Effects of terpenes on the emissions of aerosols and carbonyls from vaping delta-8- and delta-10- tetrahydrocannabinol (THC)

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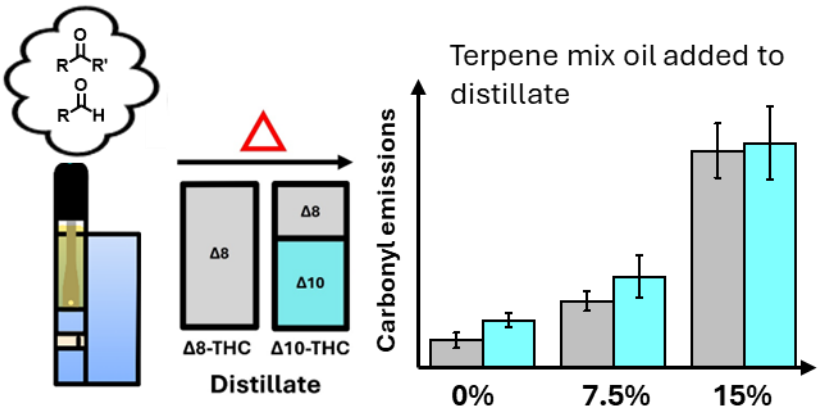
TOC Image



Abstract Cannabis electronic cigarette (CEC) products, which are used to vape purified cannabinoids or their mixtures, have rapidly proliferated in recent years and are emerging sources of indoor air pollution. Yet, chemical characterizations of the inhalable aerosol emissions from cannabinoid vaping are scarce in the literature, particularly for the highly popular synthetic cannabinoids (Δ8- and Δ10- tetrahydrocannabinol, Δ8-THC and Δ10-THC). This work quantifies the chemical composition of the cannabinoid distillates, aerosol mass production, and the emissions of harmful or potentially harmful carbonyls from the CEC vaping of Δ8-THC and Δ10-THC using high-performance liquid chromatography (HPLC) coupled to high-resolution mass spectrometry (HRMS). It was found that commercial distillates of Δ8-THC and Δ10-THC had variable purity, with the Δ10-THC distillate comprising roughly one-third of Δ8-THC. Often,

cannabinoid distillates are mixed with terpene oil in vape products. This work shows that the addition of a commercial terpene oil mixture (rich in limonene, β-caryophyllene, β-myrcene, and others) to Δ8-THC and Δ10-THC distillates at 0%, 7.5%, and 15% terpene content by mass significantly increases carbonyl formation up to 9-fold. On average, the CEC vaping of Δ8-THC and Δ10-THC distillates produced 6 ± 1 mg/puff of aerosol, which did not significantly vary with added terpenes. Molecular analysis confirmed that a majority of the carbonyl products originate from the chemical oxidation of terpenes during vaping. The most abundantly observed carbonyls were acetone, acetaldehyde, propionaldehyde, and terpene-specific carbonyls. Cannabinoid oxidation products were also observed but did not increase with terpene content. It can be concluded that high terpene content in CEC products gives rise to more carbonyl emissions in the aerosol due to terpene oxidation, which have adverse implications for inhalation toxicology in an indoor environment.

Introduction

The 2018 Farm Bill legalized the growth, processing, marketing, and sale of hemp, which contains primarily cannabidiol (CBD) along with lower levels of other cannabinoids and < 0.3% of delta-9-tetrahydrocannabinol (Δ9-THC).[1, 2] This has led to the introduction of synthetic isomers of Δ9-THC from relatively simple syntheses involving CBD, such as delta-8-tetrahydrocannabinol (Δ8-THC) and delta-10-tetrahydrocannabinol (Δ10-THC), that retain psychoactive properties but do not have a legal status.[3] Thus, the Δ8- and Δ10- analogs of THC have emerged to be popular choices for cannabis use, with Δ8-THC becoming the fastest growing product in the hemp industry.[4] As "vaping," or aerosolizing liquids, oils, or solids with an electronic (e-) cigarette device, is rapidly emerging as a popular form of intake for cannabinoids among adolescents and young adults, it is increasingly common to find e-cigarette or vaping products that feature Δ8-THC and Δ10-THC as primary ingredients.[5-8] Cannabis electronic cigarettes (CEC), or cannabis vape devices, are similar to nicotine electronic cigarettes, except that they contain a ceramic coil that is optimized to aerosolize a range of different cannabis materials with variable viscosity, including: plant/flower material, oily concentrates (e.g., distillate), waxy concentrates (e.g. resin, rosin), or "e-liquids" that contain cannabinoids at various concentrations (mg/mL) in solvents (e.g. terpenes, propylene glycol (PG)/vegetable glycerin (VG), or polyethylene glycol).[9]

CEC vaping has been shown to be an emerging source of indoor air pollution, which introduces particles, cannabinoids, volatile organic compounds (VOCs), and harmful or potentially harmful components (HPHCs) such as toxic carbonyls to indoor environments.[10-14] For example, cannabis vaping has been shown to emit more fine particles compared cigarettes in general [12], and more than cannabis smoking when compared at close proximity (< 1 m).[15] The chemical composition of cannabis vape emissions are undercharacterized, which may be due to regulatory barriers and the rapid evolution of the cannabinoid market. [16, 17] In particular, the potential health and indoor air quality effects vaping the newly introduced synthetic products, Δ8-THC and Δ10-THC, are poorly understood.[18-21] To date, there are no chemical assessments of Δ8-THC and Δ10-THC vape aerosol emissions in the literature. Furthermore, there are no currently established standards for testing or labeling for these products,[3, 22] which prevents consumers and researchers from using the labelled content ingredients to extrapolate risks. The approximately 150 reported cases per year reported to the U.S. National Poison Center involving vaping Δ8-THC, Δ10-THC, and their acetylated analogs,[23] and the aforementioned impacts on indoor air quality, underscore the need to better characterize vape emissions from synthetic cannabinoids.

