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Time to Regulate Hazardous Flavouring Additives in Reintroduced "Absinthe-Green Fairy"

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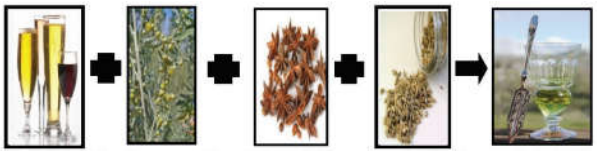
Abstract

"Absinthe" a strong aromatic green coloured alcoholic beverage with addictive, psychotropic and hallucinogenic properties has been the most popular and intriguing intoxicant since 19th century. Owing to its apparent illusive perception it was named "la fe'e verte" a French word means "the green fairy". It was condemned for inducing insane and criminal act and was also stigmatised as madness in a bottle. Later, owing to detection of psychedelic ingredient 'thujone', the absinthe remained banned for 95 years; however, its fame ride over the suppleness in laws and in 2007, it was reintroduced with varying concentration of thujone laced with harmful flavouring additives. The avaricious manufactures have been lucratively selling absinthes without printing its chemical composition on the bottle labels by taking advantage of loopholes in govt. policies. The government agencies remain focused on lowering the concentration of thujone in "green fairy" than publishing the harmful effects of its flavouring additives. To unequivocally establish a technique for the detection of harmful flavouring additives in absinthe remained a scientific challenge for decades. Henceforth, we attempted to analyse samples of popular foreign liquor brand "Paranasse Absinth" by GC-MS technique. Our research outcome led to successful chemical profiling of absinthe by detection of multiple flavouring additives viz. maltose, sucrose, anethole and methyl ethyl ketone. Amongst the detected additives, anethole is toxic, irritant, estrogenic and cytotoxic; methyl ethyl ketone is irritant, allergic, causes dizziness, cancer hazard and reproductive hazard, effect respiratory tract and CNS. Moreover, these two additives can also act as chemical precursors of Narcotic Drug and Psychotropic Substances (NDPS). Hence, through this research an effort is made to secure public health and to alert the private/govt. agencies regarding these health/immunity hazardous alcoholic beverage with high alcohol content and flavouring additives especially in COVID-19 pandemic. Our research outcome will attribute a legal check in the uncontrolled trade of potentially unsafe herbal beverages such as absinthe.

Keywords: Absinthe; Flavouring additives; Anethole; Methyl ethyl ketone, Thujone; Green fairy liquor.

Introduction

Absinthe is a distilled alcoholic beverage with high alcohol content (45–74% ABV).[1] It is an anise-flavoured spirit made from botanicals including the flowers and leaves of Artemisia absinthium (grand wormwood) together with green anise, sweet fennel and other medicinal and culinary herbs (Fig. 1).



Ethyl alcohol[2] Wormwood[3] Anise seeds[4] Fennel seeds[5] Absinthe[1]

Fig. 1: Composition of Absinthe.

It came in light in 1840s when it was used by French troops as malaria preventive and promptly

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it became popular in bars, cafes and cabarets.[6] Later, absinthe was condemned for inducing insane and criminal act and was stigmatised as madness in a bottle. It has also been portrayed as a dangerously addictive psychoactive drug and hallucinogen.[7] It is still presumed that one can see singing and dancing beautiful green fairy after the intake of absinthe (Fig. 2).

Fig. 2: Hallucinations (Auditory and Visual hallucination)[1]

Owing to this presumption, absinthe is affectionately referred as "la fee verte" means 'the green fairy' in French translation[8] and the term 'Absinthism' is generally used to describe its state as alcoholism characterized by delirium, hallucinations, tremors and seizures. A famous poet Mr. Cros has beautifully described absinthe on his poem.[9]

"With Flowers, and with Women,
With Absinthe, and with this Fire,
We can divert ourselves a while,
Act out our part in some drama.
Absinthe, on a winter evening,
Lights up in green the sooty soul;
And Flowers, on the beloved,
Grow fragrant before the clear Fire.
Later, kisses lose their charm
Having lasted several seasons;
And after mutual betrayals
We part one day without a tear.
We burn letters and bouquets.
And fire takes our bower;
And if sad life is salvaged
Still there is Absinthe and its hiccups.
The portraits are eaten by flames.
Shrivelled fingers tremble.
We die from sleeping long
With Flowers, and with Women."

