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Hemp seed-based food products as functional foods: A comprehensive characterization of secondary metabolites using liquid and gas chromatography methods

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ABSTRACT

Despite hemp has a long history as food, in the last years the interest in cannabis cultivars, including new varieties, requires a deeper investigation of hemp seed-based food products as a precious source of biomolecules. In the present work, a comprehensive characterization of the minor components occurring in hemp seed-based food products *i.e.* oil, flour and flour by-product, is reported. For this goal, volatile (*i.e.* terpenes, hydrocarbons, furans and ketones) and non-volatile (*i.e.* tocopherols, cannabinoids and phenolic compound) metabolites were investigated by means of different chromatographic techniques. HPLC in combination with PDA, fluorescence, and MS detection was employed to analyse non-volatile fraction. Furthermore, GC coupled with FID and MS detectors were used for the analysis of volatiles and unsaponifiable compounds, the latters after conversion into more volatile trimethylsylil derivatives. Terpenes represented the most abundant compounds among volatiles. A total of 58 compounds belonging to the unsaponifiable matter was identified only in hempseed oils. Among tocopherols, γ-tocopherol was quantified at the highest level. Phenols and cannabinoids were also investigated, and a total of 52 compounds were identified and quantified. To the best of our knowledge, this is the first study providing a thorough chemical characterization of minor fraction of hemp products.

1. Introduction

In the last few years, an increasing trend to use non-conventional foods worldwide was observed, as a consequence of their beneficial property and nutritional effects that could improve the health status by changing only eating habits.

In this context, functional foods and natural products play an important role to health promotion and prevention of disease risks. Functional foods are referred as "Natural or processed foods that contain known or unknown biologically-active compounds which in defined, effective non-toxic amounts, provide a clinically proven and documented health benefit for the prevention, management, or treatment of chronic disease" (Martirosyan and Singh, 2015).

Recently, it has been reported that canola (*Brassica napus* L.), Indian mustard (*Brassica juncea* L.), chia (*Salvia hispanica* L.), quinoa (*Chenopodium quinoa* Willd.) and hemp (*Cannabis sativa* L.) seed oils can be considered excellent examples of functional foods thanks to the presence of macro and micronutrients that have disease-prevention benefits (Frassinetti and Giorgetti, 2018; Oulad El Majdoub et al., 2020; Teh and Birch, 2014).

Abbreviations: BSTFA, [N,O-bis(trimethylsilyl)trifluoroacetamide]; CBC, cannabicromene; CBCA, cannabicromenic acid; CBD, cannabidiol; CBDA, cannabidiolic acid; CBDV, cannabivarin; CBDVA, Cannabivarinic acid; CBEA, cannabielsoin acid; CBG, cannabigerol; CBGA, cannabigerolic acid; CBL, cannabicyclol; CBN, cannabinol; CBNA, cannabinolic acid; FAMEs, fatty acids methyl esters; LRIs, linear retention indices; PUFAs, polyunsaturated fatty acids; THC, tetrahydrocannabinol; THCA, tetrahydrocannabinolic acid; THCV, Tetrahydrocannabivarin; THCVA, Tetrahydrocannabivarinic acid; TMCS, trimethylchlorosilane.

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The term hemp or industrial hemp refers solely to some *Cannabis sativa* varieties for which cannabidiol (CBD) and its acid precursor (CBDA) are the main constituents, while Δ^9-tetrahydrocannabinol (Δ^9-THC), responsible for the well-known psychotropic activity of cannabis is below 0.3% in weight (Protti et al., 2019).

According to its possible usage, hemp is also known as fiber-type *Cannabis*, since it can be employed for the production of fiber for clothes, animal feed and in human nutrition. Conversely, Cannabis sativa cultivars with Δ^9-THC above 0.3% is classified as drug type (*i.e.* marijuana), used for both medical (therapeutic) and non medical (illicit) purposes.

Due to the noticeable pharmacological activity of CBD, hemp *viz.* the fiber-type cannabis, has been attracting great interest worldwide even for its seed products, usable for the production of different foodstuffs.

Regarding human nutrition, hempseed can be consumed raw or as its processing products *e.g.* oil, flour, protein powder, or incorporated into food preparation (yogurt, snack bars, cookies, bread), in order to obtain a food product with higher nutritional and sensory qualities.

Due to the uniqueness of its composition hemp seed can be considered as one of the most nutritionally complete food sources, as it contains around 30–40% fiber, 25–30% protein, 25–30% oil and 6–7% moisture. These values can vary largely among different cultivars (Leonard et al., 2020).

The beneficial and nutritional effects of hemp seed derivatives are mainly attributed to the high content (80%) of polyunsaturated fatty acids (PUFAs), in particular linoleic (ω-6) and α-linolenic (ω-3) acids with 4:1 ratio, that is an optimal balance for human nutrition (Arena et al., 2022). These components play beneficial effects on the cardiovascular system and contribute to maintain low blood cholesterol and triglycerides levels.

The unsaponifiable lipid fraction, including sterols, phytol and tocopherols, is well-known for biological activity, thanks to inhibition of the absorption of cholesterol from dietary fat, reduction of the risk of cardiovascular disease and antiviral, antifungal, and anti-inflammatory properties (Siano et al., 2019).

The potential use of hemp seed products as ingredients for the human diet is not only related to the fatty acid profile but also to the high content of bioactive compounds such as carotenoids and polyphenols, which mainly include hydroxycinnamic acid and lignanamides (Leonard et al., 2020). Typically, the production of these components is related to plant defence mechanisms against pathogens or ultraviolet radiation. In addition, they have a potent antioxidant activity and play an important role to scavenge free radicals. Therefore, the antioxidant components safeguard the chemical stability of a cold-pressed oil against oxidative rancidity and the related shelf life.

Furthermore, the other minor components, such as terpenes and cannabinoids could contributes to the overall beneficial effects.

Actually, it has been reported that hemp seeds should not possess cannabinoids, whereas the presence of the latter in hemp seed-based food products is principally due to the bad selection of the bracts of the perigonium, which have the highest cannabinoid content, or they derive from the resin secreted by the epidermal gland located on leaves or flowers (Citti et al., 2018).

As a consequence, cannabinoids are considered "impurities" of hemp seed-based products and then their concentration depends on the cultivar and the industrial process. In most European countries, the actual legal limit for the cultivation of industrial hemp seed is 0.2% of the psychoactive constituent Δ^9-THC on dry basis (Russo and Reggiani, 2013).

Since recent studies on hemp have dealt with the main components (*e.g.* lipids and proteins) (Alonso-Esteban et al., 2023; Arena et al., 2022; Leonard et al., 2020); we decided to focus on secondary metabolites; in particular, the aim of this work was to characterize the minor components occurring in hemp seed-based food products *i.e.* oil, flour and flour by-product: volatile compounds, being manly terpenes, unsaponifiable fraction, tocopherols, cannabinoids and phenols by mean of different chromatographic techniques.

To the best of our knowledge, no study has been conducted to compare the content of the above mentioned classes of compounds present in hempseed oils, flours and flour by-product.

For this purpose, gas chromatography (GC) was employed to determine the volatile profile and the unsaponifiable fraction. Furthermore, normal-phase liquid chromatography (NPLC) coupled to a fluorescence detector (FLD) was used to separate and quantify tocopherols (all vitamers, α, β, γ, δ), while reversed-phase LC (RP-LC) coupled to a photodiode array and electrospray ionization MS (HPLC-PDA/ESI-MS) was employed for the quali-quantitative analysis of cannabinoids and phenolic compounds.

Such characterization could promote a significant increase in the knowledge of hemp seed-based food products as a functional food, which confers enhanced benefits in the human health.

2. Materials and methods

2.1. Materials and reagents

All solvents, standard materials and reagents, were purchased from Merck KGaA (Darmstadt, Germany), apart for tocopherols and tocotrienols standards that were purchased by Extrasynthese (Genay Cedex, France). LC-MS grade water, acetonitrile (ACN), formic acid, reagent grade ammonium formate and water from aMilli-Q SP ReagentWater System, were used for HPLC-PDA/ESI-MS analyses and sample preparation of cannabinoids and polyphenols.

Reagent grade *n*-Hexane, 2-propanol (IPA) were used for NPLC-FLD analyses of tocopherols.

Reagent grade *n*-Hexane, methanol (MeOH), IPA and distilled water were used for polyphenols, tocopherols and cannabinoids extraction.

Reagent grade Ethanol (EtOH), diethyl ether (Et_2O) chloroform ($CHCl_3$), potassium hydroxide (KOH), powdered anhydrous sodium sulphate (Na_2SO_4), BSTFA [N,O-bis(trimethylsilyl) trifluoroacetamide] + 1% TMCS (trimethylchlorosilane) kit, anhydrous pyridine and distilled water were used for the extraction of the unsaponifiable fraction.

A C7-C40 saturated alkanes (1000 g/mL) standard mixture in hexane and C4-C24 even chain fatty acid standard mixture were used as reference homologue series for linear retention indices (LRIs) calculation.

The α, β, γ, δ-tocopherol and α-tocotrienol standards were used for quantitative analysis of vitamin E.

Luteolin-7-O-Glucoside, Hydroxytyrosol 4-O-Glucoside and N-Trans-Caffeoyltyramine standards were employed for quantitative analysis of phenolic compounds.

Cannabidivarinic acid (CBDVA), cannabidivarin (CBDV), cannabidiolic acid (CBDA), cannabigerolic acid (CBGA), cannabigerol (CBG), cannabidiol (CBD), etrahydrocannabivarin (THCV), tetrahydrocannabivarinic acid (THCVA), cannabinolic acid (CBNA), cannabinol (CBN), Δ^9-tetrahydrocannabinol (Δ^9-THC), Δ^8-tetrahydrocannabinol (Δ^8-THC), Δ^9-tetrahydrocannabinolic acid (Δ^9-THCA), cannabicyclol (CBL), cannabichromene (CBC), cannabichromenic acid (CBCA) standards were used for quali-quantitative analyses.

2.2. Samples

A total of seven hemp seed-based food products were investigated: four different hemp seed oils, two hemp seed flours (variety Futura 75) and one flour by-product (variety Futura 75). Oils 1–4 (variety Futura 75 for oils 1, 2 and 4, and variety Jubileu for oil 3) were provided by Canapar (Ragusa, Italy), Molino Crisafulli (Caltagirone, Italy), Canapuglia (Bari, Italy) and Marishanti (Ragusa, Italy) companies and they were obtained by cold pressing of hemp seeds (without any filtration). Flours were supplied by Canapar and Molino Crisafulli and were obtained by stone milling of hemp seed after cold pressing and sieving, while the flour by-product was provided by Canapar and represents the coarse

residue of the sieving process.

2.3. Sample preparation, instrumentation and analytical conditions

2.3.1. GC-FID/MS

2.3.1.1. Volatile profile analysis by GC-FID/MS. Volatile profile of hemp seed oils, flours and by-products was investigated coupling headspace solid phase micro-extraction (SPME) with GC analysis, by using a gas chromatograph coupled to mass spectrometer (GC-MS) or flame ionization detector (GC-FID) for qualitative and quantitative purposes, respectively. In particular, for the extraction were selected the following condition: sample amount 2 mL for oil, 1.0 g. for flours and flour by-product; DVB/CAR/PDMS 50/30 μm SPME fiber, 1 cm long (Merck KGaA, Darmstadt, Germany); conditioning time of 5 min at 60 °C; extraction time of 50 min at 60 °C and stirring rate of 300 rpm.

