Characterizing the Odor of Marijuana using Direct Analysis in Real Time Mass Spectrometry

By

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Table of Contents

Table of Contents for Figures and Tables

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Abstract

Whether or not odor is sufficient enough for probable cause to start a search, warranted or warrantless, is often raised and debated in the court system. A person's ability to recognize a scent is very subjective. But the molecules responsible for odor, terpenes, are present in marijuana like many other plants. Determining the terpene signature, and showing the uniqueness of the terpene signature, can offer objective evidence that the odor of marijuana is unique. The fundamental issue here is whether the odor of marijuana, as perceived by a law enforcement officer, is sufficient to constitute probable cause for a further search or arrest. Probable cause is a rather low bar to be crossed, but is a bar that cannot be ignored and must be satisfied for a criminal case to proceed. The present study contributes to meeting and enforcing that bar.

This study has investigated the relative terpene signatures of marijuana in comparison to catnip, tobacco, oregano, and the closest plant relative of marijuana, hops. Using the AccuTOF™ DART™ Mass Spectrometer, the samples were analyzed both directly and indirectly. To analyze indirectly, samples were held adjacent to the sample airstream of the mass spectrometer and a gentle heat source was applied. Resulting spectra of the volatiles were compared. All samples gave different spectra signatures for their volatiles. The odor profile of marijuana is distinct from hops and any other plants commonly used as mimics for marijuana.

Introduction

Probable Cause

The Fourth Amendment to the United States Constitution provides protection from illegal search and seizure of their persons or property. The amendment essentially has two main parts. The first part explicitly specifies that the search and seizure must be reasonable. The second part is equally explicit, and specifies that a warrant will not be issued unless *probable cause* has been *properly* established and the scope of the search is specifically set. The term *probable cause* may be defined [1] as "reasonable ground to suspect that a person has committed or is committing a crime or that a place contains specific items connected with a crime".

Legal Status of Marijuana Odor

It is common practice for a police officer to use the perceived odor of marijuana as probable cause when making an arrest or searching a person's property. The possession of marijuana (*Cannabis sativa*) is a criminal offense under Federal law [2], and under the laws of most nations. In the United States, possession of a small amount has to some extent been decriminalized in fifteen states (Alaska, California, Colorado, Connecticut, Maine, Massachusetts, Minnesota, Mississippi, Nebraska, Nevada, New York, North Carolina, Ohio, Oregon, and Washington). In these states, possession of a small amount is typically an infraction, akin to a traffic violation. In other states, possession of any amount is a misdemeanor, and in all of the United States, possession of a larger amount – presumed to indicate that the material is being held for sale rather than for personal use – is a felony, punishable by a term in state prison. While marijuana use is becoming increasingly decriminalized in the United States, this is not the case in other countries which can have stricter regulations. Thus, the question of marijuana and marijuana odor – especially use of marijuana odor as probable cause – remains an important question.

The use of odor as probable cause is constantly being raised and debated. Some courts have held that odor is sufficient for probable cause of a warrantless search, while others believe odor provides enough probable cause to obtain a search warrant, but not offering sufficient cause for a warrantless search. The odor of marijuana in particular, related to probable cause and search In United States v Ramos in 2006 [3] the court came down strongly that the odor of marijuana could serve as probable cause: "It is well settled that the smell of marijuana alone, if articulable and particularized, may establish probable cause."

This case involved a routine traffic stop. When officers detected the odor of marijuana a subsequent search of the vehicle turned up handguns. The defendants moved to suppress the evidence due to unlawful search and seizure. However, the court decided that the odor of marijuana was sufficient probable cause for a warrantless search of the vehicle and the verdict was upheld. The Ramos court cited United States vs. McGlory (968 F. 2d. 308, 3rd. Cir): "Probable cause exists when the facts and circumstances within the arresting officer's knowledge are sufficient to warrant a reasonable person to believe an offense has been committed."

One other issue is relevant here. A police officer may base an arrest or a search on probable cause to suspect marijuana, but with the arrest or search then leading by further investigation to an arrest on a more serious charge. The probable cause aspect may then be scrutinized by courts to determine whether the arrest for a more serious charge may pass legal muster.

An obvious challenge to the odor of marijuana being used as probable cause for an arrest or a search is that the odor is not unique to marijuana, or possibly even characteristic to the extent that it could be relied upon. The Fourth Amendment challenge would be directed toward whether the odor constitutes a reasonable basis for the search or arrest.

While there is no scientific proof that the odor of marijuana is unique, courts have consistently ruled that the odor of a controlled material, perceived by a properly trained law enforcement official, will be accepted as constituting reasonable cause. The U.S. Supreme Court, in U.S. v Ventresca [4] ruled that "the smell of contraband by a trained officer supports finding of probable cause." (The "contraband" in this case was the odor of marijuana. It was the odor of an illegal distillery as perceived by an Alcohol and Tobacco Tax investigator). While of lesser legal significance, similar rulings occurred in the Fourth and Ninth Circuit Courts of Appeals (U.S. v Humphries, 372 F. 3d. 654, 4th Cir. 2004, U.S v Shates, 915 F. Supp. 1483, 9th Circuit, N.Dist. Cal, 1995, U.S. v Boger, 755 F. Supp. 338, 9th Circuit, E. Dist. Wash., 1990). The Humphries, Shates and Boger cases specifically involved the odor of marijuana. The wording of the Humphries decision is typical of the holdings of the various courts:

> We have repeatedly held that the odor of marijuana alone can provide probable cause to believe that marijuana is present in a particular place. In *United States v. Scheetz,* 293 F.3d 175, 184 (4th Cir.2002), for example, we held that the smell of marijuana emanating from a properly stopped automobile constituted probable cause to believe that marijuana was in the vehicle, justifying its search. Similarly, in *United States v. Cephas,* 254 F.3d 488, 495 (4th Cir.2001), we recognized that the strong smell of marijuana emanating from an open apartment door "almost certainly" provided the

> officer with probable cause to believe that marijuana was present in the apartment. *See also United States v. Sifuentes,* 504 F.2d 845, 848 (4th Cir.1974) (holding that officers' sight of boxes inside a van coupled with the strong odor of marijuana permitted seizure of the boxes because they were in "plain view, that is, obvious to the senses"). While smelling marijuana does not assure that marijuana is still present, the odor certainly provides probable cause to believe that it is. Thus, when marijuana is believed to be present in an automobile based on the odor emanating therefrom, we have found probable cause to search the automobile, and when the odor of marijuana emanates from an apartment, we have found that there is "almost certainly" probable cause to search the apartment. A separate question, of course, remains in these circumstances — whether an exception to the warrant requirement applies, such as the automobile exception in *Scheetz* or the exigent circumstances in *Cephas.* Humphries contends that these cases are inapposite because the present case raises the issue of probable cause *to arrest,* not to search. It is true that the inquiries about whether the facts justify a search are different from whether they justify a seizure. In the search context, the question is whether the totality of circumstances is sufficient to warrant a reasonable person to believe that contraband or evidence of a crime will be found in a particular place. *Ornelas,* 517 U.S. at 696, 116 S.Ct. 1657; *Illinois v. Gates,* 462 U.S. 213, 238, 103 S.Ct. 2317, 76 L.Ed.2d 527 (1983). Whereas in the arrest context, the question is whether the totality of the circumstances indicate to a reasonable person that a "suspect has committed, is committing, or is about to commit" a crime. *DeFillippo,* 443 U.S. at 37, 99 S.Ct. 2627. But in both cases, the quantum of facts required for the officer to search or to seize is "probable cause," and the quantum of evidence needed to constitute probable cause for a search or a seizure is the same. 2 Wayne R. LaFave, *Search & Seizure* § 3.1(b) (3d ed.1996); *compare Pringle,* 124 S.Ct. at 799-800 (arrest context), *with Gates,* 462 U.S. at 230-32, 103 S.Ct. 2317.

While courts have in the past ruled that marijuana odor may constitute probable cause, the issue cannot be considered as totally closed. At any point the odor of marijuana as probable cause may be challenged in court on the basis of the distinctness of the odor, or how well an officer was trained to recognize the odor. In the Federal jurisdiction and in those states following Daubert this could be raised in a Daubert Hearing. In California, the equivalent would be a Kelley-Frye Hearing [5].

Police officers are typically trained early on in the police academy to identify the smell of marijuana, both unburned and burning. Training and experience in the recognition of the odor of marijuana is not restricted entirely to humans. For years dogs have been used successfully to identify drugs, explosives, and food items that may be illegally transported. Law enforcement literature states that drug sniffing dogs are trained to recognize the terpene caryophyllene oxide, a known constituent of marijuana.

However, some judges have held the odor of marijuana is not enough for probable cause, or at the least, not enough for probable cause to search without a warrant. In the case Commonwealth v Cruz [6], the judge ruled that given the decriminalization of small amounts of marijuana, smelling a faint odor of marijuana was insufficient for a law enforcement officer to ask Cruz to step out of the vehicle. But again, not every state has decriminalized small amounts of marijuana, and possession is still illegal on a federal level.

All of these cases have involved the use of trained officers or detectives and their recognition of a specific odor. A person's ability to distinguish an odor, however, is subjective. Therefore, the issue is still debated even though many courts have upheld that odor is sufficient for probable cause. The issue becomes: is the odor discernible and is it distinct? To answer the first part, is the odor of marijuana discernible, trained officers and other individuals must have the ability to accurately discern the odor of marijuana.

Studies Relating to Law Enforcement use of Marijuana Odor

An Alaskan State Trooper study focused on three years of data from the Alaska State Trooper investigations relating to the reliable detection of marijuana odor for establishing its presence upon subsequent searches. The study found 91.5% of the time that troopers smelled marijuana, they did, upon subsequent search; find four or more ounces of the plant material.

The Alaska State Troopers found four or more ounces of marijuana in 83.1% of searches that were not based on the odor of marijuana. This is significant because it indicates that the marijuana odor is discernible to trained law enforcement officers and a reliable investigative lead [7].

In 2004, Doty et al. performed two separate studies on the perception of marijuana odor. The first asked nine participants to sniff two bags; one bag containing marijuana and the other containing balled up paper. Nine out of nine participants correctly identified the bag with marijuana as having an odor characteristic of marijuana. The second study focused on real life examples of cases involving debates of probable cause. An elaborate experiment was set-up to see if car exhaust would mask the odor of marijuana. They found that the exhaust did mask the odor of marijuana in these same nine participants. Despite this result, it does not mean that a highly trained law enforcement officer would not be able to recognize the odor of marijuana when other scents could potentially mask the odor.

The study by Doty et al. established that a trained person in law enforcement, as well as the average person could accurately recognize the odor of marijuana. However, this study does not indicate what gives marijuana its characteristic odor [8].

Cause of Odor of Marijuana - Terpenes

Terpenes have been shown to be prominent volatile odor-producing compounds in marijuana [9]. Terpenes are organic molecules produced by plants. They have the basic chemical structure of isoprene.

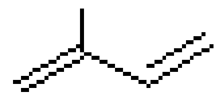


Figure 1 – The structure of isoprene.

Isoprene is a volatile organic hydrocarbon, with conjugated double bonds or double bonds that are separated by single bonds. Isoprene is commonly found in petroleum and is susceptible to retro-Deils Alder reactions. Retro-Deils Alder reactions are reverse Diels-Alder reactions. While Diels-Alder reactions occur when a compound with conjugated double bonds reacts with another compound to form a ring, retro-Diels Alder reactions break a ring down into two compounds, one of which contains a conjugated double bond. Consequently terpenes are various combinations of the basic isoprene structure.

Terpenes are categorized as volatile organic compounds (VOCs) and are often found as essential oils, so they are easily vaporized at room temperature. Fragrance companies use terpenes to make their scents. Terpenes are responsible for numerous plant odors. A prominent example is pinene. Pinene is an abundant terpene found in resinous pine trees, which gives them their specific odor. However, pinene is also found in many other plants. Pinene is also found in many other European conifers besides pine trees, as well as *Eucalyptus*, rosemary, and sage. The monoterpene myrcene, is a terpene found in mangos, lemon grass, verbena, hops, ylang-ylang, bay, and wild thyme. Using gas chromatography-mass spectrometry (GC-MS) and liquid chromatography-mass spectrometry (LC-MS) experiments, Brenneseisen and Elsohy [9] found myrcene to be the most abundant terpene in marijuana. Thus, terpenes, including myrcene are not limited to a single species and may be present in many unrelated plants. As a result, while terpenes are found in marijuana, this does not provide evidence that they, individually, give a unique and characteristic odor. It is the group of terpenes as a whole, the signature mixture of terpenes that would be the cause for the unique odor of marijuana.

Terpenes are characterized into many subgroups; monoterpenes, sesquiterpenes, diterpenes, and many others. The terpenes that have been isolated in *Cannabis* are limited to monoterpenes and sesquiterpenes. At one point Brenneseisen [10] states, there are 140 terpenes in marijuana. However, in his chapter in *Forensic Science and Medicine: Marijuana and the Cannabinoids,* he only lists 43 of them.

Table 1 — List of terpenes found in marijuana as described by Brenneseisen (2006). The structures can be found in Appendix 1

Name	Terpene Type	Molecular Formula	Formula Weight
Myrcene	**monoterpene**	$C_{10}H_{16}$	**136**
Limolene			
trans-Ocimene			
Pinene			
beta-Pinene			
alpha-Pinene			
delta-3-Carene			
beta-Phellandrene			
cis-Ocimene			
Terpinolene			
Camphene			
alpha-Thujene			
Linalool	**monoterpene**	$C_{10}H_{16}O$	**152**
Fenchone			
Borneol			
Ipsdienol			
cis-Sabinene Hydrate	**monoterpene**	$C_{10}H_{18}O$	**154**
beta-Fenchol			
alpha-Terpineol			
trans-gamma-Bisabolene	**sesquiterpene**	$C_{15}H_{24}$	**204**
Guajol			
alpha-Guaiene			
alpha-Humulene			**(alpha-Caryophyllene)**
trans-alpha-Farnesene			
trans beta-Caryophyllene			

Name	Terpene Type	Molecular Formula	Formula Weight
alpha-Selinene			
beta-Selinene			
gamma-Curcumene			
alpha-trans-Bergamotene			
cis-gamma-Curcumene			
cis-beta Farnesene			
apha-cis-Bergamotene			
gamma-Muurolene			
alpha-Longipinene			
alpha-Cadinene			
beta-Elemene			
Caryophyllene Oxide		$C_{15}H_{24}O$	**220**
beta-Eudesmol		$C_{15}H_{26}O$	**222**
alpha-Eudesmol			
gamma-eudesmol			
epi-alpha-Bisabolol			
alpha-Ylangene		$C_{16}H_{28}$	**220**

In another work reported by Brenneseisen and Elsohly [9], they only show 47 terpenes in spectrographical results using Gas Chromatography-Mass Spectrometry and Liquid Chromatography-Mass Spectrometry, compared to the 43 reported by Brenneseisen [10]. Thus, there seems to be little consistency among authors on the total number of terpenes found in marijuana. Clearly, however, terpenes are numerous and the mixtures are complex.