It has been recently observed that the consumer preference for cannabis vaping products in the US and Canada is shifting from dry herb to cannabis oil or distillates.[24] Cannabis vape products that use cannabinoid distillates (often > 90% purity) are often mixed with an oily mixture of cannabis-derived terpenes (monoterpenes $C_{10}H_{16}$, or sesquiterpenes $C_{15}H_{24}$) for added flavor, aroma, and to reach the lower viscosity necessary to vape.[25] A lowered viscosity via the addition of terpenes may impact the aerosol emissions of the distillate. Terpenes are known to have high or moderate volatility. It was found that monoterpenes emitted from cannabis vaping are comparable or at higher concentration compared to cannabis smoking in an indoor environment, and may be subject to thirdhand transport to other living spaces.[10] Terpenes are also chemically labile due to double bonds in their chemical structure,[26] known to react quickly[27] with the reactive oxygen species (ROS) that are produced during vaping.[28-30] Thus, the addition of terpenes to the cannabinoid distillates may impact the emission of oxidation products in the aerosols such as carbonyls.[31]

There are many cannabis-derived terpene mixtures in commerce, each advertising a different aroma that is achieved by different compositional distribution of terpenes. Common major components are limonene, myrcene, and caryophyllene alongside several other terpenes as

minor components. To date, research on cannabis vaping has primarily focused on the dose transfer of terpenes and cannabinoids to the aerosol from both dabbing and vaping, specifically focusing on Δ9-THC.[32-36] The effects of added terpenes on the emission of air pollutants, such as aerosol particles and toxic carbonyls, from the cannabinoid vapes are not well understood. Recently, Meehan-Atrash et al. reported that increasing the percent mass of β-myrcene in CEC vaping of Δ9-THC and cannabinol (CBN) decreased the formation of some VOCs (isoprene, methylbutene, etc.) and isoprene-specific carbonyls (methacrolein, methyl vinyl ketone, etc.) and decreased the degradation of the starting cannabinoid, though the effects on volatile compounds may be opposite for dabbing.[32, 37, 38] This work complements prior studies by characterizing aerosols generated from the CEC vaping of the synthetic cannabinoids Δ8-THC and Δ10-THC, with and without the addition of a commercial mixture of terpene oil. Moreover, we examine a large suite of carbonyl emissions with semi-targeted analytical techniques.

2. Methods

2.1 Vape Oil Formulations and Analysis

Distillates of Δ8-THC and Δ10-THC (with a color and viscosity resembling honey) were obtained from commercial vendors without added terpenes and used without further purification. Δ8-THC distillate was obtained from The Hemp Collect (Portland, OR) and was advertised to contain 89.5% Δ8-THC (with minor contributions from cannabinol (0.67%), cannabichromene (0.18%), and cannabidiolic acid (0.03%)) according to the certificate of analysis. Δ10-THC distillate was obtained from Gilded Extracts (San Antonio, TX) and was advertised to contain 87.7% Δ10-THC (with minor contributions from Δ8-THC (0.352%), cannabinol (4.357%), and others) according to the certificate of analysis. An oily mixture of terpenes labeled "Watermelon Splash" was obtained from Abstrax Tech (Tustin, CA). The terpene mixture was advertised to contain d-Limonene, β-caryophyllene, and β-myrcene as major components, and a "candy" or "melon" flavor and aroma. The available documentation does not provide the specific mass distribution for the terpene mixture. The terpene mix was added to the THC distillates at 0, 7.5, and 15% (w/w) to mimic commercially available formulations and those studied in the scientific literature.[37, 39]

The chemical composition of cannabinoids and terpenes in vape oils were analyzed by gas chromatography-mass spectrometry (GC-MS, Agilent 5890 GC with 5973 MSD) after dilution with ethyl acetate. Analytes were separated with an HP5-MS capillary column (30 m, 0.25 mm ID, 0.25 um film, Agilent Technologies Inc., Santa Clara, CA) with the following oven program: 60ºC (1.5 min), 10ºC/min (24 min), and 300ºC (3.5 min). Quantification was performed using certified reference standards of cannabinoids and terpenes: Δ8-THC in methanol and Δ10-THC in methanol (Cerilliant, Round Rock, TX), and Cannabis Terpene Mix A (20 component mixture in methanol) and Cannabis Terpene Mix B (14 component mixture in methanol) (Supelco TraceCERT, Bellefonte, PA).

2.2 Generation of Aerosol from a Cannabis e-Cigarette Device

The THC-derived vape oils were aerosolized or "vaped" with a representative cannabis electronic cigarette (CEC) device, the CCell Palm Pro with a battery capacity of 500 mAh (Shenzhen Smoore Technology Limited, Shenzhen, China, **Fig. 1A**). CCell Kera cartridges (1.4 Ω, 1.0 mL, Shenzhen Smoore Tech. Ltd., Shenzhen, China), hereinafter referred to as the "pod" for brevity, were selected based on their refillable ability and the specialized Zirconia ceramic coil designed to effectively vaporize viscous fluids. The device was vaped using the 3.6V setting with the adjustable airflow collar kept closed for the most efficient aerosolization at the same vacuum flow rate and puff duration.

Cannabis vape users engage in longer and deeper puffs compared to nicotine e-cigarette users.[9, 40] As a result, parameters were selected at the upper end of the conventional range for e-cigarette users in previous studies.[41] The device was activated with an average applied vacuum flow of 1.8 ± 0.1 L/min for a 4 second puff duration, corresponding to a puff volume of 121 ± 5 mL. The flow rate was measured by a primary flow calibrator (4000 Series Model 4043, TSI Inc., Shoreview, MN) and the puffing regimen was regulated by solenoid valves controlled by a time relay controller (PTR4-SP, Changzhou Xuchuang Info. Tech. Co., Changzhou, China). The puff frequency was 2 puffs/min. Aerosol mass was determined by gravimetric analysis of the post-vaped pod minus the pre-vaped pod using a calibrated Shimadzu microbalance.

