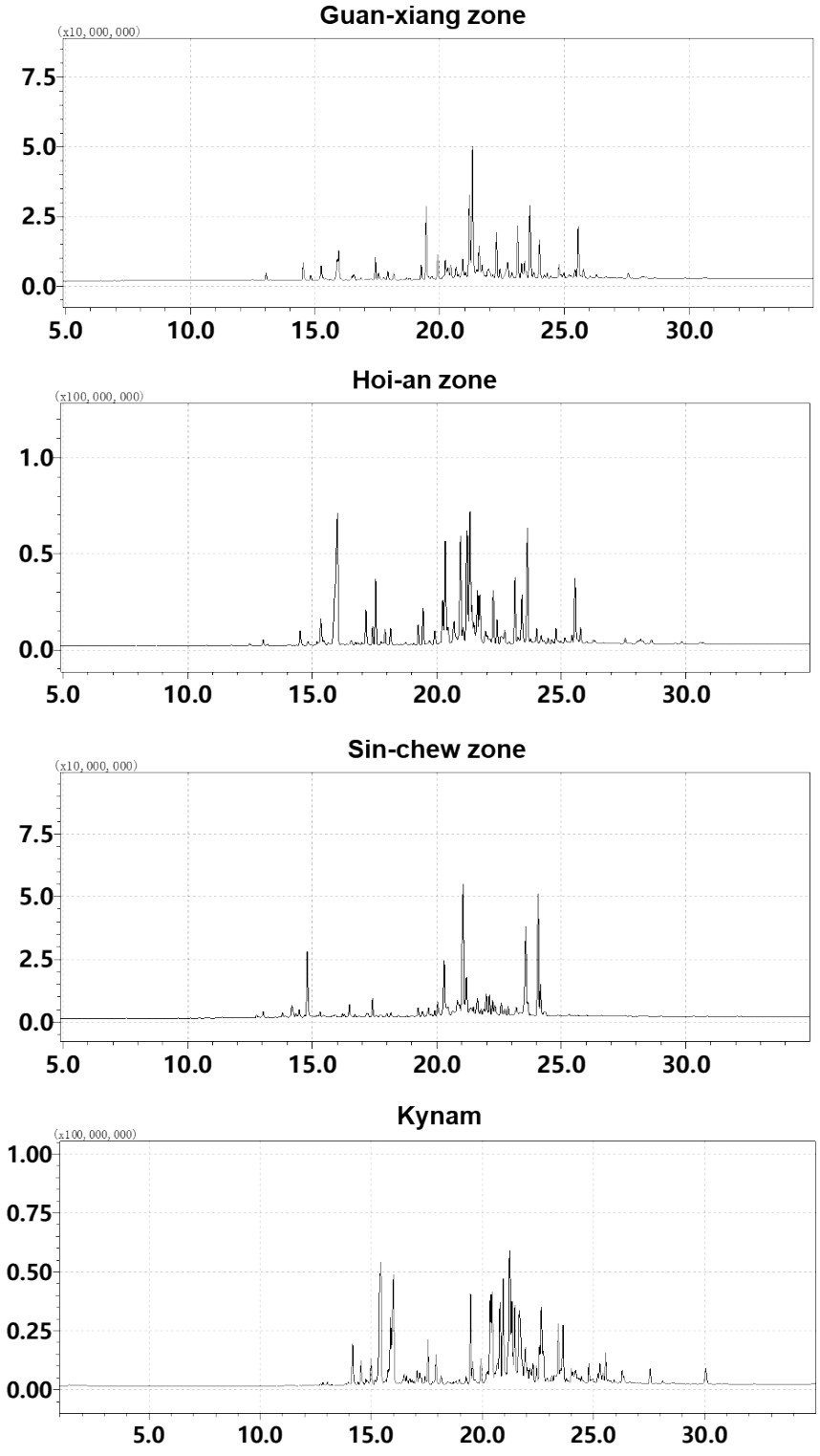


Fig. S6 Representative gas-chromatogram of agarwood from different zones and different species.

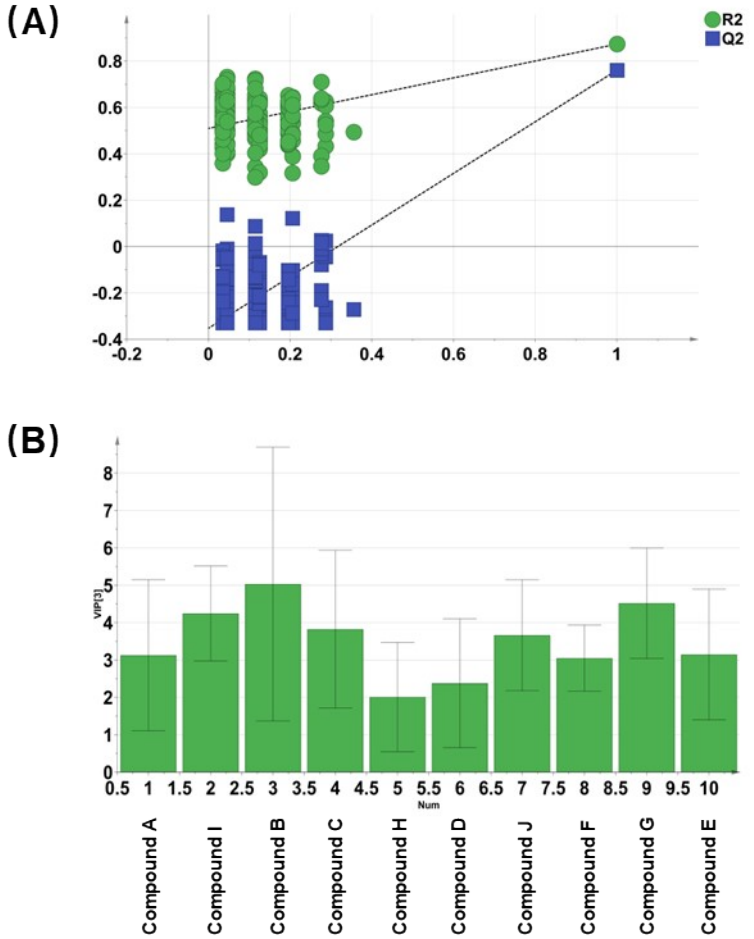


Fig. S7 (A) Replacement verification results of agarwood Samples (200 times of cross verification) for the PLS-DA model, (B) VIP value plot of PLS-DA model based on SCAN mode (Compound A: α-Guaiene, Compound B: (4S,4aR,6R)-4,4a-Dimethyl-6-(prop-1-en-2-yl)-1,2,3,4,4a,5,6,7-octahydronaphthalene, Compound C: α-Bulnesene, Compound D: (-)-Nootkatene, Compound E: Eremophila-1(10),11-dien-9-one, Compound F: 1,1,4,7-Tetramethyldecahydro-1H-cyclopropa[e]azulene-4,7-diol, Compound G: (-)-Aristolene, Compound H: Guaiol, Compound I: (3S,3aS,6R,8aS)-3,8,8-Trimethyl-7-methyleneoctahydro-1H-3a,6-methanoazulene, Compound J: (3S,3aS,6R,7S,8aS)-3,7,8,8-Tetramethyloctahydro-1H-3a,6-methanoazulen-7-ol)).

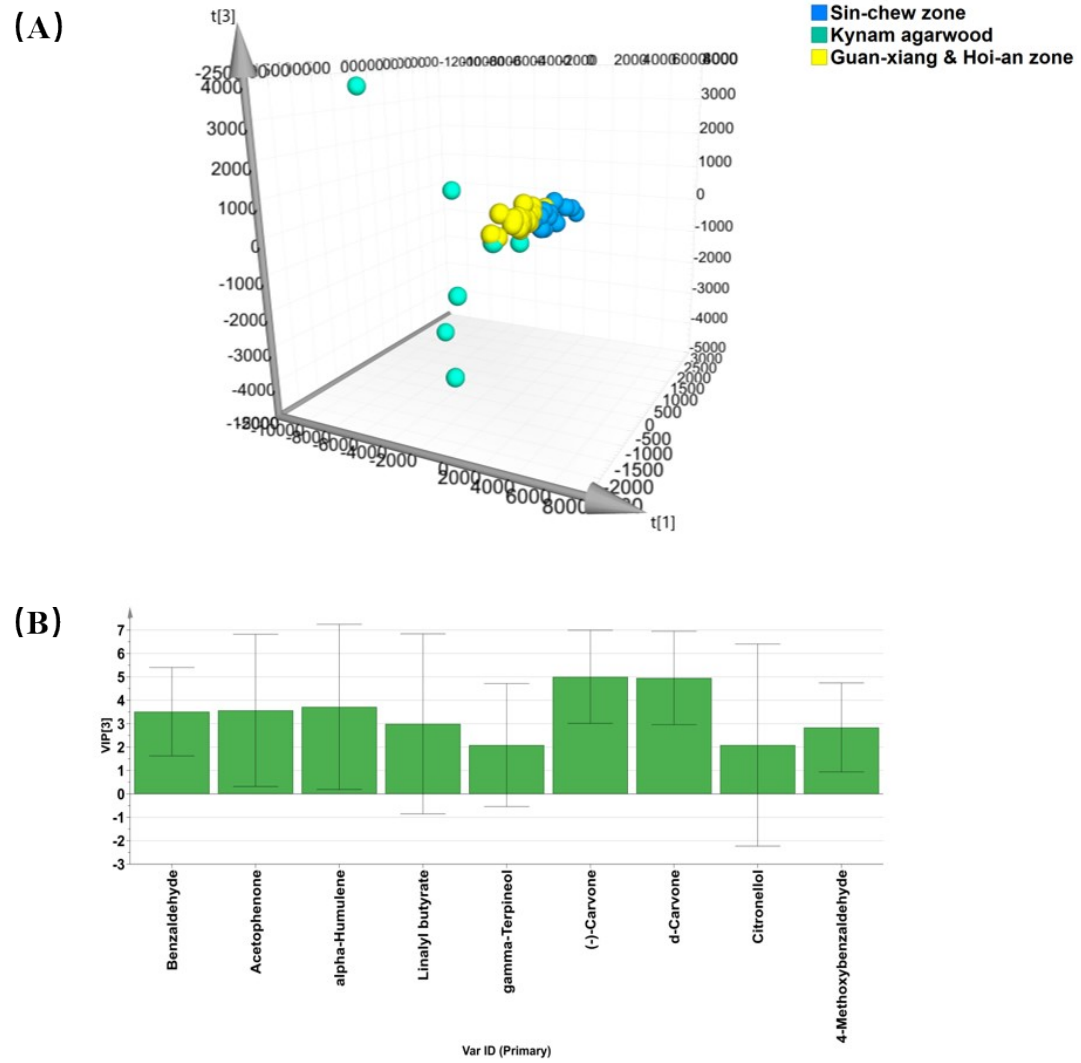


Fig. S8 Multivariate statistical analysis of different zones of agarwood based on MRM mode ((A) PLS-DA score plot; (B) VIP value (>1)).