Some consideration must be given to the cannabinoids. These are an extended family of materials unique to *Cannabis*. In the quest for a technique to characterize the odor of *Cannabis*, it would be preferable to be able to detect the cannabinoids, unique to *Cannabis*, rather than terpenes, which are not. The emphasis here is again the issue of probable cause. A consideration of the structures of the cannabinoids explains why a police officer would be unable to smell tetrahydrocannabinol, the principle psychopharmacological agent, or any other cannabinoid.

The structures of the cannabinoids are given in Appendix 2. Their structures are much more complex than terpenes or even sesquiterpenes, and consequently their vapor pressures are so much higher that they will be reluctant to enter into the vapor phase where their odor may be perceived. Cannabinol, a relatively simple cannabinoid, has a formula weight of 310, while several of the Cannabis terpene ensemble have a formula weight of only 136.

In this study, the relative terpene and volatile signatures of marijuana in comparison to catnip, tobacco, oregano, and the closest plant relative of marijuana, hops was investigated. These are plant materials that have relevancy to the issue of *Cannabis* odor.

Catnip and oregano are occasionally sold, in lieu of, or mixed with marijuana, to increase a dealer's profit. Being able to show that marijuana has a distinct and separate odor from dried catnip and oregano, which are visibly similar to *Cannabis sativa*, gives credibility to an officer's claim of probable cause for a search when they detect the odor of marijuana.

Figure 2 – (Left) **Cannabis sativa***, marijuana. (Right)* **Humulus lupulus***, hops. Although the plants are closely related, their physical appearance is quite different [11].*

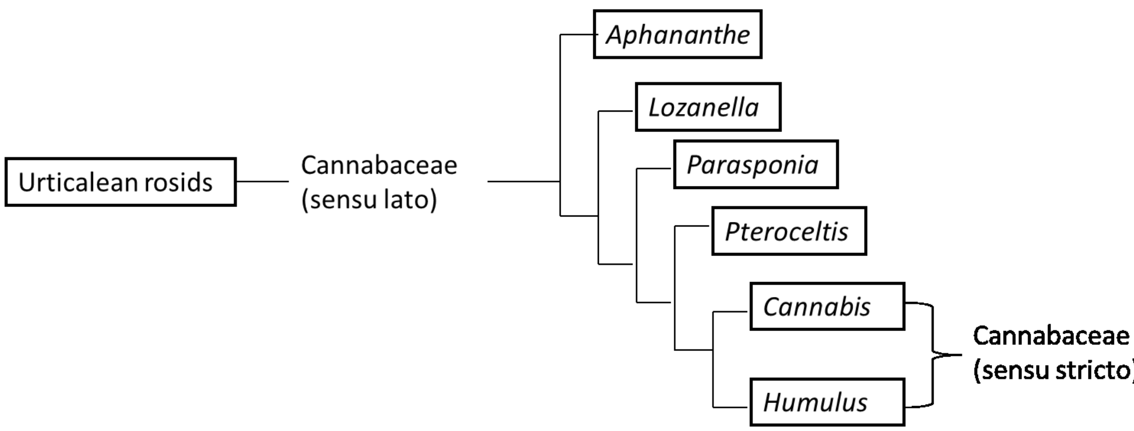


Figure 3 – The phylogeny of genera within the **Cannabaceae** *sensu strico (strict sense), which shows that the genera* **Cannabis** *and* **Humulus** *are classified within the same plant family. (Sensu lato-broad sense)*

Hops, *Humulus lupulus,* was used in this study because it is part of the same plant family, *Cannabaceae*, as marijuana. If the odor profile of marijuana is distinct from hops and any other plants commonly confused, or used as mimics, for marijuana, it can be scientifically argued that the odor of marijuana is distinct or at least characteristic to the point where probable cause is shown.

Conventional Gas Chromatography and Mass Spectrometry of Marijuana Terpenes

The traditional method for sampling volatile compounds is by headspace collection coupled with gas chromatography and mass spectrometry, or alternatively, steam distillation followed by gas chromatography and mass spectrometry. Essentially, with headspace collection, a sample is heated in a closed container and the volatiles are pushed through to a gas chromatography instrument. Recently, the addition of the Solid-Phase Micro-Extraction (SPME) fiber columns has made it easier for ambient atmospheric collection of volatiles. The SPME fibers can sample on a much smaller scale without the need for a large and bulky headspace instrument. A fiber is exposed to volatiles for a time, and then the fiber is inserted into a gas chromatography instrument. Headspace collection and SPME fiber sampling generally start with an extraction. As with all extractions of interest, the extraction will always favor certain compounds that are soluble in the solvent. In addition, as with any extraction process, some of the analyte being extracted is lost with each step of the procedure. If a compound is in a sample, but in relatively small concentration, it is possible that it will be lost in the extraction process. The AccuTOF™ DART™ Mass Spectrometer, however, requires no sample preparation, and thus no compound within a sample will be favored over another. The AccuTOF™ DART™ reveals the relative abundance of each compound that is present in the native state of the sample.

AccuTOF™ DART™ Mass Spectrometry

This study used the sensitivity of the AccuTOF™ DART™ Mass Spectrometry in determining marijuana's odor profile. The AccuTOF™ DART™ Mass Spectrometer machine uses Direct Analysis in Real Time (DART) ionization using helium gas to ionize the sample. The Time-of-Flight (TOF) detection gives accurate mass information, to the hundred-thousandths of a mass unit, and allows for the identification of isotopes and elemental composition.

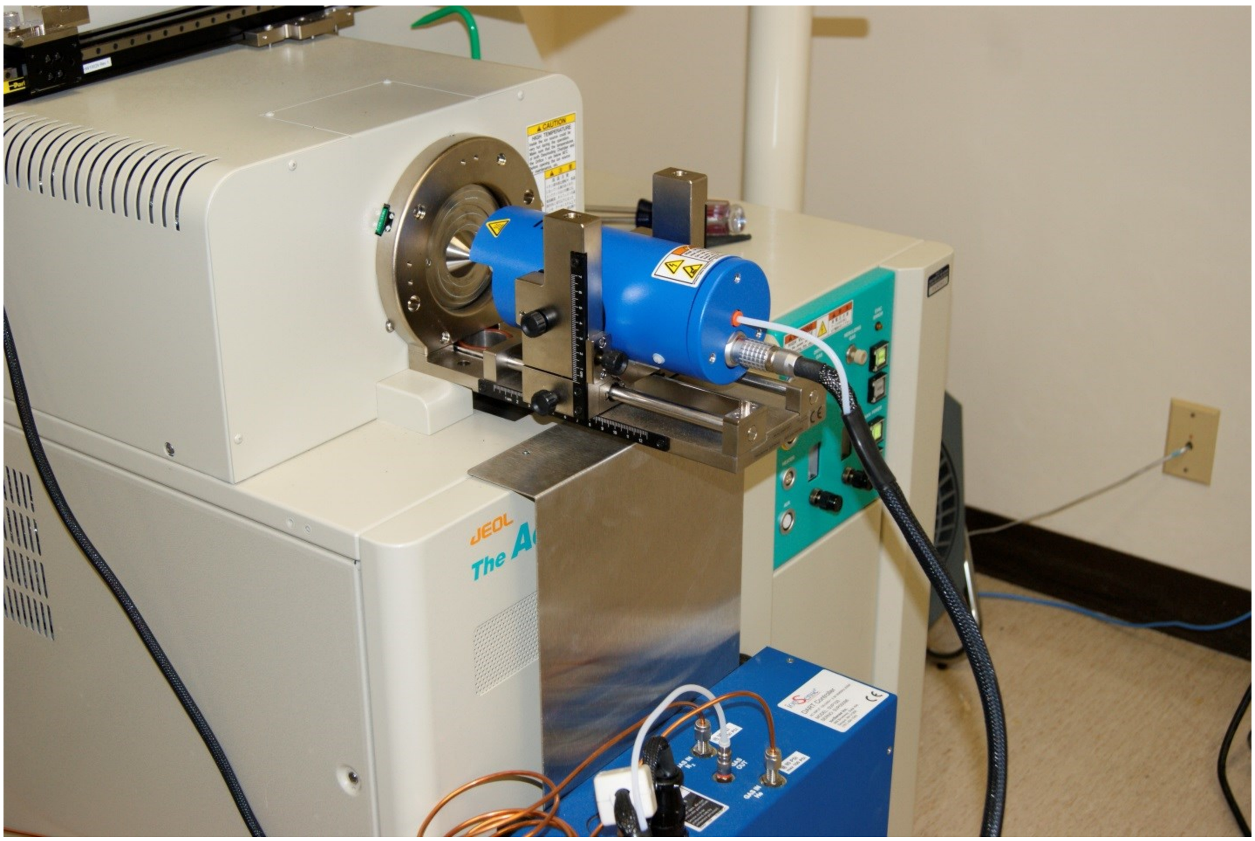


Figure 4 – The* AccuTOF™ DART™ Mass Spectrometer*. The DART™ ionizer is the smaller instrument that rests on the Time-of-Flight mass spectrometer detector.

An example of the applicability of the AccuTOF™ DART™ is the following: The AccuTOF™ DART™ was validated in studies where scientists used US one dollar bills in their natural and native states, uncut and unprepared, and held this to the airstream of the DART™ [12]. The results showed that 94% of the US one dollar bills contain traces of cocaine. In this analytical modality, Items placed in the air stream can detect traces of substances without requiring any sample preparation from the operator.

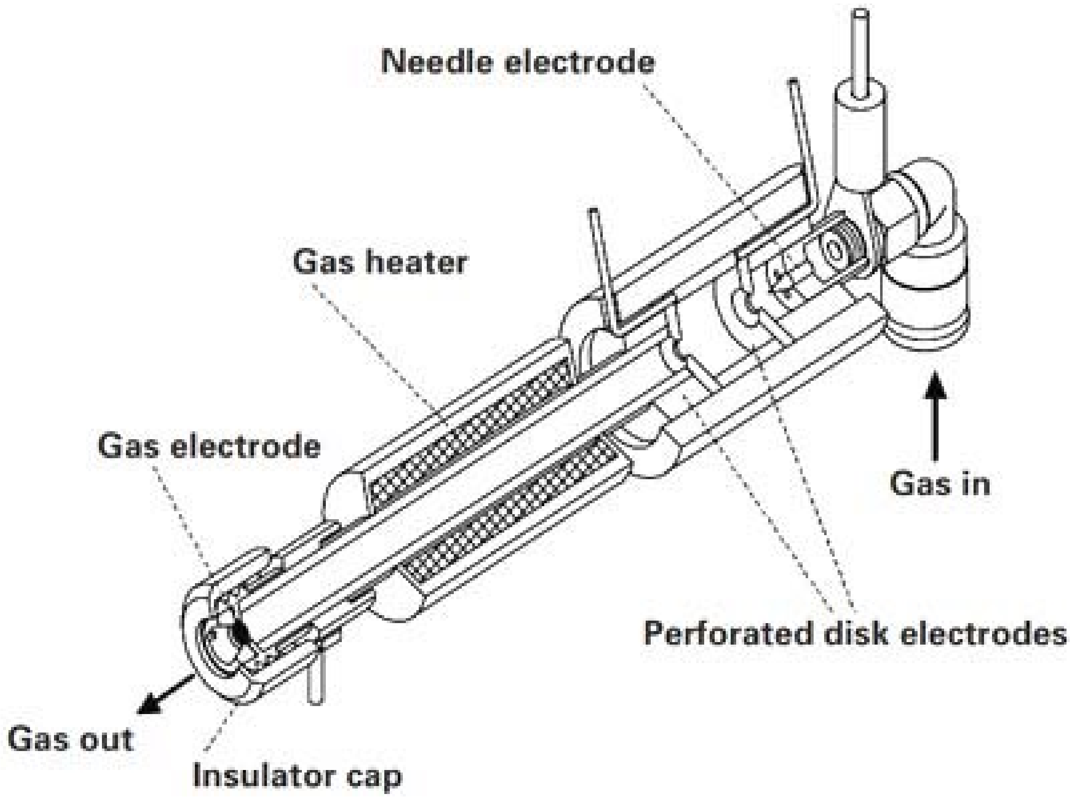


Figure 5 — Direct Analysis in Real Time ion source.

The DART™ forms ions using Penning ionization. Gas flows into the chamber where the needle electrode produces an electrical discharge that produces ions, electrons, and molecules. When the gas passes through the disk electrodes, or lenses, charged particles are removed leaving only neutral gases and metastable species. The lens prevents ion-ion and ion-electron recombination, acts as a source of electrons by Penning ionization, and acts as an electrode to direct the flow of ions into the mass spectrometer. The DART™ produces simple mass spectra as M^+ or $[M+H]^+$ in positive-ion mode [12].

Marijuana Identification Testing

Marijuana plants have several distinct morphological characteristics that can be used to distinguish it from other plants, but the two different types of trichomes are most often used by forensic scientists during a visual examination. Trichomes are very fine outgrowths from the epidermis of plants. They are often described as hairs or hair-like structures. Marijuana leaves have distinctive hair-like structures called cystolithic trichomes. These are bear-claw shaped hairs found on the upper side of the leaves, and are still present on dried marijuana. The second structure, called a non-cystolithic trichome, or a clothing trichome resemble little hairs and are found on the underside of the marijuana leaves [13].