2.3 Collection and Analysis of Carbonyls using HPLC-HRMS

The methods for the collection and analyses of carbonyls used in this work have been described previously.[14, 42, 43] Briefly, carbonyls produced from vaping Δ8-THC and Δ10-THC were collected onto 2,4-dinitrophenylhydrazine (DNPH) cartridges (350 mg DNPH, Supelco Inc., Bellefonte, PA) for conversion into hydrazones. A total of 15 puffs was collected for each analysis. 2 mL of acetonitrile (LC-MS grade, Fisher Scientific Inc., Hampton, NH) was used to extract the DNPH and hydrazones.[42] The temperature of the pod, connector, and collection media were regulated to ~ 35 ºC with a fiberglass heating tape (Dwyer Omega, Michigan City, IN) to prevent aerosol condensation and clogging and to mimic body temperature during the transport of the aerosol from source to collection.

Carbonyl quantification was performed utilizing high performance liquid chromatography-high resolution mass spectrometry (HPLC-HRMS) using a Thermo Q-Exactive HF (High-field Orbitrap) at 45,000 m/Δm mass resolving power at m/z 400. Separation of hydrazones was done with a Dionex Ultimate 3000 HPLC using an Agilent Poroshell EC-C18 column (2.1 mm × 100 mm, 2.7 μm, 120 Å) with the following gradient program: 40% B (3.33 min), 50% B (14.6 min), 60% B (20 min), 100% B (32 min), 40% B (37 min). Concentrations of formaldehyde, acetaldehyde, acetone, acrolein, propionaldehyde, methacrolein, hexaldehyde, benzaldehyde, butanone, butyraldehyde, crotonaldehyde, valeraldehyde, glyoxal, and methylglyoxal were quantified using commercially-available certified reference standards (AccuStandard, New Haven, CT).[42] Acetic acid, glycolaldehyde, and hydroxyacetone standards were synthesized as described previously.[44] Concentrations of each carbonyl were normalized by the amount of aerosol collected on the cartridge, which was determined by weighing the cartridge before and after aerosol collection using a 51g × 0.1 mg, 120 V analytical balance (Mettler Toledo, Columbus, OH).

$$\text{Normalized carbonyl yield} = \left(\frac{\mu g}{mL} \times \text{mL extraction solvent}\right) \times \left(\frac{1}{\text{mg aerosol collected}}\right) \quad \textbf{[Eqn. 1]}$$

Carbonyls for which analytical standards were unavailable were identified using accurate mass but not quantified. These carbonyls are discussed in semi-quantitative terms according to their HPLC peak areas. The quantified carbonyl values in this work should be considered a lower limit.

3. Results and Discussion

3.1 Cannabinoid and terpene content from distillate mixtures

Composition analysis of the cannabinoid content of the distillates (**Fig. 1B and C**) showed that the Δ8-THC distillate contains mostly Δ8-THC (98.7% THC isomer purity by mass) with minor contribution from cannabidiol (CBD, 0.044%). This result is in rough agreement with the certificate of analysis. In contrast, we found that the Δ10-THC distillate purchased for this research is only two-thirds Δ10-THC with the remaining one-third of the composition comprising of Δ8-THC (**Fig. 1C**). This result is in discrepancy to the product certificate of analysis, which stated an approximate 90% Δ10-THC content with < 1% of Δ8-THC. It is not clear if storage-related degradation occurred prior to purchase; however, THC has been reported to degrade to cannabinol (CBN) instead of migrate the location of the double bond to a different THC isomer.[45] As Δ10-THC is synthesized from other cannabinoids, unintended byproducts[37] and incomplete purification[4] are likely reasons for the large impurity of Δ8-THC in the Δ10-THC distillate.

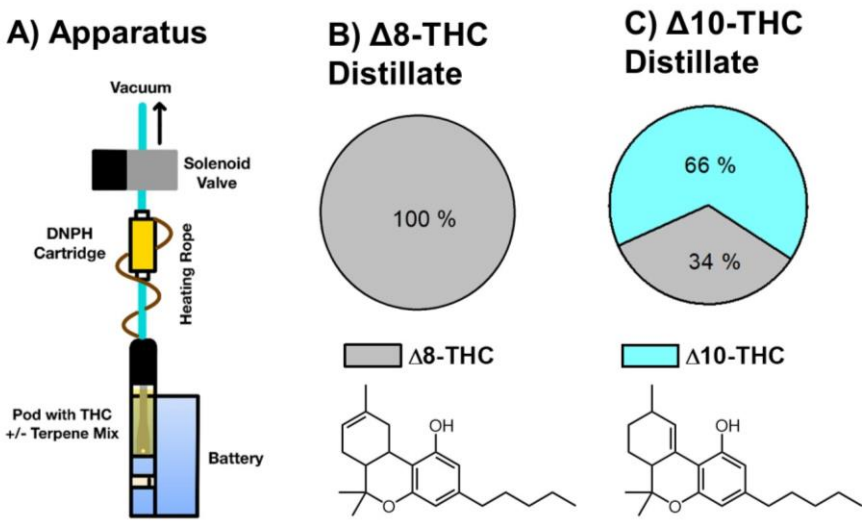


Figure 1. Cannabinoid distillate vaping apparatus (A) and GC/MS quantified THC isomer distribution in commercial Δ8-THC distillate (B) and commercial Δ10-THC distillate (C).

The composition analysis of the terpene mix (**Fig. 2**) used for this research

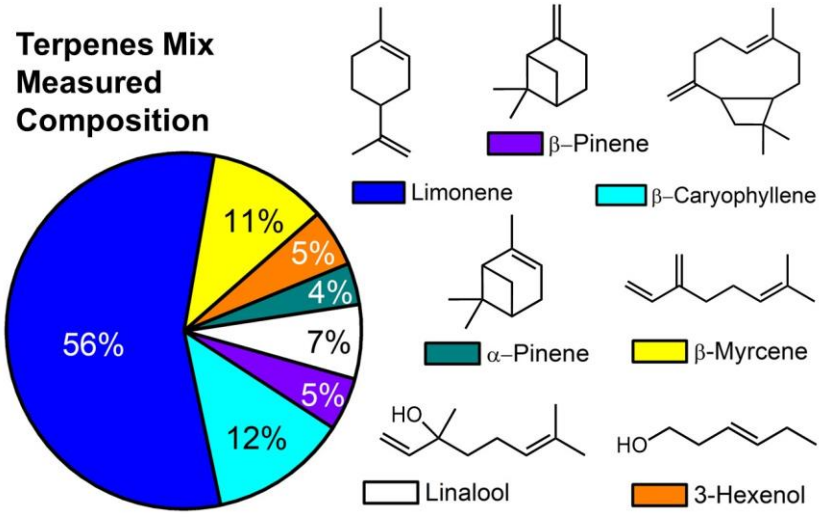


Figure 2. GC/MS quantified terpene composition from the commercial Watermelon Splash terpene oil mix that was used for study.