After the extraction, the analytes were thermally desorbed for 1 min at 260 °C in the GC injector port in splitless mode.

GC-MS analysis were performed by using a GCMS-QP2020 instrument (Shimadzu, Duisburg, Germany), equipped with a split-splitless injector and an inlet liner, direct SPME type, straight design unpacked (Merck KGaA, Darmstadt, Germany). The injector was equipped with a Thermogreen LB-2 Septa, plug (Merck KGaA, Darmstadt, Germany), and the temperature was set at 260 °C. The separation was achieved on a SLB-5 ms [silphenylene polymer with similar polarity to poly(5% diphenyl/95% dimethyl siloxane)] (30 m L. × 0.25 mm I.D., 0.25 μm *d.f.*) capillary column (Merck KGaA (Darmstadt, Germany)).

GC analytical parameters were as follows: carrier gas (He at constant linear velocity, 30 cm/s), initial pressure of 24.6 kPa; temperature program from 40 °C held for 1 min to 350 °C at 3 °C /min held for 5 min.

With regard to the MS conditions, the samples were analyzed in full scan mode, using a mass range of 40–500 *m/z,* with a scanning rate interval of 0.2 s.

MS interface and ion source temperatures were 250 °C and 220 °C, respectively. Data were acquired and processed by using the GCMSsolution ver. 4.50 software (Shimadzu, Duisburg, Germany). The mass spectral databases used were: the W11N17 (Wiley11-Nist17, Wiley, Hoboken, USA); and FFNSC 4.0 (Shimadzu, Kyoto, Japan). The identification was performed applying spectral similarity match over 85% and linear retention index (LRI) filter window (calculated using a C7-C40 saturated *n*-alkane homologue series) of ± 10 LRI units.

GC-FID analyses were carried out on a GC-2010 instrument (Shimadzu, Duisburg, Germany), equipped with the same injector and liner described above for the GC-MS system. The analytical condition in terms of column, temperature program, carrier gas, linear velocity, injection parameters were the same as for MS applications. The initial inlet pressure was 97.4 kPa. FID parameters were as follows: temperature, 280 °C (sampling rate 200 ms), H_2 flow rate, 40 mL/min; make-up gas (N_2), 30 mL/min; air flow rate, 400 mL/min.

Data acquisition and processing were performed by using the LabSolution ver. 5.92 software (Shimadzu, Duisburg, Germany). Quantitative results were determined as peak area percentage. Samples were analyzed in triplicates.

2.3.1.2. Unsaponifiable profile by GC-FID/MS. The phytosterols were extracted from hemp seed oils according to a procedure reported by Aloisi et al. (2020). For this purpose, 10 mL of a 2 N KOH/EtOH solution was added to 1 g of oil, subsequently heated to 80 °C. The mixture was maintained under reflux condition and magnetic stirring for 2 h, and then extracted once with 20 mL and other two times with 15 mL of Et_2O. The extracted fractions were combined, washed with 10 mL of distilled water and dried with anhydrous Na_2SO_4. The solvent was evaporated under low-pressure conditions at 37 °C.

Finally, the unsaponifiable fraction was dissolved in 500 μL of $CHCl_3$, as derivatization mixture 200 μL of BSTFA (1% TMCS) and 200 μL of pyridine were added. The solution was heated at 70 °C for 20 min, and then the derivatized sample was injected.

The analyses of unsaponifiable fraction were carried out on a GCMS-QP2020 instrument (Shimadzu, Duisburg, Germany) equipped with a split-splitless injector (280 °C) and an AOC-20i autosampler. Separations were performed on a SLB-5 ms [silphenylene polymer with similar polarity to poly (5% diphenyl/95% dimethyl siloxane)] 30 m × 0.25 mm I.D. × 0.25 μm *d.f.* capillary column Merck KGaA (Darmstadt, Germany) and the temperature program was as follows: from 50 °C to 360 °C at 3.0 °C/min. The injection volume was 0.5 μL with a split ratio of 1:50. Helium was employed as carrier gas, with a constant linear velocity of 30 cm/s and an initial inlet pressure of 26.6 kPa.

The following MS parameters were employed: mass range, 40–550 *m/z*; ion source temperature, 220 °C; interface temperature, 250 °C; event time, 0.20 s. Data were acquired and processed by using GCMSsolution ver. 4.50 software (Shimadzu, Duisburg, Germany). The identification procedure was performed automatically by the software, based on a dual-filter LRI/MS search algorithm after the loading of the LIPIDS Mass Spectral Library ver. 1.0 and FFNSC Library 4.0 (Shimadzu, Kyoto, Japan). LRI values were calculated after the injection of FAMEs C4-C24 and saturated *n*-alkanes C7-C40 standard mixture as references homologue series. Peak assignment was based on a MS spectral similarity higher than 85% and a ± 10 LRI tolerance window.

GC-FID analyses were carried out on a GC-2010 instrument (Shimadzu, Duisburg, Germany) equipped with a split-splitless injector, an AOC-20i/s autosampler and an FID detector. The analytical condition in terms of column, temperature program, carrier gas, linear velocity, injection parameters were the same as for MS applications. The initial inlet pressure was 97.4 kPa. The injector temperature was set at 280 °C.

FID parameters were as follows: temperature, 280 °C (sampling rate 200 ms), H_2 flow rate, 40 mL/min; make-up gas (N_2), 30 mL/min; air flow rate, 400 mL/min.

Data acquisition and processing were performed using the LabSolution ver. 5.92 software (Shimadzu, Duisburg, Germany). Quantitative results were determined as peak area percentage. Samples were analyzed in triplicates.

2.3.2. HPLC-FLD and UHPLC-PDA/MS

2.3.2.1. Tocopherol profile by NPLC-FLD. Hemp seed oils were prepared by dissolving 0.2 g of oil in 1 mL of hexane, while seed flour and seed flour by-product were extracted by solvent maceration. Briefly, 40 g of sample was mixed with 50 mL of *n*-hexane and stirred for 40 min. The hexane fraction was recovered after centrifugation (10 min at 3000 rpm) and the solvent was completely evaporated by using a rotary evaporator. The dried residue was re-dissolved in *n*-hexane. Quantification was carried out by external calibration curves of α, β, δ, γ tocopherols and α tocotrienol, in the range between 0.05 and 2.5 ppm, according to the validation reported in a recent paper (Dugo et al., 2020).

The analyses of tocopherols were carried out by using a Shimadzu Nexera-X2 (Shimadzu, Duisburg, Germany), including a CBM-20A controller, two LC-30 AD dual-plunger parallel-flow pumps, a DGU-20ASR on-line degasser, an autosampler SIL-30 AC, a CTO-20 AC column oven, and a RF-20AXS fluorescence detector with cell capacity 12 μL and xenon lamp. Excitation and emission wavelengths were 290 nm and 330 nm, respectively.

Chromatographic separations were performed by keeping the oven temperature at 25 °C using an Ascentis Si (250 L. × 4.6 mm I.D., 5 μm *d.p.*) Merck KGaA (Darmstadt, Germany) column, in isocratic mode: *n*-hexane and IPA (99:1, *v/v*). Flow rate was set at 1.7 mL/min and injection volume was 5 μL.

Data acquisition and processing were performed using the LCsolution software ver. 5.85 (Shimadzu, Duisburg, Germany).

2.3.2.2. Cannabinoid profile by UHPLC-PDA. Cannabinoids were

extracted from hemp seed oils by using the procedure described in Citti et al. (2018). Briefly, 100 µL of the hemp seed oils were diluted with 400 µL of IPA. The mixtures were placed for 10 min in an ultrasonic bath and then filtered with 45 µL nylon filter. The quantification was performed using external calibration curve for each cannabinoid. The analyses of cannabinoids were performed on the integrated UHPLC system LC-2040 3D Nexera-i PDA (Shimadzu, Duisburg, Germany).

The separation was carried out on an Ascentis Express C18 column (150 L. × 3.0 mm I.D., 2.7 µm *d.p.*; Merck KGaA, Darmstadt, Germany) with 5 mM of ammonium formiate in water with 0.1% formic acid as solvent A and ACN with 0.1% formic acid as solvent B, under the following gradient: 0–4.5 min, 67% B; 4.5–6 min, 67–95% B, 6–8 min, 95% B.

Injection volume, flow rate and oven temperature were 5 µL, 1 mL/min, and 40 °C, respectively.

The PDA parameters were as follow: sampling frequency, 4.1667 Hz; time constant, 0.480 s; wavelength range 200–400 nm. The chromatograms were extracted at 228 nm.

Labsolutions Ver. 5.85 (Shimadzu, Duisburg, Germany) was used for data collection and processing.

2.3.2.3. Phenolic compounds by UHPLC-PDA/ESI-MS. Phenolic compounds from hemp oils, flours and by-products were extracted by using a slightly modified procedure by Montedoro et al. (1992). In brief, 1 mL of *n*-hexane were added to 1 g of hemp seed-based food products and the mixtures were homogenized for a few minutes. Then, 1 mL of MeOH/-water (80:20 *v/v*) was added to the mixture and, after 5 min agitation, the sample was extracted for 5 min in an ultrasonic bath. Finally, the mixture was centrifuged for 10 min at 3000 rpm and the MeOH/water phase was collected. The oil and solid matrices were then extracted twice more with the same procedure described above. Afterward, the three MeOH/water phases were pooled and washed with 1 mL of *n*-hexane. The external calibration method was employed for the semi-quantification of all the analytes of interest.

The semi-quantification of phenylpropionamides was performed by UHPLC-PDA analysis using *N-trans*-caffeoyltyramine in the range between 0.5 and 150 mg/L at 320 nm extraction wavelenght, while luteolin-7-O-Glucoside and hydroxytyrosol-4-O-Glucoside in the range 0.5–50 mg/L were used for the semi-quantification of flavone glycosides and phenolic acids at 320 nm and 268 nm extraction wavelenghts, respectively. Finally, the semi-quantitative analysis of cannabinoids was carried out by using calibration curves of CBDA and CBD in the range of 0.5–150 mg/L and CBGA and THCA in the range between 0.5 and 50 mg/L at 228 nm extraction wavelenght. Specifically, CBDA was used as standard compounds for the (semi-)quantification of CBDA and CBDA-C4; CBD was the standard compounds for the (semi-)quantification of CBEA-A, CBEA-B, CBDVA, CBDV, CBEA and CBD; CBGA was the reference compound for the (semi-)quantification of CBGA and 6,7-Epoxy-CBGA; the curve of THCA was employed for the semi-quantification of CBTA.

The UHPLC-PDA/ESI-MS analyses of phenolic compounds were performed on a Nexera Series LC-40 (Shimadzu, Duisburg, Germany) equipped with a CBM-40 controller, one LC-40B X3 dual-plunger parallel-flow pumps, a CTO-40C column oven, a SIL-40CX3 autosampler, an SPD-M40 photo diode array detector, and LCMS-8050 triple quadrupole mass spectrometer equipped with an ESI interface (Shimadzu, Duisburg, Germany) and used in MS mode only, while the collision cell and the second quadrupole act as fly-through zone.