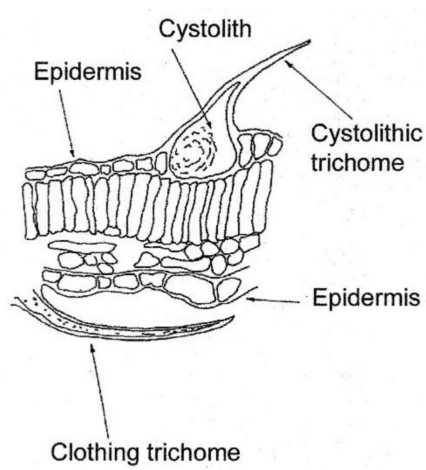
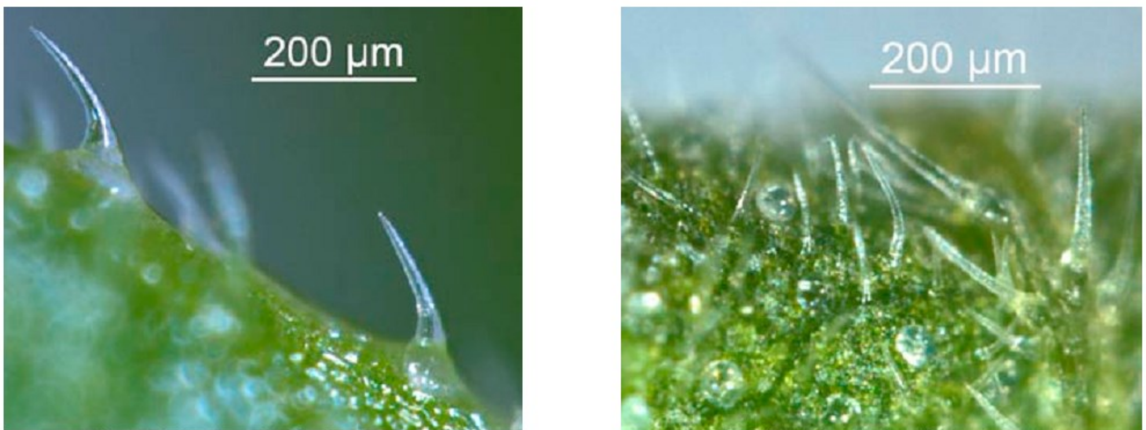


Figure 6 – Cross-section of the marijuana leaf showing the adaxial cystolithic trichome and the abaxial non-csytolithic trichome, or clothing trichome [14].

Both these morphological features together are distinct for marijuana. Trichomes are by no means unique to *Cannabis*, but no plant material other than *Cannabis* has been reported as having the cystolithic bear claw trichome on the top surface of the leaf, exclusively, and the non-cystolithic trichome on the bottom of the leaf exclusively. These trichomes can be imaged using a stereomicroscope, which allows a three-dimensional view of the marijuana plant [15].



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Cystolithic trichomes Non-cystolithic trichomes

Figure 7 – Cystolithic and non-cystolithic trichomes found on marijuana leaves.

The Duquenois-Levine test is a color change chemical test that is used in crime laboratories to confirm whether a sample is marijuana [16]. First, the vanillin acetaldehyde Duquenois reagent is added to the marijuana and the mixture is shaken. Next, concentrated hydrochloric acid is added and the sample mixture is again shaken. If the sample is marijuana the color will change to dark blue or deep violet. The addition of chloroform to the Duquenois and hydrochloric acid mixture is the Levine modification. Chloroform should not react with the other phenols to give a color change. The lack of further color change ensures that the marijuana resin is responsible for the color change. Besides marijuana, there are no other reported plant species to produce the same precise color reaction from this test [16].

Note: “Odor” in this paper will refer to the volatiles and terpenes.

Experimental

Napa Sample

Microscopy and Duquenois-Levine Test

Marijuana was obtained from the Napa County Sheriff’s Department from evidence marked for destruction. The Napa County Sheriff’s Department sent the marijuana directly to the US Fish and Wildlife National laboratory to abide by drug possession laws.

The marijuana sample was weighed on an electronic scale and was 3.015 grams. A small subsample of the marijuana was placed on a piece of wax paper under a reflective light stereomicroscope at 30 and 60x magnification.

The sample was observed for the two different types of trichomes: cystolithic trichomes found on the top-side of the leaf, and non-cystolithic trichomes found on the under-side of the leaf. As marijuana leaves dry the edges of the leaf curl up and inward. This allowed for proper determination of the surface area being observed. The bear claw-like cystolithic trichomes were found on the top of the leaves (adaxial), and non-cystolithic trichomes were found on the bottom (abaxial) of the leaves. This evaluation confirmed the sample to be marijuana.

The sample was then chemically confirmed to be marijuana by the Duquenois-Levine Regeant NIK test that was obtained from the Napa County Sheriff's Department. These NIK tests are packets used to identify specific substances in the field. It is a small pouch consisting of three capsules. The first capsule contains the Duquenois reagent, the second capsule contains the concentrated hydrochloric acid, and the third capsule contains the Levine modification, chloroform. A small portion of marijuana was added into the pouch. Once sealed, the first capsule was broken and the pouch was shaken to mix the Duquenois reagent and the marijuana. The second capsule was then broken to add the concentrated hydrochloric acid, and again the pouch was shaken. The sample turned a violet color. Once the color change stopped, the third capsule was broken to add the chloroform. The pouch was shaken again, and the sample deepened in color. The color of the sample remained dark violet, this confirmed the sample was marijuana.

Ashland

One of the remarkable things about the AccuTOF™ DART™ Mass Spectrometer is that the operator creates the dataset for the software to use in identifying peaks of interest. All that is needed is the molecular formulas and names of the compounds uploaded into a spreadsheet and then uploaded into the system. This allows the software to search for specific ions. The software automatically calculates the mass of the molecule, and then the calculated mass is used to search against the molecular ion peaks from the scans. To create the dataset, compilations of the known terpenes found in marijuana, hops, catnip, oregano, and tobacco were listed on one spreadsheet. Since many terpenes have the same mass and molecular formula, the formula is entered into the spreadsheet and identified by a number (*i.e.,* 1-4). The list of the numbers and the names of the compounds they correspond to are included in Appendix 4.

The experimental method for testing odor was developed by trying various sampling methods until we were satisfied the instrument registered the sample. First, marijuana was placed into a stainless steel tea infuser, and was held to the side of the airstream to see if volatiles would register on the DART™. Various distances were tested, starting about 15 centimeters from the airstream and then moving to approximately one centimeter away from the airstream. The process was repeated using a heat gun to push hot air through the sample to force any volatiles into the airstream. This heating method worked well and was thereafter used for the odor portion of the experiment.

All standards and samples were run, and completed, using 2,500 volts and 350 °C discharge tip on the AccuTOF™ DART™ Mass Spectrometer. Helium gas was used as the ionizing medium to create the metastable species. TSS Pro 3.0 software was used to eliminate background and average the peaks. The peaks were turned into total ion spectra with the software and then translated with Mass Mountaineer to evaluate the mass spectra from TSS Pro 3.0. Mass Mountaineer was also used to apply statistics to show statistical difference in the marijuana, hops, catnip, oregano, and tobacco samples.

A calibration curve was made to calibrate the mass spectrometer. Polyethylene glycol (PEG 600) was used as an instrument standard and was run between all standards and samples. This was considered the “blank” used between runs and ensured that sample spectras were not affected by the previous samples. The terpene standards were in both liquid and solid form.

The solid terpene standards were dissolved in methanol. The terpene standards were then picked up with a glass melting point tube and held directly into the airstream.

For the heat induced odor tests, samples were placed into stainless steel tea diffusers and held at an average of 15 centimeters away from the airstream. A heat gun was used to gently heat the samples and volatilize any compounds with vapor pressures higher than atmospheric conditions. The vaporized compounds were then carried into the airstream of the AccuTOF™ DART™ Mass Spectrometer inlet. Sample order for the heat induced odor tests was as follows; PEG 600, marijuana, PEG 600, catnip, PEG 600, oregano, PEG 600, hops, PEG 600, tobacco, and PEG 600. For direct analysis tests, a leaf of each sample was taken with forceps and placed directly into the AccuTOF™ DART™ airstream for no more than 10 seconds. The sample run order was the same for direct analysis as for the heat-induced odor analysis.

Results

Napa

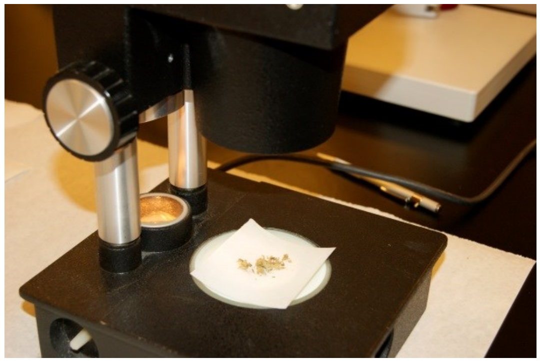

Figure 8 – The plant sample under the stereomicroscope. Using this scope it was possible to visualize the two types of trichomes used for identification of marijuana.

Figure 9 – The plant sample tested positive for marijuana using the NIK test from the Napa County Sherriff's Department Crime Laboratory.

The visual identification coupled with the positive chemical reaction from the Duquenois-Levine modification confirmed the sample was marijuana.

Ashland

The fit of the calibration curve using the AccuTOF DART™ was 5 x 10^{-11}. This indicated that the difference between the calculated mass of the PEG mass standard and the actual mass readings of the instrument is extremely small.

The scans of the terpene standards contained many other molecular ion peaks. These standards were purchased through Sigma Aldrich, and although some were certified as >96% pure their mass spectra from the AccuTOF™ DART™ showed that the standards had many other compounds present.

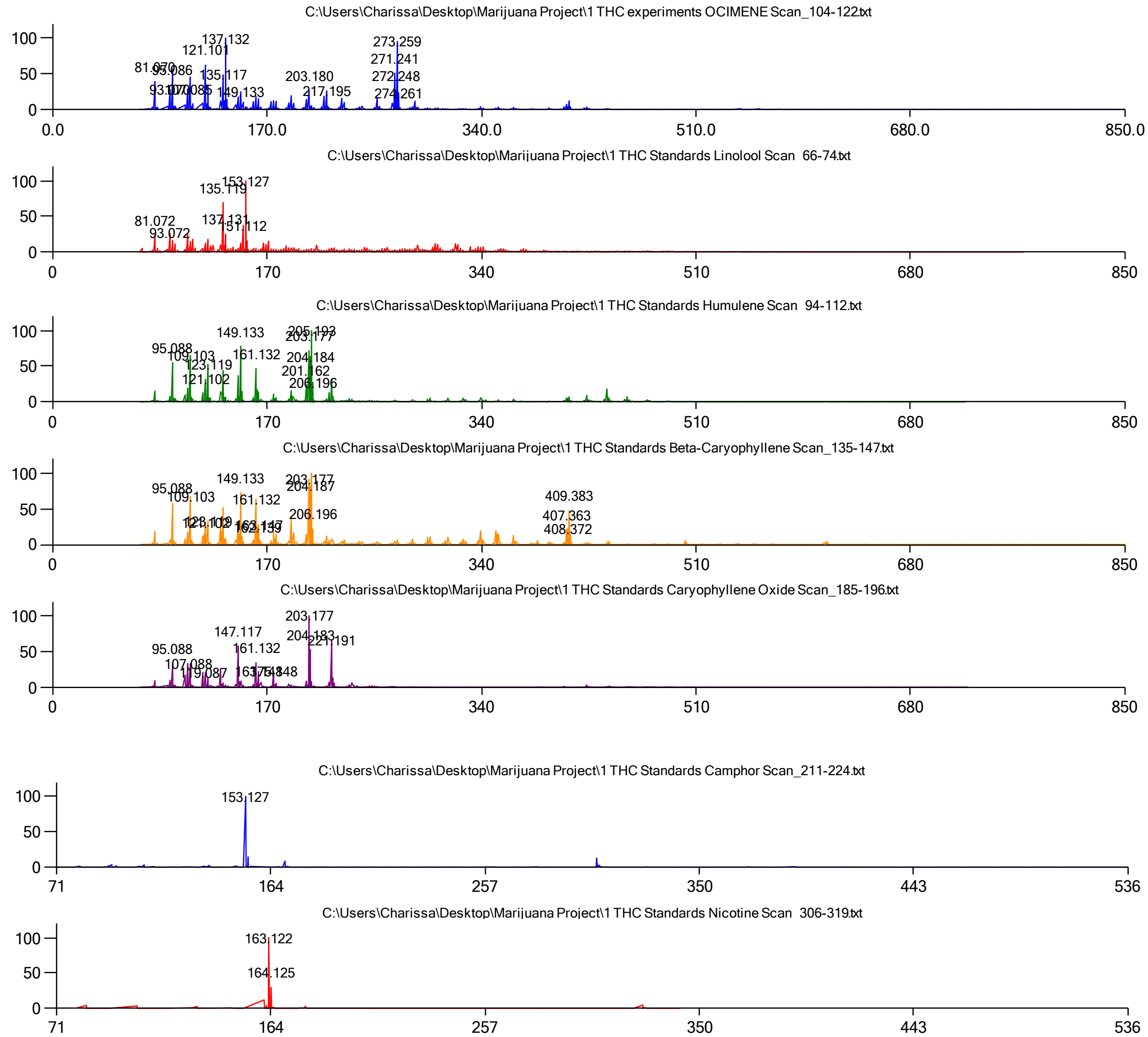

Figure 10 – The mass spectra for the terpene standards and nicotine.

Unlike other purchased standards, the standards for camphor and nicotine were extremely pure. One possible reason for the impurities in most standards is that testing for purity was done using gas chromatography, which separates the compounds and is visualized with a peak for each compound. It is possible they only showed the peak that corresponded to the standard. It is also possible that since the AccuTOF™ DART™ does not separate compounds like gas chromatography, but instead shows all compounds present, that the AccuTOF™ DART™ simply picked up compounds that were unknown to also be present in the standard.

