Ecology-friendly highly efficient extraction of industrial hemp

Ana M. Dobreva[1] & George H. Stantchev[2]

[1] Insitute for Roses and Aromatic Plants, 49 Osvobojdenie Blvd, 6100, Kazanlak, Bulgaria, e-mail: anadobreva@abv.bg (corresponding author)

[2] Comerg LLC, 85022, Phoenix AZ, USA

Received: December 13, 2021 ▹ Accepted: February 08, 2022

Abstract. Industrial hemp is the only plant that produces chemicals known as cannabinoids. They are well known for their human biology influence, but the plant also produces essential oil with many benefits. There are different methods of extraction of hemp substances and most commented are the supercritical solvents, but conditions for their processing and investment costs make them impractical. Subcritical extraction of industrial hemp with 1,1,1,2- tetrafluoroethane gives a high-yield product and, on the average, up to 90 % efficiency of the derived cannabinoids and terpenes.

Key words: *Cannabis sativa*, extraction, freon, cannabinoids, essential oil

Citation: Dobreva, A.M. & Stantchev, G.H. 2022. Ecology-friendly highly efficient extraction of industrial hemp. -- Phytologia Balcanica, 28 (1): 39-42. -- ISSN 1310-7771 (print), 1314-0027 (online).

Introduction

Industrial hemp is another name for *Cannabis sativa* L., with several subspecies or chemotypes. It is the only plant producing chemicals known as cannabinoids. Their number reaches 80, but the most important for human biology are Δ^9-tetrahydrocannabinol (THC) and cannabidiol (CBD). The chemicals in fact are odorless and the specific aroma of the plant is rendered by the essential oil, which consists of monoterpenes (50 – 90 %) and sesquiterpenes (5 – 50%). It can be also a source of flavonoids and polyunsaturated fatty acids. All substances are valuable and have entourage effect. For decades, hemp and hemp-derived products have been classified as a federally illegal substances, but in recent years their restricted status was removed and they were fully or partially legalized as an agricultural commodity. The value of cannabis products in 2018 has been estimated conservatively close to $10 billion (USA) and 5.5 billion (Canada) and expected to rapidly increase (Ataman 2018; King 2018). Manufacturing of these end products involves such processes as extraction, phase transformation and steam distillation. Although some minimal amounts of cannabinoids can be obtained by distillation, the only efficient method for producing all valuable substances is extraction with a critical fluid technology, using not only CO_2, but pro-

© Institute of Biodiversity and Ecosystem Research, Bulgarian Academy of Sciences, 2022
DOI 10.7546/PhB.28.2022.3

pane or butane, dimethyl ether, ethanol, or mixtures thereof (King 2018). Particularly, the use of CO_2 in its sub- and supercritical states, with ethanol as a co-solvent is widely practiced. Solubility of cannabinoids in CO_2 is low under subcritical conditions and this can be improved by higher pressure (Perrotin-Brunel & al. 2010). Unfortunately, a high level of unwanted solutes will be also extracted from the hemp matrix (King 2019). The nature of liquefied 1,1,1,2 tetrafluoroethane (R134a) and the treatment conditions (low pressure, easy operation, low energy, and investment costs) make it a suitable extractant for the target substances, and particularly for cannabinoids and terpenes. It is generally recognized as safe (GRAS) and consumer-friendly.

The aim of this work was to evaluate the efficiency of the cannabis subcritical extraction with respect to the yield and chemical composition of the product.

Material and methods

Dried inflorescences of five hemp cultivars (Charlotte's Web, Pineapple Chunk, White Fire, Candy Land, and Futura 75) were purchased from the local growers in the USA. They had different chemotypes (THC, CBD) or were cultivated as fibre crops. A patented installation with 20L volume extractor was used (Stantchev 2018). Food grade 1,1,1,2-tetrafluoroethane (CAS number 811-97-2) was used as a solvent. Each charging of the vessel was 2kg. The plant material was placed in the extractor, wherein it was decarboxylated (145 °C for 7 min) before extraction. That routine procedure aimed to release the cannabinoids from their acid forms. Exhaustive extraction was performed at the following parameters: pressure 0.9 – 1.0 MPa; temperature 35–45 °C; and 3–5 cycles of 20 minutes (Stantchev 2020). All extractions were carried out in triplicate. After measuring the quantities, the products of each hemp cultivar were mixed in their natural ratio and stored in refrigerator before analysis.

HPLC/UV analysis was performed to quantify the cannabinoids (identified as THC, CBD, their acid forms THCA, CBDA, and cannabinol (CBN)) and GC/MS analytical method was used to determine the essential oil compounds. The protocols were produced by an accredited laboratory, licensed for hemp testing (https://www.sclabs.com/licenses-accreditation/). For efficient verification of the process, parallel with the yield (%), the starting plant material, the obtained product and the exhausted plant material were evaluated.