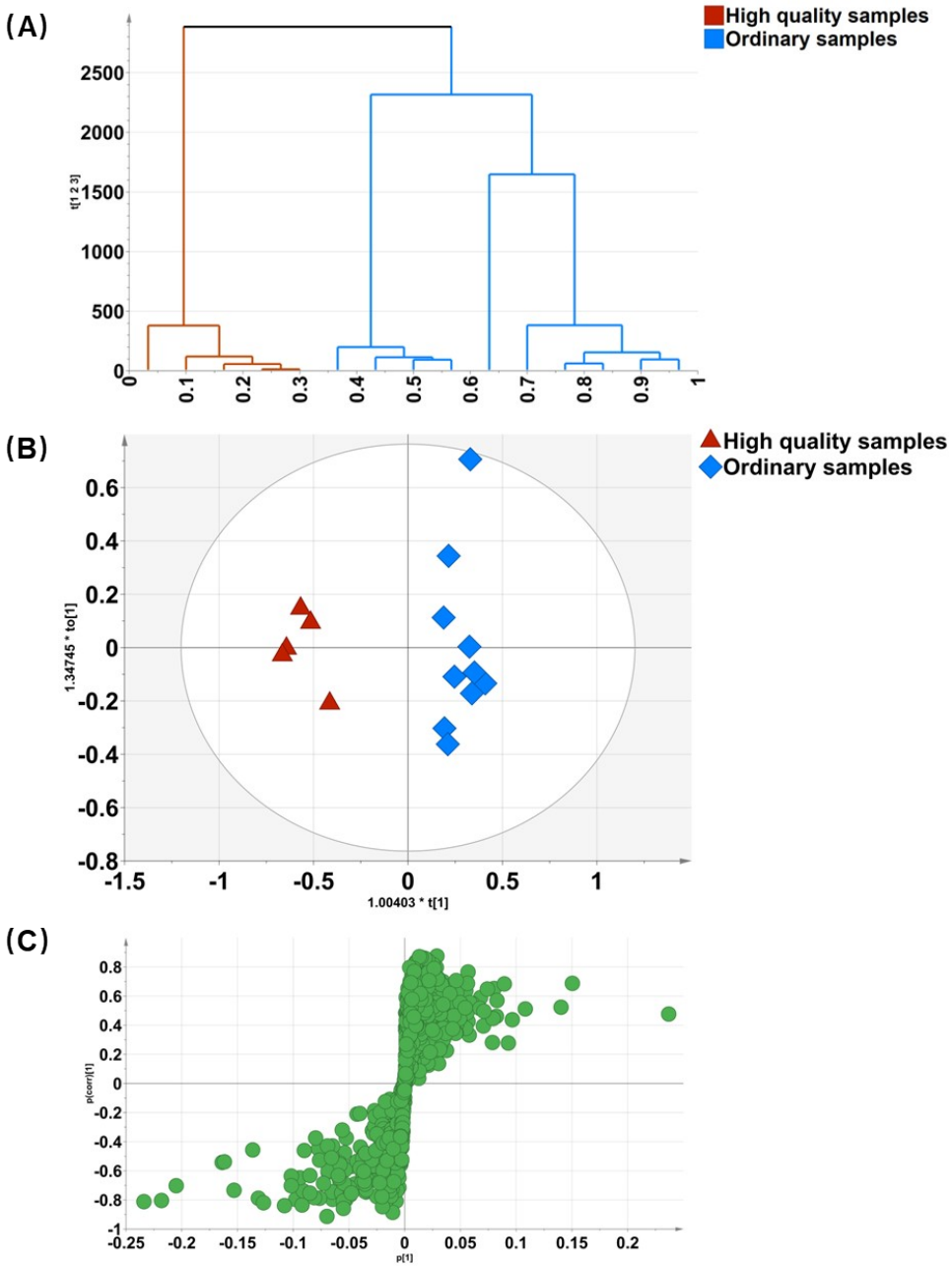


Fig. S9 Multivariate statistical analysis of different quality agarwood from Guan-xiang zone based on SCAN mode ((A) HCA analysis diagram; (B) OPLS-DA score plot; (C) S-plot).

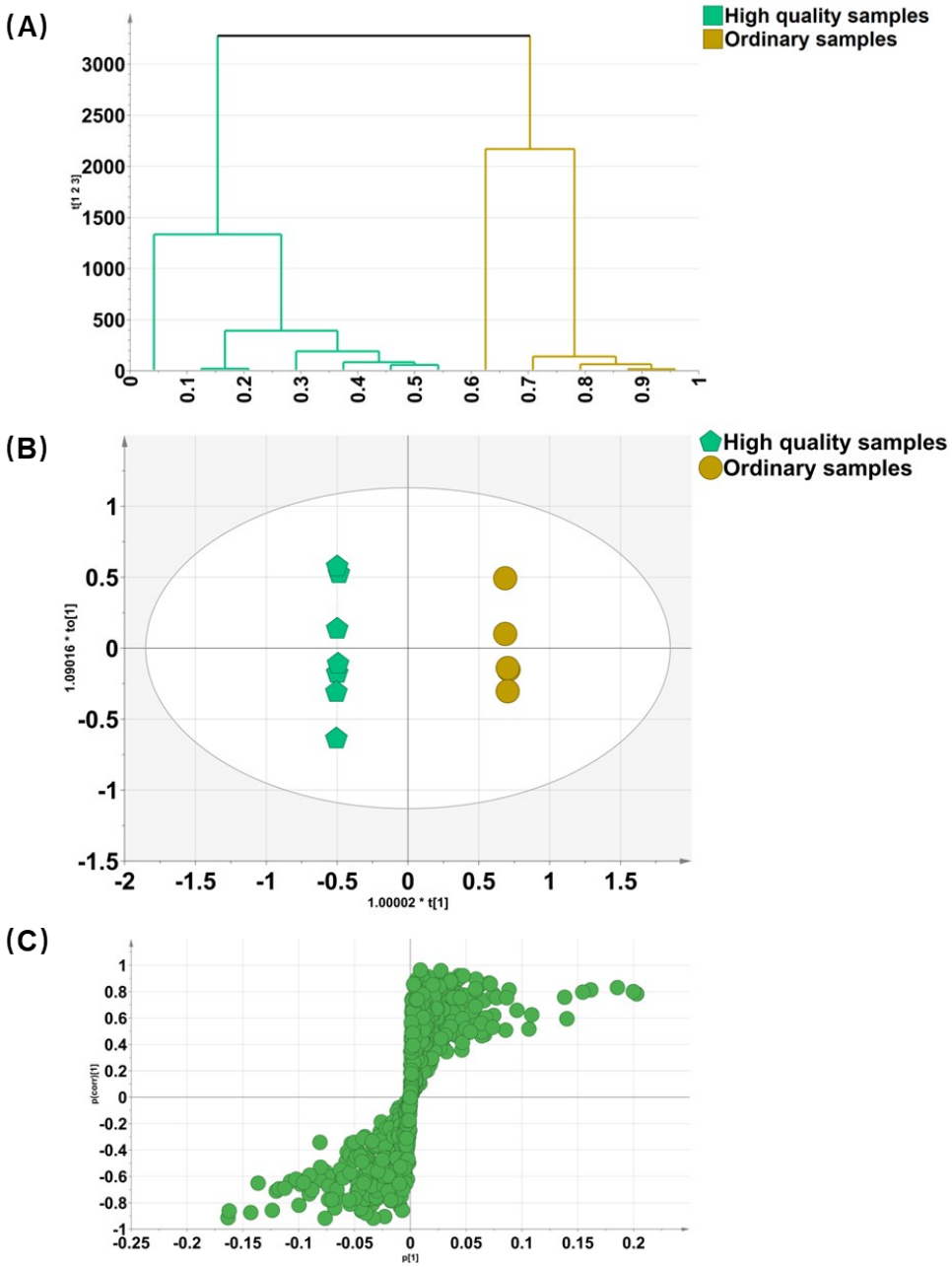


Fig. S10 Multivariate statistical analysis of different quality agarwood from Sin-chew zone based on SCAN mode ((A) HCA analysis diagram; (B) OPLS-DA score plot; (C) S-plot).

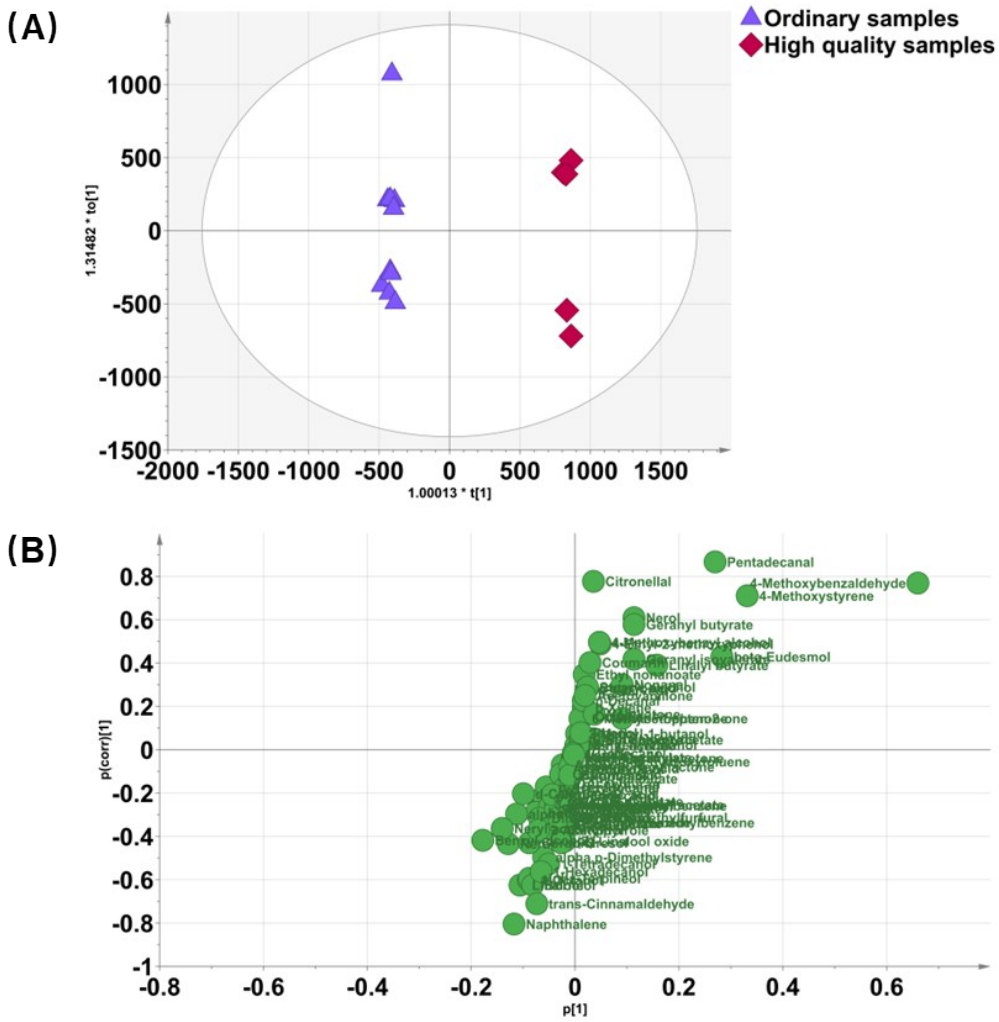


Fig. S11 Multivariate statistical analysis of different quality agarwood from Guan-xiang zone based on MRM mode ((A) OPLS-DA score plot; (B) S-plot).