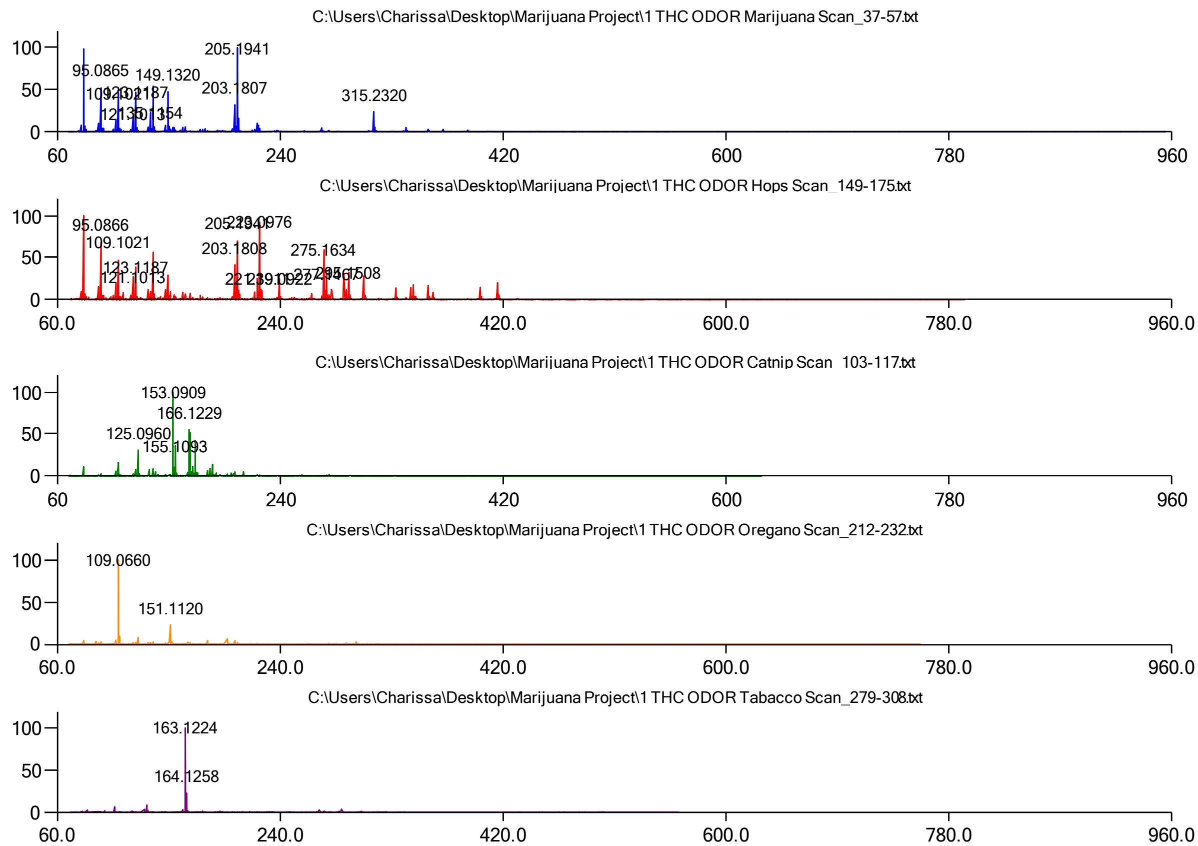

Figure 11 – Spectra from the odor portion of the experiment. From top to bottom; Spectrum A-marijuana, Spectrum B-hops, Spectrum C-catnip, Spectrum D-oregano, Spectrum E-tobacco. See Appendix 5 for detailed individual spectra.

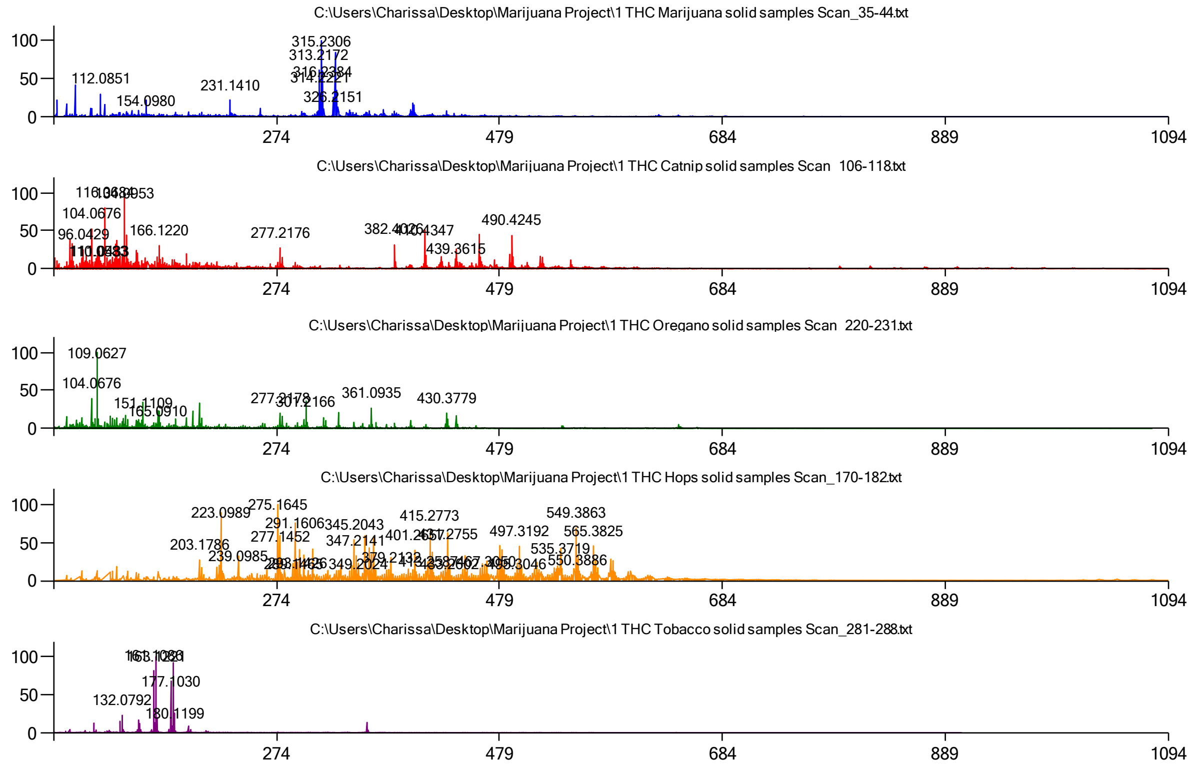

Figure 12 – Solid sample spectra. In order from top to bottom Spectrum A-marijuana, Spectrum B-catnip, Spectrum C-oregano, Spectrum D-hops, Spectrum E-tobacco. See Appendix 5 for detailed individual spectra.

Principle component analysis was done on the odor sample results. As can be determined in the graph (figure 11), all samples are statistically different. As might be expected, Marijuana is closest on the graph to hops, given they are close relatives and share many of the same terpenes.

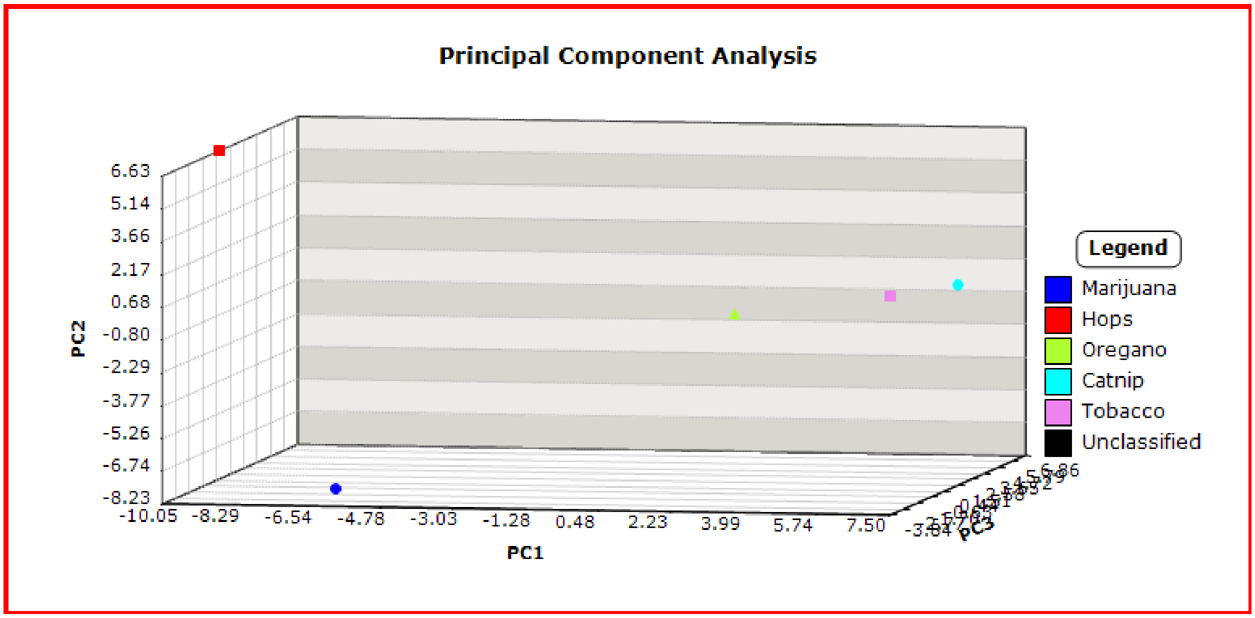

Figure 13 – Principal Component Analysis graph showing the statistical difference between the samples.

Discussion

The present work has satisfactorily shown that marijuana terpenes, and thereby by extraction, odor, is distinguishable from other common plants that could conceivably be confused with *Cannabis.* The difference is not just subjective, but objective and statistically different as well; this work appears to premise that marijuana odor can be used for probable cause. This is the fundamental question the present work attempted to answer, and the DART™ approach does in fact support the odor study. Though this study does not directly prove that humans can distinguish among the terpene profiles of the various plants, it does provide evidence that these odor profiles are different and thus gives more credibility to law enforcement officer's claims that marijuana can be distinguished from other plants by its odor.

Nearly all previous research about terpene concentrations in marijuana has stated that the monoterpenes, more specifically myrcene, are the most abundant terpenes found in marijuana. According the results from the AccuTOF™ DART™ Mass Spectrometer, the sesquiterpenes were found to be the most abundant in marijuana. This does not mean that myrcene is not the most abundant terpene. The AccuTOF™ DART™ Mass Spectrometer produces a molecular ion, thus any and all monoterpenes are shown in the same peak, likewise with sesquiterpenes. It is quite possible that the number of sesquiterpenes, not the abundance, far outweighs the monoterpenes, which accounts for the higher abundance of sesquiterpenes in the spectrograph.

There are many avenues of future research that can follow this experiment. More samples and their terpenes and volatiles can be compared to further encourage the objectivity of the distinctness of marijuana odor. Since delta-9-tetrahydrocannabinol was one of the volatiles that was identified on the spectra, the AccuTOF™ DART™ Mass Spectrometer seems to be a new and faster method of identification of marijuana. There is some research now into using the AccuTOF™ DART™ Mass Spectrometer for identification of synthetic cannabinoids. Coupling the identification of synthetic cannabinoids with the identification of marijuana could become a useful tool to prevent fraud in the marijuana medical business or in forensic drug identification.

When comparing the results of the terpene standards using mass spectra from the AccuTOF™ DART™ and the gas chromatograph it seems possible that the AccuTOF™ DART™ could be used to create purer standards. Considering the AccuTOF™ DART™ shows the user what is in the sample or what is not, it can quickly show if there is contamination.

The sampling ease of the AccuTOF™ DART™ and the applicability to marijuana odor and probable cause cases make this an invaluable tool for the forensic science community and for future odor studies.

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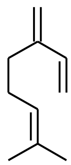
(15) United Nations Office of Drugs and Crime. Recommended Method for Identification and Analysis of Cannabis and Cannabis Products-Manual for Use by National Drug Analysis Laboratories. Revised and Updated 2009.

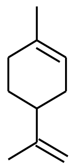
(16) Thornton, J. and Nakaurma, G. The Identification of Marijuana. Journal of Forensic Science Society. 1972. 12, 461. Pages 461-519.

Appendix 1 — Cannabis Terpenes; structures and chemical formulas

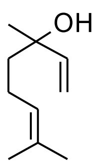
Myrcene, Monoterpenoid, $C_{10}H_{16}$ FW= 136



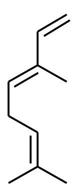
Limonene, Monoterpenoid, $C_{10}H_{16}$, FW = 136



Linalool, Monoterpenoid, $C_{10}H_{16}O$, FW= 152



trans-Ocimene, Monoterpenoid, $C_{10}H_{16}$, FW= 136



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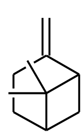
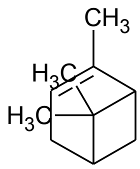
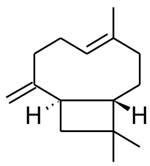


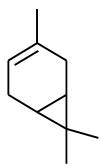
Alpha-Pinene, Monoterpenoid, $C_{10}H_{16}$, FW = 136



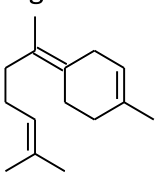
Beta-Caryophyllene, Sesquiterpenoid, $C_{15}H_{24}$, FW = 204



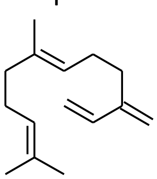
Delta-3-Carene, Monoterpenoid, $C_{10}H_{16}$, FW = 136



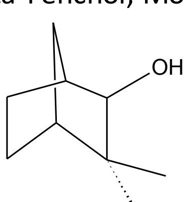
trans-gamma-Bisabolene, Sesquiterpenoid, $C_{15}H_{24}$, FW = 204



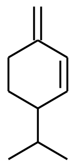
trans-alpha-Farnasene, Sesquiterpenoid, $C_{15}H_{24}$, FW = 204



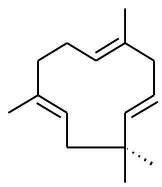
Beta-Fenchol, Monoterpenoid, $C_{10}H_{18}O$, FW = 154



Beta-Phellandrene, Monoterpenoid, $C_{10}H_{16}$, FW = 136



Alpha-Humulene (alpha-Caryophyllene), Sesquiterpenoid, $C_{15}H_{24}$, FW = 204



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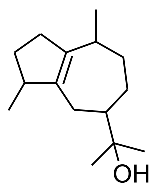

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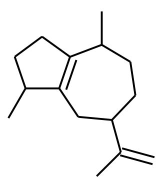

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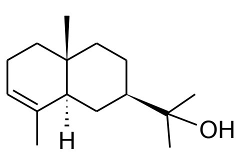

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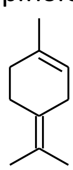

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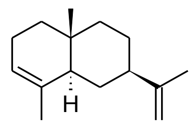