revealed that the major component is limonene (56% by mass), with smaller contributions from β-caryophyllene (12%), β-myrcene (11%), linalool (7%), β-pinene (5%), 3-hexenol (5%), and α-pinene (4%). Although the product specifications do not indicate concentrations, it was determined that the major components listed on the product page (limonene, β-caryophyllene, β-myrcene) are indeed accurate after validation with the GC-MS analysis.

3.2 Aerosol mass and carbonyl yields that were quantified in the aerosol

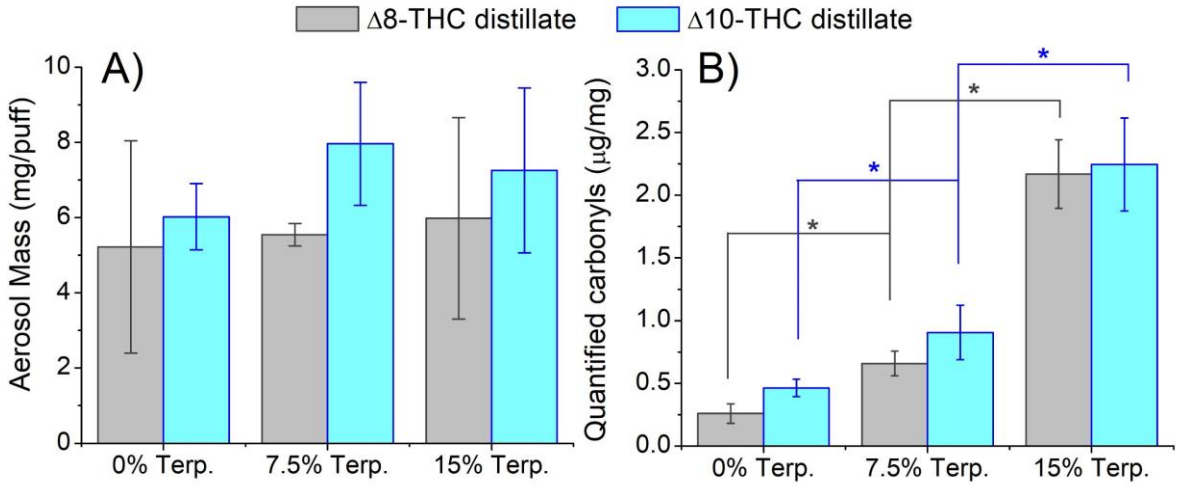


Figure 3. Aerosol mass (mg puff^{-1}) measurements for Δ8-THC (light grey) and Δ10-THC (light blue) vape oils with 0.0, 7.5, and 15.0% terpenes. Asterisks (*) denote statistically significant differences ($p < 0.05$) using one-way ANOVA. Average aerosol mass between the three terpene mix concentrations are not statistically different. Terpenes have no significant effect on aerosol mass production.

It was found that both Δ8-THC and Δ10-THC vape oils produce approximately 6 ± 1 mg/puff of aerosol, which is not significantly different within uncertainty of the measurement regardless of cannabinoid isomer or added terpene content (**Fig. 3A**). E-cigarette aerosol yields are reflective of both the vape material and the device construction and settings,[43, 46] however, we can qualitatively assess that the aerosol yield from distillate vaping using a CEC in this work is comparable to the yields produced from vaping cannabinoid e-liquids using pod type e-cigarettes (50 mg/mL in PG/VG) and extracts of cannabidiol.[47, 48] The uncertainties associated with triplicate gravimetric determinations of aerosol mass loss from the device were relatively large for distillate vaping (up to 50% individually), potentially due to the challenges associated with consistently aerosolizing the viscous distillates and their mixtures. It is possible that finer trends in aerosolization efficiency associated with added terpene content are obscured by the large

uncertainties. Unfortunately, to our knowledge, reports of aerosol mass yields in cannabinoid distillate vaping with added terpene content are not available in the literature for comparison.

Summed aerosol yields of the quantified carbonyls (**Fig. 3B**) had smaller standard deviation compared to the quantification of aerosol mass, likely due to the fact that the variations in aerosol mass are accounted for in the yield normalization (**Eqn. 1**). It was found that increasing terpene concentration in the distillate mixture significantly increased the yields of total carbonyls compared to each previous sample ($p < 0.05$, using one-way ANOVA). This trend was observed for both the Δ8-THC and Δ10-THC distillate samples. The 15% terpene sample showed the clearest increase in carbonyl production compared to both the 7.5% and 0% terpene samples.