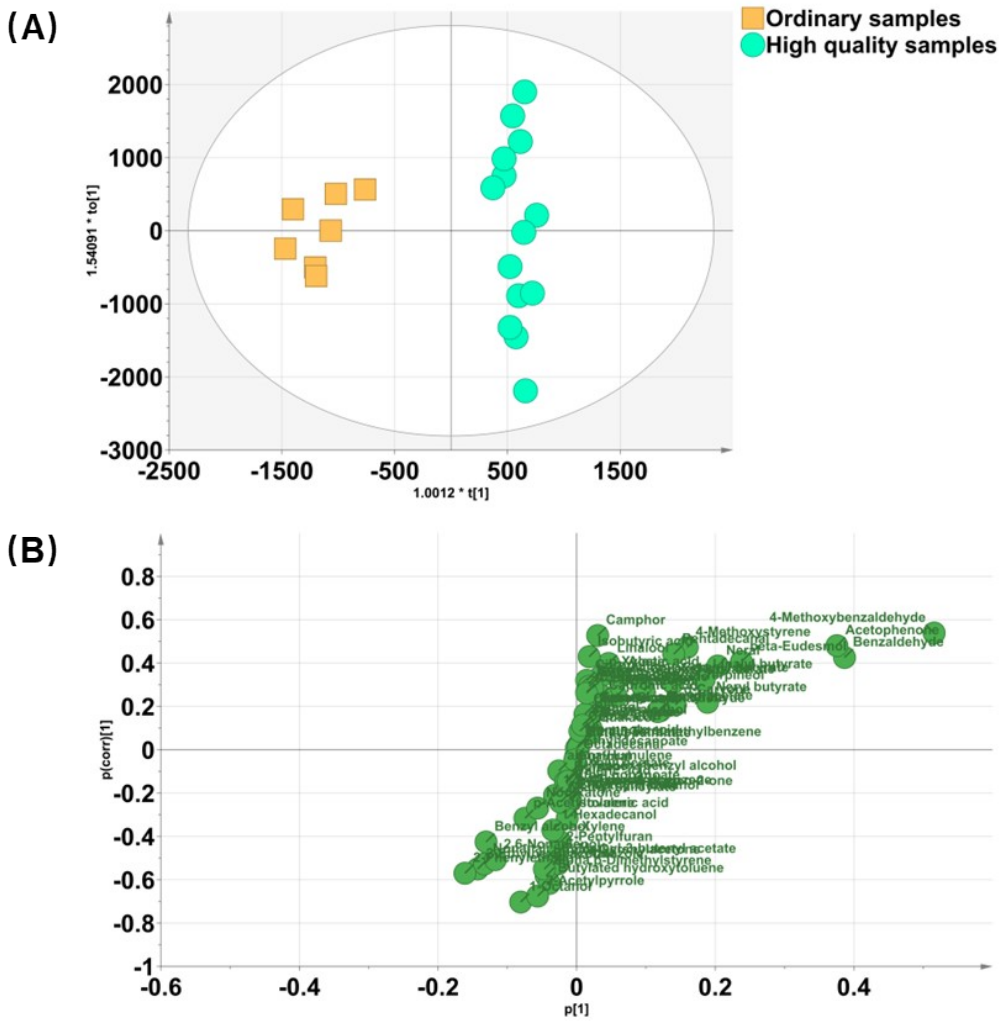


Fig. S12 Multivariate statistical analysis of different quality agarwood from Hoi-an zone based on MRM mode ((A) OPLS-DA score plot; (B) S-plot).

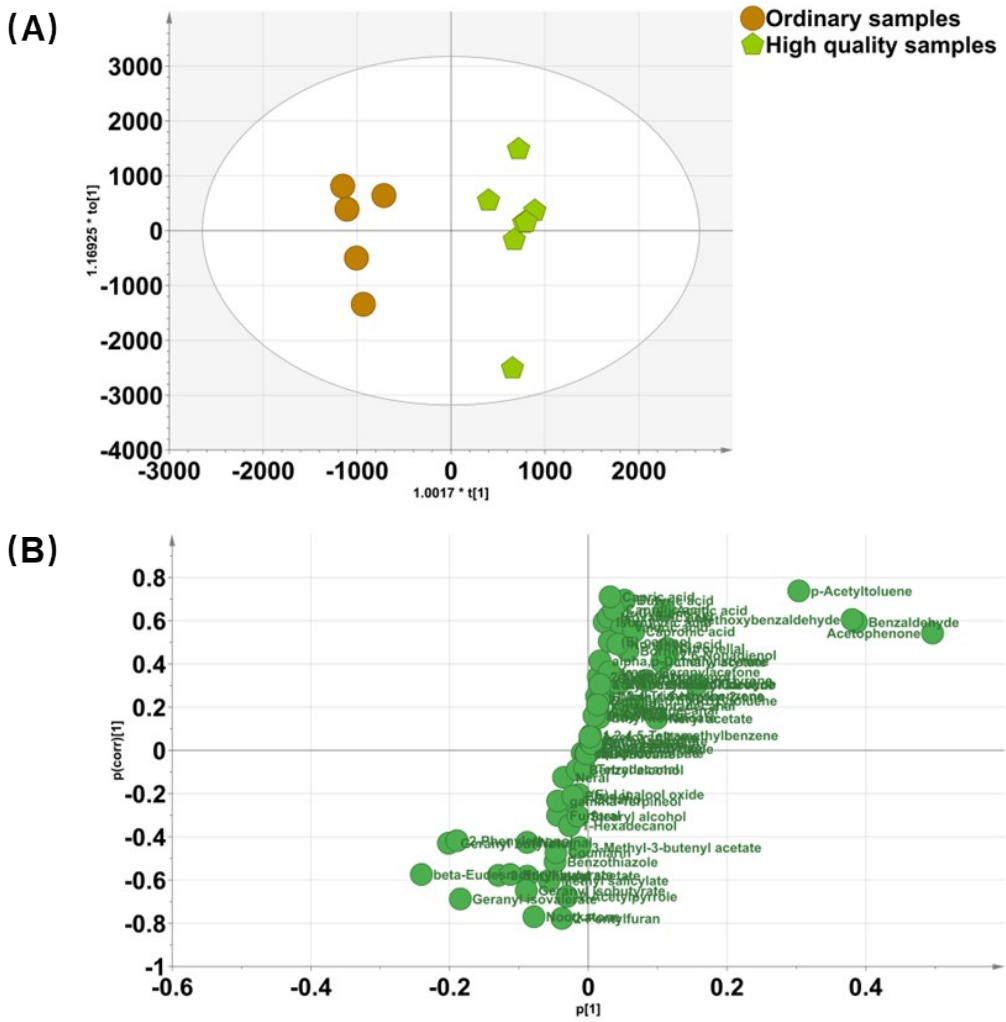
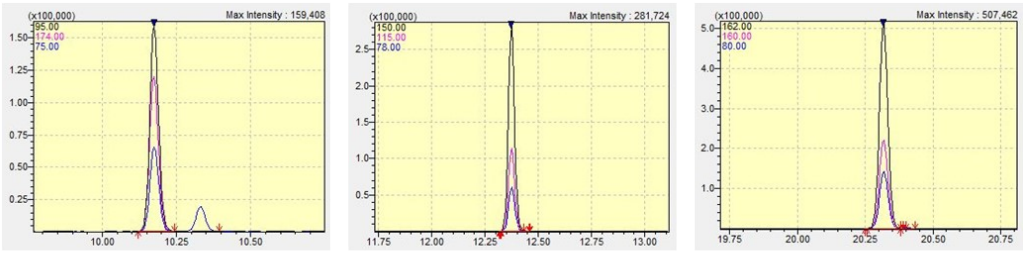
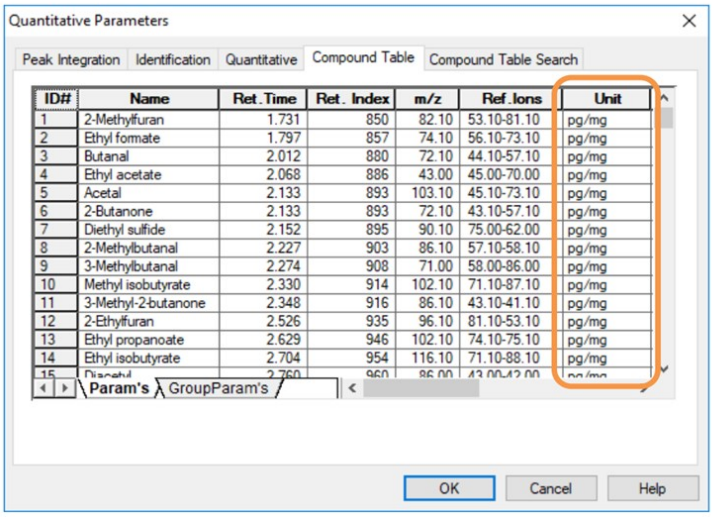


Fig. S13 Multivariate statistical analysis of different quality agarwood from Sin-chew zone based on MRM mode ((A) OPLS-DA score plot; (B) S-plot).

(A)



(B)



ID#	Name	Ret.Time	Ret. Index	m/z	Ref.Ions	Unit
1	2-Methylfuran	1.731	850	82.10	53.10-81.10	pg/mg
2	Ethyl formate	1.797	857	74.10	56.10-73.10	pg/mg
3	Butanal	2.012	880	72.10	44.10-57.10	pg/mg
4	Ethyl acetate	2.068	886	43.00	45.00-70.00	pg/mg
5	Acetal	2.133	893	103.10	45.10-73.10	pg/mg
6	2-Butanone	2.133	893	72.10	43.10-57.10	pg/mg
7	Diethyl sulfide	2.152	895	90.10	75.00-62.00	pg/mg
8	2-Methylbutanal	2.227	903	86.10	57.10-58.10	pg/mg
9	3-Methylbutanal	2.274	908	71.00	58.00-86.00	pg/mg
10	Methyl isobutyrate	2.330	914	102.10	71.10-87.10	pg/mg
11	3-Methyl-2-butanone	2.348	916	86.10	43.10-41.10	pg/mg
12	2-Ethylfuran	2.526	935	96.10	81.10-53.10	pg/mg
13	Ethyl propanoate	2.629	946	102.10	74.10-75.10	pg/mg
14	Ethyl isobutyrate	2.704	954	116.10	71.10-88.10	pg/mg

Fig. S14 (A) Mass spectra of internal standard compounds (B) Diagram of the results of semi-quantitative calculations.

Table S1 Specific information for odor components in smart aroma database.