Phenolic compounds were separated on an Ascentis Express C18 column (150 L. × 4.6 mm I.D., 2.7 µm *d.p.;* Merck KGaA, Darmstadt, Germany), with 0.1% formic acid in water (pH = 3; solvent A) and 0.1% formic acid in acetonitrile (solvent B) was employed under the following conditions: 0–15 min, 5–50%B; 15–35 min, 50–70%B; 35–41 min, 100% B. The flow rate was 1 mL/min.

The injection volume was 5 µL and the oven temperature was set at 30 °C.

The PDA parameters were performed in the wavelenght range 200–400 nm, sampling frequency 40 Hz, time constant 0.025 s. The chromatograms were extracted at 228 nm, 268 and 320 nm for cannabinoids, phenolic acids (and derivatives) and lignanimides, hydroxycinnamic acids (and derivatives) and flavonoids (and derivatives), respectively.

The MS acquisitions were performed using ESI source operating both in positive (+) and negative ionization modes (-), with the following parameters: interface and desolvation temperature were set at 300 °C and 525 °C, respectively; heat block temperature, 400 °C; nebulizing gas flow (N_2), 3 L/min; drying gas flow (N_2), 10 L/min; acquisition range, 100–1500 *m/z* (+/-).

Data acquisition and processing was handled by the LabSolution ver. 5.95 software X2 (Shimadzu, Duisburg, Germany).

3. Results and discussion

3.1. Volatile profile composition

Hemp volatile fraction is responsible for the typical aroma and flavor, and may also be responsible for a wide range of biologically relevant effects.

Fig. 1 shows GC-MS volatile fraction profiles of oil 1, flour 1 and flour by-product. A total of 253 compounds were identified in hemp samples: 10 furans, 5 amines, 43 alcohols, 9 esters, 103 terpene hydrocarbons, 31 hydrocarbons, 22 aldehydes, 20 ketones and 10 acids as reported in Table S-1.

In general, the GC data of the analysed hemp products are in accordance with previous findings in literature related to the volatile fraction of hemp flowers (Palmieri et al., 2020; Pellati et al., 2018).

All the hemp samples analysed in this study displayed the same qualitative profile: terpene hydrocarbons were the most represented class of compounds, ranging between 27% and 67% of the total peak area. Among them, the most abundant were β-myrcene (14%), α-pinene (11%) and limonene (8%).

It is noteworthy that β-myrcene is the prominent compound in the volatiles fraction of all sample, except in oil 3, that showed a notably high amount of α-pinene.

As for sesquiterpene hydrocarbons, the flour samples showed higher abundance of this class of compounds than hemp seed oils. In particular, (*E*)-caryophyllene was the most abundant compound found in all the samples, followed by α-humulene; in literature it is reported that the latter possess anti-inflammatory activity due to interaction with cannabinoid receptors and gastric cytoprotective activity (Pellati et al., 2018; Stenerson and Halpenny, 2017; Tambe et al., 1996).

Hemp seed flour samples resulted richer in hydrocarbons and esters than hemp seed oil samples, which showed higher relative percentage concentration of ketones and aldehydes.

In general, a considerable variability in quantitative composition was observed also within the same type of samples, as reported in Fig. S1. In this respect, oil 4 resulted to significantly differ from other hemp seed oils for a lower amount of terpene hydrocarbons and a higher amount of alcohols. Oils 1, 2 and 3 were more similar, with comparable quantities of esters; hemp seed oil 2 was found to be richer in acids than the other samples, as shown in Fig. S1.

Concerning hemp seed flour samples, the most representative compounds are terpene hydrocarbons, alcohols, hydrocarbons, and aldehydes, while the flour by-product showed a lower percentage of hydrocarbons and acids and a higher percentage of terpene hydrocarbons. The use of recycling strategies of this kind of by-products is therefore useful for the recovery of such biomolecules with beneficial properties.

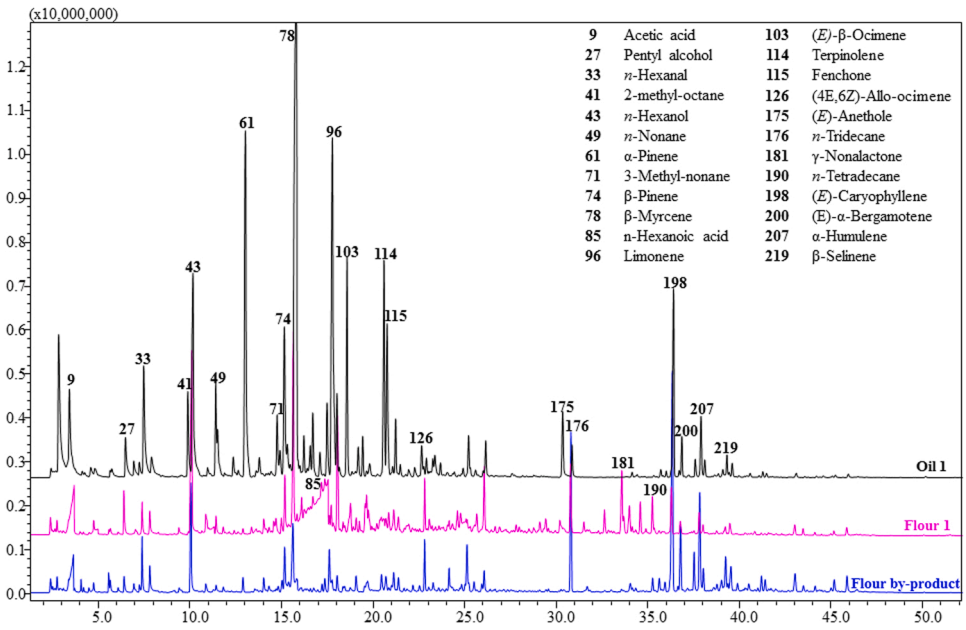

Fig. 1. GC-MS volatile fraction profiles of oil 1, flour 1 and flour by-product.

3.2. *Unsaponifiable fraction composition*

The health benefits of the unsaponifiable fraction of vegetable origin are correlated to the prevention of cardiovascular diseases. However, this class of compounds in hemp products has been poorly investigated by researchers despite the potential relevance that it may have for the development of plant-derived pharmaceutical drugs and nutraceutical compounds.

In this research, after extraction and conversion into more volatile compounds, the determination of this interesting fractions in hemp seed oils (n = 4) was performed by GC−MS/FID.

Fig. 2 reports the representative GC-MS profile obtained for one of the oils, since all the samples showed similar profiles.

As shown in Table S2, 57 compounds was positively identified in the unsaponifiable fraction. Regard to the sterols, β-sitosterol was the most abundant phytosterol, followed by campsterol and Δ-5-avenasterol.

From a quantitative point of view, considering only the phytosterol fraction, β-sitosterol ranged from a minimum of 61.44% (oil 2) to a maximum of 64.13% (oil 3). As regard campesterol, the higher level was encountered in oil 3 (12.02%). The minimum amount of Δ-5-avenasterol was found in oil 1 (8.67%), and a higher content was reached in oil 2 (10.24%).

These results are in accordance with Montserrat-de la Paz et al. (2014) and Blasi et al. (2022) that reported β-Sitosterol (> 60%), campsterol (~ 18%) and Δ-5-avenasterol (> 5%) as predominant compounds in the phytosterol fraction of hemp seed oils.

In comparison to the common vegetables oils, the sterol content in hemp seed oils was similar to canola, soybean and sunflower oils (Ghazani and Marangoni, 2013) and twice the olive oil (Montserrat-de la Paz et al., 2014).

Another interesting compound, belonging to the aliphatic alcohol fraction, is phytol, which accounts for a minimum of 1.59% (oil 2) and a maximum of 2.63% (oil 1) of the total unsaponifiable fraction. Phytol, a constituent of chlorophyll, is mainly found in food, such as spinach, beans, raw vegetables, and asparagus, and has both anticancer and antioxidant activities (Vetter et al., 2012).

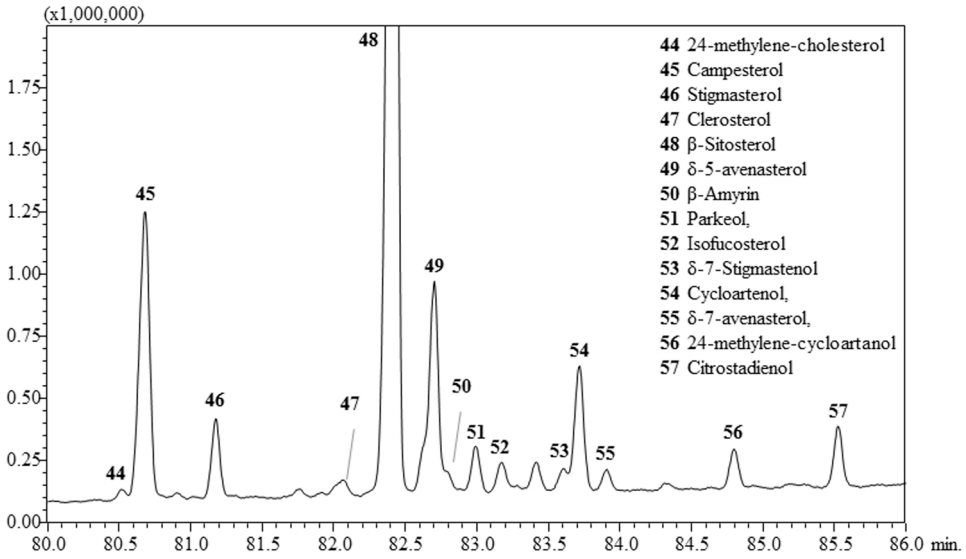

Fig. 2. Six-minutes expansion of the GC-MS chromatogram relative to the unsaponifiable profile of a hempseed oil. Sterols were detected as trimethylsilyl ether.

As the linear aliphatic alcohol, hexacosanol represent the most representative compounds, with a mean value of 0.2% in oils 2–4, up to 0.43% in oil 1. The second abundant compounds in this chemical class is tetracosanol, going from an average percentage of 0.05% for oil 2 to 0.17% for oil 1. Several studies have shown that mixtures of a long-chain primary alcohols extracted from a by-product of olive oil has a potent effect on some mediators involve in inflammatory response (Fernandez-Arche et al., 2009).

Regarding squalene, it was found in low concentrations in all samples. The maximum amount was detected in oil 1 (0.36%) and the minimum amount in oil 3 (0.18%). These values are completely different in comparison to other plants (*e.g.* olive tree) where are rich in squalene (Ostlund et al., 2002).

3.3. Tocopherol composition

Tocopherols were analyzed by NPLC coupled with a FLD. Peak identification was obtained by comparing the retention time of the sample with a standard solution.

In term of quantification, the total amount of tocopherols in hempseed oil ranged around 80–150 mg per 100 g of oil (Leonard et al., 2020).

As can be observed in Table 1, the highest total tocopherol levels were determined for flour 2 (99.73 mg/100 g), followed by flour 1 (66.12 mg/100 g) and flour by-product (64.61 mg/100 g), while no significant differences were determinated for hemp seed oils; a slightly lower value was measured in oil 3 (54.83 mg/100 g).