The trends of increasing carbonyl yields with increasing terpene content (**Fig. 3**) appear to be driven primarily by the production of acetone due to its relatively high production yield (**Fig. 4A**). **Table S1** shows the tabulated data for carbonyl yields in each sample. In the 15% terpene

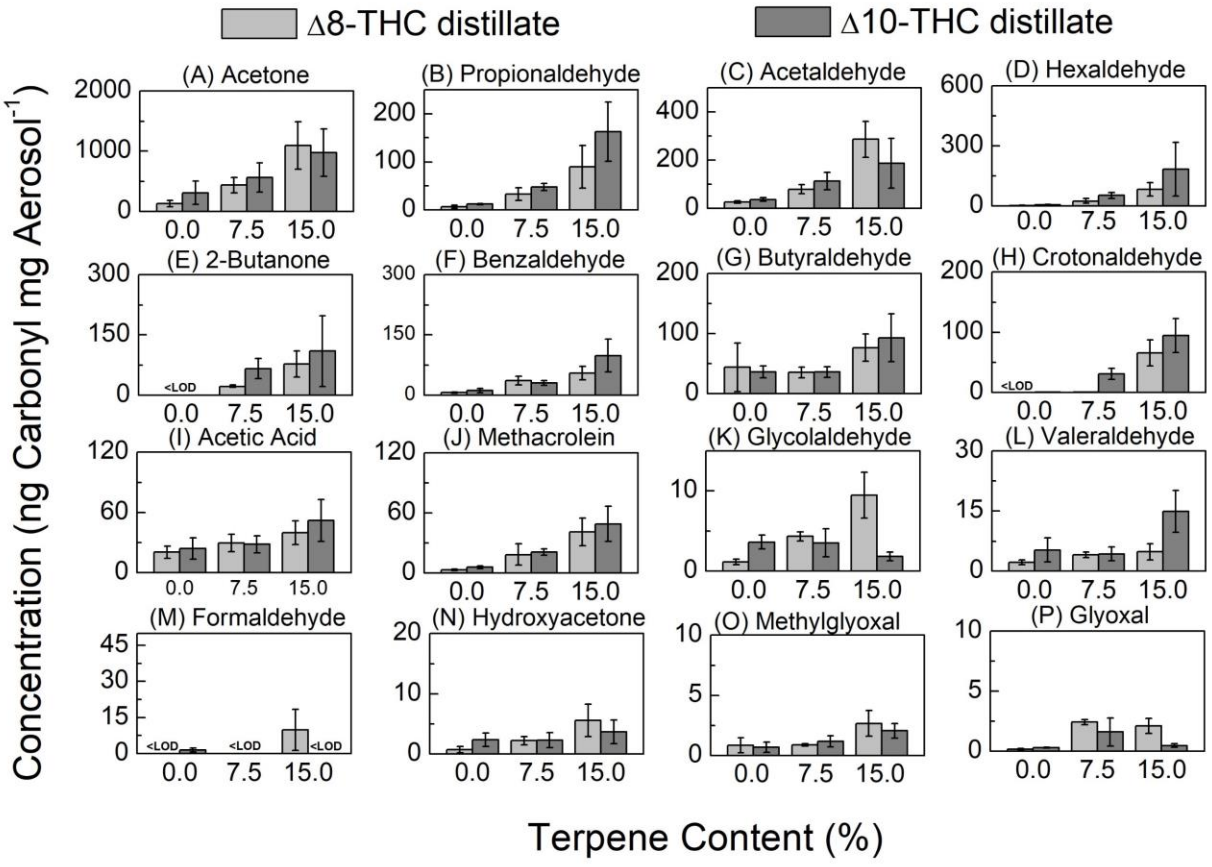


Figure 4. Concentrations of select carbonyls (ng mg aerosol^{-1} = µg mL aerosol^{-1} assuming density is 1 g/mL) that were quantified in Δ8-THC distillate samples (light grey) and Δ10-THC distillate samples (dark grey) at 0, 7.5, and 15% terpenes.

samples, acetone was observed with a yield of 1000 ng/mg aerosol, or 1 µg/mg. Assuming a density of approximately 1 g/mL for cannabis distillates (range 0.96-1.05 g/mL),[49] the concentration of acetone itself is approximately 1 mg/mL of the aerosol, similar in concentration to purposefully added ingredients in vape liquids.[50] Propionaldehyde (**Fig. 4B**), acetaldehyde (**Fig. 4C**), and hexaldehyde (**Fig. 4D**) were also observed as significant degradation products; their yields also increased with increasing terpene concentration. Because the pure distillate produced roughly 9-fold fewer carbonyls compared to the 15% terpene sample, this suggests that degradation of terpenes during the vaping process is an important source of carbonyls during CEC vaping.

Interestingly, formaldehyde, which is usually a major carbonyl product for nicotine-containing e-cigarettes that contain propylene glycol and glycerol,[42, 51, 52] is found in very low mass yields in cannabis vape distillates. The relatively high acetone yields and low formaldehyde yields in the vaped Δ8-THC and Δ10-THC aerosol are consistent with the findings of Li et al,[14] who studied Δ9-THC distillate with a third-generation e-cigarette device. It is possible that these results reflect the different chemical characteristics of vaping lower-viscosity e-liquid compared to higher-viscosity distillate, or differences in coil types of the nicotine devices and the CEC devices. However, sampling differences cannot be ruled out as a source of the discrepancy, as the DNPH-impregnated silica cartridges have not been validated for oily aerosol.

The data presented here shows that methacrolein yields increase with higher terpene concentration during CEC vaping. This differs from the report of lower HPHC emissions (specifically methacrolein, methyl vinyl ketone, and isoprene) with higher mass percentages of β-myrcene during CEC vaping of Δ9-THC vape oil.[37] The discrepancy could be due to the fact that this study examined a terpene mixture instead of a single terpene; thus, the chemical source of methacrolein in this work might be different compared to that from Meehan-Atrash et al. [37] It is also possible that the normalization with aerosol mass done in our work may reveal yield trends that are absent when the data are not normalized, due to the high uncertainties related to aerosolization from viscous THC distillates (**Fig. 3A**). Unfortunately, direct comparison of other products is not possible between this study and those in the literature.

When comparing Δ10-THC vape oil and Δ8-THC vape oil, there is no significant differences in carbonyl formations, either pure or with varying terpene mix concentrations. Glycolaldehyde (**Fig. 4K**) and valeraldehyde (**Fig. 4L**) do show variations between the Δ8- and

Δ10-THC samples at 15% terpenes; however, they were observed with low yields and thus are more susceptible to quantification inconsistencies. Generally, the trends of speciated carbonyls support the overall trend in quantified carbonyls, which increases with increasing terpene mix percentage.