The main chemical ingredients of absinthe are thujone and anethole. Thujone is the principle active ingredient found in wormwood and is a colourless liquid with a menthol-like aroma while the second ingredient anethole also known as anise camphor is found in anise and fennel. Thujone is believed to be responsible for absinthe's alleged psychedelic effects and due to this effects, absinthe was remained banned for 95 years and again came in market in 2007 after Government's declaration to have lower thujone's limit in absinthe. In the past, absinthe was thought to contain upto 260–350 mg/l of thujone but its quantity was lowered several times to reduce psychedelic effects. In 2005, three 1899 high wormwood recipes were analysed by GC-MS for thujone concentration and which was found to be 4.3 mg/l as the highest content whereas in 2008 study, thujone's concentration was found in between 0.5 and 48.3 mg/l in 13 pre-ban (1895–1910) bottles.[10] Absinthe's ingredient are found to be varied from country to country as maximum thujone level in European Union and in UK is 35 mg/l while thujone is absent in US absinthe. Due to irregularity and suppleness in laws, absinthe liquors have been coming in market with varying concentration of thujone in order to reduce the absinthism.

Anethole, the flavouring compound in absinthe is an unsaturated ether and a derivative of phenylpropene. It is distinctly 13 times sweeter than sugar. One of the common sources of this compound is Pimpinella anisum and sometimes Chinese star anise (illicium verum) is also used. The other source i.e. Japanese star anise (illicium anisatum) is scientifically recognised as highly poisonous and not fit for human consumption. Due to this European Commission has once imposed strict controls on all imports of star anise, including analytical examination. Although, the 2002 decision has been repealed but this issue needs attention when dealing with closely related sources of flavour. Other than natural source, anethole is also produced synthetically. Ignoring the fact that the anethole is harmful, this compound has always been used for aroma and flavour in absinthe.[11]

Other than anethole, different flavouring compounds have also been used by manufactures. Some products even independent of the traditional recipes have been made with readily bought finished extracts of wormwood or other plant blended with ethyl alcohol of agricultural origin with artificial dye and mild flavour.[12] The avaricious manufactures have been adding these harmful chemicals in absinthe to enhance its flavour in

order to increase the product's sale. The details of these ingredients are even not printed on the bottle labels.

Ninety-five percent of chemicals used in fragrances are synthetic compounds derived from petroleum and intake of these can cause severe health problems i.e. Inflammation to monocytes, cancer, birth defects, neurotoxic, CNS disorder and allergic reactions.[13 and 14] Study on chemical profiling of flavouring additives in absinthe has not yet been reported in any scientific literature. Till date only the role of thujone, its determination and its percentage in absinthe have been published so far. A study on flavouring additives of absinthes alongwith their harmful effects has not yet been reported. Henceforth, a forensic attempt is made to secure public health by chemically profiling hazardous flavouring additives in absinthes alongwith their harmful effects on body. Forensic study was mainly targeted to give complete forensic chemical profiling of absinthes so as to make absintheurs aware of the hidden health hazards of these products.

Materials and Method

In this research, seized samples of commercial absinthes i.e. "Parnasse Absinth" were subjected to forensic chemical analysis. These commercial absinthes were seized (under Excise Act) during a regular search in Chandigarh by Chandigarh Police and seized samples were submitted at Central Forensic Science Laboratory, Chandigarh for the detection and quantification of ethanol. The details of chemical ingredients of absinthe were not found printed on the printed label of bottles. The appropriate portions of the absinthes beverage samples were analysed by chemical tests for the detection of ethanol, methanol, copper, iron and furfural and specific gravity method was used for estimating ethanol percentage. For complete chemical profiling of flavouring additives in absinthes, the samples were analysed by gas chromatography-mass spectrometry (GC-MS) technique.

The Solvent used for extraction was of LC grade (Merck, German).

Extraction of absinthes for flavouring additives

50 ml of representative sample was extracted three times with 20 ml chloroform by liquid-liquid extraction procedure. These chloroform extracts were combined in china dish, was concentrated and stored at 4^0C.

Equipment

Thermo Finnigan Trace GC Ultra coupled with a Thermo DSQ Quadrupole MS and Thermo autosamplers 3000 were used.

