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Technical Note: Pine Rosin Identified as a Toxic Cannabis Extract Adulterant

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Abstract

Pine rosin (colophony) has been identified as a potentially new adulterant in cannabis oil. Its inhalation toxicity poses a significant health concern to users. For example, pine rosin fumes are released during soldering, and have been cited as a causative agent of occupational asthma. Symptoms also include desquamation of bronchial epithelium, which has also been observed in e-cigarette or vaping product used-associated lung injury (EVALI) patients. The sample analyzed herein was acquired from a cannabis industry source, also contains medium chain triglycerides and oleamide, the latter of which is a hypnotic that is commonly found in the synthetic marijuana product Spice, or K2. A combination of proton nuclear magnetic resonance (^{1}H NMR) and high pressure liquid chromatography-electrospray ionization mass spectrometry (HPLC-ESIMS) was used to unambiguously identify major pine rosin ingredients such as abietic and other resin acids. Comparison to commercial samples of pure pine rosin confirmed the assignment.

Keywords

Cannabis extract; BHO; marijuana; EVALI; rosin; pine rosin; adulterant; cutting agent

Introduction

Since the legalization of medical marijuana in California in 1996, and the legalization of recreational marijuana in Colorado in 2012, 33 states and the District of Colombia have medical cannabis programs, and 10 states and the District of Colombia have fully legalized recreational use as of 2020.[1] Canada first enacted medical marijuana laws in 2001, and now has recreational cannabis as of 2018.[2] With the passage of more lax laws, cannabis extracts (CEs) have surged in popularity as alternative products to cannabis flower, with expenditures on CEs in the legal Washington state cannabis market increasing 145 %

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CREDIT author statement

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between 2014 and 2016.[3] CEs are consumed by inhalation using modified e-cigarettes or via dabbing[4], and increased usage of these among teens and young adults[5] has led to concerns of safety, as up to 11 % of high schooler students[6] report lifetime use of a cannabis vaporizer.

CEs may be consumed via inhalation by three main methods/devices: cartridge vaporizers (CVs), top-loading vaporizers (TLVs), and dabbing.[4] In dabbing, a small amount of CE is placed on a hot surface (i.e. a "nail," which may be heated with a blow torch or electrically) that is connected to a water pipe.[4, 7] A TLV is an electronic vaporizer device that consists of a battery-powered resistive heating coil in an atomizer, upon which a user manually places small amounts of CE.[4] Disposable CV devices closely mimic nicotine e-cigarettes, and have surged in popularity given their ease of use and discretion, with sales of these increasing more than 10-fold to $224 million in Colorado as of 2018.[8]

The cannabis concentrate hashish, commonly consumed in Europe from illicit manufacturers in North Africa, has an extensive history of containing adulterants.[9] A recent analysis of hashish in Madrid found that 18 % suffers from contamination with glucose, sucrose, and/or abietic acid (a principal component of pine rosin).[10] Pine rosin has also been identified as a hashish adulterant in Italy,[11] Israel, and the Czeck Republic.[12]

CEs available in North America are generally manufactured via solvent extraction (most commonly with butane, though propane or supercritical CO_2 have widespread usage) followed by several refinement steps. Butane hash oil (BHO), propane hash oil (PHO) and CO_2 oil may all adopt one of several names depending on consistency: *shatter*, *wax*, *crumble*, *budder*, or *pull-nsnap*.[7] Recently, applied heat and pressure has been used to press cannabis oils from flower to make a product known as *rosin*.[13] Despite the similarity in naming, cannabis rosin and pine rosin share few chemical similarities.[13]

Cases of adulteration in North American cannabis products have only recently come into view. The synthetic cannabinoid 5-MDMB-PINACA and the antitussive dextromethorphan have been identified in certain commercially available cannabidiol e-liquids for CV devices.[14] Online reports on Reddit.com and cannabis websites have become grounds where users have aired complaints of BHO adulterated with pine rosin, and have cited specific brands and products as bad actors.[15–17] The timing of these forum posts about pine rosin being used as an adulterant for CEs, or as counterfeit BHO, coincide with the EVALI outbreak. Additionally, several recent patents mention *methyl ester of rosin*, a pine rosin derivative, as a potential additive to cannabis vaporizers.[18–20]

CEs added to CV devices often require fluidizing agents to ensure better wicking efficiency in the atomizer of a vape pen, given the high viscosity of cannabis extracts.[4] Substances such as terpenes, medium chain triglyceride (MCT) oil, and phytol, among others are commonly used.[21] One CE additive to CV devices, vitamin E acetate (VEA), has been linked with the recent outbreak of e-cigarette, or vaping, product use associated lung injury (EVALI).[22] It's use as a thickening agent has been suggested, however, the markedly lower viscosity of VEA relative to Δ^9-tetrahydrocannabinol (THC), indicates that the former is used to dilute CEs, and that a different additive is the thickening agent, which is

introduced to give the appearance of unadulterated CE. Herein is the first report of an adulterant containing pine rosin (a.k.a. rosin colophony or pine resin) for cannabis CV devices. The adulterant was acquired from a formulations consultant that works in the cannabis vaporizer formulations space, which itself acquired the adulterant from cannabis CV device manufacturer.