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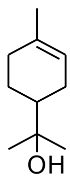
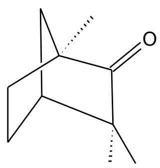
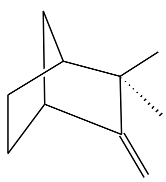


Fenchone, Monoterpenoid, C10H16O, FW = 152



Camphene, Monoterpenoid, $C_{10}H_{16}$, FW = 136



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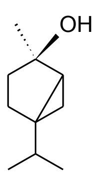
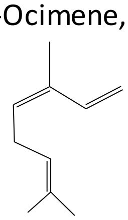


cis-Ocimene, Monoterpenoid, $C_{10}H_{16}$, FW = 136



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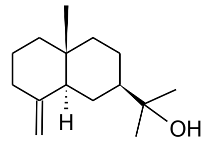
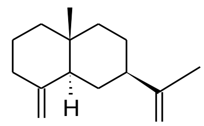


Beta-Selinene, Sesquiterpenoid, $C_{15}H_{24}$, FW = 204



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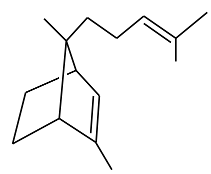

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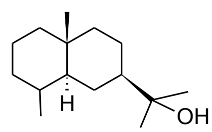

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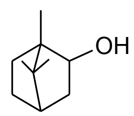

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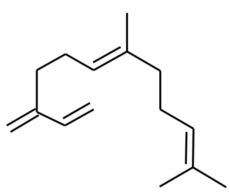

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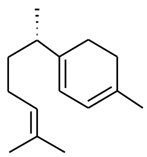

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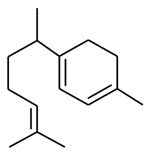

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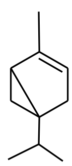
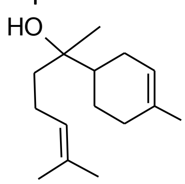
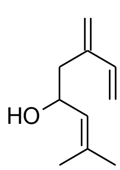


Epi-alpha-Bisabolol, Sesquiterpenoid, $C_{15}H_{26}O$, FW =



Ipsdienol, Monoterpenoid, $C_{10}H_{16}0$, FW = 152



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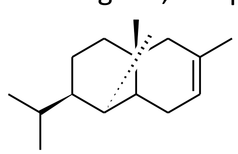

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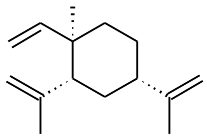

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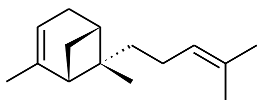

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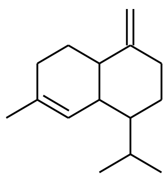

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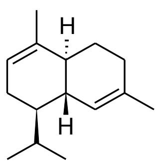

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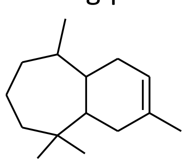
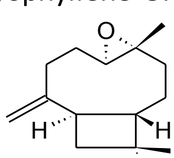


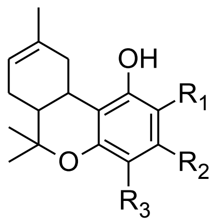
Caryophyllene Oxide, Sesquiterpenoid, $C_{15}H_{24}O$, FW = 222



