Analysis of terpenes in dried wood using thermal desorption–GC–TOFMS

Product used: Mass Spectrometer (MS)

Introduction

Terpenes are organic compounds consisting of isoprene units (C5). Depending on the number of isoprene units, they are called monoterpenes (C10), sesquiterpenes (C15), diterpenes (C20), etc. Derivatives with functional groups such as carbonyl and hydroxyl are called terpenoids. Some terpenoids have a carbon number that is not a multiple of 5 due to addition or elimination during the derivatization process. There are many types of these terpenes and their uses are diverse, such as raw materials for industrial products, foods, cosmetics, and pharmaceuticals, etc. Terpenes are also known as aromatic components of plants, and are particularly abundant in coniferous trees. In this MSTips, we will introduce the analysis of terpenes in cedar and cypress wood using thermal desorption (TD)-GC-TOFMS.

Experiment

Commercially available dried cedar and cypress wood were used as samples. 30 mg of each was sealed in a TD sample tube and heated at 120°C for 60 minutes to extract volatile components. Table 1 shows the measurement conditions of TD-GC-MS.

Table 1 Measurement conditions

TD conditions	
Thermal Desorption	TD-100xr (Markes International Ltd)
Sample tube type	Empty
Tube desorption	120°C(60min), 20mL/min, Splitless
Focusing trap type	General purpose Hydrophobic (T2)
Trap cooling	0 °C
Trap desorption	280°C(2min), 100mL/min, Split50:1

GC conditions	
Gas Chromatograph	8890 GC (Agilent Technologies)
Column	ZB-5MSi (Phenomenex) 30m x 0.25mm, 0.25µm
Oven Temperature	40°C(2min)-10°C/min -300°C(10min)
Carrier flow	He, 2.0mL/min
MS conditions	
Spectrometer	JMS-T2000GC (JEOL Ltd.)
Ion source	EI/FI combination
Ionization	EI(70eV), FI
Ion source temperature	250 °C (EI)
Mass range	*m/z* 10-800

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Results

Figure 1 shows TIC chromatograms of cedar and cypress wood. In cedar, similar amounts of sesquiterpenes and diterpenes were detected. In cypress, sesquiterpenes were mainly detected.