Materials and Methods

Two adulterants were donated by Vialpando LLC. Initial analysis by nuclear magnetic resonance spectroscopy (NMR) identified one of them to be pure VEA, while the other (Figure 1, dubbed cannabis extra adulterant [CEA]) required further analysis for identification. The CEA was initially assayed by GC-MS, which first suggested the presence of substituted abietanes and pimaranes. Analysis of the NMR spectrum showed peaks in the alkenyl region that are known to be characteristic of the resin acids in question,[23] and the characteristic glycolic methylene peaks from a triglyceride (Figure S1). 2D NMR techniques COSY and NOESY aided the confirmation of the identity of different isomeric resin acids, as well as the identification of communic acid, which was aided by semi-preparative HPLC. An HPLC-ESIMS chromatogram of CEA provided confirmation of the abietane and pimarane molecules and oleamide (Figure S2). Oleamide is not directly visible in the NMR spectrum of CEA, but the amide N-H protons are visible in the semi-preparative HPLC fraction that contains it when this is dissolved in DMSO-d_6 (Cambridge Isotope Laboratories), which was spiked with a pure standard of oleamide (TCI America) to confirmed its presence (Figure S3). Commercially available medium chain triglyceride (MCT) oil (Nature's Way) was spiked in a CEA NMR sample (Figure S4). An approximate %mass of each identified component was determined by quantitative NMR (Q-NMR).[24] See the supplementary appendix for further experimental details.

Results and Discussion

The analytical methods used discovered that the unknown CEA contains resin acids consistent with pine rosin (68 %), MCT oil (15 %), and small amounts of oleamide (Table 1). An overlay of a commercially available sample of gum rosin (Sigma Aldrich) and CEA demonstrates the similarity of these two substances (Figure 2), with the major visible difference being the presence of the triglyceride peaks from MCT oil in the CEA. Rosin, a solid at room temperature, appears to have been amended with MCT oil to thin its consistency to allow extrusion from a syringe, making its final appearance very similar to pure THC or clarified cannabis extract. For the purposes of this study, only approximate quantification was necessary to determine the composition of the sample. Given that this adulterant is destined for use in cannabis e-cigarettes, it is unknown how the final matrix will affect identification and quantification of resin acids in a black market sample. The analytical methods presented herein may serve as a guide for identifying resin acids in a cannabis sample, but a more comprehensive quantitative method will need to be developed for cannabis extracts adulterated with pine rosin and/or oleamide.

Rosin is a known respiratory tract irritant and a significant contributor to occupational asthma due to its use in soldering.[25] Occupational exposure to pine rosin vapor from

solder flux at levels of 50 μg/m^3, the 8-h Time Weighted Average (TWA) exposure limit, has not been known to produce sever acute lung injuries.[25] However, CEA added to CE at a level of just 1 % will produce nearly 0.6 g/m^3 of pine rosin in the aerosol from a cannabis vaporizer pen with each puff, or ~3,500 times the 15-min TWA exposure limit.[25] In vivo exposure of abietic acid to rat lungs produced desquamation of bronchial epithelium,[26] which has also been reported in EVALI cases.[27] We are unaware of efforts to date to test for pine rosin compounds in samples from patients with vaping-induced lung injuries. Oleamide appears to have been added to increase the psychoactivity of resulting adulterated CE, as this compound is a cannabinoid receptor agonist and sleep-inducing agent.[28] Interestingly, oleamide is a common additive to synthetic cannabinoid “Spice” mixtures.[29] It is unknown what, if any, are the health effects of inhaling oleamide. Oleamide is also mentioned as a potential additive to vaping formulations in a patent registered to a cannabis vaporizer formulations company.[30]

Conclusion

The use of pine rosin as an adulterant in cannabis oil has not been previously reported in the scientific literature. It is available through online vendors, typically used as an ingredient in industrial products such as varnishes, adhesives, soldering fluxes and sealing wax. It has significant inhalation toxicity. To date, there are no reports of testing for this substance in cannabis oil samples from patients with lung injury. Due to the significant toxicity and prevalence based on social media posts, regulators and laboratory personnel should be aware of its use in adulterated cannabis oil.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Highlights

- Pine rosin was identified as component in a sample of cannabis extract adulterant.
- The inhalation toxicology of pine rosin is well-studied.
- Current analytical methods may misidentify pine rosin as an additive.
- The prevalence of this additive is unknown.