Instrumentation conditions

Thermo Finnigan Trace GC Ultra coupled with a Thermo DSQ Quadrupole MS and Thermo auto sampler 3000 was used for chemical profiling. The GC-column was a 30 m BP-5 with 0.33 mm I.D. and 0.5 µm film thickness. Helium was used as a carrier gas at a constant flow of 1.2 ml/min. Splitless injection was used with a splitless time of 60 s. The injector and interface line temperature were held at 250^0C and 330^0C respectively. Oven initial temperature was set at 90^0C for 1 minute and increased to 310^0C at the rate of 20^0C/min and held at this temperature for 10 minutes.

The MSD conditions: Ionisation energy 70 eV, ion source temperature 200^0 C, mass range 41–410 amu, electron multiplier voltage (Auto tune + 200V).

Sample injection volume: – 1 µl.

Compound Identification

Xcaliber 1.4 software was used for data acquisition and processing and the result(s) were scrutinized via MS-library of National Institute of Standard and Technology.

Results

Various laboratory examinations such as Physical tests, Chemical tests and Specific gravity measurements were carried out with the seized samples:

A. Physical Tests

1. Volume- approx 100ml–150ml in seized samples.
2. Colour-Light green colour.
3. Odour- characteristic odour of ethanol.

B. Chemical Tests

1. Iodoform Test for Ethanol-Positive.
2. Dichromate test for Ethanol- Positive.

3. Aniline test for Furfural- Negative.

4. Chromotropic acid test for Methanol- Negative.

5. Potassium ferrocyanide test for Copper and Iron- Negative.

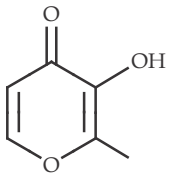
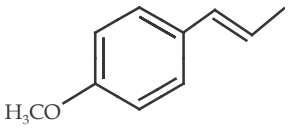
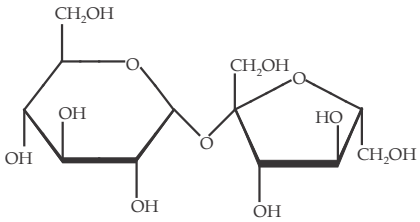
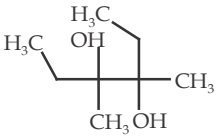
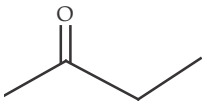
C. Specific gravity measurements

1. Average % Proof- 85.09

2. Average % Alcohol (v/v) - 46.90

The ethanol was detected in samples by chemical analysis and its percentage proof and % alcohol (V/V) were estimated at 85.09 and 46.90 by specific gravity method. Five chemical compounds detected by GC-MS technique are summarised in Table 1 and the resulting total ion chromatogram (TIC) is depicted in Fig. 3.

Table 1: Detected chemical compounds in Absinthe.

S.No.	Rt	Detected chemical compound	Molecular weight (g/mole)	Molecular formula	Structure	Important Mass Fragments
1.	3.49	Maltol	126.111	$C_6H_6O_3$		126,71,43,55,97, 27,15, 52,69,80
2.	3.63	Anethole	148.205	$C_{10}H_{12}O$		148,117,77,133,105, 121,79,91,51,39
3.	5.88	Sucrose	342.30	$C_{12}H_{22}O_{11}$		73,57,31,43,86, 77,103,49,131,113
4.	7.14	DL-3,4-dimethyl-3,4-hexanediol	146.23	$C_8H_{18}O_2$		151,43,57,29,109, 73,69, 134,81,97
5.	9.39	Methyl ethyl ketone (Butanone)	72.107	C_4H_8O		43,72,29,57,27, 15,28,42,44,28