These results are in accordance with Anwar et al., (2006) and Blasi et al. (2022) that reported the content of total tocopherol in the range of 63.03–111.8 mg/100 g for hemp seed oils from different geographical origins; similar results were obtained by Teh and Birch (2013) who showed a total tocopherol value of 59.16 mg/100 g for cold-pressed hemp seed products.

On the contrary, Smeriglio et al., (2016); and Izzo et al., (2020) reported a total tocopherols content in hemp seed oil of 11.40 mg/100 g and in the range 3.47–13.25 mg/100 g, respectively.

These different ranges of total tocopherols content might be due to the type of process conditions. Lower tocopherols content in vegetable oils can be attributed to many factors *e.g.* storage time, temperature or oxygen exposure (Blade et al., 2006).

Overall, in hempseed products the γ-tocopherol is dominant (85–91% of the total amount of tocopherols), followed by α, and δ-tocopherol, which are present at low concentrations, in the range of 1.70–4.00 mg/100 g.

From a nutritional point of view, intestinal absorption of γ-tocopherol is comparable to that of α-tocopherol, and it could play a specific role in the preventive side effects of some radicals like peroxynitrite and NO_x (Ruperez et al., 2001).

With regard to α-tocotrienol and β-tocopherols, they were not detected in the analysed samples.

3.4. Cannabinoid profiling by fast UHPLC-PDA

In the last decade, the scientific community has paid increasing attention to the role of cannabinoids in the human body, investigating both beneficial and toxic effects (Leghissa et al., 2018).

Among them, CBD is the most important non-psychoactive cannabinoid contained in the seeds of cultivars used for the production of hemp seed oil, while it is crucial to guarantee the absence of the THC, due to its psychotropic effect. Specifically, both CBD and THC derive from CBGA through reaction promoted by the CBDA-synthase and THCA-synthase, respectively.

The "legal" varieties that can be used for the production of seeds and fibers must not contain the enzyme THCA-synthase, which would convert CBGA into THCA and CBGVA (cannabigerovarinic acid) into THCVA (Citti et al., 2018). Rather, they contain the enzyme CBDA-synthase, which leads to the synthesis of cannabidiolic acid (CBDA) from CBGA and CBDVA from CBGVA. Afterward, such acidic forms can be transformed in the corresponding neutral molecules (CBD, CBDV, Δ^9-THC, THCV) through thermal decarboxylation reaction or undergo oxidation following air exposition and be converted into CBN (Russo, 2011).

Then, the total cannabinoid profile can be related to both genotype information and storage conditions. For this reason, in the last decade researchers address many efforts to the development of rapid and reliable methods for the analysis of cannabinoids to gain the needed information with minimal sample treatment and limited chemical reagents use (La Tella et al., 2022).

Within this context, in the present work a high-speed analytical method was used to obtain a preliminary investigation of the main cannabinoids in hempseed products. Using a partially porous C18 column, it was possible to obtain a satisfactory separation of 16 cannabinoid standards in about 6 min. Fig. 3 reports the UHPLC-PDA profiles obtained for the mixture above-mentioned (A) and the oil 1 (B), as representative of all the analysed oils, quite similar from a qualitative point of view. The obtained chromatographic profile for the oils was in partial accordance with a previous studies on a commercial hempseed oil, which reported the presence of CBDA as the main cannabinoid, followed by a moderate content of CBD, CBDV and CBN (Citti et al., 2018). The chromatogram in Fig. 3B is dominated by the peak of CBDA, followed by CBD and low percentages of CBDVA, CBDV and CBGA; THC, THCA, THCVA, THCV and CBN were not detected, meaning that the analyzed hempseed oils derived from "legal" varieties and they were properly stored avoiding or minimizing oxidation reactions.

3.5. Phenolic compounds and cannabinoids composition

Phenolic compounds include more than ten thousand molecules with various therapeutic properties *i.e.* antioxidant and anti-inflammatory. In particular, their presence is associated with a decrease in the risk of stroke, myocardial infarction and diabetes, but also with the improvement of insulin resistance and systemic inflammation conditions (Fraga et al., 2019; Mukherjee and Chakraborty, 2021; Lowe et al., 2021).

Among them, the main compounds in hempseed products are hydroxycinnamic acid amides, lignanamides and cannabinoids. The first ones is the results of the phenylpropanoid pathway with tyrosine and phenylalanine as precursors, on the contrary lignanamides are derived from the oxidative coupling between hydroxycinnamic acid amides

Table 1
Tocopherol content (mg/100 g ± standard deviation) in hemp seed-based food products.

Compound	Oils				Flours		Flour by-product
	Oil 1	**Oil 2**	**Oil 3**	**Oil 4**	**Flour 1**	**Flour 2**	
α -tocopherol	3.88 ± 0.00	2.91 ± 0.03	2.75 ± 0.01	2.43 ± 0.00	3.67 ± 0.09	3.42 ± 0.01	4.00 ± 0.10
α-tocotrienol	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
β-tocopherol	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
γ-tocopherol	57.10 ± 0.09	54.72 ± 1.59	50.09 ± 0.00	55.13 ± 0.06	59.81 ± 0.11	93.64 ± 0.10	58.70 ± 0.23
δ-tocopherol	1.74 ± 0.01	1.89 ± 0.01	1.99 ± 0.01	1.7 ± 0.00	2.64 ± 0.08	2.67 ± 0.02	1.91 ± 0.07
Total	62.72	59.52	54.83	59.26	66.12	99.73	64.61

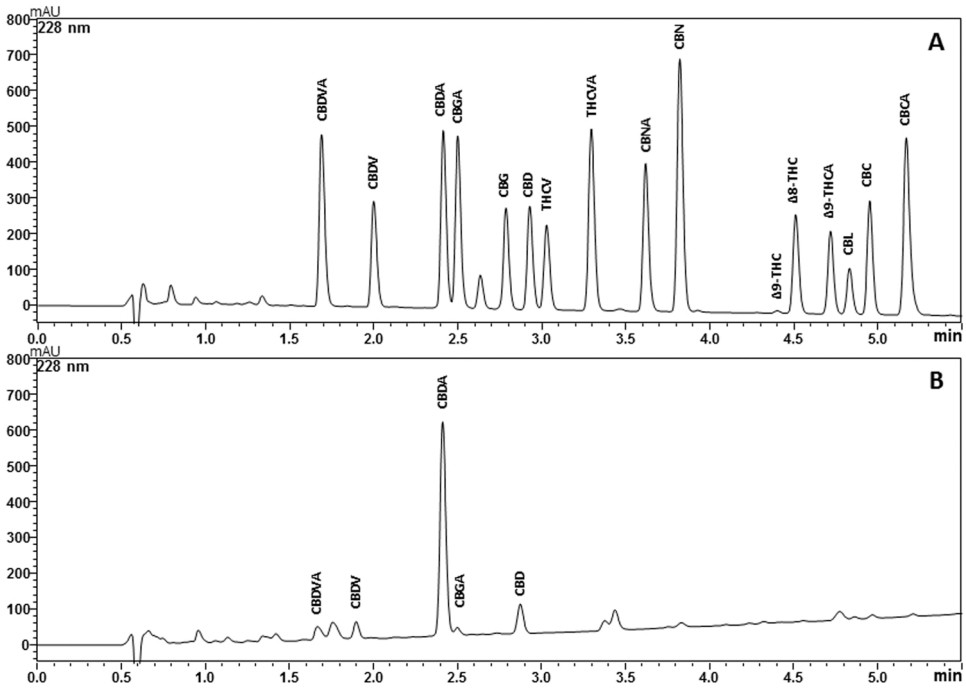

Fig. 3. LC-PDA profile of cannabinoids in A) mixture of 16 analytical standards. B) Oil 1.

monomers. As for cannabinoids, they can be also classified as terpenophenolic compounds, which are biosynthesized from the phenolic acid, olivetolitic acid and the monoterpene geranylpyrophosphate. Until now, more than 100 phytocannabinoids have been identified, most of them have demonstrated potential benefits, such as antiepileptic, analgesic, neuroprotective and anticonvulsant efficacy (Harris et al., 2016; Reddy, 2016; Yamaori et al., 2011; Zuardi et al., 1982).

In particular, due to the larger number of cannabinoids involved in real samples, the fast and sustainable approach reported in the previous section can be considered just preliminary and an untargeted characterization is needed, by exploiting the MS signals for the identification of unknown peaks for which commercial standards are not available.

For this reason, the investigation of cannabinoids and phenols compounds was carried out in hemp seed oils, hemp flour and hemp flour by-product *via* UHPLC-PDA/ESI-MS.

The profiles of phenolic and cannabinoid compounds of the oil 1, flour 1 and flour by-product are shown in Fig. 4.

The compounds were identified according to the complementary information coming from PDA and MS spectra in combination with data already reported in the literature. Two organic acids and fifty phenolic compounds were positively detected and quantified; among them, 31 phenylpropionamides (9 hydroxycinnamic acid amides and 22 lignanamides), 4 phenolic acids, 1 lignan, 2 flavones and 12 cannabinoids were identified. A detailed list of the identified and quantified (mg/L of the sample) compounds in the seven hemp derivate products is presented in Table S3.

For quantitative purposes, all the identified compounds were quantified using the external standard calibration method. Calibration curves

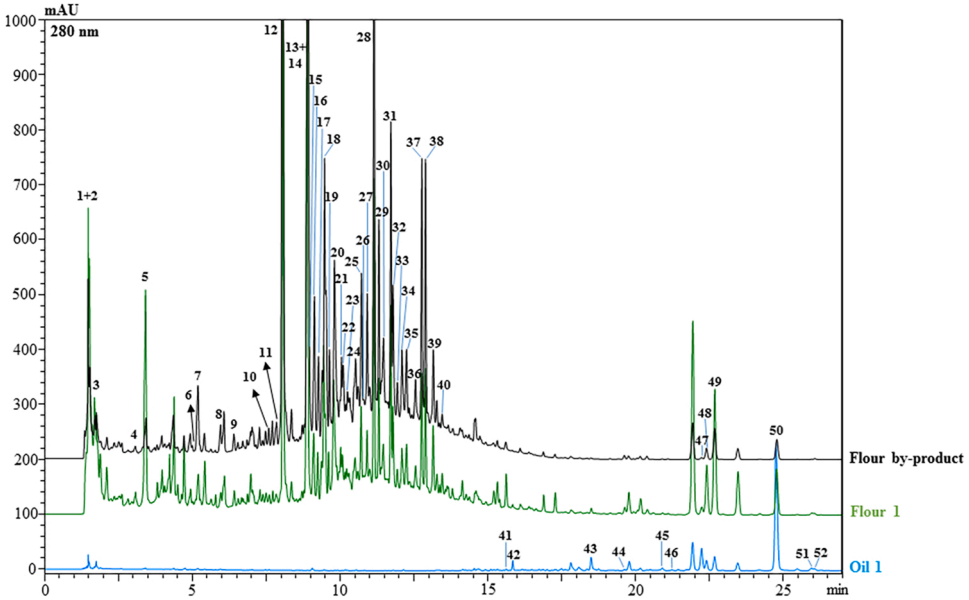

Fig. 4. LC-PDA profiles of phenolic and cannabinoid compounds of the oil 1, flour 1 and flour by-product.

for each standard compound were built using the area obtained in the chromatogram at λ 228 nm for cannabinoids, at λ 268 nm for phenolic acids and at λ 320 nm for lignanamides, hydroxycinnamic acid and flavonoids, after triplicate injections at each concentration level.

