Supporting Information

Comparison of volatile profiles and bioactive components of sun-dried Pu-erh tea leaves from ancient tea plants on Bulang Mountain measured by GC-MS and HPLC

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Table S1 Detail results of intra-day repeatability of the HS-SPME method

Compounds	RI	Peak area					RSD
		1	2	3	4	5	
Linalool	1101	448738007	400568601	432951763	400844011	402062770	4.81%
α-Terpineol	1192	124692738	115885847	127535092	116741895	116297176	4.07%
Methyl salicylate	1195	22038230	21430597	23001927	21676081	25461199	6.47%
Nerol	1230	42699351	45667533	45569752	42018502	43774982	3.36%
Geraniol	1256	134542778	120311308	133193798	118651646	134252875	5.57%
α-Ionone	1429	22955364	24061178	25551452	23271083	22978478	4.12%
β-Ionone	1487	96875958	85609915	87557542	95417283	91660054	4.75%
(*E*)-Nerolidol	1569	58647059	50037543	51395227	51049009	57438631	6.71%
Phytol	2116	43291063	38229073	39012409	43352284	44375484	6.04%

HS-SPME: headspace-solid phase microextraction; RI: retention index; RDS: relative standard deviation

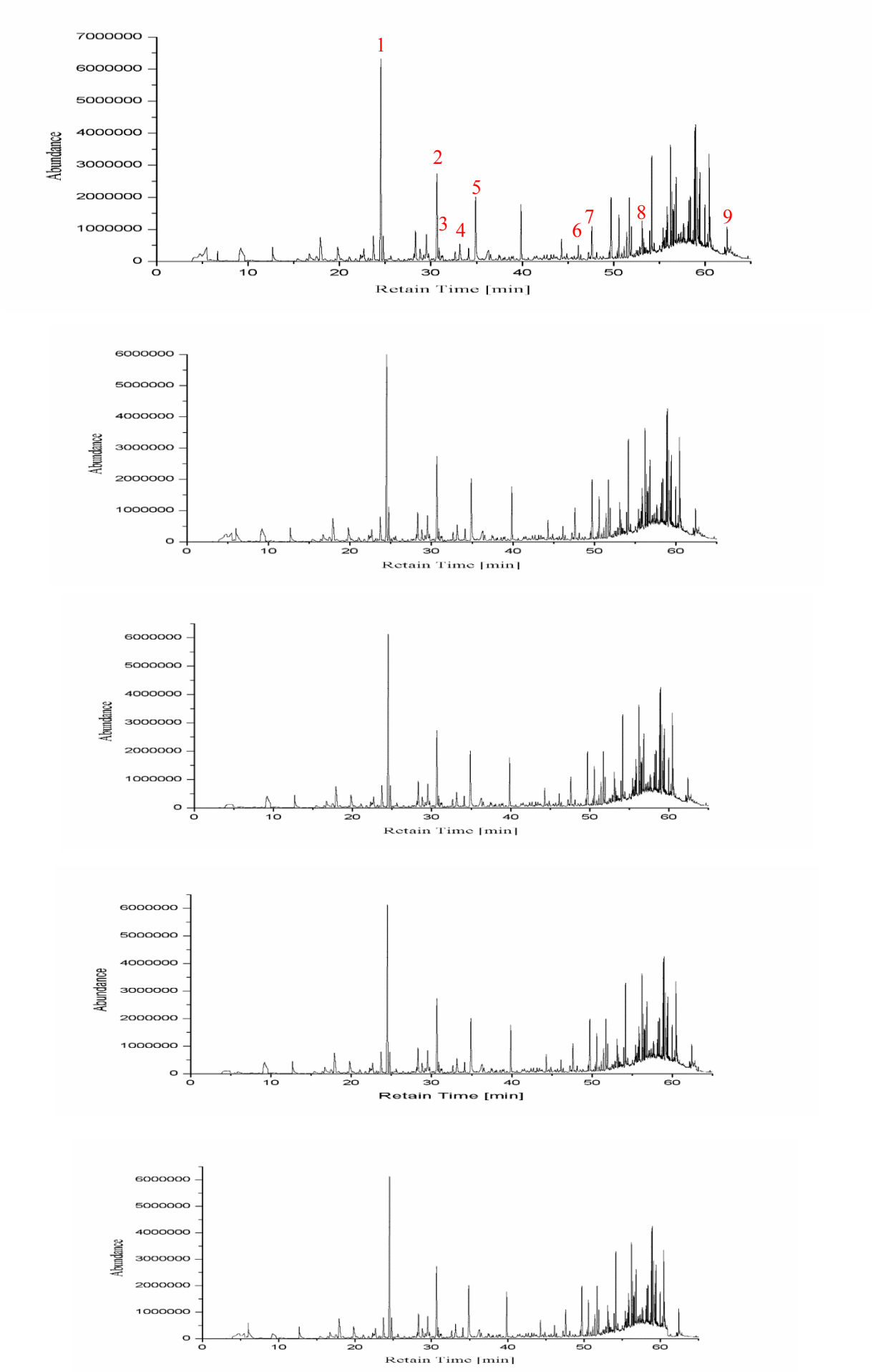

Fig. S1 Total ion chromatograms of the intra-day repeatability experiments

1: linalool; 2:α-terpineol, 3: methyl salicylate; 4: nerol; 5: geraniol; 6: α-ionone; 7: β-ionone; 8: (*E*)-nerolidol; 9: phytol