3.3 Oxidation products of cannabinoids and terpenes

Extracted ion chromatograms of major carbonyls observed in this work (**Fig. 5**) visually demonstrate that yields of carbonyls in the distillate vape aerosol increase substantially with the addition of terpene oil, regardless of whether those carbonyls were quantified with standards or observed semi-quantitatively (i.e., the peak areas correlate to concentration, but the data were not converted to concentration values). Most of the unquantified carbonyls are higher-molecular-weight or complex carbonyls, with the intact or nearly intact carbon backbone of the monoterpenes (C_9-C_{10}); the magnitude of their observed chromatographic peak areas was substantial. For example, the most abundant quantified carbonyl, acetone (**Fig. 4A**), has a chromatographic peak area that is up to 20 times smaller compared to some unquantified carbonyls (**Fig 5**). It is understood that the range of electrospray ionization sensitivities for carbonyl-DNPH hydrazones generally vary less than an order of magnitude.[53] Thus, the unquantified carbonyls may have yields exceeding that of acetone, suggesting that the quantification of targeted carbonyls in complex samples such as cannabis vape oils and liquids

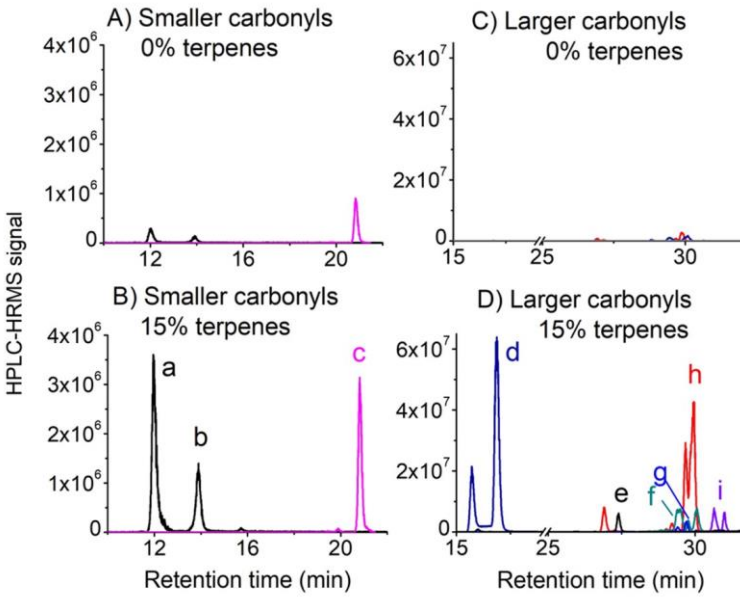


Figure 5. Extracted ion chromatograms for representative smaller (< C_6) and larger (C_9-C_{10}) carbonyl products, detected as their DNPH hydrazone negative ion (m/z = M + $C_6H_6N_4O_4$ – H_2O – H), from Δ8-THC distillate with no terpenes added (A - smaller, C - larger) and for Δ8-THC distillate + 15% terpenes by mass (B - smaller, D – larger). Chemical key, with assigned identities in parenthesis: a) C_3H_6O (acetone); b) C_3H_6O (propionaldehyde); c) C_5H_8O (3-methylbut-2-enal); d) $C_{10}H_{12}O_2$ (2 isomers); e) $C_9H_{16}O_3$; f) $C_{10}H_{16}O$ (3 isomers); g) $C_9H_{14}O$ (2 isomers); h) $C_9H_{16}O$ (3 isomers); i) $C_{10}H_{16}O$ (2 isomers).

only tells a small fraction of the full story. Both the raw and processed carbonyl data collectively suggest that the added terpenes are being chemically transformed into carbonyls, and that they are responsible for the majority of the carbonyl yields.

In contrast, observations of the of cannabinoid oxidation products show that the degradation of the parent cannabinoid either decreased slightly, or remained the same, with increasing terpene content (**Fig. 6**). While minor changes in the precursor THC content is challenging to quantify within uncertainty due to the fact that distillate contains nearly pure THC, we can monitor the peak areas of specific oxidation products of THC more precisely. **Figure 6** shows that $C_{21}H_{32}O_3$ and $C_{21}H_{30}O_3$, two select oxidation products of Δ8-THC ($C_{21}H_{30}O_2$) with high signal, had similar or smaller chromatographic peak areas in the samples with 0% and 15% added terpene content.

As these THC oxidation products were observed at the accurate mass of their deprotonated ions, their molecular formulas are accurately known and chemical structures (**Fig. 6** insert) may be proposed assuming established chemical mechanisms. These cannabinoid-derived ions have the exact molecular formula of Δ8-THC, but with the addition of O ($C_{21}H_{30}O_3$, signifying the addition of a carbonyl) or H_2O ($C_{21}H_{32}O_3$, signifying the addition of a hydroxyl), they most likely result from oxidation at the C=C double bond in the ring structure of Δ8-THC. Multiple isomers exist for each oxidation product, suggesting that the location of the added carbonyl or hydroxyl moieties can vary along the structure of Δ8-THC, which is reasonable given that Δ8-THC has two allylic H-abstraction sites adjacent to the endocyclic double bond, one tertiary benzyl H-abstraction site, two alkenyl radical addition sites