Those compounds for which a commercial standard was not available were quantified using the calibration curve of the structurally closest related standard assuming a similar response in the PDA and having similar UV-Vis absorption maxima.

Fig. 5 shows the contribution of each chemical classes and cannabinoid in terms of total concentration values (mg/Kg) in the seven hempseed products investigated.

As the result, the content of phenols in the flours (839.92–862.75 mg/Kg) and flour by-product (1345.16 mg/Kg) was significantly higher than in the hemp oils (1.03–7.91 mg/Kg). A similar trend was also found in pumpkin seeds (Peričin et al., 2009).

Cannabinoids were the most abundant class in hemp seed oils, in particular, oil 4 has been showing only the presence of cannabinoids, on the contrary, flour 1 presented almost the same amount of cannabinoids (488.21 ± 3.06 mg/Kg) and lignanamides (485.03 ± 1.51 mg/Kg), the results are showed in Fig. 5.

Among cannabinoids in the hempseed oils, cannabielsoin acid (CBEA) was the most abundant compound, in the range from 125.45 ± 0.13 mg/Kg in oil 2 to 25.63 ± 0.70in oil 4.

The second most abundant compound was CBDA in a minimum range of 10.89 ± 0.85 mg/Kg in oil 3 to a maximum of 124.75 ± 1.63 mg/Kg in oil 1, followed by CBDVA from 35.58 ± 0.23 mg/Kg (oil 1) to 83.23 ± 0.54 mg/Kg (oil 2), these significant differences in quantitative profiles between the samples could be due to the production process and storage conditions. These results are in accordance with studies previously reported for other samples (Christinat et al., 2022; Citti et al., 2018).

Conversely, cannabinoids' quali-quantitative profiles in flours were very similar between them and richer than the hempseed by-product; specifically, the most abundant were CBDVA (from a maximum of 160.15 ± 1.16 mg/Kg in flour 1 to a minimum of 29.15 ± 0.13 mg/Kg in flour by-product), followed by CBDV (130.01 ± 0.93 mg/Kg in flour 1 and 25.81 ± 0.05 mg/Kg in flour by-product), CBEA (111.58 ± 0.62 mg/Kg in flour 2) and CBDA (45.59 ± 0.43 mg/Kg in flour 2 and 20.36 ± 0.06 mg/Kg in flour by-product).

Regarding CBD, which is responsible for several pharmacological activities, it was detected in all the investigated samples.

The most abundant values were found in the hempseed oils, in the range from 4.72 ± 0.06 mg/Kg to 33.03 ± 0.09 mg/Kg; on the contrary, the lower concentrations were observed in the flours and flour by-product (from 4.81 ± 0.05–18.13 ± 0.16 mg/Kg).

Finally, the ratio between CBDA and CBD was also calculated, since it could be an important marker of genuineness for hemp seed oil regarding the cold pressing and good storage conditions. This is due to the decarboxylation reaction that transformed the CBDA into CBD. In each sample, this ratio was higher than 5:1, in particular, the ratio was around 20:1 and 10:1 in the oil 2 and oil 1, respectively.

These results suggested the high quality and a good storage of the hempseed products.

As for lignamides, which resulted the second most abundant class of phenolic compounds, they appeared only in flours and flour by-product, accounting for more than 35% of the total quantified compounds; in particular, the richest sample was flour by-product (801 ± 1.63 mg/Kg), followed by flour 2 (488.18 ± 4.02 mg/Kg) and flour 1 (485.03 ± 1.51 mg/Kg). Cannabisin A and B were the most predominant compounds of this group, being flour by-product the richest one (159.65 ± 3.39 mg/Kg).

Concerning the hydroxycinnamic acids derivatives, the biggest amount was detected in the flour by-product (450.67 ± 8.58 mg/Kg) followed by flour 2 (258.17 ± 2.25 mg/Kg) and flour 1 (248.89 ± 1.46 mg/Kg), while they were found in poor amounts in hempseed oils. The predominant compound in this fraction was *N-trans*-caffeoyl tyramine, with a concentration of 140.23 ± 2.25 mg/Kg and 270.24 ± 8.62 mg/Kg, in flour I and flour by-product, respectively.

The phenolic acid class, which consists only of benzoic acid, represented around 1% of the total quantified compounds, being flour 1 (20.44 ± 0.08 mg/Kg) and flour 2 (24.30 ± 1.53 mg/Kg) the most concentrated samples in this chemical class, while they were detected at

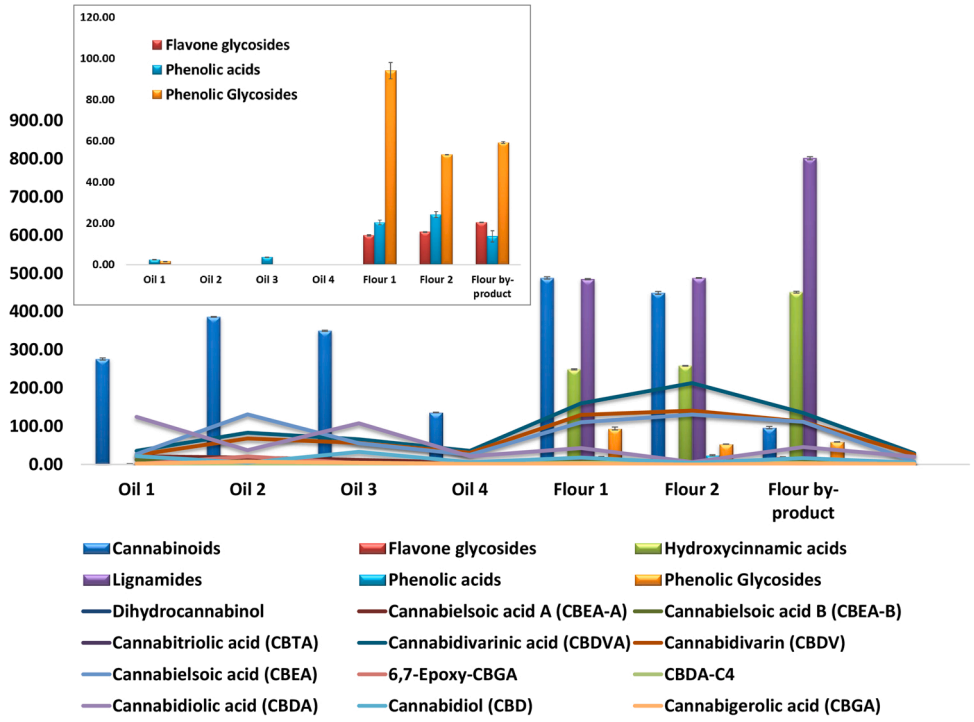

Fig. 5. Contribution of each chemical class and cannabinoid in terms of total concentration values (mg/Kg) in the seven hempseed products investigated. An enlargement of the minor classes is also provided in the insert.

low levels only in two hempseed oils.

On the other hand, flavone glycosides, which only appear in flours and flour by-product, showed overall concentrations between 14.23 ± 0.32 and 20.49 ± 0.25 mg/Kg, being flour I the sample with the lowest concentration and flour by-product the richest one.

Finally, phenolic glycosides, which are the sum of hydroxytyrosol hexoside and dihydroxybenzoic acid hexoside, were quantified at the highest level in flour I (94.16 ± 3.36 mg/Kg).

As in the case of terpenes and tocopherols, the by-product can be still considered a rich source of bioactive compounds.

4. Conclusion

The result of this study confirm the nutritional value of hemp seed-based food products, thanks to the presence of minor and secondary metabolites.

To the best of the author's knowledge, a comprehensive characterization of the minor fraction of hemp seed oils, flours and flour by-product through the analysis of volatile compounds, unsaponifiable fraction, tocopherols, phenolic compounds and cannabinoids, has been carried out in the present work for the first time.

All the investigated samples showed the same qualitative profiles with respect to all the chemical classes, while quantitative differences were detected even within the same type of samples (oils or flours). Within this context, the analysis of secondary metabolites can be extremely useful for the evaluation of storage conditions and the influence of technological processed on the chemical composition, which determines the biological activity of such food products. As an example, the noticeable content of CBDA was confirmed in all the analyzed oils, thus pointing out the effect of "contamination by inflorescences"of hemp seeds. Such contamination makes necessary the analysis of the cannabinoid profile to guarantee the absence of THC in the final products. Also, the ratio between the acidic form (CBDA) and the neutral CBD confirmed a care in preserving the raw material from oxidation prior and during the technological process leading to the production of the oil, as well as proper storage conditions.

In conclusion, hemp seed-based food products can be claimed as healthy food due to both a high nutritional value and favourable content of secondary metabolites, such as terpenes, phytosterols, tocopherols, phenolic compounds and cannabinoids.

The present work is intended to the valorisation of such unconventional food products, paying also attention to the waste product, still rich in bioactive molecules.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jfca.2023.105151.

References

Aloisi, I., Zoccali, M., Dugo, P., Tranchida, P.Q., Mondello, L., 2020. Fingerprinting of the unsaponifiable fraction of vegetable oils by using cryogenically-modulated comprehensive two-dimensional gas chromatography-high resolution time-of-flight mass spectrometry. Food Anal. Methods 13, 1523–1529. https://doi.org/10.1007/s12161-020-01773-9.

Alonso-Esteban, J.I., Gonzalez-Fernandez, M.J., Fabrikov, D., de Cortes Sanchez-Mata, M., Torija-Isasa, E., Guil-Guerrero, J.L., 2023. Fatty acids and minor functional compounds of hemp (Cannabis sativa L.) seeds and other Cannabaceae species. J. Food Compos. Anal. 115, 104962–104971. https://doi.org/10.1016/j.jfca.2022.104962.

Anwar, F., Latif, S., Ashraf, M., 2006. Analytical characterization of hemp (Cannabis sativa) seed oil from different agro-ecological zones of Pakistan. J. Am. Oil Chem. Soc. 83, 323–329. https://doi.org/10.1007/s11746-006-1207-x.

Arena, P., Rigano, F., Guarnaccia, P., Dugo, P., Mondello, L., Trovato, E., 2022. Elucidation of the Lipid Composition of Hemp (Cannabis sativa L.) Products by Means of Gas Chromatography and Ultra-High Performance Liquid Chromatography Coupled to Mass Spectrometry Detection. Molecules 23, 3358. https://doi.org/10.3390/molecules27103358.

Blade, S.F., Ampong-Nyarko, K., Przybylski, R., 2006. Fatty acid and tocopherol profiles of industrial hemp cultivars grown in the high latitude prairie region of Canada. J. Ind. Hemp 10, 33–43. https://doi.org/10.1300/J237v10n02_04.

