Headspace SPME-GC/MS Analysis of Terpenes in Cannabis

A rapid method to identify cannabis terpenes for forensic and organoleptic applications

Cannabis sativa (cannabis or marijuana) contains over 100 different terpenes and terpenoids, including mono, sesqui, di and tri, as well as other miscellaneous compounds of terpenoid orgin.[1] Terpenes give the plant distinct organoleptic properties and produce characteristic aromas when the buds are heated or vaporized.[2] Although the terpene profile does not necessarily indicate geographic origin of a cannabis sample, it can be used in forensic applications to determine the common source of different samples.[3] In addition, different cannabis strains have been developed which have distinct aromas and flavors, a result of the differing amounts of specific terpenes present.[4]

Experimental

Dried cannabis sample was obtained courtesy of Dr. Hari H. Singh, Program Director at the Chemistry and Physiological Systems Research Branch of the United States National Institute on Drug Abuse at the National Institute of Health. Terpenes were isolated using headspace solid phase microextraction (SPME) followed by chromatographic separation on an Equity®-1 capillary GC column. Peak identifications were assigned using MS spectral matching against reference spectra in the Wiley and NIST libraries. Confirmatory identification was done based on retention index, which was calculated for the compounds identified in each sample using an n-alkane standard analyzed under the same GC conditions. This data was compared with published values and peak identifications were assigned.[5,6,7] Final analytical conditions appear in **Figure 1**.

Results and Discussion

The terpenes identified in the cannabis sample (**Figure 1**) are indicated in **Table 1**. The profile was similar to those found previously in the analysis of dried cannabis.[3,5] Early eluting peaks generally were monoterpenes and monoterpenoids. The later eluting peaks consisted of sequiterpenes and caryophyllene oxide, which is a sequiterpenoid. The most abundant terpene was caryophyllene. The predominance of this compound could be due to the specific strain of cannabis tested, and/

Figure 1. Headspace SPME-GC/MS Analysis of Dried *Cannabis Sativa*

(See **Table 1** for peak identification)

sample/matrix:	0.5 g dried, ground *cannabis sativa*
SPME fiber:	50/30 µm DVB/CAR/PDMS (57298-U)
sample equilibration:	30 min, 40 °C
extraction:	20 min, headspace, 40 °C
desorption process:	3 min, 270 °C
fiber post bake:	3 min, 270 °C
column:	Equity®-1, 60 m × 0.25 mm I.D., 0.25 µm (28047-U)
oven:	60 °C (2 min), 5 °C/min to 275 °C (5 min)
inj. temp.:	270 °C
detector:	MSD
MSD interface:	300 °C
scan range:	full scan, m/z 50-500
carrier gas:	helium, 1 mL/min constant flow
liner:	0.75 mm ID SPME
instrument:	Agilent® 6890/5973N GC/MS