Figure 1:
Cannabis extract thickener provided in a glass syringe.

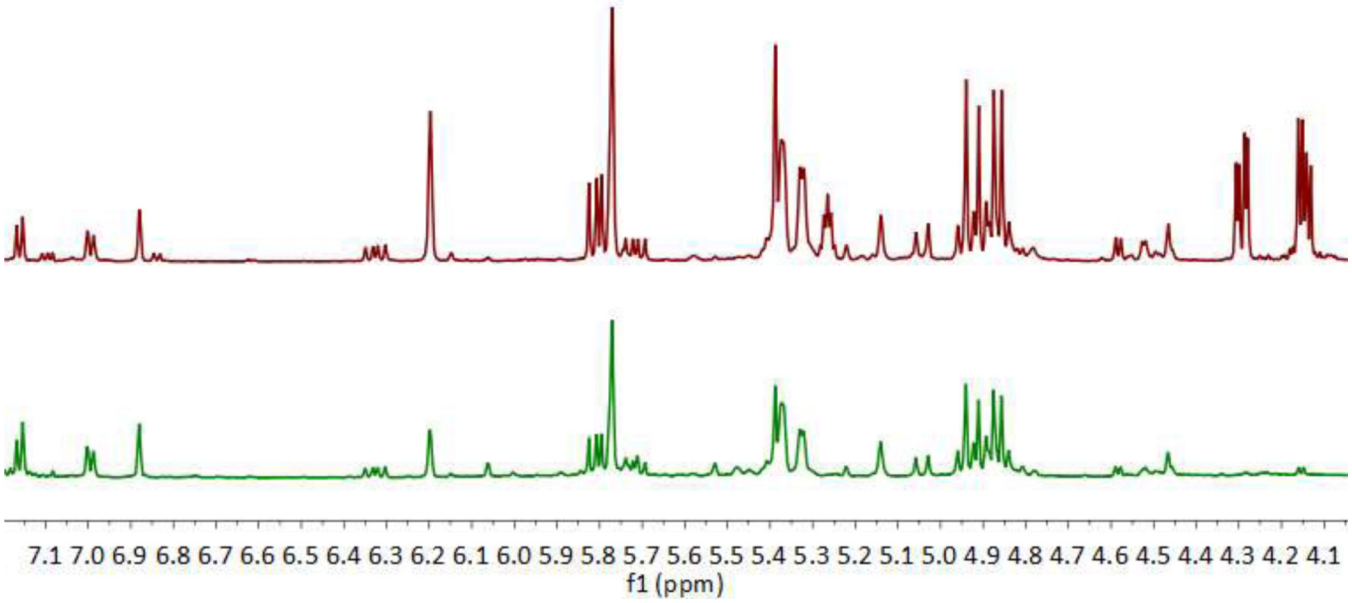

Figure 2:
Overlaid ^{1}H NMR spectra of CEA (top, maroon) and commercially-available gum rosin (bottom, green) from Sigma Aldrich (CAS no. 8050-09-7).

Table 1:

Components identified in CEA by nuclear magnetic resonance (NMR) spectroscopy and HPLC-ESIMS, and approximate %masses in the sample were determined by Q-NMR.

Common Name	CAS Number	RT in LC/MS (min.)	NMR Shift (ppm)	Mass Accuracy (ppm)	% in Sample
Dehydroabietic acid	1740-19-8	16.5	6.88	0.03	3
Communic acid	2761-77-5	21.8	6.32	0.03	4
Pimarol	1686-59-5	23.9	NA	0.52	NA
Pimaric acid	127-27-5	23.9	5.71	1.25	3.2
Sandaracopimaric acid	471-74-9	23.9	5.22	1.25	1.5
Palustric acid	1945-53-5	23.9	5.39	1.25	14
Abietic acid	514-10-3	25.1	5.77	1.25	17
Oleamide	301-02-0	25.1	6.65-7.19	0.64	NA
Neoabietic acid	471-77-2	25.1	6.2	1.25	12
Isopimaric acid	5835-26-7	25.1	5.81	1.25	13
Sandaracopimarinal	3855-14-9	30.3	5.22	0	NA
MCT oil	438544-49-1	NA	4.3	NA	15