Compound	Retention time	Retention index	Ion pair
2-Methylfuran	1.62	850	82.10>54.00
Butanal	1.893	880	72.10>57.00
Ethyl acetate	1.948	886	70.00>55.00
Acetal	2.011	893	73.10>45.10
2-Butanone	2.011	893	72.10>43.10
Diethyl sulfide	2.03	895	90.10>75.10
Methyl isobutyrate	2.203	914	71.10>43.10
3-Methyl-2-butanone	2.221	916	86.10>43.10
2-Ethylfuran	2.394	935	96.10>81.00
Ethyl propanoate	2.494	946	102.10>74.10
Ethyl isobutyrate	2.567	954	116.10>88.10
Diacetyl	2.621	960	86.00>43.00
2-Pentanone	2.631	961	86.10>71.10
3-Pentanone	2.64	962	86.10>57.10
Propyl acetate	2.658	964	61.00>43.10
Methyl Butanoate	2.749	974	71.10>43.10
2-Methyl-3-pentanone	2.84	984	71.10>43.10
Methyl isobutyl ketone	2.949	996	100.10>85.10
Methyl 2-methylbutyrate	3.045	1003	88.10>57.10
Ethyl vinyl ketone	3.103	1006	84.10>55.10
Methyl isovalerate	3.143	1008	74.10>43.00
Thiophene	3.162	1009	84.00>58.00
2-Butanol	3.182	1010	59.10>31.10
alpha-Pinene	3.221	1012	93.00>77.00
Propanol	3.378	1020	59.00>31.10
Methylbutenol	3.437	1023	71.10>43.10
Ethyl butanoate	3.457	1024	71.00>43.10
Isopropyl butyrate	3.515	1027	71.10>43.10
Propyl propionate	3.594	1031	75.10>57.10
3-Hexanone	3.633	1033	71.10>43.10
Ethyl 2-methylbutyrate	3.751	1039	102.00>74.00
Camphene	3.947	1049	121.10>93.10
Dimethyl disulfide	4.084	1056	94.00>79.00
Ethyl 3-methylbutanoate	4.124	1058	85.10>57.10
Butyl acetate	4.143	1059	73.00>43.00
2-Hexanone	4.182	1061	100.10>85.10
Hexanal	4.222	1063	82.10>67.10
S-Ethyl Thioacetate	4.32	1068	104.10>43.10
2-Methylthiophene	4.418	1073	97.00>53.10
Isobutanol	4.438	1074	43.10>41.10

1-Hexen-3-one	4.496	1077	70.10>55.00
Tetrahydrothiophene	4.693	1087	88.00>60.00
2-Methylpentan-2-ol	4.732	1089	59.10>31.10
beta-Pinene	4.81	1093	93.10>77.10
3-Pentanol	4.889	1097	59.10>31.10
Sabinene	5.204	1110	93.10>77.10
2-Pentanol	5.255	1112	73.10>55.10
2-Methylbutyl acetate	5.357	1116	70.00>55.10
Propyl butyrate	5.357	1116	71.00>43.10
(E)-2-Pentenal	5.357	1116	83.10>55.10
Mesityl oxide	5.357	1116	98.10>83.10
Isoamyl acetate	5.383	1117	70.10>55.10
p-Xylene	5.562	1124	106.00>91.00
m-Xylene	5.716	1130	106.00>91.00
Ethyl valerate	5.793	1133	85.10>57.10
1-Hexanethiol	5.844	1135	118.10>84.10
1-Butanol	5.869	1136	56.10>41.10
delta-3-Carene	5.921	1138	136.10>93.10
alpha-Phellandrene	6.33	1154	93.10>77.00
Myrcene	6.484	1160	93.00>77.10
Pyridine	6.586	1164	79.10>52.10
Pentyl acetate	6.663	1167	70.10>55.10
1,4-Cineole	6.689	1168	125.10>43.10
alpha-Terpinene	6.689	1168	121.10>93.10
o-Xylene	6.766	1171	106.00>91.00
2-Heptanone	6.791	1172	71.00>43.00
Heptanal	6.868	1175	70.10>55.10
Methyl hexanoate	6.996	1180	74.00>43.10
3-Methyl-3-butenyl acetate	7.098	1184	68.10>53.10
Ethyl isocaproate	7.15	1186	88.10>70.10
Limonene	7.175	1187	136.00>93.00
Diethyl disulfide	7.329	1193	122.00>94.00
1,8-Cineole	7.406	1196	111.10>43.10
2-Methyl-1-butanol	7.431	1197	70.10>55.10
Isoamyl alcohol	7.457	1198	70.10>55.10
2-Methylpyridine	7.457	1198	93.10>66.10
trans-2-Hexenal	7.529	1201	69.10>41.10
Butyl 2-methylbutyrate	8.056	1226	85.10>57.10
2-Pentylfuran	8.077	1227	81.00>53.00
Ethyl hexanoate	8.098	1228	88.00>61.00
(Z)-beta-Ocimene	8.098	1228	93.10>77.10
Isopropyl hexanoate	8.119	1229	99.10>43.10
(Z)-4-Heptenal	8.119	1229	94.10>79.10

gamma-Terpinene	8.288	1237	93.10>77.10
Styrene	8.33	1239	104.10>78.10
Prenyl acetate	8.351	1240	86.10>71.10
1-Pentanol	8.414	1243	70.00>55.00
1-Hexen-3-ol	8.414	1243	57.10>31.10
(E)-beta-Ocimene	8.456	1245	93.10>77.10
3-Octanone	8.519	1248	71.10>43.10
2-Methylpyrazine	8.561	1250	94.00>67.00
Isoamyl butyrate	8.73	1258	70.10>55.10
p-Cymene	8.793	1261	134.10>119.10
Hexyl acetate	8.877	1265	84.10>69.10
2,4-Dimethylthiazole	8.877	1265	113.00>72.00
2-Ethylpyridine	8.899	1266	106.10>78.10
4-Methylthiazole	8.92	1267	99.00>72.00
1,2,4-Trimethylbenzene	8.941	1268	120.10>105.10
Acetoin	8.941	1268	45.00>43.00
delta-Terpinene	8.983	1270	136.10>121.10
2-Octanone	9.109	1276	128.00>85.00
3-Mercapto-2-butanone	9.151	1278	104.10>43.00
Octanal	9.193	1280	84.00>55.00
3-Heptanol	9.362	1288	69.10>41.10
1-Octen-3-one	9.425	1291	70.10>55.00
2-Methyl-3-furanthiol	9.552	1297	114.00>86.00
trans-2-Penten-1-ol	9.633	1301	57.10>31.00
2,5-Dimethylpyrazine	9.65	1302	108.10>42.10
2,6-Dimethylpyrazine	9.721	1306	108.00>42.00
(Z)-2-Penten-1-ol	9.739	1307	57.10>31.00
3-Methyl-2-buten-1-ol	9.739	1307	71.10>43.10
(3Z)-3-Hexenyl acetate	9.757	1308	82.10>67.10
trans-2-Heptenal	9.757	1308	83.00>55.00
Pentyl butyrate	9.792	1310	71.10>43.10
Propyl hexanoate	9.792	1310	99.10>43.10
2-Heptanol	9.81	1311	83.10>55.10
2-Methoxypyrazine	9.917	1317	110.10>81.10
2-Ethylpyrazine	9.935	1318	107.00>79.00
6-Methyl-5-hepten-2-one	10.059	1325	108.10>93.10
Ethyl 2-mercaptopropionate	10.112	1328	88.00>60.00
Ethyl heptanoate	10.148	1330	88.10>61.00
2,3-Dimethylpyrazine	10.165	1331	108.00>67.00
Ethyl lactate	10.254	1336	75.10>45.00
cis-Rose Oxide	10.325	1340	139.10>69.10
2,6-Dimethyl-5-heptenal	10.343	1341	82.10>67.10
3-Mercapto-2-pentanone	10.361	1342	75.00>41.00

Allyl isothiocyanate	10.45	1347	99.10>41.10
1-Hexanol	10.467	1348	56.10>41.10
4,5-Dimethylthiazole	10.503	1350	113.00>71.00
trans-3-Hexen-1-ol	10.574	1354	82.10>67.10
trans-Rose Oxide	10.574	1354	139.10>69.10
2,4,5-Trimethylthiazole	10.645	1358	127.00>86.00
3-Ethoxy-1-propanol	10.698	1361	71.00>43.10
Methyl cyclohexanecarboxylate	10.751	1364	142.10>113.10
Dimethyl trisulfide	10.769	1365	126.00>79.00
2-Ethyl-5-methylpyrazine	10.769	1365	121.10>66.10
4-Mercapto-4-methyl-2-pentanone	10.769	1365	132.10>89.10
Heptyl acetate	10.787	1366	70.10>55.10
cis-3-Hexen-1-ol	10.929	1374	82.10>67.10
2,5-Dimethylfuran-3-thiol	10.929	1374	128.10>95.10
Benzyl methyl ether	10.929	1374	91.10>65.10
Butyl isothiocyanate	10.947	1375	115.10>100.10
2-Nonanone	10.982	1377	71.00>43.00
2-Ethylhexyl acetate	11.018	1379	70.10>55.10
2,4-Hexadienal	11.053	1381	96.00>81.10
Methyl octanoate	11.071	1382	87.00>55.00
3-Octanol	11.071	1382	83.10>55.10
Nonanal	11.089	1383	82.10>67.10
2,3,5-Trimethylpyrazine	11.16	1387	122.10>42.10
Methyl (methylthio)acetate	11.16	1387	120.00>74.10
2-Ethyl-3-methylpyrazine	11.178	1388	121.00>93.10
2-Isobutylthiazole	11.231	1391	99.00>59.00
2-Methylanisole	11.231	1391	122.00>107.10
trans-3-Octen-2-one	11.249	1392	111.10>55.10
trans-2-Hexen-1-ol	11.302	1395	82.10>67.10
alpha-Thujone	11.406	1401	110.10>95.10
(Z)-hex-2-en-1-ol	11.422	1402	82.10>67.10
Butyl hexanoate	11.484	1406	99.10>43.10
Hexyl butyrate	11.5	1407	71.10>43.10
1,2,4,5-Tetramethylbenzene	11.531	1409	119.00>91.00
2-Octanol	11.562	1411	97.10>55.10
2-Mercaptoethyl acetate	11.577	1412	60.00>45.00
trans-2-Octenal	11.608	1414	83.10>55.10
2-Cyclohexen-1-one	11.624	1415	96.10>68.00
Furfuryl mercaptan	11.639	1416	114.00>81.10
Hexyl 2-methylbutanoate	11.701	1420	85.10>57.10
alpha,p-Dimethylstyrene	11.717	1421	132.10>117.10
2-Ethyl-3,6-dimethylpyrazine	11.748	1423	135.10>107.10

2-Isopropyl-3-methoxypyrazine	11.779	1425	152.00>137.00
Ethyl (methylthio)acetate	11.779	1425	134.10>88.10
Ethyl octanoate	11.841	1429	88.10>61.00
(Z)-Linalool oxide	11.857	1430	94.10>79.10
Methional	11.857	1430	104.10>76.10
2-Methyl-1,3-dithiolane	11.888	1432	120.00>105.00
cis-Limonene oxide	11.919	1434	93.10>77.10
Acetic acid	11.919	1434	60.00>43.00
Furfural	11.981	1438	95.00>67.10
2-Ethyl-3,5-dimethylpyrazine	12.012	1440	135.10>66.00
1-Octen-3-ol	12.074	1444	57.10>31.00
5-Ethyl-2,3-dimethylpyrazine	12.089	1445	135.10>53.10
trans-Limonene oxide	12.12	1447	94.10>79.10
1-Heptanol	12.136	1448	70.10>55.10
2-Pentylthiophene	12.136	1448	97.00>53.10
Menthone	12.136	1448	112.10>97.10
Isopentyl hexanoate	12.198	1452	99.10>43.10
(Z)-3-hexenyl butyrate	12.198	1452	82.10>67.10
(E)-Linalool oxide	12.291	1458	94.10>79.10
cis-3-Hexenyl 2-methylbutanoate	12.462	1469	82.10>67.10
Citronellal	12.462	1469	121.10>93.10
Octyl acetate	12.478	1470	56.10>41.10
2,4-Heptadienal	12.54	1474	81.00>53.10
Isomenthone	12.571	1476	112.10>97.10
2-Ethylhexanol	12.586	1477	83.10>55.10
2,3-Diethyl-5-methylpyrazine	12.586	1477	150.10>135.10
Methyl nonanoate	12.71	1485	71.10>43.10
2-Acetylfuran	12.726	1486	110.10>95.00
2-Sec-Butyl-3-methoxypyrazine	12.788	1490	138.00>123.10
n-Decanal	12.804	1491	112.00>70.00
2-(Methylthio)ethanol	12.912	1498	92.00>61.10
Camphor	12.985	1503	108.10>93.10
Ethyl 3-hydroxybutyrate	12.985	1503	117.10>71.00
Benzaldehyde	13.014	1505	105.00>77.00
3-Mercapto-3-methylbutyl formate	13.028	1506	69.10>41.10
2-Nonanol	13.07	1509	69.10>41.10
4-(Methylthio)-2-butanone	13.07	1509	118.10>71.10
2-Methyltetrahydrothiophen-3-one	13.084	1510	116.10>60.00
Furfuryl Acetate	13.126	1513	140.10>98.10
Propanoic acid	13.196	1518	74.00>56.00
(E)-2-Nonenal	13.21	1519	96.10>81.10