Blasi, F., Tringaniello, C., Verducci, G., Cossignani, L., 2022. Bioactive minor components of Italian and Extra-European hemp seed oils. LWT 158, 113167–113173. https://doi.org/10.1016/j.lwt.2022.113167.

Christinat, N., Savoy, M.C., Mottier, P., 2022. Development, validation and application of a LC-MS/MS method for quantification of 15 cannabionoids in food. Food Chem. 318, 126469 https://doi.org/10.1016/j.foodchem.2020.126469.

Citti, C., Pacchetti, B., Vandelli, M.A., Forni, F., Cannazza, G., 2018. Analysis of cannabinoids in commercial hemp seed oil and decarboxylation kinetics studies of cannabidiolic acid (CBDA). J. Pharm. Biomed. Anal. 149, 532–540. https://doi.org/10.1016/j.jpba.2017.11.044.

Dugo, L., Russo, M., Cacciola, F., Mandolfino, F., Salafia, F., Vilmercati, A., Fanali, C., Casale, M., De Gara, L., Dugo, P., Mondello, L., Rigano, F., 2020. Determination of the Phenol and Tocopherol Content in Italian High-Quality Extra-Virgin Olive Oils by Using LC-MS and Multivariate Data Analysis. Food Anal. Methods 13, 1027–1041. https://doi.org/10.1007/s12161-020-01721-7.

Fernandez-Arche, A., Marquez-Martin, A., De la PuertaVazquez, R., Perona, J.S., Terencio, C., Perez-Camino, C., RuizGutierrez, V., 2009. Long-chain fatty alcohols from pomace olive oil modulate the release of proinflammatory mediators. J. Nutr. Biochem. 20, 155–162. https://doi.org/10.1016/j.jnutbio.2008.01.007.

Fraga, C.G., Croft, K.D., Kennedy, D.O., Tomás-Barberán, F.A., 2019. The effects of polyphenols and other bioactives on human health. Food Funct. 10, 514–528. https://doi.org/10.1039/C8FO01997E.

Frassinetti, S., Giorgetti, L., 2018. Nutraceutical potential of hemp (Cannabis sativa L.) seed and sprouts. Food Chem. 262, 56–66. https://doi.org/10.1016/j.foodchem.2018.04.078.

Ghazani, S.M., Marangoni, A.G., 2013. Minor components in canola oil and effects of refining on these constituents: a review. J. Am. Oil Chem. Soc., 90 *923*–932. https://doi.org/10.1007/s11746-013-2254-8.

Harris, H.M., Sufka, K.J., Gul, W., Elsohly, M.A., 2016. Effects of delta-9-tetrahydrocannabinol and cannabidiol on cisplatin-induced neuropathy in mice. Planta Med 82, 1169–11721. https://doi.org/10.1055/s-0042-106303.

Izzo, L., Pacifico, S., Piccolella, S., Castaldo, L., Narváez, A., Grosso, M., Ritieni, A., 2020. Chemical analysis of minor bioactive components and cannabidiolic acid in commercial hemp seed oil. Molecules 25, 3710. https://doi.org/10.3390/molecules25163710.

La Tella, R., Rigano, F., Guarnaccia, P., Dugo, P., Mondello, L., 2022. Non-psychoactive cannabinoids identification by linear retention index approach applied to a hand-portable capillary liquid chromatography platform. Anal. Bioanal. Chem. *5* https://doi:10.1007/s00216-021-03871-x.

Leghissa, A., Hildenbrand, Z.L., Schug, K.A., 2018. A review of methods for the chemical characterization of cannabis natural products. J. *Sep Sci.* 41, 398–415. https://doi.org/10.1002/jssc.201701003.

Leonard, W., Zhang, P., Ying, D., Fang, Z., 2020. Hempseed in food industry: Nutritional value, health benefits, and industrial applications. Compr. Rev. Food Sci. Food Saf. 19 282–308. https://doi.org/10.1111/1541-4337.12517.

Lowe, H., Steele, B., Bryant, J., Toyang, N., Ngwa, W., 2021. Non-Cannabinoid Metabolites of *Cannabis sativa* L. with Therapeutic Potential. Plants 10, 400. https://doi.org/10.3390/plants10020400.

Martirosyan, D.M., Singh, J., 2015. A new definition of functional food by FFC: What make a new definition unique? Funct. Foods Health Dis. 5, 209–223. https://doi.org/10.31989/ffhd.v5i6.183.

Montedoro, G., Servili, M., Baldioli, M., Miniati, E., 1992. Simple and Hydrolyzable Phenolic Compounds in Virgin Olive Oil. 1.Their Extraction, Separation, and Quantitative and Semiquantitative Evaluation by HPLC. J. Agric. Food Chem. 40, 1571–1576. https://doi.org/10.1021/jf00021a019.

Montserrat-de la Paz, S., Marín-Aguilar, F., García-Gimenez, M.D., Fernandez-Arche, M. A., 2014. Hemp (Cannabis sativa L.) seed oil: analytical and phytochemical characterization of the unsaponifiable fraction. J. Agric. Food Chem. 62, 1105–1110. https://doi.org/10.1021/jf404278q.

Mukherjee, C., Chakraborty, S., 2021. Study of dietary polyphenols from natural herbal sources for providing protection against human degenerative disorders. Biocatal. Agric. Biotechnol. 33, 101956 https://doi.org/10.1016/j.bcab.2021.101956.

Ostlund, R.E.M., Racette, S.B., Stenson, W.F., 2002. Effect of trace components of dietary fat on cholesterol metabolism: Phytosterols, oxysterols and squalene. Nutr. Rev. 60, 349–359. https://doi.org/10.1301/00296640260385793.

Oulad El Majdoub, Y., Alibrando, F., Cacciola, F., Arena, K., Pagnotta, E., Matteo, R., Micalizzi, G., Dugo, L., Dugo, P., Mondello, L., 2020. Chemical Characterization of Three Accessions of Brassica juncea L. Extracts from Different Plant Tissues. Molecules 25, 5421. https://doi.org/10.3390/molecules25225421.

Palmieri, S., Pellegrini, M., Ricci, A., Compagnone, D., Lo Sterzo, C., 2020. Chemical Composition and Antioxidant Activity of Thyme, Hemp and Coriander Extracts: A Comparison Study of Maceration, Soxhlet, UAE and RSLDE Techniques. Foods 9, 1221. https://doi.org/10.3390/foods9091221.

Pellati, F., Brighenti, V., Sperlea, J., Marchetti, L., Bertelli, D., Benvenuti, S., 2018. New Methods for the Comprehensive Analysis of Bioactive Compounds in *Cannabis sativa* L. (hemp) (https://). Molecules 23, 2639. https://doi.org/10.3390/molecules23102639.

Perič̆in, D., Krimer, V., Trivić, S., Radulović, L., 2009. The distribution of phenolic acids in pumpkin's hull-less seed, skin, oil cake meal, dehulled kernel and hull. Food Chem. 113, 450–456. https://doi.org/10.1016/j.foodchem.2008.07.079.

Protti, M., Brighenti, V., Battaglia, M.R., Anceschi, L., Pellati, F., Mercolini, L., 2019. Cannabinoids from *Cannabis sativa* L.: A New Tool Based on HPLC–DAD–MS/MS for a Rational Use in Medicinal Chemistry. ACS Med. Chem. Lett. 10, 539–544. https://doi.org/10.1021/acsmedchemlett.8b00571.

Reddy, D.S., 2016. The Utility of Cannabidiol in the Treatment of Refractory Epilepsy. Clin. Pharmacol. Ther. 101, 182–184. https://doi.org/10.1002/cpt.441.

Ruperez, F.J., Martín, D., Herrera, E., Barbas, C., 2001. Chromatographic analysis of α-tocopherol and related compounds in various matrices. J. Chromatogr. A 935, 45–69. https://doi.org/10.1016/S0021-9673(01)01101-3.

Russo, E.B., 2011. Taming THC: potential *Cannabis* synergy and phytocannabinoid-terpenoid entourage effects. Br. J. Pharmacol. 163, 1344–1364. https://doi.org/10.1111/j.1476-5381.2011.01238.x.

Russo, R., Reggiani, R., 2013. Variability in Antinutrional compounds in Hempseed meal of Italian and French varieties. Plant 1, 25–29. https://doi.org/10.11648/j.plant.20130102.13.

Siano, F., Moccia, S., Picariello, G., Russo, G.L., Sorrentino, G., Di Stasio, M., La Cara, F., Volpe, M.G., 2019.). Comparative study of chemical, biochemical, characteristic and ATR-FTIR analysis of seeds, oil and flour of the edible fedora cultivar hemp (*Cannabis sativa* L.). Molecules 24, 83. https://doi.org/10.3390/molecules24010083.

Smeriglio, A., Galati, E.M., Monforte, M.T., Lanuzza, F., D'Angelo, V., Circosta, C., 2016. Polyphenolic compounds and antioxidant activity of cold-pressed seed oil from finola cultivar of Cannabis sativa L. Phytother. Res. 30, 1298–1307. https://doi.org/10.1002/ptr.5623.

Stenerson, K.K., Halpenny, M.R., 2017. Analysis of terpenes in cannabis using headspace solid-phase microextraction and GC–MS. LCGC North Am. 35, 27–32.

Tambe, Y., Tsujiuchi, H., Honda, G., Ikeshiro, Y., Tanaka, S., 1996. Gastric cytoprotection of the non-steroidal anti-inflammatory sesquiterpene, β-caryophyllene. Planta Med. 62, 469–470. https://doi.org/10.1055/s-2006-957942.

Teh, S.S., Birch, J., 2013. Physicochemical and quality characteristics of cold-pressed hemp, flax and canola seed oils. J. Food Compos. Anal. 30, 26–31. https://doi.org/10.1016/j.jfca.2013.01.004.

Teh, S.S., Birch, J., 2014. Effect of ultrasonic treatment on the polyphenol content and antioxidant capacity of extract from defatted hemp, flax and canola seed cakes. Ultrason. Sonochem. 21, 346–353. https://doi.org/10.1016/j.ultsonch.2013.08.002.

Vetter, W., Schröder, M., Lehnert, K., 2012. Differentiation of refined and virgin edible oils by means of the trans- and cis-phytol isomer distribution. J. Agric. Food Chem. 60, 6103–6107. https://doi.org/10.1021/jf301373k.

Yamaori, S., Okamoto, Y., Yamamoto, I., Watanabe, K., 2011. Cannabidiol, a major phytocannabinoid, as a potent atypical inhibitor for CYP2D6. Drug Metab. Dispos. 39, 2049–2056. https://doi.org/10.1124/dmd.111.041384.

Zuardi, A.W., Shirakawa, I., Finkelfarb, E., Karniol, I.G., 1982. Action of cannabidiol on the anxiety and other effects produced by δ9-THC in normal subjects. Psychopharmacology 76, 245–250. https://doi.org/10.1007/BF00432554.