Hemp variety	Cannabinoids	Content in the plant, %	Content in the extract, %
Candy Land	THC	0.4	74.1
	THCA	24.6	2.3
	CBD	<0.1	0.4
	CBDA	0.5	0.1
	CBN	<0.1	<0.1
	Total	25.6	76.9
White Fire	THC	3.3	80.1
	THCA	21.1	0.6
	CBD	<0.1	1.3
	CBDA	1.0	<0.1
	CBN	<0.1	<0.1
	Total	25.3	82.1
Pineapple Chunk	THC	0.9	63.8
	THCA	12.2	7.0
	CBD	<0.1	<0.1
	CBDA	0.7	1.8
	CBN	<0.1	<0.1
	Total	13.8	72.7
Charlotte's Web	THC	0.1	5.1
	THCA	0.3	<0.1
	CBD	1.7	51.1
	CBDA	17.0	1.0
	CBN	<0.1	<0.1
	Total	19.2	57.2
Futura 75	THC	<0.1	4.2
	THCA	<0.1	1.5
	CBD	0.2	26.3
	CBDA	0.3	2.0
	CBN	<0.1	0.1
	Total	1.0	34.1

Table 1. Chemical profile of the main cannabinoids in the studied cultivars

Results and discussion

All cultivars produced clear viscous extracts, amber yellow in colour. The smell of natural plants was completely preserved. Here are the yields in descending order: Candy Land (26.66±1.14 %), White Fire (26.30±1.11 %), Pineapple Chunk (20.15±0.85 %), Charlotte's Web (4.25±0.49 %), and the lowest one of Futura 75 (3.45±0.24 %).

The profile of cannabinoids in the starting material and in the product is presented in Table 1.

Total concentration of cannabinoids in the extracts ranged from 34.1 % (Futura) to 82.1 % (White Fire). The varieties showed quantitative differences: the products from White Fire, Candy Land and Pineapple Chunk showed the highest content of THC (80.1, 74.1 and 63.8%, respectively), and those from Charlotte's Web and Futura manifested higher amounts of CBD (51.1 and 26.3%). Efficiency of extraction with respect to total cannabinoids ranged between 64% and 95%. THC-rich varieties showed higher results. For individual cannabinoids, on the average, extraction efficiency was very close: 91.8% for THC and 87% for CBD. The obtained data revealed the same levels of efficiency as compared with the maximum CO_2, though under harsh conditions of 34 MPa/55°C (Rovetto & Aieta 2017)

Profile of the main terpenes in the extracts is presented in Table 2.

Qualitative composition of terpenes in the extracts confirmed the literature data for cannabis and its CO_2 products (Ataman 2018; Da Porto & al. 2014). They employed the same pool of components, with limonene (from 0.09 to 4.63 %), β-myrcene (from 0.06 to 3.90 %), β-caryophyllene (from 0.07 to 0.96 %), linalool (from 0.01 to 0.60 %), and terpinolene (from 0.10 to 0.41 %) as main constituents, followed by β-pinene, α-humulene, terpineol, fenchol, borneol, α-bisabolol, and phytol. Different varieties demonstrated diverse terpene profiles: Charlotte's Web extract had the highest content of β-myrcene, while that of Pineapple Chunk was characterized by the maximum limonene. The other three varieties had a balanced composition of essential oil. Extraction efficiency of terpene compounds using R134a ranged from 90% to 97%. The values were several times higher than the 80% found in literature data for CO_2 extraction, but again it was under a much higher pressure than 10-14 MPa (Da Porto & al. 2014).

The method and installation were patent-protected (Stantchev 2018, 2020).

Conclusion

The extraction of industrial hemp with 1,1,1,2-tetrafluoroethane under subcritical conditions can be a highly efficient method for production of cannabis extractives, both cannabinoids and terpenes. The study provides pilot data on the efficacy of the method.

Table 2. Chemical profile of the main terpenes in the hemp extracts (rel. %)

Terpenes	Candy Land	White Fire	Pinapple Chunk	Charllote's Web	Futura 75
α-pinene	0.02	0.05	0.11	1.20	0.04
β-myrcene	0.06	0.09	0.19	3.90	0.31
β-pinene	0.02	0.03	0.01	0.10	0.02
Limonene	0.09	1.82	4.63	0.50	0.20
Terpinolene	0.13	0.11	0.41	0.10	0.21
Linalool	0.10	0.01	0.02	0.60	0.01
β-caryophyllene	0.36	0.07	0.11	0.96	0.52

References

Ataman, D. 2018. Beyond the smoke: Cannabis flavoring in 2018. – Perfum. Flavor., **43**: 52-55.

Da Porto, C., Decorti, D. & Natolino, A. 2014. Separation of aroma compounds from industrial hemp inflorescences (*Cannabis sativa* L.) by supercritical CO_2 extraction and on-line fractionation. – Ind. Crops Prod. **58:** 99-103.

King, J. 2018. Advancing the application of critical fluid technology in cannabis science & engineering. - In: Proceedings of 12th Int. Symp. Supercrit. Fluids, 22-25 April, Antibes, France.

King, J. 2019. The relationship between cannabis/hemp use in foods and processing methodology. – Curr. Opin. Food Sci. **28**: 32-40.

Perrotin-Brunel, H., Kroon, M., Roosmalen, M., Spronsen, J., Peters, C., Witkamp, G. 2010. Solubility of non-psychoactive cannabinoids in supercritical carbon dioxide and comparison with psychoactive cannabinoids. – J. Supercrit. Fluids, **55**(2): 603-608.

Rovetto, L. & Aieta, N. 2017. Supercritical carbon dioxide extraction of cannabinoids from *Cannabis sativa* L. – J. Supercrit. Fluids, **129:** 16- 27.

Stantchev, G. 2018. Apparatus and method for plant extraction. US Patent № 20180010066. - https://patents.justia.com/patent/20180010066 (accessed 30.09.2021).

Stantchev, G. 2020. Apparatus and method for plant extraction. US Patent 10836979B2. - https://patents.justia.com/patent/10836979 (accessed 30.09.2021).