Appendix 2 — Cannabis cannabinoid structures

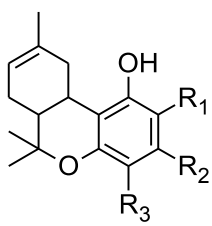
Tetrahydrocannabinol Family

Δ^9-tetrahydrocannabinol



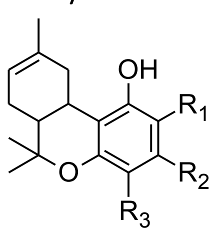
R1=H, R2= C_5H_{11}, R3= H

Δ^9-tetrahydrocannabinolic acid A



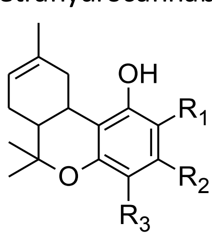
R1=COOH, R2=C_5H_{11}, R3=H

Δ^9-tetrahydrocannabinolic acid B



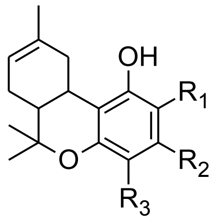
R1=H, R2= C_5H_{11}, R3= COOH

Δ^9-tetrahydrocannabinolic Acid-C_4



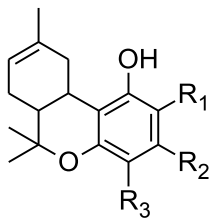
R1=H, R2=C_4H_9, R3=COOH

Δ^9-tetrahydrocannabinol-C_4



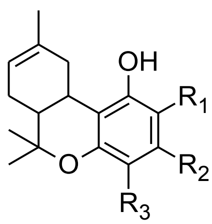
R1=H, R2=C_4H_9, R3=H

Δ^9-tetrahydrocannabivarinic acid



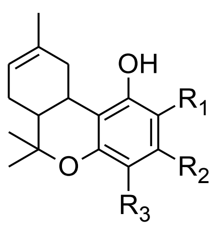
R1=COOH, R2=C_3H_7, R3=H

Δ^9-tetrahydrocannabivarin



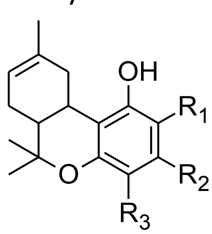
R1= H, R2=C_3H_7, R3=H

Δ^9-tetrahydrocannabiorcolic acid



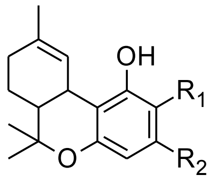
R1=COOH, R2=CH_3, R3= H

Δ^9-tetrahydrocannabiorcol



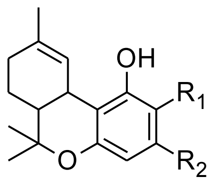
R1=H, R2=CH_3, R3=H

Δ[8]-tetrahydrocannabinol



R1= COOH, R2=C_5H_{11}

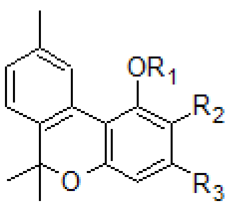
Δ[8]-tetrahydrocannabinolic acid



R1=H, R2= C_5H_{11}

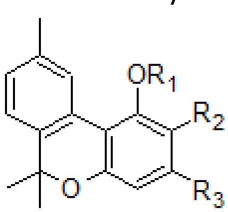
Cannabinol Family

Cannabinol



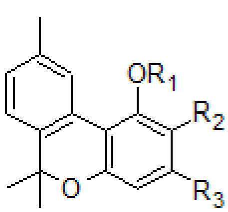
R1=H, R2=H, R3=C_5H_{11}

Cannabinol Methylether



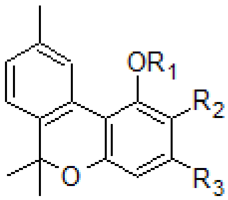
R1=CH3, R2= H, R3=C_5H_{11}

Cannabinol-C4



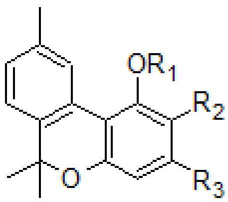
R1=H, R2=H, R3=C_4H_9

Cannabinol-C2



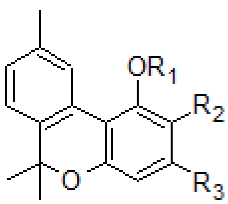
R1=H, R2=H, R3=C_2H_5

Cannabiorcol



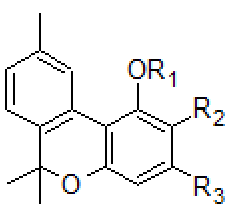
R1=H, R2=H, R3=CH_3

Cannabivarin



R1=H, R2= H, R3=C_3H_7

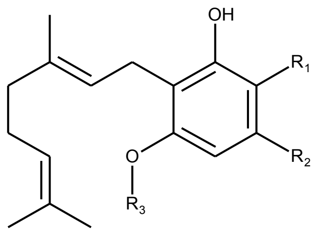
Cannabinolinolic Acid



R1=H, R2=COOH, R3=C_5H_{11}

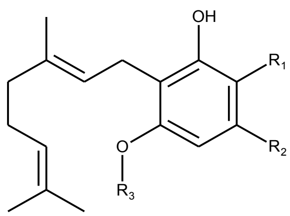
Cannabigerol Family

Cannabigerol



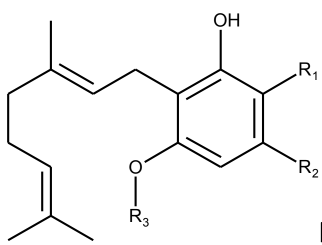
R1= H, R2=C_5H_{11}, R3=CH_3

Cannabigerolic acid



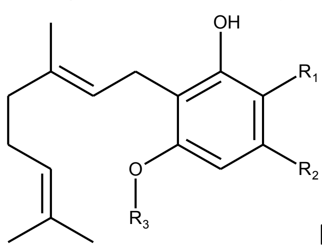
R1=COOH, R2=C_5H_{11}, R3=H

Cannabigerolic acid monomethylether



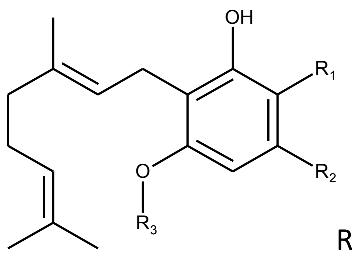
R1=COOH, R2=C_5H_{11}, R3=CH_3

Cannabigerol monomethylether



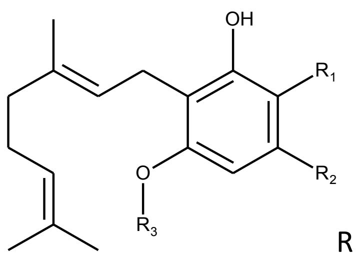
R1= H, R2=C_5H_{11}, R3=CH_3

Cannabigerovarinic acid



R1=COOH, R2=C_3H_7, R3=H

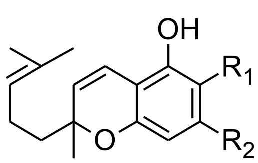
Cannabigerovarin



R1=H, R2=C_3H_7, R3=H

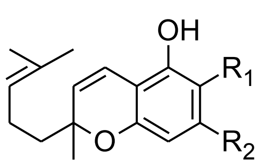
Cannabichromene Family

Cannabichromenic acid



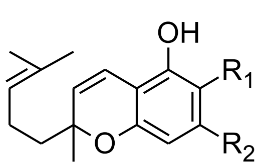
R1=COOH, R2=C_5H_{11}

Cannabichromene



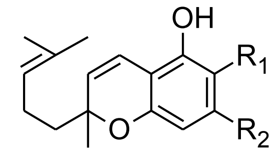
R1=H, R2=C_5H_{11}

Cannabichromevarinic acid



R1=COOH, R2=C_3H_7

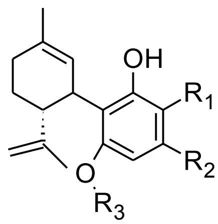
Cannabichromevarin



R1=H, R2=C_3H_7

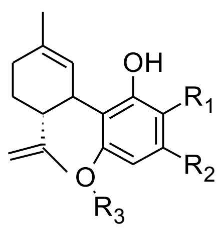
Cannabidiol Family

Cannabidiol-C_4



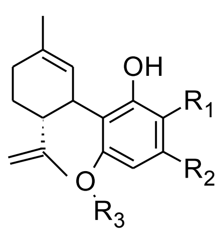
R1=H, R2= C_4H_9, R3= H

Cannabidiolic acid



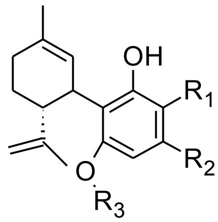
R1=COOH, R2=C_5H_{11}, R3=H

Cannabidiol monomethyl ether



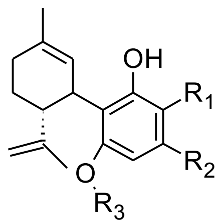
R1=H, R2=C_5H_{11}, R3=CH_3

Cannabidivarnic acid



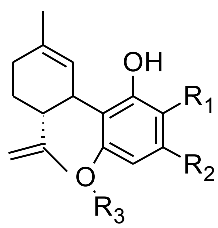
R1=COOH, R2=C_3H_7, R3=H

Cannabidivarin



R1=H, R2=C_3H_7, R3=H

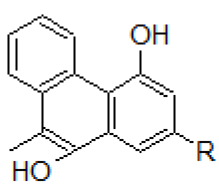
Cannabidiorcol



R1=H, R2=CH_3, R3=H

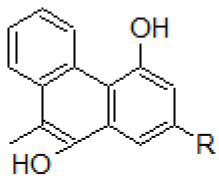
Cannabinodiol Family

Cannabinodiol



R=C_5H_{11}

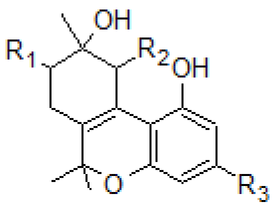
Cannabinodivarin



R=C_3H_7

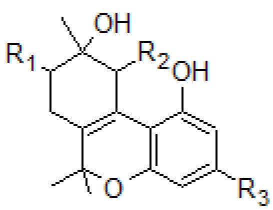
Cannabinitrol Family

Cannabinitrol



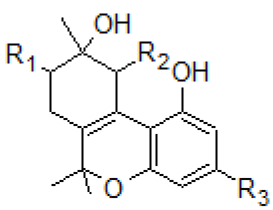
R1=H, R2=OH, R3=C_5H_{11}

10-ethoxy-9-hydroxy-Δ-^{6a}-tetrahydrocannabinol



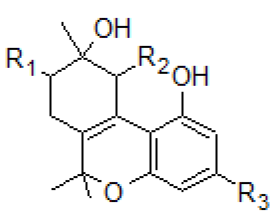
R1=H, R2=OC_2H_5, R3= C_5H_{11}

8,9-Dihydroxy-Δ-^{6a}-tetrahydrocannabinol



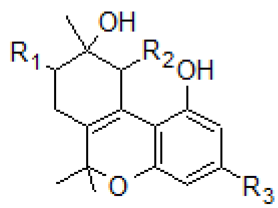
R1=OH, R2=H, R3=C_5H_{11}

Cannabitriolvarin



R1=H, R2=OH, R3=C_3H_7

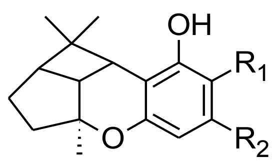
Ethoxy-cannabitriolvarin



R1=H, R2=OC_2H_5, R3= C_3H_7

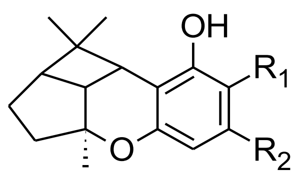
Cannabicyclol Family

Cannabicyclol



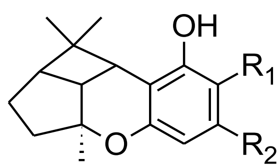
R1=H, R2=C_5H_{11}

Cannabicyclolic acid



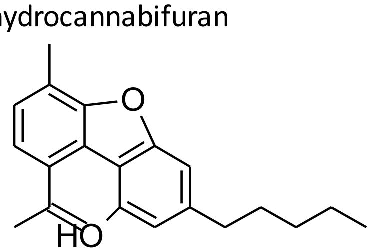
R1=COOH, R2= C_5H_{11}

Cannabicyclovarin



R1=H, R2=C_3H_7

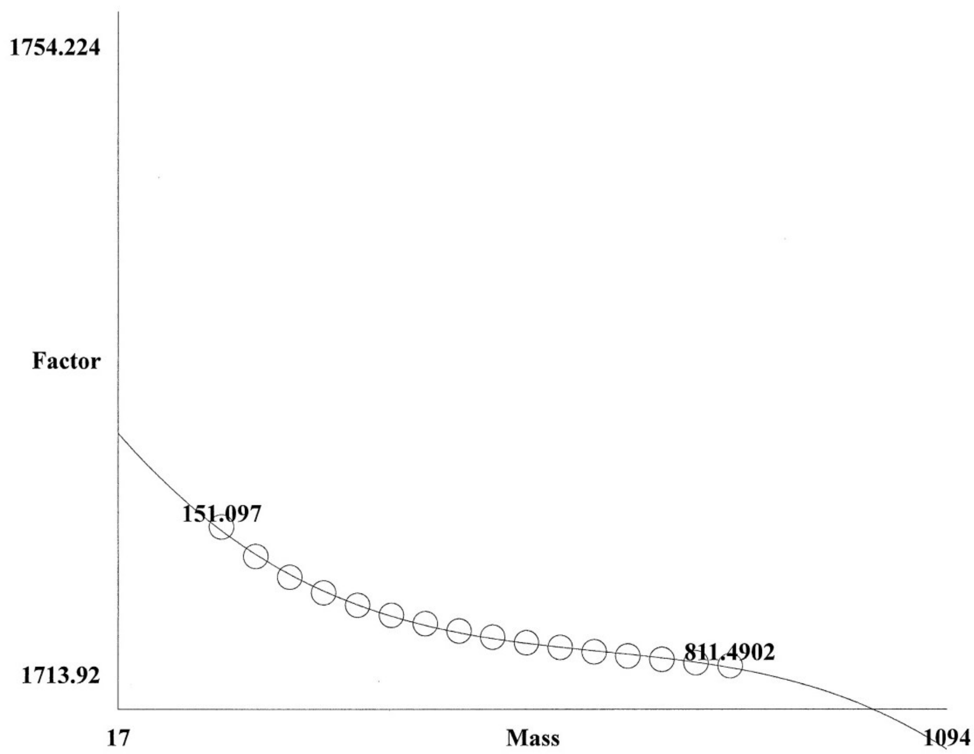
Dehydrocannabifuran



Appendix 3 - Calibration Curve

US Fish and Wildlife Service National Forensic Lab
3/4/2013

Calibration Curve
Data File : 1 THC ODOR experiments



Curve Fit: 5 E-11
TOF Calibration Constants
a: -0.112987
b: 5.855648E-04
c: -4.609301E-12
d: 4.579734E-17

Calibration Masses

151.097	591.3592
195.1232	635.3854
239.1495	679.4116
283.1757	723.4379
327.2019	767.4641
371.2281	811.4902
415.2543	
459.2805	
503.3068	
547.333	

Appendix 4 - Dataset of Terpenes

The table below is the actual dataset for the Mass Mountaineer software. When the name column contains a number, range of numbers, or series of numbers you will find the correlation in the second table of compounds in this appendix. For example, 1 – 4 of this first dataset would reference the following in the second table of compounds.

1	thymol
2	carvacrol
3	carvone
4	myrtenal

Mass Mountaineer Software Dataset

Name	Composition	Mass	Category
para-cymenene	C10H12	132.093903	monoterpene
eugenol	C10H12O2	164.083725	monoterpene
para-cymene	C10H14	134.109543	monoterpene
1 -- 4	C10H14O	150.104462	monoterpene
5 --19	C10H16	136.125198	monoterpene
20 -- 28	C10H16O	152.120117	monoterpene
29 -- 40	C10H18O	154.135773	monoterpene
41 -- 43	C10H18O2	170.130676	monoterpene
44, 45	C10H20O	156.151413	monoterpene
methylcaracrol	C11H16O	164.120117	monoterpene
46, 47	C11H18O2	182.130676	monoterpene
citronellyl formate	C11H20O2	184.146332	monoterpene
48, 49	C12H16O2	192.115036	monoterpene
50 -- 52	C12H20O2	196.146332	monoterpene
citronellyl acetate	C12H22O2	198.161987	monoterpene
beta-ionone	C13H20O	192.151413	sesquiterpenes
Cannithrene-1	C14H14O3	230.094299	Noncannabinoid Phenols
Apigenin	C15H10O5	270.052826	Flavinoids
Luteolin, Kaempferol	C15H10O6	286.047729	Flavinoids
Quercetin	C15H10O7	302.042664	Flavinoids
Cannithrene-2	C15H16O4	260.104858	Noncannabinoid Phenols
53, 54	C15H18O3	246.125595	Noncannabinoid Phenols

55 -- 85	C15H24	204.187805	sesquiterpene
86, 87	C15H24O	220.182709	sesquiterpene
88 -- 94	C15H26O	222.198364	sesquiterpene
Cannabistilbene-II	C16H19O5	291.12326	Noncannabinoid Phenols
Cannabifuran	C16H26O2	250.193283	Misc. cannabinoids class
alpha-Ylangene	C16H28	220.219101	sesquiterpene
N-p-coumaroyltyramine	C17H15O3	267.102112	Amides
N-trans-caffeoyltyramine	C17H15O4	283.097046	Amides
95, 96	C17H22O2	258.161987	cannabidiols, tetrahydrocannabinol
N-trans-feruloyltyramine	C18H17O4	297.112671	Amides
Cannabinol-C2	C18H20O2	268.146332	Cannabinol and Cannabinodiol class
delta-9-tetrahydrocannabiorcolic acid	C18H22O4	302.151825	Delta-9-tetrahydrocannabinols
Cannabiorcol	C19H18O2	278.130676	Cannabinol and Cannabinodiol class
97, 98	C19H22O2	282.161987	Cannabinol and Cannabinodiol class
Cannabistilbene-I	C19H23O3	299.164734	Noncannabinoid Phenols
99, 100	C19H25O2	285.185455	cannabichromenes
101 -- 103	C19H26O2	286.193268	cannabidiols, tetrahydrocannabinol
Cannabitriolvarin	C19H26O4	318.183105	Cannabitriol Class
cannabigerovarin	C19H27O2	287.201111	cannabigerol class
3,4,5,6-tetrahydro-7-hydroxy-alpha-alpha-2-trimethyl-9-n-propyl-2,6-methano-2H-1-benzoxocin-5-methanol	C19H29O3	305.21167	Misc. cannabinoids class
Cannflavin B	C20H20O6	356.125977	Flavinoids
Vitexin	C20H21O11	437.108398	Flavinoids
Orientin	C20H21O12	453.103302	Flavinoids
104, 105	C20H24O2	296.177643	Cannabinol and Cannabinodiol class
cannabichromevarinic acid	C20H25O4	329.175293	cannabichromenes
106, 107	C20H27O4	331.190948	cannabigerol class
cannabidiol-C4, delta-9-tetrahydrocannabinol-C4	C20H28O2	300.208923	cannabidiols, tetrahydrocannabinol
delta-9-tetrahydrocannabivarinic acid	C20H28O4	332.198761	Delta-9-tetrahydrocannabinols
phytol	C20H40O	296.307922	sesquiterpenes
108, 109	C21H26O2	310.193268	Cannabinol and Cannabinodiol class
10-oxo-delta-6a-tetrahydrocannabinol	C21H28O3	328.203857	Misc. cannabinoids class
delta-9-tetrahydrocannabinolic acid-C4	C21H28O4	344.198761	Delta-9-tetrahydrocannabinols

110 -- 113	C21H29O2	313.216766	cannabichromenes
114, 115	C21H30O2	314.224579	Delta-9-tetrahydrocannabinols
Cannabielsoin	C21H30O3	330.219482	Cannabielsoin class
116 -- 119	C21H30O4	346.214417	Cannabitriol Class
trihydroxy-delta-9-tetrahydrocannabinol	C21H30O5	362.20932	Misc. cannabinoids class
cannabigerol	C21H32O2	316.240234	cannabigerol class
cannabiripsol	C21H32O4	348.230072	Misc. cannabinoids class
cannabigerol monomethylether	C21H33O2	317.248047	cannabigerol class
Cannabinolic Acid	C22H26O4	354.183105	Cannabinol and Cannabinodiol class
Cannabinol methylether	C22H28O2	324.208923	Cannabinol and Cannabinodiol class
delta-8-tetrayhydrocannabinolic acid	C22H29O2	325.216766	delta-8-tetrahydrocannabinols
cannabichromenic acid	C22H29O4	357.206573	cannabichromenes
120 -- 123	C22H30O4	358.214417	cannabidiols
124, 125	C22H30O5	374.20932	Cannabielsoin class
cannabigerolic acid	C22H31O4	359.222229	cannabigerol class
cannabidiol monomethylether	C22H32O2	328.240234	cannabidiols
C23H34O4	C23H34O4	374.245697	cannabigerol class
Cannflavin A	C24H26O6	410.172943	Flavinoids
hex-3-en-1-ol	C6H12O	100.088814	monoterpene
benzaldehyde	C7H6O	106.041862	monoterpene
6-methyl-5-hepten-2-one	C8H14O	126.104462	monoterpene

Dataset used for Mass Mountaineer Software

Table of Compounds

Molecular Formula	Compound Name
$C_{10}H_{14}O$	
1	thymol
2	carvacrol
3	carvone
4	myrtenal
$C_{10}H_{16}$	
5	myrcene
6	limolene
7	α-pinene
8	β-pinene
9	δ-3-carene
10	cis-ocimene

11	trans-ocimene
12	α-thujene
13	tricyclene
14	α-phellandrene
15	β-phellandrene
16	α-terpinene
17	γ-terpinene
18	terpinolene
19	camphene
$C_{10}H_{16}O$	
20	linalool
21	fenchone
22	borneol
23	Ipsdienol
24	cis-carcaveol
25	neral
26	citral
27	camphor
28	trans-carveol
$C_{10}H_{18}O$	
29	α-terpineol
30	β-terpineol
31	β-fenchol
32	terpinen-4-ol
33	cis-Sabinene hydrate
34	geraniol
35	terpinen-1-ol
36	1,8-cineole
37	cis-rose oxide
38	trans-rose oxide
39	citronellal
40	isodihydrocarveol
$C_{10}H_{18}O_2$	
41	cis-linaloxides
42	trans-linaloxides
43	cis-para-meth-2-en-1-ol
$C_{10}H_{20}O$	
44	cintronellol
45	menthol
$C_{11}H_{18}O_2$	
46	neryl formate
47	geranyl formate

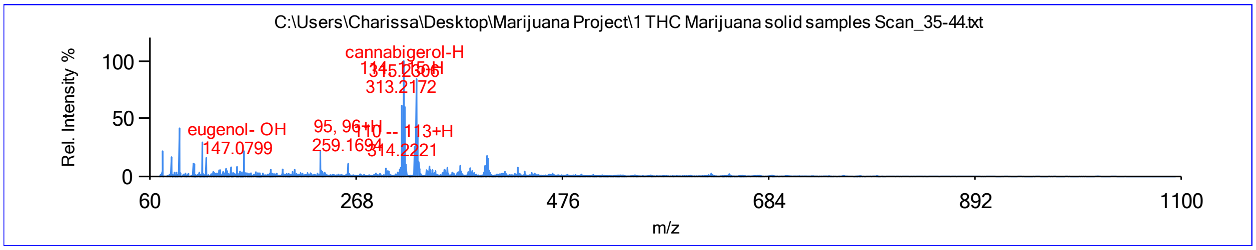
$C_{12}H_{16}O_2$	
48	thyml acetate
49	carvacryl acetate
$C_{12}H_{20}O_2$	
50	α-terpinyl acetate
51	neryl acetate
52	geranyl acetate
$C_{15}H_{18}O_3$	
53	cannabispiran
54	isocannabispiran
$C_{15}H_{24}$	
55	α-humulene
56	guajol
57	trans-γ-bisabolene
58	α-guaiene
59	trans-α-farnesene
60	β-caryophyllene
61	α-selinene
62	β-selinene
63	γ-curcumene
64	α-trans-bergamotene
65	cis-γ-curcumene
66	cis-β-farnesene
67	α-cis-bergamotene
68	γ-muurolene
69	α-longipinene
70	α-cadinene
71	β-elemene
72	sabinene
73	α-copaene
74	β-funebrene
75	Germacrene B
76	Germacrene D
77	γ-cadinene
78	β-bisabolene
79	isocaryophyllene
80	camphene
81	α-muurolene
82	α-gurgunene
83	β-gurgunene
84	γ-gurgunene
85	alloaromadendrene

$C_{15}H_{24}O$	
86	caryophyllene oxide
87	spathulenol
$C_{15}H_{26}O$	
88	α-eudesmol
89	β-eudesmol
90	epi-α-bisbalol
91	γ-eudesmol
92	2 cis, 6 cis-farnesol
93	α-cardinol
94	cis-nerolidol
$C_{17}H_{22}O_2$	
95	cannabidiorcol
96	Δ-9-tetrahydrocannabiorcol
$C_{19}H_{22}O_2$	
97	cannabivarin
98	cannbinodivarin
$C_{19}H_{25}O_2$	
99	cannabichromevarin
100	Δ-7-cis-iso-tetrahydrocannabivarin
$C_{19}H_{26}O_2$	
101	cannabidivarinic acid
102	Δ-9-tetrahydrocannabivarin
103	cannabicyclovarin
$C_{20}H_{24}O_2$	
104	cannabinol-C4
105	dehydrocannabifuran
$C_{20}H_{27}O_4$	
106	cannabigerovarinic acid
107	cannabichromanon
$C_{21}H_{26}O_2$	
108	cannabinol-C4
109	cannabinodiol
$C_{21}H_{29}O_2$	
110	cannabichromene
111	cannabidiol
112	Δ-8-tetrahydrocannabinol
113	Δ-9-cis-tetrahydrocannabinol
$C_{21}H_{30}O_2$	
114	Δ-9-tetrahydrocannabinol
115	cannabicyclol

$C_{21}H_{30}O_4$	
116	cannabitriol
117	8,9, dihydroxy-Δ-6a-tetraydrocannabinol
118	ethoxy-cannabitriolvarin
119	cannabicitran
$C_{22}H_{30}O_4$	
120	cannabidilolic acid
121	Δ-9-tetrahydrocannabinolic acid A
122	Δ-9-tetrahydrocannabinolic acid B
123	cannabicyclolic acid
$C_{22}H_{30}O_5$	
124	cannabielsoic acid A
125	cannabielsoic acid B
$C_{23}H_{34}O_4$	
126	cannabigerolic acid monomethylether
127	10-ethoxy-9-hydroxy-Δ-6a-tetrahydrocannabinol

Appendix 5 – Individual Spectra

Marijuana solid samples scan



Compounds identified by mass with isotope checks.