Supplementary Material

Hemp seed-based food products as functional foods: a comprehensive characterization of secondary metabolites

Supporting Information Table of Contents:

Table 1s: Analysis of volatile fraction in hemp seed-based food products expressed in area % ± SD as measurement acquired by GC-FID analysis.

n.	Compound	LRI_{ex}	LRI_{lib}	Similarity %	Oils				Flours		Flour by-product
					Oil 1	Oil 2	Oil 3	Oil 4	Flour 1	Flour 2	
1	Acetaldehyde	468	-	89	0.34 ± 0.03	0.88 ± 0.07	0.38 ± 0.03	0.08 ± 0.01	0.07 ± 0.01	0.16 ± 0.01	0.13 ± 0.01
2	Ethanol	488	-	97	0.18 ± 0.01	0.27 ± 0.02	0.17 ± 0.01	0.25 ± 0.02	0.20 ± 0.02	0.27 ± 0.02	0.09 ± 0.01
3	Acetone	506	-	94	4.62 ± 0.37	3.25 ± 0.26	5.54 ± 0.44	2.39 ± 0.19	0.65 ± 0.05	0.48 ± 0.04	0.37 ± 0.03
4	Methyl acetate	532	526	91	-	-	-	-	-	0.02 ± 0.00	-
5	Propyl alcohol	560	555	92	-	-	-	0.39 ± 0.03	0.12 ± 0.01	0.05 ± 0.00	-
6	Methylpropionaldehyde	572	554	92	-	-	-	0.56 ± 0.04	0.19 ± 0.02	-	0.07 ± 0.01
7	2,3-Butanedione	596	595	89	-	-	-	-	-	-	0.04 ± 0.00
8	2-Methylfuran	608	606	89	-	-	-	0.14 ± 0.01	-	-	-
9	Acetic acid	618	661	98	2.93 ± 0.23	4.20 ± 0.34	2.94 ± 0.24	1.26 ± 0.10	3.57 ± 0.29	3.68 ± 0.29	0.90 ± 0.07
10	Isobutyl alcohol	627	621	91	0.19 ± 0.02	-	-	-	0.17 ± 0.01	-	0.01 ± 0.00
11	Isovaleric aldehyde	653	656	96	-	0.11 ± 0.01	-	-	0.15 ± 0.01	0.04 ± 0.00	0.13 ± 0.01
12	(*E*)-2-Butenal	655	650	94	0.09 ± 0.01	-	0.12 ± 0.01	0.24 ± 0.02	0.04 ± 0.00	0.06 ± 0.01	-
13	Butyl alcohol	662	653	91	-	-	-	0.25 ± 0.02	-	0.07 ± 0.01	-
14	2-Methylbutyraldehyde	663	662	93	0.14 ± 0.01	0.08 ± 0.01	0.52 ± 0.04	0.02 ± 0.00	0.16 ± 0.01	-	0.06 ± 0.01
15	1-Penten-3-ol	684	691	95	-	-	-	-	0.22 ± 0.02	0.02 ± 0.00	0.03 ± 0.00
16	3-Pentenone	685	677	89	-	-	-	-	-	0.08 ± 0.01	-
17	Propyl methyl ketone	686	682	91	0.32 ± 0.03	0.04 ± 0.00	1.73 ± 0.14	2.38 ± 0.19	-	-	-
18	*n*-Heptane	700	700	94	-	0.94 ± 0.08	-	-	0.03 ± 0.00	-	-
19	2-Ethylfuran	701	702	92	-	-	-	-	-	0.63 ± 0.05	-
20	*n*-Pentanal	702	696	94	0.35 ± 0.03	0.03 ± 0.00	2.42 ± 0.19	2.42 ± 0.19	0.32 ± 0.03	0.15 ± 0.01	0.21 ± 0.02
21	Propanoic acid	710	698	98	0.03 ± 0.00	0.02 ± 0.00	0.04 ± 0.00	0.02 ± 0.00	0.01 ± 0.00	0.21 ± 0.02	0.01 ± 0.00
22	Acetoin	715	716	90	-	-	-	-	0.03 ± 0.00	-	0.01 ± 0.00
23	Isopentyl alcohol	733	729	89	0.10 ± 0.01	0.08 ± 0.01	0.09 ± 0.01	0.03 ± 0.00	0.60 ± 0.05	0.13 ± 0.01	0.04 ± 0.00
24	*sec*-Butylcarbinol	736	733	92	0.26 ± 0.02	0.17 ± 0.01	0.28 ± 0.02	0.12 ± 0.01	0.47 ± 0.04	0.19 ± 0.02	0.09 ± 0.01
25	(*E*)-2-Pentenal	752	751	95	0.03 ± 0.00	0.05 ± 0.00	0.49 ± 0.04	0.49 ± 0.04	0.17 ± 0.01	0.15 ± 0.01	0.01 ± 0.00
26	Pyridine	755	746	92	0.01 ± 0.00	-	-	-	-	0.01 ± 0.00	0.01 ± 0.00
27	Pentyl alcohol	764	763	96	1.10 ± 0.09	0.20 ± 0.02	1.07 ± 0.09	3.12 ± 0.25	0.64 ± 0.05	1.39 ± 0.11	0.14 ± 0.01
28	2,3-Butadienol	785	788	96	0.50 ± 0.04	0.09 ± 0.01	0.33 ± 0.03	0.31 ± 0.02	0.14 ± 0.01	0.19 ± 0.02	0.24 ± 0.02
29	Butyl methyl ketone	786	786	89	-	-	-	0.14 ± 0.01	-	-	-
30	Butanoic acid	788	818	95	-	0.24 ± 0.02	0.20 ± 0.02	0.17 ± 0.01	-	0.05 ± 0.00	-
31	α-Octene	790	788	91	-	-	0.79 ± 0.06	0.14 ± 0.01	-	-	-
32	Butadienol <2,3-> ISOMER	792	-	94	0.35 ± 0.03	-	0.66 ± 0.05	0.50 ± 0.04	0.28 ± 0.02	-	0.17 ± 0.01
33	*n*-Hexanal	801	801	95	2.85 ± 0.23	2.16 ± 0.17	10.22 ± 0.82	9.41 ± 0.75	2.07 ± 0.17	0.93 ± 0.07	1.67 ± 0.13
34	Oct-(4E)-ene	805	796	92	-	-	3.54 ± 0.28	0.76 ± 0.06	-	0.03 ± 0.00	-
35	(2E, 4E)-Octadiene	812	818	90	-	-	0.70 ± 0.06	0.39 ± 0.03	-	-	-
36	2-Methylpyrazine	827	820	90	0.06 ± 0.00	-	-	0.09 ± 0.01	-	-	0.01 ± 0.00
37	Isovaleric acid	845	842	94	0.01 ± 0.00	0.18 ± 0.01	0.07 ± 0.01	0.04 ± 0.00	0.19 ± 0.02	0.04 ± 0.00	0.01 ± 0.00
38	2-Methybutyric acid	851	881	89	0.02 ± 0.00	0.11 ± 0.01	0.02 ± 0.00	0.03 ± 0.00	0.04 ± 0.00	0.04 ± 0.00	0.01 ± 0.00
39	(*Z*)-2-Hexenal	853	842	90	0.05 ± 0.00	0.12 ± 0.01	0.48 ± 0.04	0.40 ± 0.03	0.26 ± 0.02	0.32 ± 0.03	0.03 ± 0.00
40	Ethyl benzene	859	857	95	0.02 ± 0.00	0.03 ± 0.00	0.07 ± 0.01	0.12 ± 0.01	0.03 ± 0.00	0.04 ± 0.00	0.01 ± 0.00
41	Octane, 2-methyl-	861	865	92	1.63 ± 0.13	-	-	1.78 ± 0.14	-	-	0.05 ± 0.00
42	(*E*)-2-Hexenol	865	864	93	-	-	0.02 ± 0.00	-	0.02 ± 0.00	0.09 ± 0.01	-

Table 1s (*continued*)