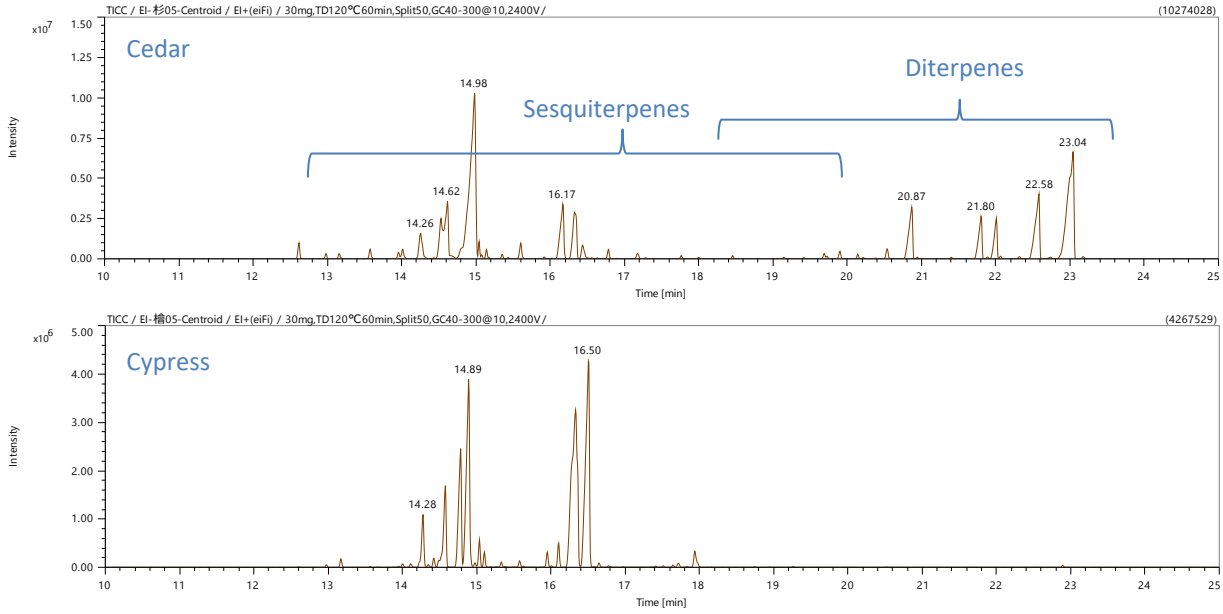

Figure 1 TIC chromatograms

Figure 2 shows the difference analysis results of msFineAnalysis AI (focused on 12:00-17:00). ID017-19 are all sesquiterpenoids with the chemical formula $C_{15}H_{26}O$. ID017 epi-Cubenol was strongly detected in cedar, ID018 τ-Muurolol was detected with the same intensity in both, and ID019 α-Cadinol was strongly detected in cypress. These components have similar structures, so their mass spectra are also similar. msFineAnalysis AI can select them correctly using the retention index (RI) analysis.