4-Pentenyl isothiocyanate	13.238	1521	99.00>72.00
Ethyl nonanoate	13.337	1528	88.10>61.10
Ethyl DL-Leucate	13.351	1529	87.10>69.10
Linalool	13.506	1540	71.00>43.00
Dimethyl sulfoxide	13.534	1542	133.10>115.10
Ethyl 3-(methylthio)propionate	13.576	1545	148.10>74.10
1-Octanol	13.59	1546	69.00>41.00
Isobutyric acid	13.604	1547	73.10>55.00
Linalyl acetate	13.632	1549	93.10>77.10
5-Methyl furfural	13.745	1557	110.00>53.00
2-Pentylpyridine	13.773	1559	93.10>66.10
Diethyl malonate	13.871	1566	133.10>115.10
Fenchol	13.927	1570	107.10>91.10
2,5-Dimethyl-4-methoxy-3(2H)-furanone	13.927	1570	142.10>85.00
Nonyl acetate	13.956	1572	97.10>55.10
(2E,6Z)-nona-2,6-dienal	13.956	1572	70.10>42.10
2-Acetylpyridine	14.138	1585	79.10>52.00
Terpinen-4-ol	14.152	1586	136.10>93.10
Benzonitrile	14.166	1587	103.10>76.10
Methyl decanoate	14.18	1588	87.00>55.00
2-Undecanone	14.18	1588	71.00>43.00
(+)-Dihydrocarvone	14.209	1590	152.10>109.10
beta-Caryophyllene	14.223	1591	133.10>105.10
Undecanal	14.251	1593	82.10>67.10
(E)-2-Octen-1-ol	14.335	1599	81.10>79.10
5-Methyl-6,7-dihydro-5H-cyclopenta[b]pyrazine	14.335	1599	134.10>119.10
Hexyl hexanoate	14.388	1603	99.10>43.10
3-(Methylthio)propyl acetate	14.414	1605	88.00>73.10
Methyl benzoate	14.427	1606	105.10>77.10
Butyl octanoate	14.44	1607	127.10>57.10
Butyric acid	14.48	1610	60.00>42.00
(+)-Isodihydrocarvone	14.48	1610	152.10>95.10
cis-beta-Terpineol	14.493	1611	121.10>93.10
Acetylpyrazine	14.493	1611	122.10>94.10
Benzyl mercaptan	14.519	1613	124.00>91.00
Methyl nerate	14.623	1621	114.10>83.10
2-Acetylthiazole	14.623	1621	127.00>99.10
L-Menthol	14.714	1628	95.00>67.00
Phenylacetaldehyde	14.753	1631	91.10>65.10
Ethyl decanoate	14.779	1633	101.10>73.10
(Z)-2-Decenal	14.792	1634	83.10>55.10

Acetophenone	14.792	1634	105.00>77.00
trans-2-Decenal	14.806	1635	107.00>79.00
1-Nonanol	14.871	1640	70.10>55.10
3-Mercapto-3-methyl-1-butanol	14.871	1640	86.10>71.10
Isopropyl benzoate	14.884	1641	105.00>77.10
Furfuryl alcohol	14.884	1641	98.10>42.10
Methyl 2-octynoate	14.897	1642	95.10>67.10
(Z)-3-Hexenyl hexanoate	14.988	1649	82.10>67.10
Citronellyl acetate	15.014	1651	123.10>81.10
Isovaleric acid	15.027	1652	60.00>42.00
Isoamyl octanoate	15.04	1653	70.10>55.10
2-Methyl butyric acid	15.053	1654	74.00>56.00
Isoborneol	15.079	1656	110.10>95.10
Methyl 2-methyl-3-furyl disulfide	15.092	1657	160.00>112.00
4-Methoxystyrene	15.105	1658	134.10>91.10
Ethyl benzoate	15.131	1660	105.00>77.10
trans-beta-Terpineol	15.145	1661	136.10>107.20
beta-Farnesene	15.158	1662	93.10>77.10
Dihydrocarvyl acetate	15.158	1662	107.10>91.10
Estragole	15.171	1663	148.10>117.10
Diethyl succinate	15.171	1663	129.00>101.10
Ethyl 3-hydroxyhexanoate	15.197	1665	89.10>45.00
alpha-Humulene	15.21	1666	93.10>77.10
3-(Acetylthio)-2-methylfuran	15.223	1667	156.10>114.00
alpha-Terpinyl acetate	15.249	1669	121.10>93.10
Decyl acetate	15.288	1672	97.10>55.10
Neral	15.288	1672	94.10>79.10
2-Formylthiophene	15.327	1675	111.00>39.10
Linalyl butyrate	15.366	1678	93.10>77.10
alpha-Terpineol	15.366	1678	136.00>121.00
gamma-Terpineol	15.405	1681	121.10>93.10
Borneol	15.405	1681	110.10>95.10
Methyl geranate	15.431	1683	114.10>83.10
2-Thiophenemethanethiol	15.431	1683	97.00>53.10
(E,E)-2,4-nonadienal	15.523	1690	81.00>53.00
gamma-Caprolactone	15.523	1690	85.00>57.10
Methionol	15.64	1699	106.10>58.00
2-Phenylethanethiol	15.653	1700	91.10>65.10
n-Dodecanal	15.665	1701	110.00>67.00
Linalyl isovalerate	15.714	1705	93.10>77.10
3-Methyl-2(5H)-furanone	15.714	1705	69.10>41.10
3-Methyl-2,4-nonanedione	15.727	1706	99.10>43.10
3-Mercaptohexyl acetate	15.751	1708	88.10>59.00

Valencene	15.763	1709	161.20>105.10
Neodihydrocarveol	15.776	1710	136.10>107.20
Piperitone	15.776	1710	110.10>95.10
Neryl acetate	15.812	1713	93.10>77.10
Benzyl acetate	15.812	1713	150.10>108.10
Valeric acid	15.824	1714	60.00>42.00
(-)-Carvone	15.849	1716	108.10>93.10
d-Carvone	15.849	1716	108.10>93.10
Geranial	15.922	1722	94.10>79.10
Epoxylinalool isomer-1	15.922	1722	94.10>79.10
4-Ethylbenzaldehyde	15.935	1723	134.00>105.10
Naphthalene	15.971	1726	128.00>102.00
Dihydrocarveol	16.069	1734	121.00>93.10
Ethyl undecanoate	16.082	1735	101.10>73.00
2-Acetyl-2-thiazoline	16.082	1735	129.00>101.10
trans-2-Undecenal	16.167	1742	83.10>55.10
Methyl 2-nonynoate	16.192	1744	107.10>79.10
Geranyl acetate	16.192	1744	136.10>121.20
Epoxylinalool isomer-2	16.216	1746	94.10>79.10
1-Decanol	16.278	1751	83.10>55.10
2,6-Nonadienol	16.302	1753	69.10>41.00
Furfuryl thioacetate	16.302	1753	81.10>53.10
5-Methyl-2-thiophenecarboxaldehyde	16.302	1753	125.00>53.10
Cuminaldehyde	16.327	1755	133.10>105.20
Citronellol	16.339	1756	82.10>67.10
p-Acetyltoluene	16.339	1756	119.10>91.10
Carvyl acetate	16.351	1757	152.10>109.10
2-Acetylthiophene	16.388	1760	126.00>111.00
Methyl salicylate	16.425	1763	120.00>92.00
Neoisodihydrocarveol	16.461	1766	136.00>107.10
Ethyl phenylacetate	16.535	1772	91.10>65.10
Perillaldehyde	16.547	1773	122.10>107.10
gamma-Heptalactone	16.621	1779	85.00>57.10
Nerol	16.682	1784	93.10>77.10
Methyl furfuryl disulfide	16.706	1786	81.10>53.10
Isodihydrocarveol	16.755	1790	121.10>93.10
Ethyl nicotinate	16.78	1792	106.00>78.00
Methyl laurate	16.817	1795	87.00>55.00
2,4-Decadienal	16.829	1796	81.00>53.10
Cyclotene	16.853	1798	112.10>84.10
Geranyl isobutyrate	16.878	1800	93.10>77.10
Ethyl salicylate	16.878	1800	120.00>92.10

2-Phenylethyl acetate	16.889	1801	104.00>78.10
Hexyl octanoate	16.924	1804	127.10>57.10
beta-Damascenone	16.924	1804	121.10>105.10
(E)-beta-Damascone	16.982	1809	192.20>177.20
Butyl decanoate	17.017	1812	173.20>43.10
cis-Geranylacetone	17.052	1815	151.20>93.10
(E)-carveol	17.064	1816	109.10>94.00
3-Mercapto-1-hexanol	17.145	1823	82.10>67.10
Capronic acid	17.168	1825	73.00>55.00
trans-p-Methane-8-thiol-3-one	17.25	1832	112.10>97.10
p-Cymenol	17.261	1833	135.10>43.10
Guaiacol	17.273	1834	109.10>81.10
Geraniol	17.296	1836	69.10>41.10
Ethyl laurate	17.32	1838	88.10>61.00
trans-Geranylacetone	17.354	1841	151.20>93.10
alpha-Ionone	17.378	1843	121.00>77.00
Alpha-isomethylionone	17.389	1844	150.10>135.10
2-Dodecenal	17.424	1847	121.00>93.10
(Z)-carveol	17.424	1847	134.10>119.10
Neryl butyrate	17.447	1849	93.10>77.00
1-Undecanol	17.494	1853	83.00>55.00
Butyl benzoate	17.506	1854	105.10>77.10
Safrole	17.506	1854	162.10>104.10
Benzyl butyrate	17.575	1860	108.10>79.10
cis-p-Methane-8-thiol-3-one	17.587	1861	112.10>97.10
Benzyl alcohol	17.61	1863	79.00>77.10
Ethyl 3-phenylpropionate	17.622	1864	178.10>104.10
12-Methyltridecanal	17.633	1865	82.00>67.10
(E)-Whiskey lactone	17.645	1866	99.10>43.10
Neryl isovalerate	17.703	1871	121.10>93.10
5-Methylhexanoic acid	17.831	1882	87.10>45.10
Geranyl butyrate	17.843	1883	93.10>77.10
2-Phenylethanol	17.959	1893	91.00>65.00
gamma-Octalactone	18.017	1898	85.00>57.00
Butylated hydroxytoluene	18.051	1901	220.00>205.00
Geranyl isovalerate	18.129	1908	121.10>93.10
Tetradecanal	18.173	1912	96.00>81.10
cis-Jasmone	18.229	1917	164.10>122.10
beta-Ionone	18.339	1927	177.00>162.00
Hydroxycitronellal	18.339	1927	96.10>81.10
(Z)-whiskey lactone	18.428	1935	99.00>43.10
Maltol	18.472	1939	126.00>71.00
delta-Octalactone	18.483	1940	114.10>71.10