Table S2 Volatile compounds in seventeen tea samples

Num	Compound	ID	RI[a]	Average relative percentage content (%)															
				LME1	LME2	LME3	LME4	LME5	LBZ1	LBZ2	LBZ3	LBZ4	LBZ5	LBZ6	BL1	BL2	BL3	BL4	BL5	BL6
V1	1-Octen-3-ol	MS, RI	982	0.595	0.536	1.406	0.845	0.53	0	0	0	0.879	1.141	0.84	1.356	0	2.095	0.495	1.337	0
V2	β-Myrcene	MS, RI	991	0.529	0.724	0.73	0.621	0.686	0	0.896	0	0.996	0	0	0.608	0.547	0	0	0.641	0
V3	D-Limonene	MS, RI	1028	1.431	1.798	2.643	1.438	1.727	0	0.612	0	1.178	0.894	1.096	1.267	1.54	1.503	1.1	0.904	0
V4	Z-Ocimene	MS, RI	1037	0.497	0.659	0.565	0.493	0.42	0	0.869	0	0.741	0.763	0.691	0.612	0.497	0.358	0.51	0	0
V5	(Z)-2-Octen-1-ol	MS, RI	1062	0	0.51	0.805	0.69	0.27	0	0	0	0	0	0	0	0	1.236	0.542	0	0
V6	1-Octanol	MS, RI	1064	0.428	0.563	0	0	0	0	0	0	0	0	0	0.897	0.284	1.24	0	1.087	0
V7	Linaloloxide Ⅰ	MS, RI	1068	0	1.873	0	0	1.626	0	0	0	0.491	0.395	0.652	0	2.333	0	1.944	1.452	0
V8	Linaloloxide Ⅱ	MS, RI	1072	3	1.149	0.835	3.317	0	0	0	0	1.014	1.271	2.313	4.732	1.868	2.707	0.802	3.267	1.99
V9	Linalool	MS, RI	1101	14.217	22.077	16.247	18.471	12.736	6.857	13.337	7.549	13.836	14.786	18.639	21.124	16.193	14.288	16.231	23.604	10.646
V10	Hotrienol	MS, RI	1106	2.168	1.941	1.52	2.018	2.562	0	0	0	0.964	1.268	0.831	2.182	3.917	1.828	1.4	2.296	0
V11	Phenylethyl alcohol	MS, RI	1118	0.355	0	0	0	0	0	0	0	0	0	0	0	0.246	0	0	0.304	0
V12	L-Menthone	MS, RI	1160	0.397	0.723	0.903	0.566	0.373	0	0	0	0	0	0	0.566	0.302	0.619	0.488	0.785	0
V13	Benzyl acetate	MS, RI	1165	0.925	1.709	2.404	1.112	1.293	1.641	1.718	0	0	0.344	0	1.418	1.002	1.891	1.119	2.093	2.306
V14	Linaloloxide Ⅲ	MS, RI	1169	2.659	2.398	3.439	3.219	2.572	2.045	2.723	0	5.334	1.819	1.764	4.068	3.025	3.832	1.267	3.48	4.304