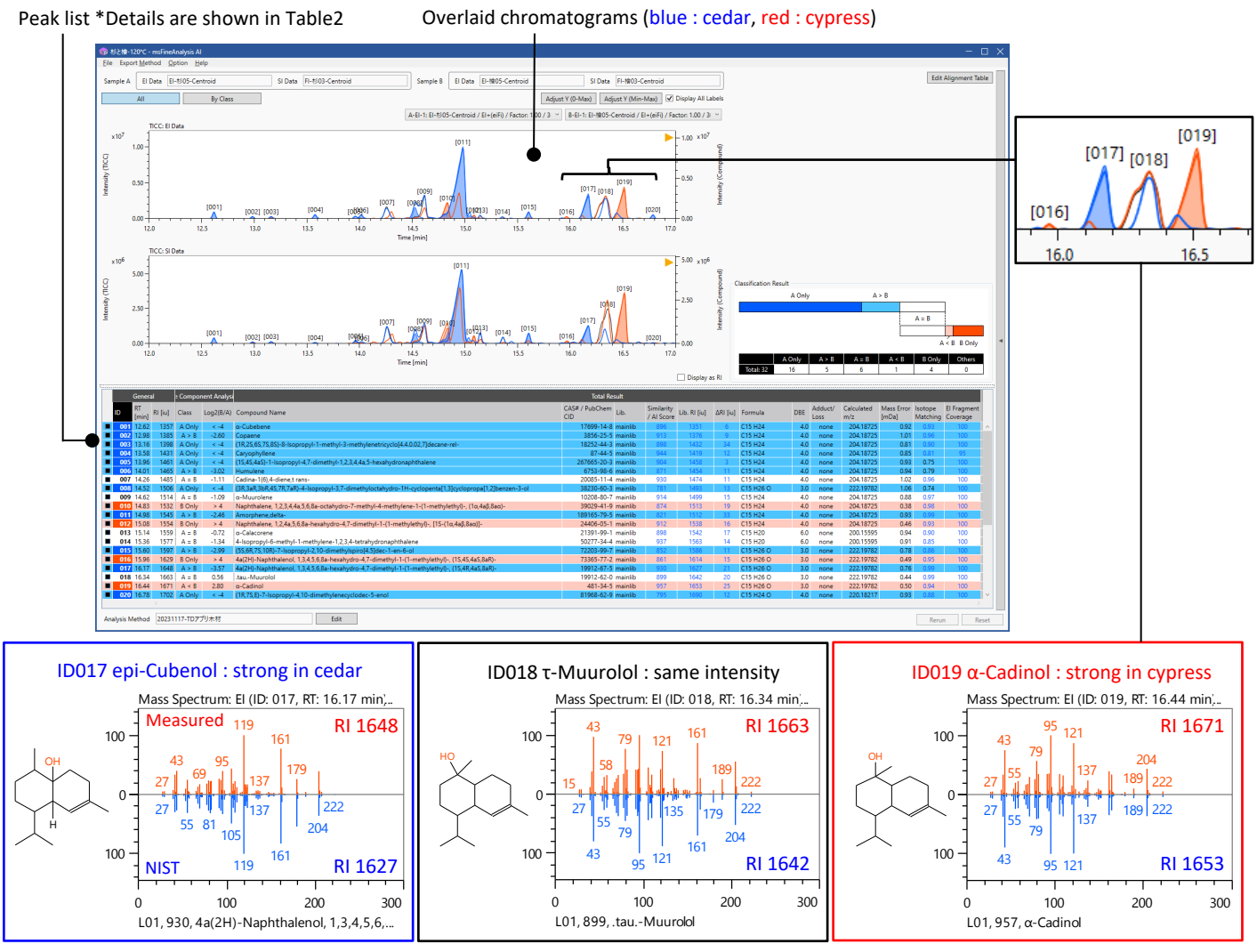

Figure 2 Difference analysis result using msFineAnalysis AI

Table 2 shows the peak list. Two (ID021, ID025) of 32 components were not registered in the NIST library, but their structural formulas could be obtained by AI structural analysis.

Table 2 Peak list of msFineAnalysis AI

(blue : Strong in Cedar, red : Strong in Cypress, White : Same intensity)