Benzothiazole	18.494	1941	135.00>108.00
(E)-2-Hexenoic acid	18.539	1945	73.10>55.00
2-Acetylpyrrole	18.55	1946	109.10>94.10
1-Dodecanol	18.594	1950	97.10>55.10
2-Methylquinoxaline	18.605	1951	144.10>117.10
Furaneol acetate	18.694	1959	128.10>85.00
Caryophyllene oxide	18.815	1970	161.10>105.10
o-Cresol	18.926	1980	108.00>77.00
Phenol	18.959	1983	94.00>66.00
(Z)-Nerolidol	18.981	1985	136.20>121.10
Methyl eugenol	19.158	2001	178.10>107.10
Methyl myristate	19.169	2002	87.10>55.00
4-Ethyl-2-methoxyphenol	19.19	2004	152.10>137.10
(E)-2-dodecen-1-ol	19.211	2006	96.10>81.10
Furaneol	19.211	2006	128.10>85.10
4-Methoxybenzaldehyde	19.232	2008	135.10>77.10
gamma-Nonalactone	19.253	2010	85.00>57.10
2-Propionylpyrrole	19.275	2012	123.00>94.10
Pantolactone	19.306	2015	71.10>43.10
Butyl laurate	19.317	2016	201.00>57.10
Diethyl malate	19.327	2017	117.10>71.10
trans-Cinnamaldehyde	19.327	2017	103.10>77.10
Pentadecanal	19.338	2018	96.10>81.10
3-Phenyl-1-propanol	19.402	2024	117.10>115.10
(E)-Nerolidol	19.412	2025	136.20>121.10
Caprylic acid	19.508	2034	101.10>55.10
Lilial	19.561	2039	189.10>131.10
Ethyl myristate	19.603	2043	101.10>73.10
p-Cresol	19.677	2050	107.10>77.10
1-Tridecanol	19.709	2053	97.10>55.10
Methyl cinnamate	19.772	2059	131.10>103.10
Homofuraneol	19.783	2060	142.10>127.10
4-Propylguaiacol	20.016	2082	137.10>122.10
Ethyl cinnamate	20.349	2114	131.10>103.10
Hexadecanal	20.47	2126	82.10>67.10
gamma-Decalactone	20.491	2128	85.00>57.00
4-Ethylphenol	20.521	2131	107.10>77.10
Bis(2-methyl-3-furyl)disulfide	20.562	2135	226.00>113.00
Nonanoic acid	20.612	2140	129.10>87.10
Thymol	20.653	2144	150.10>135.10
Eugenol	20.764	2155	164.10>149.10
3-Ethylphenol	20.785	2157	107.10>77.10
p-Vinylguaiacol	20.785	2157	150.10>135.10

1-Tetradecanol	20.795	2158	111.00>69.00
delta-Decalactone	20.856	2164	99.10>71.10
Sotolon	20.967	2175	83.00>55.10
o-Aminoacetophenone	21.16	2194	135.10>120.10
alpha-Bisabolol	21.23	2201	109.10>67.10
Massoia lactone	21.308	2209	97.00>69.10
Methyl palmitate	21.318	2210	87.10>55.00
Methyl anthranilate	21.377	2216	119.00>92.10
beta-Eudesmol	21.416	2220	108.10>93.10
5-Ethyl-3-hydroxy-4-methylfuran-2(5H)-one	21.416	2220	97.10>69.10
2,6-Dimethoxyphenol	21.552	2234	154.10>139.10
Isopropyl palmitate	21.562	2235	102.10>60.00
gamma-Undecalactone	21.63	2242	85.00>57.10
Ethyl palmitate	21.699	2249	101.10>73.10
Capric acid	21.699	2249	129.00>87.00
alpha-Amylcinnamaldehyde	21.709	2250	202.10>129.10
Neric acid	21.738	2253	100.10>82.10
Sulfurol	21.816	2261	143.10>112.00
4-Methoxybenzyl alcohol	21.826	2262	109.00>77.10
Cinnamyl alcohol	21.884	2268	134.10>92.10
delta-Undecalactone	22.06	2286	99.10>71.10
Geranic acid	22.148	2295	100.10>82.10
Farnesol isomer-1	22.215	2302	93.00>77.10
Diethyl L-tartrate	22.243	2305	104.10>76.00
Farnesol isomer-2	22.337	2315	81.00>41.10
Methyl jasmonate	22.374	2319	156.10>83.10
Isoeugenol	22.515	2334	164.10>149.10
Octadecanal	22.543	2337	124.20>82.10
trans,trans-Farnesol	22.59	2342	93.00>77.10
alpha-Hexylcinnamaldehyde	22.684	2352	145.00>117.10
Undecanoic acid	22.749	2359	129.10>87.10
1-Hexadecanol	22.796	2364	111.10>69.10
gamma-Dodecalactone	22.815	2366	85.00>57.10
delta-Dodecalactone	23.151	2402	99.10>71.10
Benzoic acid	23.269	2415	122.10>105.10
Methyl stearate	23.287	2417	143.10>55.10
Indole	23.35	2424	117.00>90.00
Coumarin	23.503	2441	146.00>118.10
Ethyl stearate	23.621	2454	101.10>73.10
Lauric acid	23.684	2461	157.00>87.00
5-Hydroxymethylfurfural	23.693	2462	97.00>69.10
Lyral	23.711	2464	136.10>79.10

Skatole	23.783	2472	130.00>77.00
6-Methoxyeugenol	23.982	2494	194.10>91.10
Nootkatone	24.088	2506	133.10>105.10
alpha-Amylcinnamyl alcohol	24.228	2522	133.00>55.00
Styrene glycol	24.28	2528	107.00>79.10
Vanillin	24.349	2536	152.00>123.00
Methyl vanillate	24.576	2562	182.00>151.10
Stearyl alcohol	24.645	2570	111.10>69.10
Hydrocinnamic acid	24.915	2601	150.10>104.10
Ethyl vanillate	24.933	2603	151.00>123.10
Acetovanillone	24.933	2603	166.10>151.10
Methyl arachidate	25.121	2624	143.10>55.10
Benzyl benzoate	25.13	2625	105.00>77.10
Ethyl arachidate	25.426	2658	157.10>129.10
Benzyl salicylate	26.658	2784	91.00>65.10
Cinnamic acid	27.095	2823	147.00>91.00
Methyl docosanoate	27.178	2830	354.40>101.10
Ethyl docosanoate	27.558	2862	157.10>129.10
7-Methoxycoumarin	27.962	2896	176.10>148.10
Tyrosol	28.38	2926	107.10>77.10
Raspberry ketone	28.422	2929	107.10>77.10

Table S2 List of compounds identified in agarwood samples by SCAN mode.

RT	Compound	Formula	m/z	CAS	Type
8.44	Styrene	C_8H_8	104.15	100-42-5	Aromatics
10.52	4-hydroxy-4-methyl-2-Pentanone	$C_6H_{12}O_2$	116.16	123-42-4	Aliphatic ketones
11.14	Nonanal	$C_9H_{18}O$	142.24	124-19-6	Aliphatic aldehydes
11.39	Tetradecane	$C_{14}H_{30}$	198.39	629-59-4	Alkanes
11.76	1-methoxy-4-methyl-Benzene	$C_8H_{10}O$	122.16	104-83-8	Aromatics
12.70	2-ethyl-1-hexanol	$C_8H_{18}O$	130.23	104-76-7	Aliphatic alcohols
12.93	Hexadecane	$C_{16}H_{34}$	226.44	544-76-3	Alkanes
13.03	Phenylglyoxal	$C_8H_6O_2$	134.13	1074-12-0	Aromatics
13.51	Linalool	$C_{10}H_{18}O$	154.25	78-70-6	Aliphatic alcohols
13.66	1-Octanol	$C_8H_{18}O$	130.22	111-87-5	Aliphatic alcohols
13.80	2-epi-.alpha.-Funebrene	$C_{15}H_{24}$	204.35	854154-70-4	Sesquiterpenes
13.90	Hexadecane, 2,6,10,14-tetramethyl-	$C_{20}H_{42}$	282.50	638-36-8	Alkanes
14.13	α-Guaiene	$C_{15}H_{24}$	204.35	3691-12-1	Sesquiterpenes
14.35	Hexacosane	$C_{26}H_{54}$	366.7	630-01-3	Alkanes
14.79	(3S,3aS,6R,8aS)-3,8,8-Trimethyl-7-methyleneoctahydro-1H-3a,6-methanoazulene (Preziza-7(15)-ene)	$C_{15}H_{24}$	204.35	31145-21-8	Sesquiterpenes
14.82	Acetophenone	C_8H_8O	120.15	98-86-2	Aromatics
14.91	Eicosane	$C_{20}H_{42}$	282.50	112-95-8	Alkanes
15.17	2-hydroxy-benzaldehyde	$C_7H_6O_2$	122.12	1990-2-8	Aromatics
15.18	Benzene, 1-ethenyl-4-methoxy-	$C_9H_{10}O$	134.17	637-69-4	Aromatics
15.27	4a,8-Dimethyl-2-(prop-1-en-2-yl)-1,2,3,4,4a,5,6,7-octahydronaphthalene	$C_{15}H_{24}$	204.35	103827-22-1	Sesquiterpenes
15.40	(4S,4aR,6R)-4,4a-Dimethyl-6-(prop-1-en-2-yl)-1,2,3,4,4a,5,6,7-octahydronaphthalene	$C_{15}H_{24}$	204.35	54868-40-5	Sesquiterpenes
15.63	Aristolochene	$C_{15}H_{24}$	204.35	26620-71-3	Sesquiterpenes
15.70	Naphthalene, 1,2,3,5,6,7,8,8a-octahydro-1,8a-dimethyl-7-(1-methylethenyl)-, [1R-(1.alpha.,7.beta.,8a.alpha.)]-	$C_{15}H_{24}$	204.35	4630-7-3	Sesquiterpenes
15.80	Azulene, 1,2,3,5,6,7,8,8a-octahydro-1,4-dimethyl-7-(1-methylethenyl)-, [1S-(1.alpha.,7.alpha.,8a.beta.)]-	$C_{15}H_{24}$	204.35	3691-11-0	Sesquiterpenes