V15	(-)-4-Terpineol	MS, RI	1174	0.451	0.926	0.407	0	1.08	0	0	0	0	0	0	0.372	0.836	0.336	0	0.41	0
V16	α-Terpineol	MS, RI	1192	5.486	9.118	6.76	5.362	8.364	4.908	7.93	4.166	6.205	5.182	7.03	7.607	7.975	5.408	5.175	6.289	6.13
V17	Methyl salicylate	MS, RI	1195	0.781	0.673	0.748	1.467	0.362	1.303	0	0	0	0	0	1.578	0.57	0.51	0.867	1.847	0
V18	Estragole	MS, RI	1199	0.325	0.517	0.945	0.182	0.38	0	0	0	0	0	0	0.168	0.31	0.408	0.378	0.566	0
V19	Safranal	MS, RI	1207	0.367	0.42	0	0	0.581	0	0	0	0	0	0	0	0.536	0.314	0.296	0.4	0
V20	β-Cyclocitral	MS, RI	1213	0	0.918	0	0	0.423	0	1.187	0	0.764	0.761	0	0	0.477	1.197	0	0	0
V21	Nerol	MS, RI	1230	1.514	2.41	1.858	2.036	2.526	0	0	0	0.551	0.74	0.532	2.708	2.542	2.254	1.356	2.09	0
V22	5-Methyl-isothiazole	MS, RI	1247	0.668	0	1.138	0	0.478	1.698	0	0	0.551	0.462	0	0.876	0.423	0.574	0.857	0.875	1.33
V23	Geraniol	MS, RI	1256	4.208	6.433	3.911	5.308	4.536	1.915	2.291	1.742	3.821	3.287	4.783	0.876	5.256	3.67	5.585	7.227	2.88
V24	Nonanoic acid	MS, RI	1278	1.292	1.906	0.909	1.411	1.129	1.512	1.528	0	0.911	0.797	0.767	1.747	1.776	1.595	1.334	1.707	0
V25	2-Methyl-naphthalene	MS, RI	1298	0.37	0	0.478	0.941	0.596	1.239	0.917	0	0	0	0	0	0	0	0.5	0	0
V26	Indole	MS, RI	1303	0.265	0	0.907	0.404	0	2.765	0.563	0	0.165	0.256	1.083	0	0.348	1.202	0.385	1.002	0
V27	1-Methyl-naphthalene	MS, RI	1312	0	0.192	0.62	0	0	0	0	0	0	0	0	0	0.372	0.375	0.259	1.053	0
V28	Geranic acid	MS, RI	1354	0.435	0	0	0.466	0	0	0	0	0	0	0	0	0	0	0.498	0	0
V29	3-Methyl-tridecane	MS, RI	1372	0.391	0	0.563	0	0	0	0.737	0	0.514	0.306	0	0	0	0	0	0	0
V30	3,5-Dimethyldodecane	MS, RI	1373	0	0	1.083	0	0	1.759	0.814	0	0.586	0	0.514	0	0	3.928	0	0	1.148
V31	(Z)-3-Hexenyl hexanoate	MS, RI	1381	0.278	0.38	0.444	0.429	0	1.335	0.271	0	0	0.999	0.796	0.271	0	0.364	0.695	0.704	0