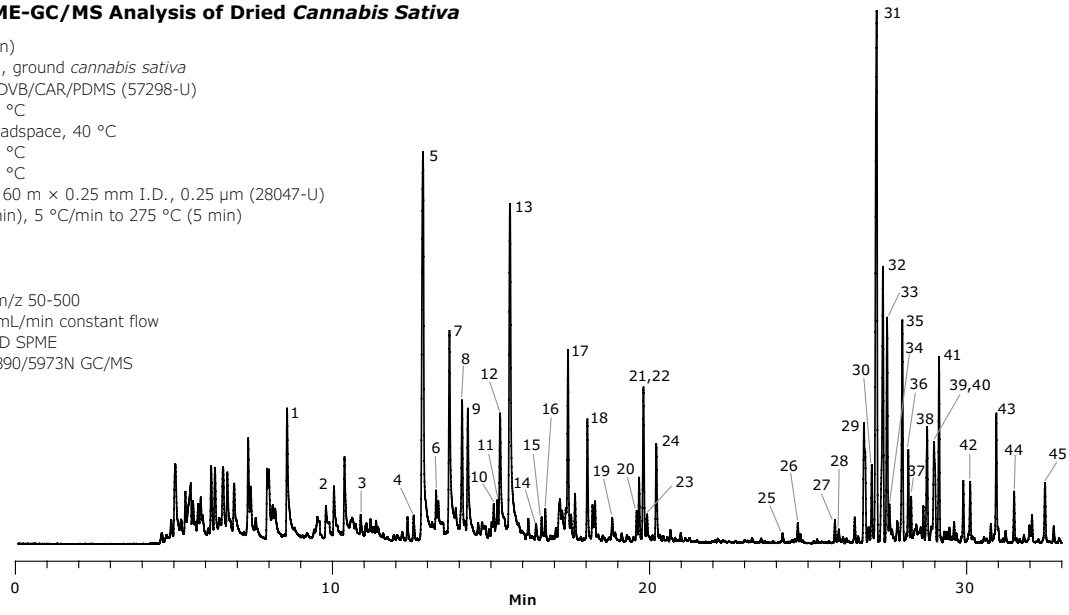

Table 1. Terpenes in Dried Cannabis Identified by MS Spectral Library Match and Retention Index

Peak No.	RT (min)	Name	RI (calculated)	RI (literature)
1	8.57	Hexanal	—	—
2	10.05	Hexene-1-ol	—	—
3	10.89	2-Heptanone	—	—
4	12.56	α-Thujene	928	938
5	12.86	α-Pinene + unknown	939	942
6	13.27	Camphene	953	954
7	13.69	6-Methyl-5-hepten-2-one	966	968
8	14.09	β-Pinene	979	981
9	14.27	β-Myrcene	984	986
10	15.09	Δ-3-Carene	1010	1015
11	15.20	α-Terpinene	1014	1012
12	15.29	Cymene	1018	1020
13	15.60	d-Limonene	1028	1030
14	16.42	γ-Terpinene	1056	1057
15	16.60	*trans*-Sabinene hydrate	1062	1078
16	16.72	cis-Linalool oxide	1066	1068
17	17.43	Linalool	1087	1092
18	18.04	d-Fenchyl alcohol	1107	1110
19	18.82	*trans*-Pinocarveol	1135	1134
20	19.59	Borneol L	1161	1164
21	19.81	1,8-Methandien-4-ol	1168	1173
22	19.81	p-Cymen-8-ol	1168	1172
23	19.92	Terpinene-4-ol	1172	1185
24	20.22	α-Terpineol	1181	1185
25	24.20	Piperitenone	1322	1320
26	24.76	Piperitenone oxide	1344	1352
27	25.85	α-Ylangene	1384	1373
28	25.97	α-Copaene	1388	1398
29	26.76	γ-Caryophyllene	1419	1403
30	27.01	α-Santalene	1429	1428
31	27.16	Caryophyllene	1435	1428
32	27.36	*trans*-α-Bergamotene + unknown	1443	1443
33	27.49	α-Guaiene	1448	1441
34	27.56	*trans*-β-Farnesene	1451	1446
35	27.98	Humulene	1467	1465
36	28.17	Alloaromadendrene	1475	1478
37	28.25	α-Curcumene	1478	1479
38	28.75	β-Selinene	1497	1487
39	28.97	α-Selinene	1507	1497
40	28.97	β-Bisobolene	1507	1506
41	29.13	α-Bulnesene	1514	1513
42	30.12	Selina-3,7(11)-diene	1556	1542
43	30.94	Caryophyllene oxide	1590	1595
44	31.50	Humulene oxide	1614	1599
45	32.48	Caryophylla-3,8(13)-dien-5-ol A	1658	1656

or the nature of the sample tested, which was dried. Previous studies have shown the level of this compound to increase significantly relative to other terepenes and terpenoids with drying.[3] Consequently, the levels of the more volatile monoterpenes and terpenoids would be expected to be less, and this was observed to some degree. Among the monoterpenes and terpenoids, the most abundant were α-pinene and limonene.

References

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2017-08269
01/2020