	(α-Bulnesene)				
15.89	2H-3,9a-Methano-1-benzoxepin, octahydro-2,2,5a,9-tetramethyl-, [3R-(3.alpha.,5a.alpha.,9.alpha.,9a.alpha.)]-（Dihydro-β-agarofuran）	$C_{15}H_{26}O$	222.37	5956-09-2	Sesquiterpenes
16.00	1,1,4,7-Tetramethyldecahydro-1H-cyclopropa[e]azulene-4,7-diol (Aromadendrane-4,10-diol)	$C_{15}H_{26}O_2$	238.37	136458-41-8	Sesquiterpenes
16.16	3,5,11-Eudesmatriene	$C_{15}H_{22}$	202.33	193615-7-5	Sesquiterpenes
16.48	Benzene, 1-(1,5-dimethyl-4-hexenyl)-4-methyl- (α-Curcumene)	$C_{15}H_{22}$	202.33	644-30-4	Aromatics
16.71	Ethanol, 2-(2-butoxyethoxy)-	$C_8H_{18}O_3$	162.23	112-34-5	Aliphatic alcohols
17.05	(2R,8R,8aS)-8,8a-Dimethyl-2-(prop-1-en-2-yl)-1,2,3,7,8,8a-hexahydronaphthalene ((-)-Nootkatene)	$C_{15}H_{22}$	202.33	5090-61-9	Sesquiterpenes
17.41	4-Phenyl-2-Butanone	$C_{10}H_{12}O$	148.20	2550-26-7	Aromatics
17.80	10,11-Epoxycalamenene	$C_{15}H_{20}O$	216.32	143785-42-6	Sesquiterpenes
18.00	Phenylethyl Alcohol	$C_8H_{10}O$	122.16	1960-12-8	Aromatics
18.95	3-Buten-2-one, 4-(2,6,6-trimethyl-1-cyclohexen-1-yl)- (β-Ionone)	$C_{13}H_{20}O$	192.3	14901-7-6	Sesquiterpenes
19.26	4-Methoxybenzaldehyde	$C_8H_8O_2$	136.15	123-11-5	Aromatics
19.91	Cyclohexanemethanol, 4-ethenyl-.alpha.,.alpha.,4-trimethyl-3-(1-methylethenyl)-, [1R-(1.alpha.,3.alpha.,4.beta.)]-	$C_{15}H_{26}O$	222.37	639-99-6	Sesquiterpenes
20.23	2-Naphthalenemethanol, 1,2,3,4,4a,5,6,7-octahydro-.alpha.,.alpha.,4a,8-tetramethyl-, (2R-cis)- (γ-Eudesmol)	$C_{15}H_{26}O$	222.37	1209-71-8	Sesquiterpenes
20.36	Cedrol	$C_{15}H_{26}O$	222.37	77-53-2	Sesquiterpenes
20.44	α-Santalol	$C_{15}H_{24}O$	220.35	115-71-9	Sesquiterpenes
20.58	2-Furanmethanol, tetrahydro-.alpha.,.alpha.,5-trimethyl-5-(4-methyl-3-cyclohexen-1-yl)-, [2S-[2.alpha.,5.beta.(R*)]]-	$C_{15}H_{26}O_2$	238.37	26184-88-3	Sesquiterpenes
20.69	1H-Benzocyclohepten-7-ol, 2,3,4,4a,5,6,7,8-octahydro-1,1,4a,7-tetramethyl-, cis-	$C_{15}H_{26}O$	222.37	6892-80-4	Sesquiterpenes

20.92	Agarospirol	$C_{15}H_{26}O$	222.37	1460-73-7	Sesquiterpenes
21.06	(3S,3aS,6R,7S,8aS)-3,7,8,8-Tetramethyloctahydro-1H-3a,6-methanoazulen-7-ol (Prezizaan-7-ol)	$C_{15}H_{26}O$	222.37	312296-11-0	Sesquiterpenes
21.18	(-)-Aristolene	$C_{15}H_{24}$	204.35	6831-16-9	Sesquiterpenes
21.30	Guaiol	$C_{15}H_{26}O$	222.37	489-86-1	Sesquiterpenes
21.47	2-Naphthalenemethanol, 2,3,4,4a,5,6,7,8-octahydro-.alpha.,.alpha.,4a,8-tetramethyl-, [2R-(2.alpha.,4a.beta.,8.beta.)]-（Rosifoliol）	$C_{15}H_{26}O$	222.37	63891-61-2	Sesquiterpenes
21.65	1(2H)-Naphthalenone, 3,4,4a,5,6,7-hexahydro-4a,5-dimethyl-3-(1-methylethenyl)-, [3S-(3.alpha.,4a.alpha.,5.alpha.)]-(Eremophila-1(10),11-dien-9-one)	$C_{15}H_{22}O$	218.33	562-23-2	Sesquiterpenes
21.70	Neointermedeol	$C_{15}H_{26}O$	222.37	5945-72-2	Sesquiterpenes
22.12	2,4-Di-tert-butylphenol	$C_{14}H_{22}O$	206.32	96-76-4	Aromatics
23.61	2(3H)-Naphthalenone, 4,4a,5,6,7,8-hexahydro-4a,5-dimethyl-3-(1-methylethylidene)-, (4ar-cis)-(Dehydrofukinone)	$C_{15}H_{22}O$	218.33	19598-45-9	Sesquiterpenes
24.18	Nootkatone	$C_{15}H_{22}O$	218.33	4674-50-4	Sesquiterpenes
24.68	n-Pentadecanol	$C_{15}H_{32}O$	228.41	629-76-5	Aliphatic alcohols
24.97	7-(2-Hydroxypropan-2-yl)-1,4a-dimethyldecahydronaphthalen-1-ol	$C_{15}H_{28}O_2$	240.38	92857-25-5	Sesquiterpenes
26.02	7,9-Di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione	$C_{17}H_{24}O_3$	276.40	82304-66-3	Ketones
26.86	(3R,3aR,4aS,5R,9aS)-3,5,8-Trimethyl-3a,4,4a,5,6,7,9,9a-octahydroazuleno[6,5-b]furan-2(3H)-one (Dihydrocolumellarin)	$C_{15}H_{22}O_2$	234.33	66873-38-9	Sesquiterpenes

Table S3 Screening results of odor components in agarwood samples by MRM mode.

RT	Compound	Formula	m/z	CAS	Odor characteristic
3.22	alpha-Pinene	$C_{10}H_{16}$	136.23	80-56-8	pine, turpentine
6.48	Myrcene	$C_{10}H_{16}$	136.23	123-35-3	balsamic, must, spice
7.10	3-Methyl-3-butenyl acetate	$C_7H_{12}O_2$	128.16	5205-07-2	—
7.17	Limonene	$C_{10}H_{16}$	136.23	138-86-3	lemon, orange
7.43	2-Methyl-1-butanol	$C_5H_{12}O$	88.15	137-32-6	wine, onion, malt
8.08	2-Pentylfuran	$C_9H_{14}O$	138.21	3777-69-3	green bean, butter
8.45	(E)-beta-Ocimene	$C_{10}H_{16}$	136.23	3779-61-1	sweet, herb
8.79	p-Cymene	$C_{10}H_{14}$	134.22	99-87-6	solvent, gasoline, citrus
8.94	1,2,4-Trimethylbenzene	C_9H_{12}	120.19	95-63-6	—
9.19	Octanal	$C_8H_{16}O$	128.21	124-13-0	fat, soap, lemon, green
10.06	6-Methyl-5-hepten-2-one	$C_8H_{14}O$	126.2	110-93-0	pepper, mushroom, rubber
10.34	2,6-Dimethyl-5-heptenal	$C_9H_{16}O$	140.22	106-72-9	fruit, green, melon
10.47	1-Hexanol	$C_6H_{14}O$	102.17	111-27-3	resin, flower, green
11.02	2-Ethylhexyl acetate	$C_{10}H_{20}O_2$	172.26	103-09-6	fruit
11.09	Nonanal*	$C_9H_{18}O$	142.24	124-19-6	fat, citrus, green
11.53	1,2,4,5-Tetramethylbenzene	$C_{10}H_{14}$	134.22	95-93-2	rancid, sweet
11.72	alpha,p-Dimethylstyrene	$C_{10}H_{12}$	132.2	1195-32-0	citrus, pine
11.84	Ethyl octanoate	$C_{10}H_{20}O_2$	172.26	106-32-1	fruit, fat
11.86	(Z)-Linalool oxide	$C_{10}H_{18}O_2$	170.25	60047-17-8	flower
11.98	Furfural	$C_5H_4O_2$	96.0	98-01-1	bread, almond, sweet
12.14	1-Heptanol	$C_7H_{16}O$	116.2	111-70-6	chemical, green
12.29	(E)-Linalool oxide	$C_{10}H_{18}O_2$	170.25	34995-77-2	flower
12.46	Citronellal	$C_{10}H_{18}O$	154.25	106-23-0	fat, lemon, rose
12.58	2-Ethylhexanol	$C_8H_{18}O$	130.22	104-76-7	rose, green
12.73	2-Acetylfuran	$C_6H_6O_2$	110.11	1192-62-7	balsamic
12.99	Camphor	$C_{10}H_{16}O$	152.23	76-22-2	camphor
13.01	Benzaldehyde	C_7H_6O	106.12	100-52-7	almond, burnt sugar
13.34	Ethyl nonanoate	$C_{11}H_{22}O_2$	186.29	123-29-5	fruity, rose, nutty
13.51	Linalool*	$C_{10}H_{18}O$	154.25	78-70-6	flower, lavender
13.59	1-Octanol*	$C_8H_{18}O$	130.229	111-87-5	chemical, metal, burnt
13.60	Isobutyric acid	$C_4H_8O_2$	88.11	79-31-2	rancid, butter, cheese
13.63	Linalyl acetate	$C_{12}H_{20}O_2$	196.29	115-95-7	sweet, fruit
13.87	Diethyl malonate	$C_7H_{12}O_4$	160.17	105-53-3	apple
14.13	2-Acetylpyridine	C_7H_7NO	121.14	1122-62-9	popcorn
14.42	Methyl benzoate	$C_8H_8O_2$	136.15	93-58-3	prune, lettuce, herb, sweet
14.71	L-Menthol	$C_{10}H_{20}O$	156.26	2216-51-5	peppermint
14.78	Ethyl decanoate	$C_{12}H_{24}O_2$	200.32	110-38-3	grape