V32	β-Damascenone	MS, RI	1385	0.303	0.711	0	0	0	0	0	0	0	0	0	0	0.392	0	0	0	0
V33	Hexyl hexanoate	MS, RI	1386	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.415	0.445	0
V34	(E)-2-Hexenyl hexanoate	MS, RI	1392	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.261	0.172	0
V35	(Z)-Jasmone	MS, RI	1397	0	0	0	0	0	5.766	0	0	1.91	1.192	1.599	0	0	0	0	0	0
V36	Cyclododecanone	MS, RI	1407	0	0	0	0	0	0	0	0	0	0	0	0.469	0	0.736	0	0.672	0
V37	β-Caryophyllene	MS, RI	1418	0.334	0	0.716	0.786	0.54	0	1.416	0	0.475	1.552	0.906	0.61	0.42	0.938	0.586	0.797	0
V38	α-Ionone	MS, RI	1429	0.814	0.455	0.717	0.733	0.976	2.447	1.772	1.634	2.108	2.044	2.336	0.743	0.785	4.218	0.718	5.761	7.734
V39	Geranyl acetone	MS, RI	1454	1.693	0.354	3.038	3.288	1.955	6.953	4.716	4.894	2.093	3.292	2.499	2.711	2.714	3.383	2.868	2.478	5.575
V40	(Z)-β-Farnesene	MS, RI	1458	0	0	0.341	0.45	0	0	0.87	0	0	0	0	0	0	0.51	0	0	1.472
V41	Dehydro-β-ionone	MS, RI	1484	0.456	5.671	0.282	0.249	0.643	1.044	0.62	0	0	1.35	0.939	0.273	0.539	0	0.304	0.334	0
V42	β-Ionone	MS, RI	1487	3.282	0.37	3.254	3.188	3.049	8.468	5.878	8.54	7.005	7.04	7.307	3.465	3.129	0	3.662	0	0
V43	α-Farnesene	MS, RI	1507	0.363	0	0.991	0.649	0.445	0	0.623	0	1.851	2.049	1.255	0.979	0.394	0.93	0.989	0.848	0
V44	Butylated hydroxytoluene	MS, RI	1516	0	0	1.35	1.334	0.791	6.504	2.013	0	0.873	0.538	0.819	0	0.741	1.591	2.097	1.163	1.782
V45	α-Amorphene	MS, RI	1517	0	0	0	0	0.191	0	0	0	0	0	0	0	0	0.292	0	0	0
V46	5-Pentylresorcinol	MS, RI	1531	0	1.974	4.303	4.238	2.821	0	0	0	0	6.802	0	4.176	2.576	3.573	4.307	2.933	9.549
V47	Dihydroactinidiolide	MS, RI	1539	1.558	0.398	1.082	0.991	2.037	3.332	1.981	4.893	3.082	3.298	2.497	0.992	1.485	1.321	1.293	0.869	1.88
V48	α-Calacorene	MS, RI	1543	0.586	0.173	0	0.846	0.909	0	0.966	1.328	0	0	0	0	0.897	0	0	0	1.273
V49	Cyclopentadecane	MS, RI	1549	0.634	0	0	0	0.763	1.455	0	0	0	0	0	0	0	0	0	0	0.622
V50	4-Methyl-pentadecane	MS, RI	1559	0	0	0	0	0.566	0	0.599	0	0	1.102	0	0.782	0.633	1.047	0.79	0.447	0.749
V51	(E)-Nerolidol	MS, RI	1569	1.917	0.499	2.916	2.264	0	0	0	0	2.711	2.675	4.163	3.237	1.431	3.843	2.312	2.505	0
V52	3-Methyl-pentadecane	MS, RI	1571	0	0	1.468	0	0	3.306	2.504	2.278	0	0	0	1.027	0	1.385	0	0	0
V53	Farnesyl acetaldehyde	MS, RI	1580	0	0	1.593	0	0	0	0	0	0	0	0	1.376	0	2.214	0	0	0
V54	Diethyl phthalate	MS, RI	1602	0	0.201	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
V55	Cedrol	MS, RI	1605	0	0	0	0	1.044	0	0	0	0	0	0	2.031	0	0	0	1.803	0
V56	Benzophenone	MS, RI	1621	1.32	0	0	0	1.761	0	0.762	0.73	0	0	0	0	0.478	0	0	0	0
V57	τ-Muurolol	MS, RI	1643	0	0	0	0	0	0	0	0	0	0	0	0	1.533	0	0	0	0
V58	α-Cadinol	MS, RI	1658	0.856	0.266	0	0.693	1.11	0	0	0	0	0	0	0	1.296	0	0	0	0
V59	2,2',5,5'-Tetramethyl-1,1'-biphenyl	MS, RI	1665	3.867	2.276	2.984	4.683	0.69	2.06	5.358	3.045	2.986	5.331	3.587	0.984	0.705	3.426	1.172	0.677	5.073
V60	4'-Benzylacetophenone	MS, RI	1697	2.151	0.494	1.453	2.284	1.366	2.02	2.713	3.096	0	1.616	2.022	0	1.306	0	1.753	0.939	1.922
V61	2,6,10,14-Tetramethyl-pentadecane	MS, RI	1705	2.292	0.736	1.385	3.112	4.691	0	3.155	3.838	3.048	2.663	2.711	3.255	1.43	0	1.801	0	2.952
V62	3-Methyl-heptadecane	MS, RI	1771	0	0.258	0.994	0.851	1.377	0	0.97	0	0	0	0	0	0.446	0	0.61	0	0
V63	2,6,10,14-Tetramethyl-hexadecane	MS, RI	1808	2.507	1.88	1.234	1.404	2.844	1.378	2.222	3.419	0	2.301	0	1.079	1.153	1.005	2.319	0.504	0.737
V64	3-Octadecyne	MS, RI	1833	3.315	3.76	1.693	2.024	0	4.38	3.404	8.625	0	0	0	2.805	1.093	0	2.861	1.662	7.149
V65	6,10,14-Trimethyl-2-pentadecanone	MS, RI	1839	3.591	2.385	1.49	1.423	3.687	5.976	5.312	10.668	2.881	3.813	3.123	2.205	4.91	3.645	1.988	1.496	5.602