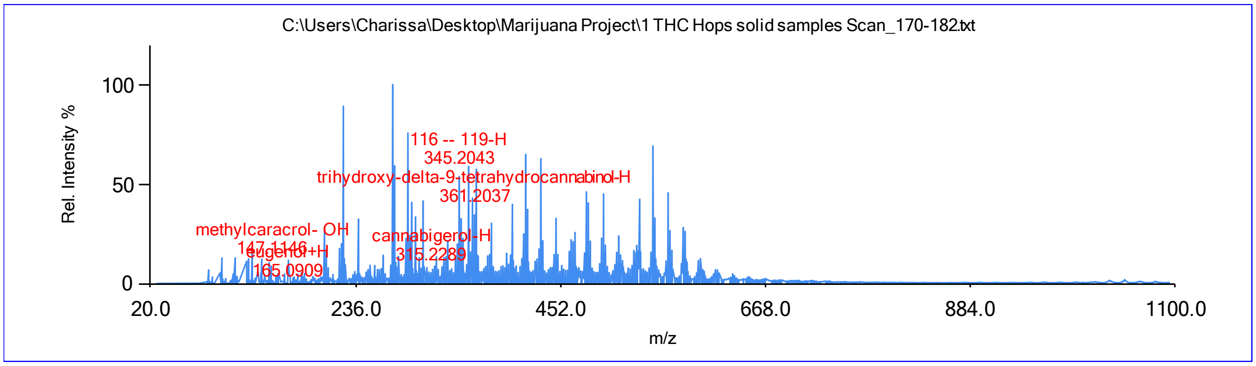
Tolerance: 5 (mmu)   Threshold: 5 %

Compound list(s): mj workbook search list.xlsx

Name	Composition	Adduct	Measured	Calculated	mmu	Abund.	#	Score
48, 49 monoterpene	C12H16O2	+H	193.12460	193.12286	-1.74	6.200	192.115036	
55 -- 85 sesquiterpene	C15H24	+H	205.19490	205.19563	0.73	5.800	204.187805	
95, 96 cannabidiols, tetrahydrocannabinol	C17H22O2*	+H	259.16940	259.16981	0.41	11.000	258.161987	
108, 109 Cannabinol and Cannabinodiol class	C21H26O2	+H	311.20361	311.20109	-2.52	6.100	310.193268	
110 -- 113 cannabichromenes	C21H29O2	+H	314.22211	314.22459	2.48	31.300	313.216766	
114, 115 Delta-9-tetrahydrocannabinols	C21H30O2	+H	315.23059	315.23240	1.81	100.000	314.224579	
Cannabielsoin Cannabielsoin class	C21H30O3	+H	331.23199	331.22731	-4.69	6.100	330.219482	
120 -- 123 cannabidiols	C22H30O4*	+H	359.22299	359.22224	-0.75	7.600	358.214417	
eugenol monoterpene	C10H12O2	- OH	147.07990	147.08098	1.09	8.300	164.083725	
88 -- 94 sesquiterpene	C15H26O	- OH	205.19490	205.19562	0.72	5.800	222.198364	
10-oxo-delta-6a-tetrah Misc. cannabinoids class	C21H28O3	- OH	311.20361	311.20112	-2.50	6.100	328.203857	
ydrocannabinol								
Cannabielsoin Cannabielsoin class	C21H30O3	- OH	313.21719	313.21674	-0.45	61.300	330.219482	
cannabiripsol Misc. cannabinoids class	C21H32O4	- OH	331.23199	331.22733	-4.66	6.100	348.230072	

110 -- 113 cannabichromenes	C21H29O2	-H	312.21060	312.20894	-1.66	7.600	313.216766
114, 115 Delta-9-tetrahydrocannabinols	C21H30O2	-H	313.21719	313.21675	-0.44	61.300	314.224579
cannabigerol cannabigerol class	C21H32O2	-H	315.23059	315.23241	1.82	100.000	316.240234
cannabigerol monomethy cannabigerol class	C21H33O2*	-H	316.23840	316.24022	1.82	60.200	317.248047
lether							
cannabichromenic acid cannabichromenes	C22H29O4	-H	356.19601	356.19875	2.73	5.800	357.206573

Hops solid samples scan



Compounds identified by mass with isotope checks.

Tolerance: 5 (mmu)   Threshold: 5 %

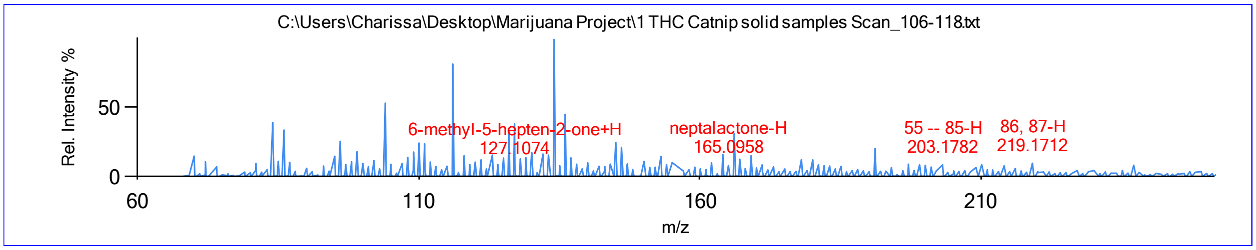
Compound list(s): mj workbook search list.xlsx

Name	Composition	Adduct	Measured	Calculated	mmu	Abund.	#	Score
eugenol monoterpene	C10H12O2*	+H	165.09090	165.09155	0.65	11.600	164.083725	
55 -- 85 sesquiterpene	C15H24*	+H	205.19440	205.19563	1.23	17.100	204.187805	
86, 87 sesquiterpene	C15H24O*	+H	221.18900	221.19053	1.54	19.900	220.182709	
methylcaracrol monoterpene	C11H16O	- OH	147.11459	147.11738	2.78	8.700	164.120117	
86, 87 sesquiterpene	C15H24O	- OH	203.17860	203.17997	1.36	27.000	220.182709	
88 -- 94 sesquiterpene	C15H26O*	- OH	205.19440	205.19562	1.23	17.100	222.198364	
Cannabinolic Acid Cannabinol and Cannabinodiol class	C22H26O4	- OH	337.18079	337.18036	-0.42	7.300	354.183105	
6-methyl-5-hepten-2-one monoterpene	C8H14O*	- OH	109.09840	109.10172	3.32	12.800	126.104462	
55 -- 85 sesquiterpene	C15H24	-H	203.17860	203.17998	1.38	27.000	204.187805	
88 -- 94 sesquiterpene	C15H26O*	-H	221.18900	221.19054	1.54	19.900	222.198364	
Cannabitriolvarin Cannabitriol Class	C19H26O4	-H	317.17911	317.17528	-3.83	7.000	318.183105	
116 -- 119 Cannabitriol Class	C21H30O4	-H	345.20432	345.20659	2.28	53.700	346.214417	
cannabigerol cannabigerol class	C21H32O2	-H	315.22891	315.23241	3.50	5.300	316.240234	

124, 125	C22H30O5	-H	373.19949	373.20150	2.00	8.500	374.20932

Cannabielsoin class

Catnip solid samples scan

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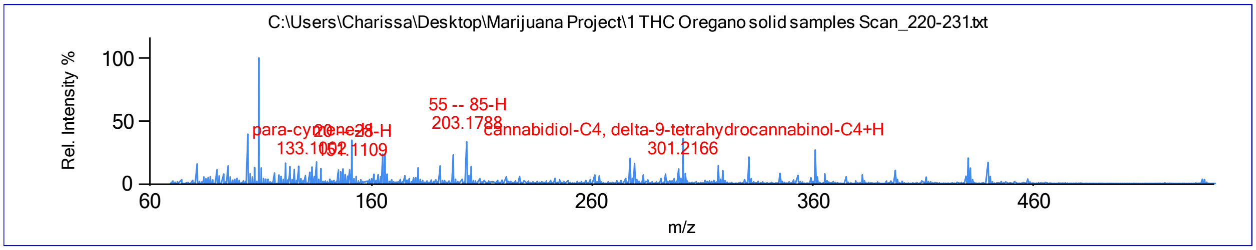
Compounds identified by mass with isotope checks.