14.79	Acetophenone*	C_8H_8O	120.15	98-86-2	must, flower, almond
15.10	4-Methoxystyrene*	$C_9H_{10}O$	134.17	637-69-4	sweet
15.16	beta-Farnesene	$C_{15}H_{24}$	204.35	18794-84-8	wood, citrus, sweet
15.16	Dihydrocarvyl acetate	$C_{12}H_{20}O_2$	196.29	20405-60-1	mint, camphor, medicine
15.17	Diethyl succinate	$C_8H_{14}O_4$	174.19	123-25-1	wine, fruit
15.21	alpha-Humulene	$C_{15}H_{24}$	204.35	6753-98-6	wood
15.29	Neral	$C_{10}H_{16}O$	152.23	106-26-3	lemon
15.37	Linalyl butyrate	$C_{14}H_{24}O_2$	224.34	78-36-4	pear, sweet
15.37	alpha-Terpineol	$C_{10}H_{18}O$	154.25	98-55-5	oil, anise, mint
15.40	gamma-Terpineol	$C_{10}H_{18}O$	154.25	586-81-2	clove
15.40	Borneol	$C_{10}H_{18}O$	154.25	10385-78-1	camphor
15.71	Linalyl isovalerate	$C_{15}H_{26}O_2$	238.37	1118-27-0	sweet, apple, citrus
15.76	Valencene	$C_{15}H_{24}$	204.35	4630-07-3	green, oil
15.81	Neryl acetate	$C_{12}H_{20}O_2$	196.29	141-12-8	fruit
15.82	Valeric acid	$C_5H_{10}O_2$	102.13	109-52-4	sweat
15.85	(-)-Carvone	$C_{10}H_{14}O$	150.22	6485-40-1	mint
15.85	d-Carvone	$C_{10}H_{14}O$	150.22	2244-16-8	caraway
15.97	Naphthalene*	$C_{10}H_8$	128.16	91-20-3	Tar, green, oil
16.0	Dihydrocarveol	$C_{10}H_{18}O$	154.25	619-01-2	mint, spice
16.30	2,6-Nonadienol	$C_9H_{16}O$	140.22	5820-89-3	cucumber
16.33	Cuminaldehyde	$C_{10}H_{12}O$	148.20	122-03-2	acid, sharp
16.34	Citronellol	$C_{10}H_{20}O$	156.26	106-22-9	rose
16.34	p-Acetyltoluene	$C_9H_{10}O$	134.17	122-00-9	bitter almond
16.42	Methyl salicylate	$C_8H_8O_3$	152.15	119-36-8	peppermint
16.68	Nerol	$C_{10}H_{18}O$	154.25	106-25-2	sweet
16.75	Isodihydrocarveol	$C_{10}H_{18}O$	154.25	18675-35-9	wood, spice
16.78	Ethyl nicotinate	$C_8H_9NO_2$	151.16	614-18-6	medicinal, tincture, anis
16.87	Geranyl isobutyrate	$C_{14}H_{24}O_2$	224.34	2345-26-8	floral
16.88	Ethyl salicylate	$C_9H_{10}O_3$	166.17	118-61-6	wintergreen, mint
17.06	(E)-carveol	$C_{10}H_{16}O$	152.23	2102-58-1	caraway, solvent
17.17	Capronic acid	$C_6H_{12}O_2$	116.16	142-62-1	sweat
17.27	Guaiacol	$C_7H_8O_2$	124.14	90-05-1	smoke, sweet, medicine
17.30	Geraniol	$C_{10}H_{18}O$	154.25	106-24-1	rose, geranium
17.32	Ethyl laurate	$C_{14}H_{28}O_2$	228.37	106-33-2	leaf
17.35	trans-Geranylacetone	$C_{13}H_{22}O$	194.31	3796-70-1	—
17.45	Neryl butyrate	$C_{14}H_{24}O_2$	224.34	999-40-6	—
17.61	Benzyl alcohol	C_7H_8O	108.14	100-51-6	sweet, flower
17.84	Geranyl butyrate	$C_{14}H_{24}O_2$	224.34	106-29-6	fruit, rose, apple
17.96	2-Phenylethanol*	$C_8H_{10}O$	122.16	60-12-8	honey, spice, rose, lilac

18.05	Butylated hydroxytoluene	$C_{15}H_{24}O$	220.35	128-37-0	Musty
18.13	Geranyl isovalerate	$C_{15}H_{26}O_2$	238.37	109-20-6	fruit, rose, apple
18.34	beta-Ionone	$C_{13}H_{20}O$	192.3	14901-07-6	seaweed, violet, flower, raspberry
18.49	Benzothiazole	C_7H_5NS	135.19	95-16-9	gasoline, rubber
18.55	2-Acetylpyrrole	C_6H_7NO	109.13	1072-83-9	nut, walnut, bread
18.59	1-Dodecanol	$C_{12}H_{26}O$	186.33	112-53-8	fat, wax
18.81	Caryophyllene oxide	$C_{15}H_{24}O$	220.35	1139-30-6	herb, sweet, spice
18.93	o-Cresol	C_7H_8O	108.14	95-48-7	phenol
18.96	Phenol	C_6H_6O	94.11	108-95-2	phenol
19.16	Methyl eugenol	$C_{11}H_{14}O_2$	178.23	93-15-2	clove, spice
19.19	4-Ethyl-2-methoxyphenol	$C_9H_{12}O_2$	152.19	2785-89-9	spice, clove
19.23	4-Methoxybenzaldehyde*	$C_8H_8O_2$	136.15	123-11-5	mint, sweet
19.31	Pantolactone	$C_6H_{10}O_3$	130.139	599-04-2	—
19.33	trans-Cinnamaldehyde	C_9H_8O	132.16	104-55-2	cinnamon, paint
19.34	Pentadecanal	$C_{15}H_{30}O$	226.4	2765-11-9	fresh
19.41	(E)-Nerolidol	$C_{15}H_{26}O$	222.37	7212-44-4	wood, flower, wax
19.51	Caprylic acid	$C_8H_{16}O_2$	144.21	124-07-2	sweat, cheese
19.56	Lilial	$C_{14}H_{20}O$	204.31	80-54-6	floral
19.68	p-Cresol	C_7H_8O	108.14	106-44-5	medicine, phenol, smoke
20.35	Ethyl cinnamate	$C_{11}H_{12}O_2$	176.21	103-36-6	honey, cinnamon
20.47	Hexadecanal	$C_{16}H_{32}O$	240.42	629-80-1	cardboard alpha-Bisabolol
20.61	Nonanoic acid	$C_9H_{18}O_2$	158.24	112-05-0	green, fat
20.76	Eugenol	$C_{10}H_{12}O_2$	164.20	97-53-0	clove, honey
20.78	p-Vinylguaiacol	$C_9H_{10}O_2$	150.17	7786-61-0	clove, curry
21.23	alpha-Bisabolol	$C_{15}H_{26}O$	222.37	515-69-5	spice, flower
21.31	Methyl palmitate	$C_{17}H_{34}O_2$	270.5	112-39-0	—
21.42	beta-Eudesmol	$C_{15}H_{26}O$	222.37	473-15-4	wood, green
21.70	Ethyl palmitate	$C_{18}H_{36}O_2$	284.5	628-97-7	wax
21.70	Capric acid	$C_{10}H_{20}O_2$	172.26	334-48-5	fat
21.83	4-Methoxybenzyl alcohol	$C_8H_{10}O_2$	138.16	105-13-5	flower
22.54	Octadecanal	$C_{18}H_{36}O$	268.50	638-66-4	oil
22.80	1-Hexadecanol	$C_{16}H_{34}O$	242.44	36653-82-4	wax, flower
23.50	Coumarin	$C_9H_6O_2$	146.14	91-64-5	green, sweet
24.09	Nootkatone*	$C_{15}H_{22}O$	218.33	4674-50-4	grapefruit
24.35	Vanillin	$C_8H_8O_3$	152.15	121-33-5	vanilla
24.64	Stearyl alcohol	$C_{18}H_{38}O$	270.5	112-92-5	oil
24.91	Hydrocinnamic acid	$C_9H_{10}O_2$	150.17	501-52-0	balsamic
24.93	Acetovanillone	$C_9H_{10}O_3$	166.17	498-02-2	vanilla

Note: – No related odor description, * The components detected in both SCAN mode and MRM mode.

Table S4 Differential odor components for appellation and quality evaluation.

Origin	RT	Characteristic components based on SCAN mode	RT	Characteristic components based on MRM mode
Wild Kynam	14.13	α-Guaiene	15.37	Linalyl butyrate
	15.17	2-hydroxy-benzaldehyde		
	15.40	(4S,4aR,6R)-4,4a-Dimethyl-6-(prop-1-en-2-yl)-1,2,3,4,4a,5,6,7-octahydronaphthalene	15.40	gamma-Terpineol
	15.80	α-Bulnesene	15.85	d-Carvone
	17.05	(-)-Nootkatene	15.85	(-)-Carvone
	18.95	β-Ionone	20.78	p-Vinylguaiacol
	21.65	Eremophila-1(10),11-dien-9-one		
High quality agarwood from Hoi-an zone	16.00	1,1,4,7-Tetramethyldecahydro-1H-cyclopropa[e]azulene-4,7-diol (Aromadendrane-4,10-diol)	13.01	Benzaldehyde
	20.23	2-Naphthalenemethanol, 1,2,3,4,4a,5,6,7-octahydro-.alpha.,.alpha.,4a,8-tetramethyl-, (2R-cis)- (γ-Eudesmol)	14.79	Acetophenone
	20.92	Agarospirol	15.10	4-Methoxystyrene
	21.18	(-)-Aristolene	19.23	4-Methoxybenzaldehyde
	21.30	Guaiol	19.34	Pentadecanal
High quality agarwood from Guan-xiang zone	16.00	1,1,4,7-Tetramethyldecahydro-1H-cyclopropa[e]azulene-4,7-diol (Aromadendrane-4,10-diol)	15.10	4-Methoxystyrene
	21.18	(-)-Aristolene	19.23	4-Methoxybenzaldehyde
	21.30	Guaiol	19.34	Pentadecanal
High quality agarwood from Sin-chew zone	14.79	(3S,3aS,6R,8aS)-3,8,8-Trimethyl-7-methyleneoctahydro-1H-3a,6-methanoazulene （Preziza-7(15)-ene）	12.46	Citronellal
	16.48	α-Curcumene	13.01	Benzaldehyde
	21.06	(3S,3aS,6R,7S,8aS)-3,7,8,8-Tetramethyloctahydro-1H-3a,6-methanoazulen-7-ol （Prezizaan-7-ol）	14.79	Acetophenone
			16.34	p-Acetyltoluene
			19.23	4-Methoxybenzaldehyde

Table S5 Quantitative results of differential components based on aroma database (pg/mg).

Origin	Sample	Citronellal	Benzaldehyde	Acetophenone	4-Methoxy-styrene	Linalyl butyrate	(-)-Carvone and d-Carvone	p-Acetyltoluene	4-Methoxy-benzaldehyde	Pentadecanal
Guan-xiang	S2	/	0.885	0.174	0.020	/	0.077	0.020	0.161	0.081
	S4		0.597	0.151	0.022	0.155	0.311	/	0.077	0.141
	S5		0.491	0.170	0.055	0.026	/	0.025	0.230	0.031
	S6		0.939	0.177	0.018	0.008	0.325	0.020	0.170	0.159
	S10		0.225	0.178	0.052	0.010	/	0.038	0.101	0.081
	S11 (H)		0.392	0.160	0.133	0.278		0.025	0.577	0.205
	S13 (H)		0.654	0.215	0.288	0.017		0.016	0.744	0.430
	S14 (H)		0.599	0.151	0.081	0.027		0.030	0.300	0.333
Hoi-an	S17	/	0.748	0.165	0.048	0.032	/	0.038	0.395	0.100
	S19		1.648	0.303	0.113	0.006	0.728	0.016	0.881	0.325
	S21		0.402	0.143	0.047	0.018	/	0.027	0.184	0.095
	S32		0.364	0.169	0.094	0.098		0.035	0.728	/
	S27 (H)		2.131	0.450	0.104	0.066		0.026	0.848	0.289
	S28 (H)		1.437	0.267	0.180	0.085		0.014	1.958	0.395
	S29 (H)		1.345	0.315	0.106	0.082		0.017	0.682	0.541
	S31 (H)		1.226	0.271	0.150	0.066		0.042	0.800	0.156
	S33 (H)		1.284	0.38	0.115	0.110		0.040	0.927	1.142
Sin-chew	S37	/	0.843	0.191	0.035	/	/	0.027	0.119	0.143
	S39		0.819	0.213	0.038		0.349	0.037	0.171	0.095
	S40		1.439	0.273	0.043		/	0.020	0.252	0.066

	S42 (H)	0.005	0.860	0.792	0.070	0.080		0.042	0.532	0.114
	S43 (H)	0.839	1.114	2.187		/	0.154	0.041	0.290	0.247
	S45 (H)	0.278	0.855	0.748	/	0.162	0.027	0.092	0.333	0.548
	S46 (H)	0.266	0.903	1.411		/	0.072	0.083	0.295	0.758
Kynam	S50 (H)	/	0.610	0.096	0.042	4.369	4.607	/	0.831	0.338
	S51 (H)		0.716	0.134	0.066	0.815	2.216		0.830	0.154
	S54 (H)		0.397	0.086	0.055	0.241	0.567		0.675	0.165

H: High quality sample.