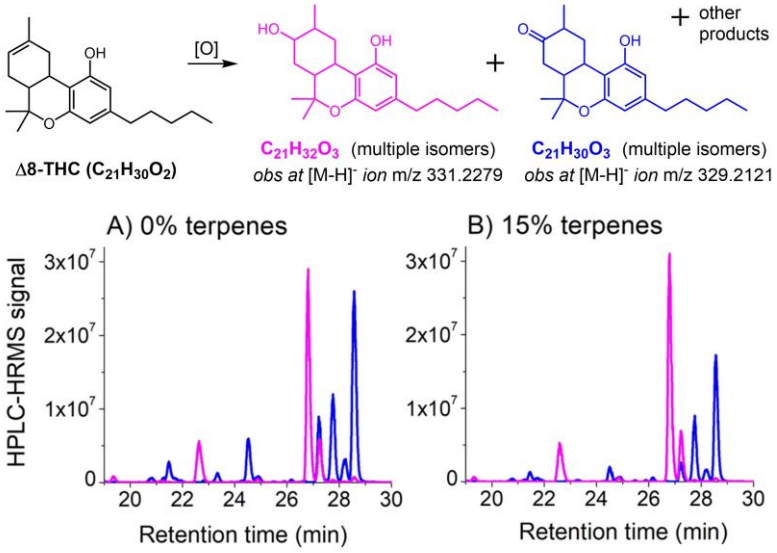
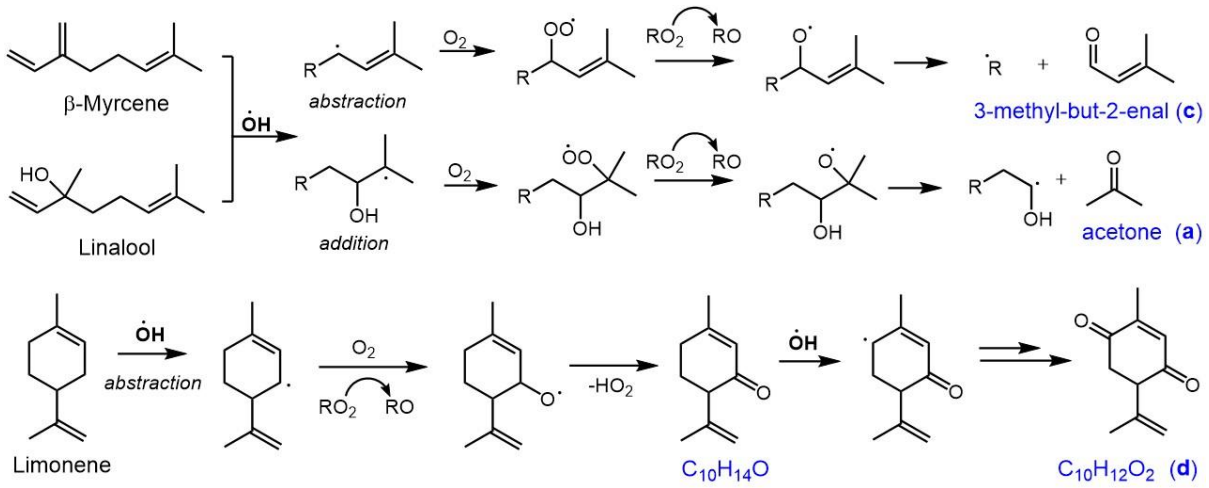


Figure 6. Extracted ion chromatograms for two representative oxidation products from Δ8-THC, $C_{21}H_{32}O_3$ (magenta) and $C_{21}H_{30}O_4$ (blue), from the following vaped aerosol samples: (A) Δ8-THC distillate (no terpenes added) and (B) Δ8-THC distillate + 15.0% terpenes by mass. One proposed chemical structure for each of the cannabinoid oxidation products are shown, although others may exist.



Scheme 1. Proposed reaction mechanism for the production of carbonyl compounds associated with the 3 largest peaks products shown in Figure 5 (a, c, d). Proposed chemical mechanisms are based on textbook radical-initiated chemistry occurring in air.

(one on each carbon of the alkene), two ring hydroxylation sites, and multiple chain oxidation sites.

Given the high chemical lability of terpenes[54] and the increasing carbonyl yields (specifically those with a terpenoid backbone) with increasing terpene content in the vape oil, it can be inferred that the terpenes in vape oil suffer substantial degradation during cannabis vaping; this was also observed by Meehan-Atrash et al.[32, 37] As some cannabinoid oxidation products decreased with terpene content, this may suggest that terpenes are shielding the cannabinoid from degradation, again in agreement with the works of Meehan-Atrash et al. With prior evidence that hydroxyl radicals (OH) are formed during the heated coil vaping process,[28-30, 55] established mechanisms of radical-initiated chemical reactions in air[56-58] can be used to rationalize the formation of major carbonyl products from some abundant terpenoids in the terpene oil mixture: limonene, linalool, and β-myrcene (**Fig. 2**). **Scheme 1** shows proposed reaction mechanisms for the three most abundant carbonyl products according to chromatographic peak areas observed in this work (**Fig. 5**): acetone, 3-methyl-but-2-enal, and the terpene oxidation product $C_{10}H_{12}O_2$. Note that there are likely more than one reaction source for these products, and multiple isomers exist for $C_{10}H_{12}O_2$; thus, the reactions in **Scheme 1** should be regarded as demonstrative only.

β-myrcene and linalool have similar chemical backbones, with linalool having one less degree of unsaturation and one more H_2O unit compared to β-myrcene at carbon 3. H abstraction at carbon 5 and OH addition at carbon 6 form the two most thermodynamically favorable alkyl

radicals (an allylic radical and a tertiary radical, respectively).[59] Further alkylperoxy (RO_2) chemistry,[60] reducing to the alkoxy radical (RO), may fragment[61] to acetone and 3-methyl-but-2-enal (**Scheme 1**, top). Acetone has also been quantified as a major OH oxidation product of myrcene previously, with yields of approximately 36%.[62] The product $C_{10}H_{12}O_2$ can be rationalized from limonene, β-myrcene, or potentially other monoterpenes (shown in **Scheme 1** for only limonene), via allylic H-abstraction and the aforementioned chemistry. The secondary alkoxy radical that is produced may lose H upon collision with oxygen ($-HO_2$) or other abundant species, forming the carbonyl – this is an established fate of secondary alkoxy radicals in air.[61] Oxidation at both allylic sites of limonene affords $C_{10}H_{12}O_2$. Not all coproducts of terpene oxidation, including the aforementioned formaldehyde,[62] are observed in high yields in this work. This could signify a deviation of the vaping chemistry compared to more dilute chemistry in air, but again, could also represent a challenge of detecting all carbonyl products when viscous aerosol is produced from thick and dense distillates.

