SPEX CertiPrep Technical Note

Terpenes: A Building Block of Cannabis

Many chemical compounds can be responsible for scent and flavor in botanicals. These chemicals are transformed into neural impulses and travel along the various facial and major nerves to centers in the brain which then interpret the impulses and create taste perception. These perceptions of taste along with texture, smell and the sensation associated with temperature, pain and pressure (chemesthesis) combine to create the impressions of flavor.

The most common functional group in flavors is carbonyls such as esters, aldehydes, ketones, etc. Other groups which produce flavors are carbohydrates, acids, salts, proteins, and terpenes. Terpenes are the common term for a large group of compounds that contribute to flavor and smell of botanical products. Isoprene or 2-methyl-1,3-butadiene (see Figure 1) and its polymers is the main base of natural rubber and the structural base for terpenes and terpenoids, even though isoprene is not part of the reactions which produce terpenes.

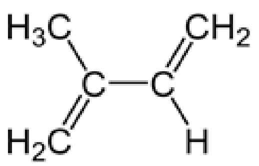

Figure 1. Isoprene Unit

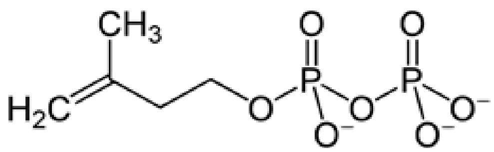

Figure 2. Isopentenyl pyrophosphate

The actual mechanisms for the synthesis of terpenes are derived from units of isopentenyl pyrophosphate (see Figure 2). The two metabolic pathways to synthesize terpenes are the mevalonic acid pathway (MVA) or the MEP/DOXP pathway. The pathways are usually exclusive to the type or organism with green algae producing terpenes via the MEP pathway; humans & fungi via the MVA pathway and plants producing terpenes from both pathways(1).

In biological processes, there are essential and nonessential terpenes. Essential terpenes are usually terpenes C15 and higher which are required by the plant, insect or algae to support life and growth. The lower weight terpenes (some C15 and below) are nonessential terpenes which assist in other biological processes or contribute to the defense and functioning of the organism but are not critical to survival. Removal of an essential terpene will damage and ultimately kill the organism whereas the removal of a nonessential terpene will not.

Terpenes are classified based on the number of isoprene units they contain. Starting with hemiterpenes that have five carbons; monoterpenes have ten carbons, sesquiterpenes have 15 carbons, etc. (see Table 1). The classification is based on the C5 rule which is the isoprene synthesis route that organisms employ for the production of terpenes.

Table 1. Terpene Groups & Examples

Terpene Group	# Isoprene Units	# Carbons	Terpene Example
Hemiterpene	1	5	Isoprene
Monoterpene	2	10	Limonene
Sesquiterpene	3	15	Humulene
Diterpenes	4	20	Taxadiene
Sesterterpenes	5	25	Ophiobolin A
Triterpenes	6	30	Squalene
Sesquarterpenes	7	35	Tetraprenylcurcumene
Tetraterpenes	8	40	Lycopene

Monoterpenes are lower molecular weight terpenes and can volatilize quickly during processing involving heat and decarboxylation. Sesquiterpenes are larger molecular weight terpenes and volatilize at higher temperatures and remain after main processing steps.

The diversity of terpenes and terpenoids is recognized by the range of scents and flavors they produce from the pine scent of Pinene (the most widely encountered terpene in nature) to the lavender and mint notes associated with Linalool. The flavor and aroma of hops are critical to beer, especially Myrcene, beta-Pinene, beta-Caryophyllene, and alpha-Humulene.

Table 2. Terpene & Terpenoid Groups Found in Cannabis

Terpene Group	Subgroup	MW	BP	Formula	Aroma
Myrcene	Monoterpene	136.2	168 ºC	$C_{10}H_{16}$	Clove-like, musky, earthy
Caryophyllene	Sesquiterpene	204.4	264 ºC	$C_{15}H_{24}$	Citrus
Humulene	Sesquiterpene	204.4	107 ºC	$C_{15}H_{24}$	Hoppy
Pinene	Monoterpene	136.2	156 ºC	$C_{10}H_{16}$	Pine
Terpinolene	Monoterpene	136.2	187 ºC	$C_{10}H_{16}$	Pine with herbal and floral notes
Limonene	Monoterpene	136.2	176 ºC	$C_{10}H_{16}$	Lemon, citrus
Carene	Monoterpene	136.2	172 ºC	$C_{10}H_{16}$	Pungent, earthy, sweet
Phellandrene	Monoterpene	136.2	172 ºC	$C_{10}H_{16}$	Citrus and mint
Linalool	Monoterpene Alcohol	154.2	199 ºC	$C_{10}H_{18}O$	Lavender and floral
Camphene	Monoterpene Alcohol	136.2	159 ºC	$C_{10}H_{16}$	Damp mine, pine notes
Terpineol	Monoterpene Alcohol	154.3	271 ºC	$C_{10}H_{18}O$	Floral

Many applications for the use of cannabinoids for health benefits have been published over the past decade. There have also been numerous publications of the health effects of various terpenes and terpenoids which suggest terpenes are often anti-inflammatories and anti-oxidants (2,3). The most common terpenes found in cannabis variants are myrcene, caryophyllene and many others (see Table 2). Current research is investigating the possible synergistic effects of cannabinoids and terpenes. Research has suggested the presence of terpenes in cannabis products can alter the pharmacokinetics of cannabinoids (4,5).

Sample Processing & Analysis for Terpenes

Cannabis compounds can be degraded by high temperatures and oxidation. In ambient temperature grinding processes, heat and energy are generated which can raise the temperature f materials to almost 100 ºC and cause up to a 60% loss of critical aromatic components (6,7). Reduction of temperature during processing can prohibit the breakdown of volatile compounds. In one study it was found that cryogenic conditions showed better retention of monoterpenes (myrcene, limonene and pinene) than grinding at ambient temperature (8,9).

The extraction and analysis of terpenes in the analytical laboratory from the various cannabis product matrices can be challenging especially in regards to sample preparation, clean-up and matrix effects. In many cases, related terpenes have the same or similar masses (Table 2) making them difficult to identify in complex mixtures where many isomers or similar compounds are present. The most common method of analysis for terpenes is gas chromatography (GC) with either a flame ionization detector (FID) or mass spectrometer (MS).

Table 3. Example of SPEX CertiPrep CAN-TERP-MIX GC/MS Instrument Conditions

Instrument Conditions	
Column	DB-624 UI Column
Size	30 m x 0.25 mm diameter
Program	50 C x 3 minute hold; 15 C/min ramp to 240; hold 20 minutes
Injection Volume	1 µL

Terpene analysis has always been an important component of many research areas including atmospheric chemistry, agricultural science, biochemistry, and environmental science to name a few. In industries dependent upon flavor and fragrance products, terpene profiles are part of their routine analytical testing procedures. The cannabis industry is just the newest industry to investigate the role of terpenes for flavor, fragrance and health benefits. As the industry continues to engineer cannabis strains to enhance specific chemical profiles, the importance of terpenes will increase.

For an in-depth look at terpenes, please read “Beyond Potency: The Importance of Terpenes” (10) in the June, 2019 issue of Cannabis Science and Technology Magazine.

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