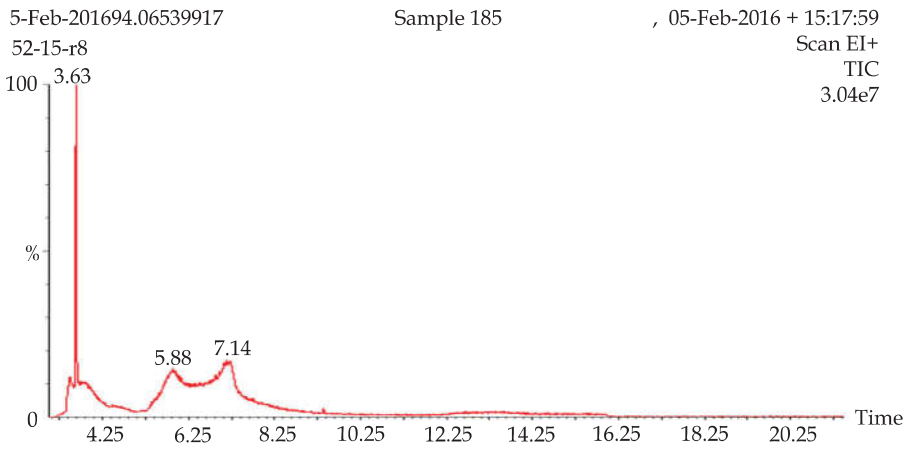


Fig. 3: Total ion chromatogram of absinthe.

Discussion

Five chemical compounds were detected in representative sample by GC-MS technique as summarised in Table 1 and its TIC is depicted in Fig. 3. Some of these detected chemical compounds are derived from plant origin while some are synthetic. These are categorised as under:

Plant origin: Maltol, Anethole, Sucrose and DL-3, 4-dimethyl-3,4-hexanediol.

Synthetic: Methyl ethyl ketone.

Among these five detected chemicals, DL-3,4-dimethyl-3,4-hexanediol is a phytochemical with antibacterial efficacy and rest four chemicals owe specific properties for imparting characteristic flavour, for that reason these four chemicals are being added by manufacturers in absinthe. The flavour of each detected chemical and their harmful effects are given below:

- Maltol
  - Flavour (aroma & taste): Sweet
  - Harmful effects: Abdominal pain, flatulence, constipation, abdominal discomfort & diarrhoea
- Anethole
  - Flavour: Sweet, anise, licorice & spicy with lingering
  - Harmful effects: In large quantity it is toxic & may act as irritant. Naturally occurring phenylpropene derivative is estrogenic at lower concentrations and cytotoxic at higher concentrations to cancer cell lines.

Table 2: Hazard Identification and International regulations for Anethole and Methyl ethyl ketone.

S.No.	Hazard identification of Anethole & Methyl ethyl ketone	International regulations on use of Anethole & Methyl ethyl ketone
1.	**For Anethole:** **1. Labelling** (i) Regulation (EC) No. 1272/2008 (ii) Directive 67/548/EEC or Directive 1999/45/EC **2. Pictogram**  **GHS07: Harmful** **3. Hazard statement** (i) H319 , H317 & H412 (ii) R36, R43 & R52/53	**For Anethole:** • **New Zealand:** Unclassified • **Canada:** No approved products containing anethole are available • **USA:** Generally Recognised as Safe • **EU:** In European Chemicals Agency (ECHA) Annex III inventory requiring REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals) Registration • **India:** No steps taken
2.	**For Methyl ethyl ketone:** **1. Labelling** (i) Regulation (EC) No. 1272/2008 (ii) 67/548/EEC or 1999/45/EC **2. Pictogram**  **GHS07: Harmful**  **GHS02: Flammable** **3. Hazard statement** (i) H225, H319 & H336 (ii) R11, R36, R66 and R67	**For Methyl ethyl ketone:** • **New Zealand:** Precursor substances in Schedule 4 of Misuse of Drugs Act, 1975 • **Canada:** As per draft screening assessment by the Minister of the Environment and the minister of Health, methyl ethyl ketone meet the criteria under paragraph 64(c) of Canadian Environment Protection Act,1999 (CEPA) i.e. it is entering or may enter the environment in a quantity that constitute a danger in Canada to human life or health. • **USA:** On 30th June, 2005, the Environmental Protection Agency (EPA) deleted methyl ethyl ketone from the list of chemical subject to reporting requirements under section 313 of the Emergency Planning and Community Right-to-Know Act (EPCRA) and section 6607 of the Pollution Prevention Act (PRA). • **EU:** Defined in the list of EU-controlled drug precursor. • **India:** Defined as Controlled chemical in Narcotic Drugs and Psychotropic Substances Act, 1985.

- Sucrose
  - Flavour: Sweet
  - Harmful effects: High level can effect blood sugar level, weight gain & heart disease
- Methyl ethyl ketone (Butanone)
  - Flavour: Sweet odour reminiscent of butterscotch & acetone
  - Harmful effects: Acute health effects: Irritate skin, burn the eyes leading to permanent damage, exposure can cause dizziness, lightheadedness, headache, nausea & blurred vision.