V66	Caffeine	MS, RI	1842	4.386	0	2.487	2.646	2.226	6.165	1.477	5.623	5.88	4.534	5.315	0.897	0.998	2.004	6.686	0	2.119
V67	Diisobutyl phthalate	MS, RI	1869	1.567	2.4	0	0	2.85	1.789	1.48	0	2.407	1.197	0	0	0.831	1.085	0	0	0
V68	Methyl palmitate	MS, RI	1927	1.834	0.425	0.496	0.577	1.177	1.402	1.085	2.465	0.688	0.758	0	0.666	0.603	0.624	0.488	0.407	1.439
V69	Isophytol	MS, RI	1947	0.518	3.568	0.86	0.302	0	0	0	0	0	0	0	0.618	0.155	0.306	0.315	0.27	0.493
V70	n-Hexadecanoic acid	MS, RI	1965	3.379	0.802	1.409	2.459	1.936	1.751	1.947	3.01	1.507	1.755	0	0.742	1.409	0.784	1.257	0.721	3.043
V71	Dibutyl phthalate	MS, RI	1969	1.075	0.452	0.528	0.93	0.966	1.243	0.928	2.918	2.833	1.846	3.223	0.478	4.656	0.546	0.363	0.337	1.578
V72	Methyl linoleate	MS, RI	2095	0.201	0	0	0.258	0	0	0.231	0	0.29	0.221	0.731	0.236	0.133	0.335	0.178	0	0
V73	Methyl linolenate	MS, RI	2098	0	0	0	0.154	0	0	0	0	0	0	0	0.152	0.107	0.357	0.185	0.14	0
V74	Phytol	MS, RI	2116	1.939	1.762	0.784	0.975	1.789	0	0.39	0	5.341	2.472	7.482	2.113	0.652	1.074	3.272	1.642	0.762
V75	Oleic Acid	MS, RI	2143	0.547	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