Tolerance: 5 (mmu)        Threshold: 5 %

Compound list(s): mj workbook search list.xlsx
```

Name	Composition	Adduct	Measured	Calculated	mmu	Abund.	#	Score
eugenol monoterpene	C10H12O2	+H	165.09579	165.09155	-4.24	7.700		164.083725
6-methyl-5-hepten-2-one monoterpene	C8H14O	+H	127.10740	127.11229	4.89	6.500		126.104462
86, 87 sesquiterpene	C15H24O	- OH	203.17821	203.17997	1.76	8.200		220.182709
55 -- 85 sesquiterpene	C15H24	-H	203.17821	203.17998	1.77	8.200		204.187805
86, 87 sesquiterpene	C15H24O	-H	219.17120	219.17488	3.68	9.300		220.182709
eugenol monoterpene	C10H12O2	+H	165.09579	165.09155	-4.24	7.700		164.083725
6-methyl-5-hepten-2-one monoterpene	C8H14O	+H	127.10740	127.11229	4.89	6.500		126.104462
neptalactone monoterpene	C10H14O2	+H	167.10620	167.10721	1.00	12.200		
86, 87 sesquiterpene	C15H24O	- OH	203.17821	203.17997	1.76	8.200		220.182709
55 -- 85 sesquiterpene	C15H24	-H	203.17821	203.17998	1.77	8.200		204.187805
86, 87 sesquiterpene	C15H24O	-H	219.17120	219.17488	3.68	9.300		220.182709
neptalactone monoterpene	C10H14O2	-H	165.09579	165.09156	-4.24	7.700		

Oregano solid samples scan



Compounds identified by mass with isotope checks.

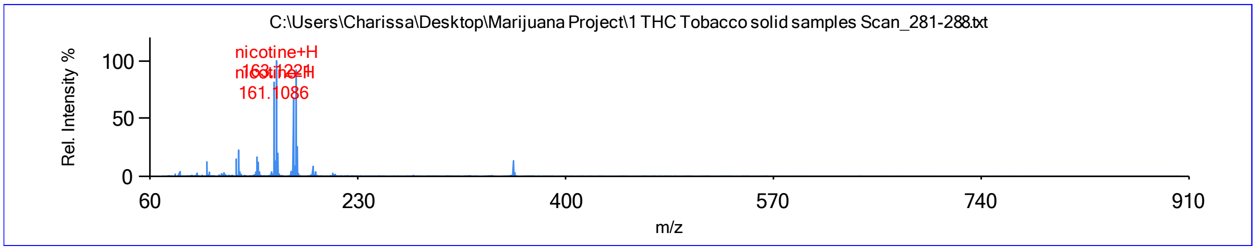
Tolerance: 5 (mmu)   Threshold: 5 %

Compound list(s): mj workbook search list.xlsx

Name	Composition	Adduct	Measured	Calculated	mmu	Abund.	#	Score
para-cymenene monoterpene	C10H12	+H	133.10020	133.10173	1.52	13.100		132.093903
eugenol monoterpene	C10H12O2	+H	165.09100	165.09155	0.55	23.400		164.083725
1 -- 4 monoterpene	C10H14O*	+H	151.11090	151.11229	1.39	34.500		150.104462
20 -- 28 monoterpene	C10H16O	+H	153.12331	153.12794	4.64	5.700		152.120117
55 -- 85 sesquiterpene	C15H24*	+H	205.19450	205.19563	1.13	13.500		204.187805
86, 87 sesquiterpene	C15H24O	+H	221.18570	221.19053	4.83	5.400		220.182709
cannabidiol-C4, delta- cannabidiols, tetrahydrocannabinol	C20H28O2*	+H	301.21661	301.21675	0.13	35.900		300.208923
9-tetrahydrocannabinol-C4								
delta-9-tetrahydrocann Delta-9-tetrahydrocannabinols	C21H28O4*	+H	345.20459	345.20659	2.00	7.200		344.198761
abinolic acid-C4								
neptalactone monoterpene	C10H14O2	+H	167.10510	167.10721	2.10	7.400		
1 -- 4 monoterpene	C10H14O	- OH	133.10020	133.10172	1.52	13.100		150.104462
41 -- 43 monoterpene	C10H18O2	- OH	153.12331	153.12794	4.63	5.700		170.130676
methylcaracrol monoterpene	C11H16O	- OH	147.11481	147.11738	2.57	11.600		164.120117
beta-ionone sesquiterpenes	C13H20O	- OH	175.14571	175.14867	2.97	6.200		192.151413
86, 87 sesquiterpene	C15H24O	- OH	203.17880	203.17997	1.17	33.300		220.182709

88 -- 94 sesquiterpene	C15H26O*	- OH	205.19450	205.19562	1.12	13.500	222.198364
cannabidiol-C4, delta- cannabidiols, tetrahydrocannabinol	C20H28O2	- OH	283.20590	283.20618	0.28	6.900	300.208923
9-tetrahydrocannabinol-C4							
trihydroxy-delta-9-tet Misc. cannabinoids class	C21H30O5*	- OH	345.20459	345.20658	1.99	7.200	362.20932
rahydrocannabinol							
para-cymene monoterpene	C10H14	-H	133.10020	133.10172	1.51	13.100	134.109543
20 -- 28 monoterpene	C10H16O*	-H	151.11090	151.11229	1.39	34.500	152.120117
29 -- 40 monoterpene	C10H18O	-H	153.12331	153.12795	4.64	5.700	154.135773
46, 47 monoterpene	C11H18O2	-H	181.12230	181.12285	0.55	12.500	182.130676
55 -- 85 sesquiterpene	C15H24	-H	203.17880	203.17998	1.18	33.300	204.187805
88 -- 94 sesquiterpene	C15H26O	-H	221.18570	221.19054	4.84	5.400	222.198364
cannabidiol-C4, delta- cannabidiols, tetrahydrocannabinol	C20H28O2	-H	299.19901	299.20110	2.09	11.700	300.208923
9-tetrahydrocannabinol-C4							
116 -- 119 Cannabitriol Class	C21H30O4*	-H	345.20459	345.20659	2.00	7.200	346.214417
neptalactone monoterpene	C10H14O2	-H	165.09100	165.09156	0.55	23.400	

Tobacco solid samples scan



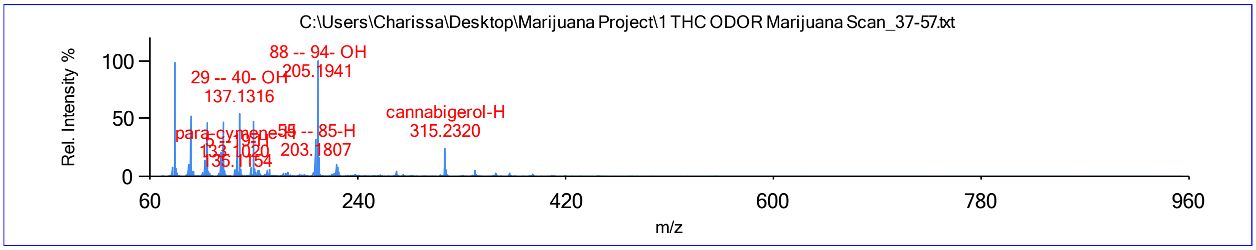
Compounds identified by mass with isotope checks.

Tolerance: 5 (mmu)   Threshold: 5 %

Compound list(s): mj workbook search list.xlsx

Name	Composition	Adduct	Measured	Calculated	mmu	Abund.	#	Score
nicotine	C10H14N2*	+H	163.12210	163.12352	1.42	100.000		tobacco
nicotine	C10H14N2	-H	161.10860	161.10787	-0.73	81.500		tobacco

Odor Marijuana Scan



Compounds identified by mass with isotope checks.

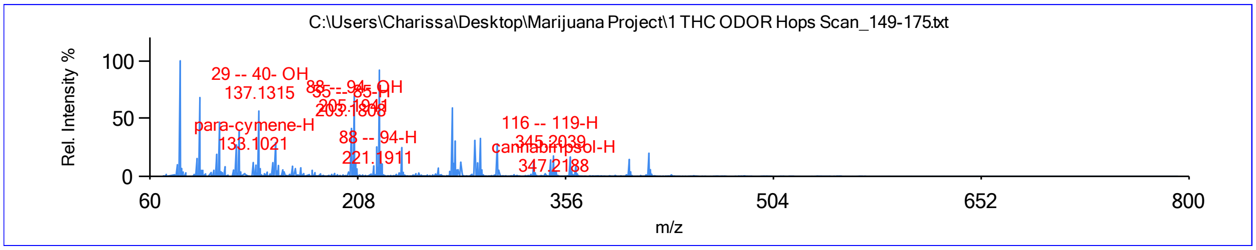
Tolerance: 5 (mmu)   Threshold: 5 %

Compound list(s): mj workbook search list.xlsx

Name	Composition	Adduct	Measured	Calculated	mmu	Abund.	#	Score
para-cymenene monoterpene	C10H12	+H	133.10201	133.10173	-0.28	5.500		132.093903
para-cymene monoterpene	C10H14	+H	135.11540	135.11737	1.97	22.700		134.109543
5 --19 monoterpene	C10H16*	+H	137.13161	137.13302	1.42	54.100		136.125198
55 -- 85 sesquiterpene	C15H24*	+H	205.19411	205.19563	1.52	100.000		204.187805
86, 87 sesquiterpene	C15H24O	+H	221.19119	221.19053	-0.66	10.000		220.182709
114, 115 Delta-9-tetrahydrocannabinols	C21H30O2*	+H	315.23199	315.23240	0.41	23.800		314.224579
1 -- 4 monoterpene	C10H14O	- OH	133.10201	133.10172	-0.28	5.500		150.104462
20 -- 28 monoterpene	C10H16O	- OH	135.11540	135.11738	1.97	22.700		152.120117
29 -- 40 monoterpene	C10H18O*	- OH	137.13161	137.13303	1.42	54.100		154.135773
methylcaracrol monoterpene	C11H16O	- OH	147.11630	147.11738	1.07	7.400		164.120117
86, 87 sesquiterpene	C15H24O	- OH	203.18069	203.17997	-0.73	31.900		220.182709
88 -- 94 sesquiterpene	C15H26O*	- OH	205.19411	205.19562	1.52	100.000		222.198364
6-methyl-5-hepten-2-one monoterpene	C8H14O*	- OH	109.10210	109.10172	-0.38	46.200		126.104462
para-cymene monoterpene	C10H14	-H	133.10201	133.10172	-0.29	5.500		134.109543
5 --19 monoterpene	C10H16	-H	135.11540	135.11737	1.97	22.700		136.125198

55 -- 85 sesquiterpene	C15H24	-H	203.18069	203.17998	-0.71	31.900	204.187805
88 -- 94 sesquiterpene	C15H26O	-H	221.19119	221.19054	-0.65	10.000	222.198364
cannabigerol cannabigerol class	C21H32O2*	-H	315.23199	315.23241	0.41	23.800	316.240234
cannabigerol monomethylether cannabigerol class	C21H33O2*	-H	316.23581	316.24022	4.41	5.400	317.248047

Odor Hops Scan



Compounds identified by mass with isotope checks.

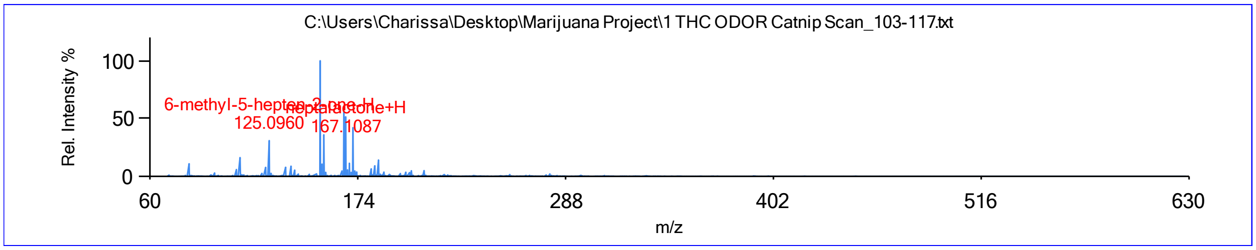
Tolerance: 5 (mmu) Threshold: 5 %

Compound list(s): mj workbook search list.xlsx

Name	Composition	Adduct	Measured	Calculated	mmu	Abund.	#	Score
para-cymenene monoterpene	C10H12	+H	133.10210	133.10173	-0.37	11.900	132.093903	
para-cymene monoterpene	C10H14	+H	135.11301	135.11737	4.36	9.700	134.109543	
1 -- 4 monoterpene	C10H14O*	+H	151.11211	151.11229	0.18	9.300	150.104462	
5 --19 monoterpene	C10H16*	+H	137.13150	137.13302	1.52	56.500	136.125198	
55 -- 85 sesquiterpene	C15H24*	+H	205.19411	205.19563	1.52	69.800	204.187805	
86, 87 sesquiterpene	C15H24O	+H	221.19110	221.19053	-0.57	25.500	220.182709	
116 -- 119 Cannabitriol Class	C21H30O4*	+H	347.21881	347.22224	3.43	17.600	346.214417	
120 -- 123 cannabidiols	C22H30O4*	+H	359.22061	359.22224	1.63	16.800	358.214417	
1 -- 4 monoterpene	C10H14O	- OH	133.10210	133.10172	-0.38	11.900	150.104462	
20 -- 28 monoterpene	C10H16O	- OH	135.11301	135.11738	4.37	9.700	152.120117	
29 -- 40 monoterpene	C10H18O*	- OH	137.13150	137.13303	1.53	56.500	154.135773	
methylcaracrol monoterpene	C11H16O	- OH	147.11639	147.11738	0.98	11.800	164.120117	
beta-ionone sesquiterpenes	C13H20O	- OH	175.14610	175.14867	2.57	5.200	192.151413	
86, 87 sesquiterpene	C15H24O	- OH	203.18080	203.17997	-0.83	41.500	220.182709	
88 -- 94 sesquiterpene	C15H26O*	- OH	205.19411	205.19562	1.52	69.800	222.198364	
6-methyl-5-hepten-2-on monoterpene	C8H14O*	- OH	109.10210	109.10172	-0.38	46.900	126.104462	

para-cymene monoterpene	$C_{10}H_{14}$	-H	133.10210	133.10172	-0.38	11.900	134.109543
5 --19 monoterpene	$C_{10}H_{16}$	-H	135.11301	135.11737	4.37	9.700	136.125198
20 -- 28 monoterpene	$C_{10}H_{16}O$*	-H	151.11211	151.11229	0.19	9.300	152.120117
55 -- 85 sesquiterpene	$C_{15}H_{24}$	-H	203.18080	203.17998	-0.82	41.500	204.187805
88 -- 94 sesquiterpene	$C_{15}H_{26}O$	-H	221.19110	221.19054	-0.56	25.500	222.198364

Odor Catnip Scan



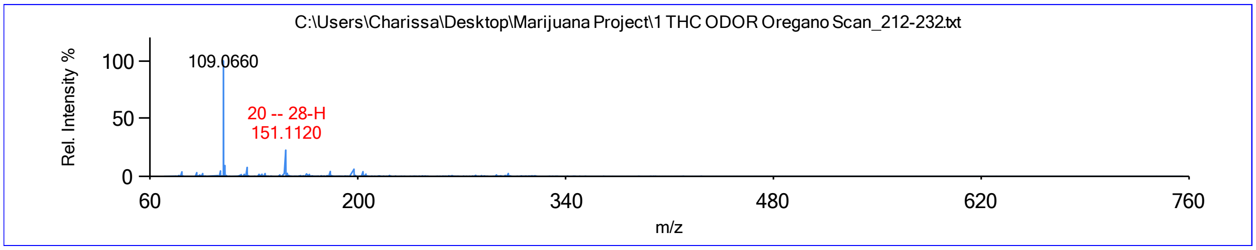
Compounds identified by mass with isotope checks.

Tolerance: 5 (mmu)   Threshold: 5 %

Compound list(s): mj workbook search list.xlsx

Name	Composition	Adduct	Measured	Calculated	mmu	Abund.	#	Score
neptalactone monoterpene	C10H14O2*	+H	167.10870	167.10721	-1.50	51.500		
6-methyl-5-hepten-2-on monoterpene	C8H14O*	- OH	109.10210	109.10172	-0.38	16.200	126.104462	
41 -- 43 monoterpene	C10H18O2	-H	169.12309	169.12285	-0.24	11.300	170.130676	
46, 47 monoterpene	C11H18O2*	-H	181.12241	181.12285	0.45	6.400	182.130676	
6-methyl-5-hepten-2-on monoterpene	C8H14O*	-H	125.09600	125.09664	0.64	30.900	126.104462	

Odor Oregano Scan



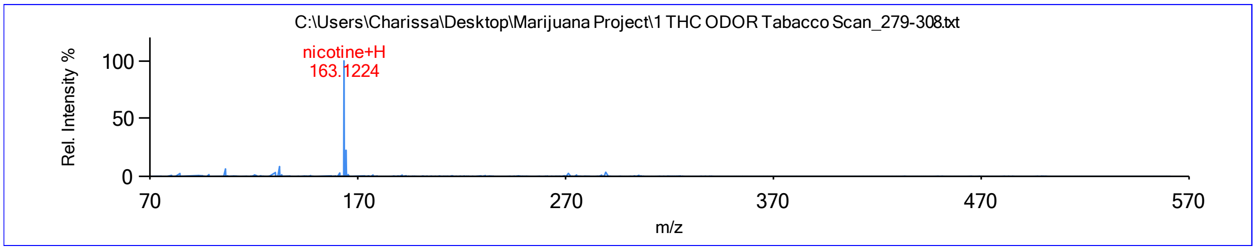
Compounds identified by mass with isotope checks.

Tolerance: 5 (mmu) Threshold: 5 %

Compound list(s): mj workbook search list.xlsx

Name	Composition	Adduct	Measured	Calculated	mmu	Abund.	#	Score
1 -- 4 monoterpene	C10H14O*	+H	151.11200	151.11229	0.29	22.700	150.10446	2
20 -- 28 monoterpene	C10H16O*	-H	151.11200	151.11229	0.29	22.700	152.12011	7

Odor Tobacco Scan



Compounds identified by mass with isotope checks.

Tolerance: 5 (mmu)   Threshold: 5 %

Compound list(s): mj workbook search list.xlsx

Name	Composition	Adduct	Measured	Calculated	mmu	Abund.	#	Score
nicotine	C10H14N2*	+H	163.12241	163.12352	1.11	100.000		tobacco