    Chronic health effects: Cancer hazard & reproductive hazard.

The additions of anethole and methyl ethyl ketone in absinthe are much harmful than other detected additives and unlike sucrose and maltose, its unwarranted presence in absinthe can't be sensed by absintheurs unless ill-effect exhibits its warning sign. These two additives have also been regulated by different laws in many countries due to their illegal use and harmful effects. Some countries have even cancelled the products containing these chemicals whereas in some countries they are still in use. The hazard identification of anethole and methyl ethyl ketone and international regulation on use of these two additives are depicted in Table 2.

As per Table 2, it is observed that there is huge variation in regulation for the use of anethole and methyl ethyl ketone across the world. It is also observed that till date no country has imposed any regulation or set up any limit for the use of anethole and methyl ethyl in absinthe.

The reason might be that the most of the countries do not have a legal definition of absinthe (unlike wine, beer and most other spirits) which allow the absinthe manufacturers to prepare absinthe as per their greed. The lack of a legal definition for absinthe means that absinthe bottlers can label their product in any way they like; regardless of how closely the procedure matches the superior traditional blend. Moreover, there is also a shortfall in quality control owing to non-availability of technical procedure(s) to identify the flavouring additives. Surprisingly, the high percentage of alcohol by volume in absinthe which may trigger severe health problems- a great concern, is also not much reviewed till date in any country.

Conclusion

There is a high health risk to consumers in the uncontrolled trade of potentially unsafe herbal beverages such as absinthe that are readily available in the market. Large varieties of absinthe are available in which the psychoactive compound thujone may be present in a very low quantity or may be absent. The differences in the varieties of absinthe may be due to the use of different species within the family, the region, the time of growth of the species, the extraction procedure and subsequent steps. Moreover, the absence of thujone doesn't indicate that the absinthe is safe to consume as the flavouring additives anethole and methyl ethyl ketone are hazardous for human health i.e. anethole- toxic, irritant, estrogenic and cytotoxic and methyl ethyl ketone- an irritant, allergic and can cause dizziness, cancer hazard and reproductive hazard. Moreover, the ignorant compound anethole is easily available chemical precursor of psychotropic para-methoxyamphetamine (PMA) and methyl ethyl ketone can act as precursor for cocaine, diacetyl morphine, MDA, MDEA, methamphetamine. Despite this, the government agencies are not alarmed with the misuse and harmful effects of these flavouring additives and focused only on lowering the concentration of thujone in absinthes. Owing to such loopholes in government policies, the manufacturers have been maliciously preparing absinthes according to their own procedures without printing the composition of absinthe on the bottle labels. The absintheurs while drinking absinthe unknowingly drink these harmful chemicals. Hence, the aforementioned health hazards need utmost attention by the private and public authorities especially in COVID-19 pandemic. A limit has also to be set up for the use of flavouring additives to protect the absintheurs and future generation from health hazard.

Forensic Significance

The addition of flavouring additives in absinthe can produce 'synergism' with thujone. Even the high proportion of alcohol in absinthe can lead to health issues like alcoholic cardiomyopathy, cirrhosis of liver, kidney failure, brain damage and diabetes and in combination with high concentration of anethole and thujone it is so hazardous that it can cause gastrointestinal problems, epilepsy and brain damage. Moreover, consuming excessive amounts of alcohol alongwith these additives can also damage the immune cells in the lungs and

upper respiratory system and thus increase the risk of developing diseases such as tuberculosis, pneumonia and respiratory distress syndrome making the drinker more susceptible to viruses such as Corona Virus (COVID-19).

Absinthe also affect the human's perception i.e. causes acute auditory and visual hallucination and due to this absintheurs tend to be more extroverted, tensed, become maniacs, show delirious behaviour and also suffer from traits of neuroticism and psychoticism which results in a number of cases pertaining to physical assault, sexual harassment and suicide. Binge drinking of absinthe can lead to alcohol poisoning.

Hence, this research publication does have a societical outreach as it makes the public at large aware about the hazardous effects of flavouring additives in absinthe and it will aid the public authority to make an absinthe free world for present and future generations, especially during COVID-19 pandemic.

Acknowledgement

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