Table S3 Contents of ten bioactive compounds in seventeen tea samples

Compounds	GA	GC	EGC	C	CAF	EC	EGCG	GCG	ECG	CG
LME1	8.497	3.807	6.648	5.634	25.787	14.885	25.939	5.636	25.163	3.841
LME2	8.074	4.343	9.271	5.424	23.597	22.540	22.878	4.410	25.313	3.351
LME3	8.181	4.368	6.058	7.940	24.190	15.894	26.368	7.243	29.769	5.603
LME4	9.1290	3.621	6.586	3.864	35.210	11.467	23.734	4.957	18.559	2.545
LME5	9.140	3.151	7.544	5.290	27.719	15.529	30.573	4.838	30.069	2.873
LBZ1	7.921	2.388	5.218	5.401	34.605	17.410	21.231	4.128	28.422	3.880
LBZ2	7.766	1.863	2.257	6.418	42.288	13.548	14.975	4.348	23.240	5.085
LBZ3	6.948	2.981	5.483	5.973	28.908	15.165	18.085	3.947	22.259	3.377
LBZ4	7.658	2.483	3.226	8.795	41.309	18.696	14.839	4.885	29.880	7.930
LBZ5	6.735	2.786	3.928	10.064	37.923	21.420	12.870	3.842	20.676	3.374
LBZ6	7.403	3.523	4.420	5.641	43.566	12.546	16.769	6.086	21.472	6.219
BL1	8.585	2.554	7.344	5.508	28.715	17.973	24.577	2.269	25.587	1.422
BL2	8.006	3.041	4.807	4.494	42.222	11.843	26.749	5.822	25.762	3.703
BL3	9.114	2.904	5.612	8.339	35.132	15.111	20.645	4.065	24.373	2.992
BL4	9.243	2.848	5.560	5.534	37.514	16.457	22.521	5.558	31.039	5.536
BL5	9.110	3.054	6.788	5.111	32.681	19.060	22.915	4.649	30.245	3.825
BL6	7.218	2.305	5.467	5.335	24.831	16.403	26.067	3.520	30.979	2.783

Table S4 Compound list with VIP value larger than 1.0

ID	RI	Compound	VIP value
Volatiles			
V50	1559	4-Methyl-pentadecane	1.590
V42	1487	β-Ionone	1.495
V3	1028	D-Limonene	1.425
V12	1160	L-Menthone	1.423
V73	2098	Methyl linolenate	1.411
V47	1539	Dihydroactinidiolide	1.373
V36	1407	Cyclododecanone	1.360
V18	1199	Estragole	1.336
V21	1230	Nerol	1.313
V38	1429	α-Ionone	1.284
V15	1174	(-)-4-Terpineol	1.212
V6	1064	1-Octanol	1.195
V62	1771	3-Methyl-heptadecane	1.177
V46	1531	5-Pentylresorcinol	1.134
V10	1106	Hotrienol	1.134
V58	1658	α-Cadinol	1.130
V57	1643	τ-Muurolol	1.118
V39	1454	Geranyl acetone	1.089
V67	1869	Diisobutyl phthalate	1.083
V19	1207	Safranal	1.078
V34	1392	(E)-2-Hexenyl hexanoate	1.072
V33	1386	Hexyl hexanoate	1.065
V5	1062	(Z)-2-Octen-1-ol	1.059
V13	1165	Benzyl acetate	1.058
V2	991	β-Myrcene	1.053
V27	1312	1-Methyl-naphthalene	1.036
V65	1839	6,10,14-Trimethyl-2-pentadecanone	1.035
V8	1072	Linaloloxide Ⅱ	1.028
V35	1397	(Z)-Jasmone	1.023
V69	1947	Isophytol	1.022
V66	1842	Caffeine	1.015
V56	1621	Benzophenone	1.011
V25	1298	2-Methyl-naphthalene	1.008
V71	1969	Dibutyl phthalate	1.005
Bioactive compounds			
1		GC	1.410
2		EGCG	1.307
3		EGC	1.160
4		GA	1.130
5		CAF	1.006