	General		e Component Analysi		Total Result										
ID	RT [min]	RI [iu]	Class	Log2(B/A)	Compound Name	CAS# / PubChem CID	Lib.	Similarity / AI Score	Lib. RI [iu]	ΔRI [iu]	Formula	DBE	Calculated m/z	Mass Error [mDa]	Isotope Matching	EI Fragment Coverage
001	12.62	1357	A Only	< -4	α-Cubebene	17699-14-8	mainlib	896	1351	6	C15 H24	4.0	204.18725	0.92	0.93	100
002	12.98	1385	A > B	-2.60	Copaene	3856-25-5	mainlib	913	1376	9	C15 H24	4.0	204.18725	1.01	0.96	100
003	13.16	1398	A Only	< -4	(1R,2S,6S,7S,8S)-8-Isopropyl-1-methyl-3-methylenetricyclo[4.4.0.02,7]decane-rel-	18252-44-3	mainlib	898	1432	34	C15 H24	4.0	204.18725	0.81	0.90	100
004	13.58	1431	A Only	< -4	Caryophyllene	87-44-5	mainlib	944	1419	12	C15 H24	4.0	204.18725	0.85	0.81	95
005	13.96	1461	A Only	< -4	(1S,4S,4aS)-1-Isopropyl-4,7-dimethyl-1,2,3,4,4a,5-hexahydronaphthalene	267665-20-3	mainlib	904	1458	3	C15 H24	4.0	204.18725	0.93	0.75	100
006	14.01	1465	A > B	-3.02	Humulene	6753-98-6	mainlib	871	1454	11	C15 H24	4.0	204.18725	0.94	0.79	100
007	14.26	1485	A = B	-1.11	Cadina-1(6),4-diene,t rans-	20085-11-4	mainlib	930	1474	11	C15 H24	4.0	204.18725	1.02	0.96	100
008	14.52	1506	A Only	< -4	(3R,3aR,3bR,4S,7R,7aR)-4-Isopropyl-3,7-dimethyloctahydro-1H-cyclopenta[1,3]cyclopropa[1,2]benzen-3-ol	38230-60-3	mainlib	781	1493	13	C15 H26 O	3.0	222.19782	1.06	0.74	100
009	14.62	1514	A = B	-1.09	α-Muurolene	10208-80-7	mainlib	914	1499	15	C15 H24	4.0	204.18725	0.88	0.97	100
010	14.83	1532	B Only	> 4	Naphthalene, 1,2,3,4,4a,5,6,8a-octahydro-7-methyl-4-methylene-1-(1-methylethyl)-, (1α,4aβ,8aα)-	39029-41-9	mainlib	874	1513	19	C15 H24	4.0	204.18725	0.38	0.98	100
011	14.98	1545	A > B	-2.46	Amorphene,delta-	189165-79-5	mainlib	821	1512	33	C15 H24	4.0	204.18725	0.93	0.99	100
012	15.08	1554	B Only	> 4	Naphthalene, 1,2,4a,5,6,8a-hexahydro-4,7-dimethyl-1-(1-methylethyl)-, [1S-(1α,4aβ,8aα)]-	24406-05-1	mainlib	912	1538	16	C15 H24	4.0	204.18725	0.46	0.93	100
013	15.14	1559	A = B	-0.72	α-Calacorene	21391-99-1	mainlib	898	1542	17	C15 H20	6.0	200.15595	0.94	0.90	100
014	15.36	1577	A = B	-1.34	4-Isopropyl-6-methyl-1-methylene-1,2,3,4-tetrahydronaphthalene	50277-34-4	mainlib	937	1563	14	C15 H20	6.0	200.15595	0.91	0.85	100
015	15.60	1597	A > B	-2.99	(5S,6R,7S,10R)-7-Isopropyl-2,10-dimethylspiro[4.5]dec-1-en-6-ol	72203-99-7	mainlib	852	1586	11	C15 H26 O	3.0	222.19782	0.78	0.86	100
016	15.96	1629	B Only	> 4	4a(2H)-Naphthalenol, 1,3,4,5,6,8a-hexahydro-4,7-dimethyl-1-(1-methylethyl)-, (1S,4S,4aS,8aR)-	73365-77-2	mainlib	861	1614	15	C15 H26 O	3.0	222.19782	0.49	0.95	100
017	16.17	1648	A > B	-3.57	4a(2H)-Naphthalenol, 1,3,4,5,6,8a-hexahydro-4,7-dimethyl-1-(1-methylethyl)-, (1S,4R,4aS,8aR)-	19912-67-5	mainlib	930	1627	21	C15 H26 O	3.0	222.19782	0.76	0.99	100
018	16.34	1663	A = B	0.56	.tau.-Muurolol	19912-62-0	mainlib	899	1642	20	C15 H26 O	3.0	222.19782	0.44	0.99	100
019	16.44	1671	A < B	2.80	α-Cadinol	481-34-5	mainlib	957	1653	25	C15 H26 O	3.0	222.19782	0.50	0.94	100
020	16.78	1702	A Only	< -4	(1R,7S,E)-7-Isopropyl-4,10-dimethylenecyclodec-5-enol	81968-62-9	mainlib	795	1690	12	C15 H24 O	4.0	220.18217	0.93	0.88	100
* 021	17.18	1739	A Only	< -4	3,5,8a-trimethyl-6,9-dihydrobenzo[f][1]benzofuran-4-one	792, 162897448	AI	832	-	-	C15 H16 O2	8.0	228.11448	0.47	0.78	95
022	17.76	1793	A = B	-1.15	Khusinol acetate	78405-34-2	mainlib	728	1825	32	C17 H26 O2	5.0	-	-	-	100
023	17.96	1813	B Only	> 4	Tau-Cadinol acetate	149197-48-8	mainlib	867	1805	8	C17 H28 O2	4.0	264.20838	0.40	0.88	100
024	19.69	1985	A Only	< -4	Phenanthrene, 7-ethenyl-1,2,3,4,4a,4b,5,6,7,9,10,10a-dodecahydro-1,1,4a,7-tetramethyl-, [4aS-(4aα,4bβ,7β,10aβ)]-	1686-56-2	mainlib	882	1960	25	C20 H32	5.0	272.24985	0.70	0.88	100
* 025	19.90	2008	A Only	< -4	(2-acetyloxy-4,4,8-trimethyl-9-tricyclo[6.3.1.01,5]dodecanyl) acetate	419, 163050904	AI	781	-	-	C19 H30 O4	5.0	322.21386	0.64	0.78	100
026	20.14	2033	A Only	< -4	(4aS,10aS)-7-Isopropyl-1,1,4a-trimethyl-1,2,3,4,4a,5,6,9,10,10a-decahydrophenanthrene	41577-36-0	mainlib	893	2036	3	C20 H32	5.0	272.24985	1.19	0.92	100
027	20.54	2076	A Only	< -4	Phenanthrene, 1,2,3,4,4a,9,10,10a-octahydro-1,1,4a-trimethyl-7-(1-methylethyl)-, (4aS-trans)-	19407-28-4	mainlib	922	2054	22	C20 H30	6.0	270.23420	0.96	0.92	100
028	20.87	2112	A Only	< -4	(4aS,4bR,10aS)-7-Isopropyl-1,1,4a-trimethyl-1,2,3,4,4a,4b,5,6,10,10a-decahydrophenanthrene	35241-40-8	mainlib	933	2080	32	C20 H32	5.0	272.24985	1.07	0.86	100
029	21.80	2217	A Only	< -4	(1R,4aR,4bS,7R,10aR)-1,4a,7-Trimethyl-7-vinyl-1,2,3,4,4a,4b,5,6,7,9,10,10a-dodecahydrophenanthrene-1-carbaldehyde	3855-14-9	mainlib	931	2185	32	C20 H30 O	6.0	286.22912	0.60	0.98	100
030	22.00	2241	A Only	< -4	Phyllocladanol	27898-42-6	mainlib	869	2210	31	C20 H34 O	4.0	290.26042	0.79	0.89	100
031	22.57	2308	A Only	< -4	((1R,4aR,4bS,7R,10aR)-1,4a,7-Trimethyl-7-vinyl-1,2,3,4,4a,4b,5,6,7,9,10,10a-dodecahydrophenanthren-1-yl)methanol	24563-84-6	mainlib	857	2270	38	C20 H32 O	5.0	288.24477	0.76	1.00	100
032	23.03	2364	A Only	< -4	Ferruginol,cis-	-	mainlib	862	2370	6	C20 H30 O	6.0	286.22912	1.20	0.99	100