4. Conclusions It was found that commercial sources of Δ8-THC and Δ10-THC had varying purity levels for the major cannabinoid, which may be different than the advertised information and may not necessarily be used for modeling, research, or risk assessment in absence of chemical characterization. The terpene oil composition analysis matched the top three advertised components, although the specific composition again required chemical analysis. The addition of a commercial terpene oil mixture to distillates of Δ8-THC and Δ10-THC substantially increased the formation of harmful or potentially harmful carbonyls but no discernable (within the uncertainty of this work) effects on aerosolization efficiency of the distillate mixture when vaped using a commercial CEC device. The data suggest that the degradation processes of terpenoid compounds in the mixture were chemically responsible for the majority of carbonyls in the aerosol. The most abundant quantified carbonyl was acetone, but substantial chromatographic peaks for terpene-derived oxidation products were observed, which were not quantified but rivaled or exceeded the observed peak of acetone. The major carbonyl products can be rationalized from the known air oxidation chemistry of the major terpene components with OH radicals. The data suggests that oxidation of the cannabinoid occurred, but did not increase due to the addition of terpenes and may decrease for some products. This work may be used to support an increasing body of knowledge on how cannabis vaping impacts health risks and indoor air quality. Overall,

the popular practice of adding high levels of terpene oils to cannabinoid distillates may have adverse effects on HPHC formation, which may increase toxicity to the users and those in the immediate vicinity compared to vaping distillate alone.

5. Author Contributions EYC and TBN designed the experiment; EYC developed the sampling protocols; EYC, LNT, and HCH developed the data analysis protocols; EYC, LNT, and HCH collected and analyzed the data; SCTN and TBN secured the funding; EYC, LNT, and TBN wrote the manuscript; all authors reviewed the manuscript and made intellectual contributions to the project.

6. Conflicts of Interest The authors declare no conflict of interests.

7. Data Availability The data supporting this article have been included as part of the Supplementary Information.

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Supporting Information

Effects of terpenes on the emissions of aerosols and carbonyls from vaping delta-8- and delta-10- tetrahydrocannabinol (THC)

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Table S1: Aerosol mass yields (mg/puff) and speciated carbonyl yields (µg/mg aerosol) that were quantified in this work. Uncertainties are reported as one standard deviation of triplicate sample analyses.

Sample	Aerosol Mass (mg/puff)	Form-aldehyde	Acetald-ehyde	Acetone	Acrolein	Propion-aldehyde	Glycol-aldehyde
Δ8-THC	5.2 ± 2.8	< LOD	0.026 ± 0.005	0.129 ± 0.053	< LOD	0.007 ± 0.003	0.0012 ± 0.0003
Δ8-THC + 7.5% terpenes	5.5 ± 0.3	< LOD	0.079 ± 0.019	0.435 ± 0.131	< LOD	0.033 ± 0.013	0.0043 ± 0.0006
Δ8-THC + 15% terpenes	6.0 ± 2.7	0.009 ± 0.008	0.286 ± 0.075	1.093 ± 0.394	< LOD	0.090 ± 0.045	0.0095 ± 0.0028
Δ10-THC	6.0 ± 0.9	0.0015 ± 0.001)	0.036 ± 0.007	0.310 ± 0.195	0.378 ± 0.270	0.012 ± 0.001	0.0036 ± 0.0009
Δ10-THC + 7.5% terpenes	8.0 ± 1.6	< LOD	0.112 ± 0.036	0.562 ± 0.244	< LOD	0.048 ± 0.007	0.0036 ± 0.0017
Δ10-THC + 15% terpenes	7.3 ± 2.9	< LOD	0.186 ± 0.103	0.975 ± 0.393	< LOD	0.163 ± 0.061	0.0018 ± 0.0006

Sample	Hydroxy-acetone	Glyoxal	Methyl-glyoxal	Croton-aldehyde	Meth-acrolein	Butyr-aldehyde	Benz-aldehyde
Δ8-THC	0.001 ± 0.001	0.0002 ± 0.0001	0.0008 ± 0.0006	0.0000 ± 0.0000	0.0032 ± 0.0007	0.0440 ± 0.0401	0.0062 ± 0.0019
Δ8-THC + 7.5% terpenes	0.002 ± 0.001	0.0024 ± 0.0002	0.0009 ± 0.0001	0.0006 ± 0.0002	0.0183 ± 0.0106	0.0353 ± 0.0091	0.0358 ± 0.0108
Δ8-THC + 15% terpenes	0.006 ± 0.003	0.0021 ± 0.0006	0.0027 ± 0.0011	0.0655 ± 0.0218	0.0411 ± 0.0139	0.0767 ± 0.0230	0.0550 ± 0.0167
Δ10-THC	0.002 ± 0.001	0.0003 ± 0.0000	0.0007 ± 0.0004	0.0005 ± 0.0002	0.0057 ± 0.0012	0.0364 ± 0.0098	0.0111 ± 0.0055
Δ10-THC + 7.5% terpenes	0.002 ± 0.001	0.0016 ± 0.0012	0.0012 ± 0.0004	0.0306 ± 0.0092	0.0209 ± 0.0030	0.0361 ± 0.0090	0.0299 ± 0.0060
Δ10-THC + 15% terpenes	0.004 ± 0.002	0.0005 ± 0.0001	0.0020 ± 0.0006	0.0947 ± 0.0284	0.0491 ± 0.0177	0.0929 ± 0.0398	0.0983 ± 0.0409

Table S2 (continued)

Sample	Valer-aldehyde	Hexaldehyde	Acetic Acid
Δ8-THC	0.0022 ± 0.0005	0.0023 ± 0.0007	0.0204 ± 0.0061
Δ8-THC + 7.5% terpenes	0.0041 ± 0.0007	0.0251 ± 0.0116	0.0295 ± 0.0089
Δ8-THC + 15% terpenes	0.0048 ± 0.0020	0.0831 ± 0.0337	0.0399 ± 0.0120
Δ10-THC	0.0053 ± 0.0030	0.0062 ± 0.0016	0.0239 ± 0.0105
Δ10-THC + 7.5% terpenes	0.0043 ± 0.0017	0.0522 ± 0.0152	0.0283 ± 0.0085
Δ10-THC + 15% terpenes	0.0149 ± 0.0052	0.1836 ± 0.1343	0.0520 ± 0.0210