VIP: variable importance in the projection. They may have potential to distinguish the sun-dried Pu-erh tea of ancient tea plants

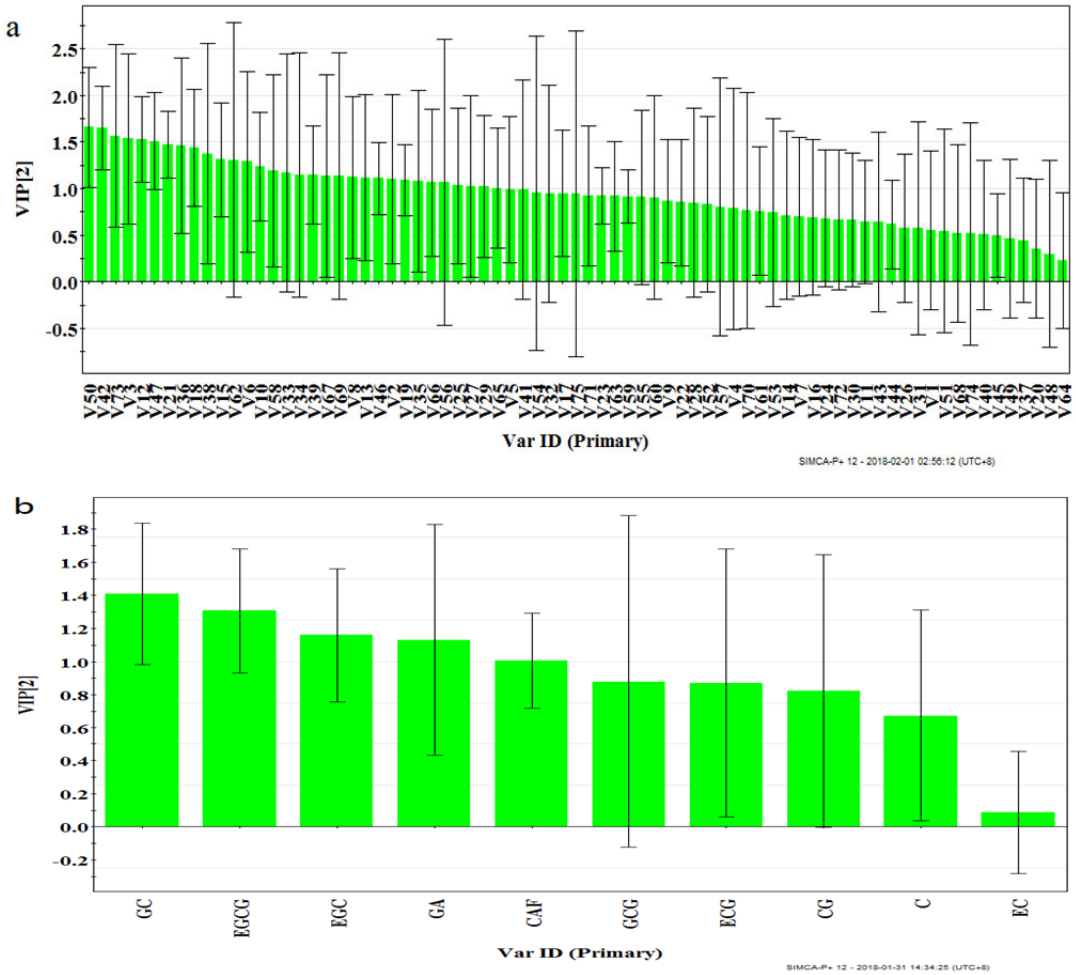

Fig. S2 VIP plots of PLS-DA based on volatiles data and bioactive compounds data

(a) Volatiles data; (b) Bioactive compounds data