Figure 3 shows the structural analysis results of ID025. Clovanediol diacetate which is one of the terpenoids was obtained as a higher candidate (6th /643 candidates).

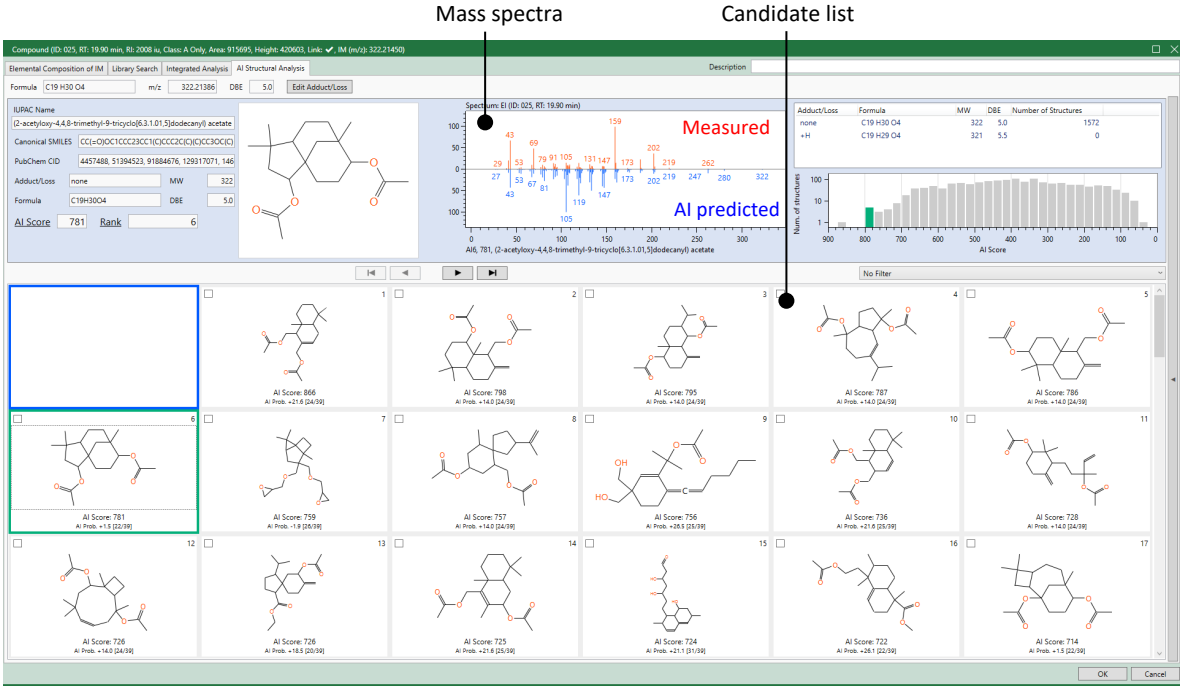

Figure 3 AI structure analysis result of peak ID025

Conclusion

Terpenes in wood were analyzed using TD-GC-TOFMS and msFineAnalysis AI. Although analysis of terpenes is complex, the good results were obtained by msFineAnalysis AI using difference analysis, retention index analysis and AI structure analysis.

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