n.	Compound	LRI_{ex}	LRI_{lib}	Similarity %	Oils				Flours		Flour by-product
					Oil 1	Oil 2	Oil 3	Oil 4	Flour 1	Flour 2	
43	*n*-Hexanol	868	867	96	4.48 ± 0.36	2.77 ± 0.22	2.48 ± 0.20	15.18 ± 1.21	5.08 ± 0.41	8.31 ± 0.66	1.51 ± 0.12
44	*n*-Pentanoic acid	885	911	89	0.01 ± 0.00	0.01 ± 0.00	0.04 ± 0.00	0.02 ± 0.00	0.04 ± 0.00	0.59 ± 0.05	0.04 ± 0.00
45	2,6-Lutidine	887	878	89	0.01 ± 0.00	-	-	-	0.11 ± 0.01	-	0.01 ± 0.00
46	2-Butyl furan	890	890	91	-	-	-	0.42 ± 0.03	0.09 ± 0.01	-	-
47	Butyl methyl ketone	891	887	94	0.18 ± 0.01	0.46 ± 0.04	0.65 ± 0.05	1.17 ± 0.09	0.28 ± 0.02	1.13 ± 0.09	0.09 ± 0.01
48	o-Xylene	893	887	92	0.05 ± 0.00	0.07 ± 0.01	0.08 ± 0.01	0.13 ± 0.01	0.15 ± 0.01	0.30 ± 0.02	0.02 ± 0.00
49	*n*-Nonane	902	900	90	1.63 ± 0.13	0.03 ± 0.00	0.11 ± 0.01	1.07 ± 0.09	0.03 ± 0.00	0.03 ± 0.00	0.04 ± 0.00
50	2-Heptanol	904	913	94	-	-	-	-	-	0.58 ± 0.05	-
51	*n*-Heptanal	905	906	96	0.49 ± 0.04	0.31 ± 0.02	0.35 ± 0.03	1.05 ± 0.08	0.40 ± 0.03	0.01 ± 0.00	0.12 ± 0.01
52	Pentyloxirane	907	905	89	0.14 ± 0.01	-	0.09 ± 0.01	0.53 ± 0.04	-	-	-
53	2-Ethyl pyridine	909	902	89	-	-	-	-	0.03 ± 0.00	-	0.02 ± 0.00
54	γ-Butyrolactone	912	910	98	0.10 ± 0.01	0.25 ± 0.02	0.14 ± 0.01	0.16 ± 0.01	0.24 ± 0.02	0.32 ± 0.03	0.09 ± 0.01
55	Pentyl acetate	913	915	88	0.05 ± 0.00	0.04 ± 0.00	0.07 ± 0.01	0.15 ± 0.01	0.02 ± 0.00	0.11 ± 0.01	0.01 ± 0.00
56	2,5-Dimethyl pyrazine	915	912	88	0.06 ± 0.00	0.11 ± 0.01		0.05 ± 0.00	0.07 ± 0.01	-	0.01 ± 0.00
57	Hashishene	919	925	93	0.41 ± 0.03	0.36 ± 0.03	0.57 ± 0.05	0.37 ± 0.03	0.05 ± 0.00	0.04 ± 0.00	0.05 ± 0.00
58	Methyl hexanoate	923	922	94	0.10 ± 0.01	-	0.07 ± 0.01	0.24 ± 0.02	-	0.19 ± 0.02	0.02 ± 0.00
59	α-Thujene	926	927	93	0.20 ± 0.02	0.05 ± 0.00	0.19 ± 0.02	0.08 ± 0.01	0.03 ± 0.00	0.02 ± 0.00	0.03 ± 0.00
60	Hexyl formate	928	929	93		-	0.08 ± 0.01	0.45 ± 0.04	-	0.22 ± 0.02	-
61	α-Pinene	933	933	97	7.74 ± 0.62	3.38 ± 0.27	11.39 ± 0.91	3.78 ± 0.30	0.57 ± 0.05	0.24 ± 0.02	0.63 ± 0.05
62	α-Tujene	935	927	91	-	0.27 ± 0.02	-	-	0.18 ± 0.01	0.05 ± 0.00	0.04 ± 0.00
63	(*Z*)-3-Hepten-1-ol	948	960	90	-		-	-	-	0.11 ± 0.01	-
64	Camphene	950	953	93	0.41 ± 0.03	0.09 ± 0.01	0.75 ± 0.06	0.26 ± 0.02	0.11 ± 0.01	0.32 ± 0.03	0.08 ± 0.01
65	γ-Pentalactone	951	954	89	-	0.03 ± 0.00	-	-	0.04 ± 0.00	0.02 ± 0.00	-
66	Thuja-2,4(10)-diene	953	953	88	0.07 ± 0.01	0.09 ± 0.01	0.09 ± 0.01	0.13 ± 0.01	0.06 ± 0.01	0.05 ± 0.00	0.07 ± 0.01
67	(*E*)-2-Heptenal	957	956	92	0.05 ± 0.00	1.15 ± 0.09	0.41 ± 0.03	0.65 ± 0.05	0.64 ± 0.05	0.64 ± 0.05	0.08 ± 0.01
68	Benzene, 1-ethyl-3-methyl-	960	957	91	0.07 ± 0.01	0.08 ± 0.01	0.14 ± 0.01	0.18 ± 0.01	0.12 ± 0.01	0.09 ± 0.01	0.13 ± 0.01
69	Benzaldehyde	962	960	97	0.07 ± 0.01	0.18 ± 0.01	0.23 ± 0.02	0.13 ± 0.01	0.41 ± 0.03	0.38 ± 0.03	0.41 ± 0.03
70	(*Z*)-2-Heptenol	968	967	88	-	-	-	-	-	0.58 ± 0.05	-
71	3-Methyl-nonane	969	971	94	1.25 ± 0.10	-	0.05 ± 0.00	0.51 ± 0.04	0.09 ± 0.01	-	0.05 ± 0.00
72	*n*-Heptanol	970	970	89	-	0.11 ± 0.01	-	-	0.16 ± 0.01	0.38 ± 0.03	0.04 ± 0.00
73	Sabinene	973	976	89	0.59 ± 0.05	0.93 ± 0.07	0.41 ± 0.03	0.55 ± 0.04	0.29 ± 0.02	0.22 ± 0.02	0.16 ± 0.01
74	β-Pinene	978	978	94	3.23 ± 0.26	1.69 ± 0.14	5.04 ± 0.40	1.63 ± 0.13	0.63 ± 0.05	0.69 ± 0.06	0.28 ± 0.02
75	Octan-3-one	984	986	92	-	1.37 ± 0.11	0.35 ± 0.03	0.98 ± 0.08	0.68 ± 0.05	-	-
76	6-Methyl-5-hepten-2-one	985	986	94	0.31 ± 0.02	-	0.61 ± 0.05	-	-	-	0.08 ± 0.01
77	Purolan	989	993	90	-	-	-	-	-	-	-
78	β-Myrcene	992	994	93	14.72 ± 1.18	8.80 ± 0.70	10.22 ± 0.82	9.72 ± 0.78	4.58 ± 0.37	8.55 ± 0.68	1.54 ± 0.12
79	2-Pentyl furan	993	991	94	0.84 ± 0.07	0.78 ± 0.06	0.99 ± 0.08	0.75 ± 0.06	0.45 ± 0.04	1.08 ± 0.09	0.51 ± 0.04
80	Mesitylene	996	994	95	0.05 ± 0.00	-	0.34 ± 0.03	-	-	-	0.05 ± 0.00
81	2-Methyl-2-hepten-6-ol	994	995	89	0.10 ± 0.01	0.25 ± 0.02	0.12 ± 0.01	0.04 ± 0.00	-	-	0.19 ± 0.02
82	*n*-Decane	1000	1000	92	0.52 ± 0.04	0.57 ± 0.05	0.16 ± 0.01	0.13 ± 0.01	0.21 ± 0.02	0.58 ± 0.05	0.12 ± 0.01
83	3-Octanol	1002	999	91	-	0.21 ± 0.02	-	-	-	-	-
84	2-Octanol	1003	1004	97	-	-	-	-	-	1.75 ± 0.14	-

Table 1s (*continued*)

n.	Compound	LRI_{ex}	LRI_{lib}	Similarity %	Oils				Flours		Flour by-product
					Oil 1	Oil 2	Oil 3	Oil 4	Flour 1	Flour 2	
85	*n*-Hexanoic acid	1004	997	88	-	0.69 ± 0.06	-	0.34 ± 0.03	0.22 ± 0.02	1.69 ± 0.14	0.47 ± 0.04
86	*n*-Octanal	1005	1006	90	0.05 ± 0.00	1.60 ± 0.13	0.17 ± 0.01	0.52 ± 0.04	0.03 ± 0.00	0.22 ± 0.02	0.11 ± 0.01
87	α-Phellandrene	1007	1007	90	0.40 ± 0.03	0.75 ± 0.06	0.37 ± 0.03	0.54 ± 0.04	0.15 ± 0.01	2.08 ± 0.17	0.08 ± 0.01
88	2-δ-Carene	1010	1000	89	-	-	-	-	-	1.50 ± 0.12	-
89	3-δ-Carene	1011	1009	96	0.85 ± 0.07	0.61 ± 0.05	1.11 ± 0.09	0.72 ± 0.06	0.17 ± 0.01	-	0.08 ± 0.01
90	Hexyl acetate	1012	1012	97	0.06 ± 0.00	-	-	0.45 ± 0.04	-	2.52 ± 0.20	0.01 ± 0.00
91	(2*E*,4E)-Heptadienal	1013	1013	94	-	0.65 ± 0.05	0.38 ± 0.03	-	0.19 ± 0.02	-	0.01 ± 0.00
92	α-Terpinene	1017	1018	89	0.51 ± 0.04	0.37 ± 0.03	0.25 ± 0.02	0.22 ± 0.02	0.13 ± 0.01	0.16 ± 0.01	0.11 ± 0.01
93	Octylacetylene	1022	1021	95	-	-	-	-	0.38 ± 0.03	7.89 ± 0.63	0.07 ± 0.01
94	Pseudocumene	1023	1020	91	0.07 ± 0.01	0.10 ± 0.01	0.07 ± 0.01	0.09 ± 0.01	-	-	-
95	p-Cymene	1024	1025	95	1.51 ± 0.12	1.06 ± 0.08	1.20 ± 0.10	1.01 ± 0.08	0.62 ± 0.05	0.42 ± 0.03	0.55 ± 0.04
96	Limonene	1029	1030	96	8.84 ± 0.71	2.76 ± 0.22	2.94 ± 0.24	1.85 ± 0.15	1.85 ± 0.15	0.20 ± 0.02	1.70 ± 0.14
97	β-Phellandrene	1032	1031	88	-	0.14 ± 0.01	0.12 ± 0.01	0.25 ± 0.02	-	-	-
98	Eucalyptol	1033	1032	89	-	0.68 ± 0.05	1.08 ± 0.09	0.27 ± 0.02	0.59 ± 0.05	0.33 ± 0.03	0.27 ± 0.02
99	2-Ethyl hexanol	1034	1030	90	-	-	-	-	0.27 ± 0.02	0.06 ± 0.01	-
100	(*Z*)-β-Ocimene	1035	1036	95	1.37 ± 0.11	1.89 ± 0.15	0.63 ± 0.05	0.44 ± 0.04	0.14 ± 0.01	0.05 ± 0.00	0.18 ± 0.01
101	Oct-3-en-2-one	1038	1036	94	0.24 ± 0.02	0.65 ± 0.05	0.22 ± 0.02	0.82 ± 0.07	0.80 ± 0.06	3.92 ± 0.31	0.17 ± 0.01
102	Phenylacetaldehyde	1045	1045	92	-	0.05 ± 0.00	-	-	0.23 ± 0.02	0.19 ± 0.02	0.05 ± 0.00
103	(*E*-β-Ocimene	1046	1046	97	3.87 ± 0.31	4.50 ± 0.36	1.78 ± 0.14	1.56 ± 0.12	0.24 ± 0.02	0.54 ± 0.04	0.26 ± 0.02
104	γ-Hexalactone	1053	1060	89	0.16 ± 0.01	0.66 ± 0.05	0.22 ± 0.02	0.78 ± 0.06	0.16 ± 0.01	1.01 ± 0.08	0.09 ± 0.01
105	(*E*)-2-Octenal	1058	1058	91	0.15 ± 0.01	0.55 ± 0.04	-	1.50 ± 0.12	0.68 ± 0.05	0.46 ± 0.04	0.29 ± 0.02
106	γ-Terpinene	1060	1058	94	0.61 ± 0.05	-	0.40 ± 0.03	-	-	-	-
107	2-Methyl decane	1064	1062	90	0.67 ± 0.05	0.13 ± 0.01	0.02 ± 0.00	0.18 ± 0.01	0.01 ± 0.00	0.07 ± 0.01	0.13 ± 0.01
108	(*E*)-2-Octenol	1068	1067	94	-	0.21 ± 0.02	-	0.43 ± 0.03	0.25 ± 0.02	0.79 ± 0.06	-
109	(3E,5E)-Octadien-2-one	1070	1073	92	0.14 ± 0.01	1.09 ± 0.09	0.11 ± 0.01	0.54 ± 0.04	0.35 ± 0.03	0.62 ± 0.05	0.43 ± 0.03
110	(*Z*)-Sabinene hydrate	1071	1069	90	0.37 ± 0.03	0.24 ± 0.02	0.14 ± 0.01	-	0.69 ± 0.06	-	0.37 ± 0.03
111	*n*-Octanol	1072	1076	92	-	0.31 ± 0.02	-	0.53 ± 0.04	0.18 ± 0.01	0.17 ± 0.01	-
112	(5-Ethylcyclopent-1-enyl)methanol	1076	1073	90	0.05 ± 0.00	0.65 ± 0.05	0.14 ± 0.01	0.33 ± 0.03	0.13 ± 0.01	0.15 ± 0.01	0.08 ± 0.01
113	*n*-Heptanoic acid	1088	1116	91	0.10 ± 0.01	0.42 ± 0.03	0.06 ± 0.00	0.33 ± 0.03	0.06 ± 0.01	0.07 ± 0.01	0.01 ± 0.00
114	Terpinolene	1089	1086	96	3.98 ± 0.32	2.90 ± 0.23	1.67 ± 0.13	1.87 ± 0.15	0.93 ± 0.07	0.12 ± 0.01	0.78 ± 0.06
115	Fenchone	1090	1090	97	-	-	-	-	-	-	1.76 ± 0.14
116	p-Cymenene	1092	1093	95	3.23 ± 0.26	0.56 ± 0.04	0.58 ± 0.05	0.76 ± 0.06	0.95 ± 0.08	0.22 ± 0.02	0.62 ± 0.05
117	Linalool	1101	1101	91	0.82 ± 0.07	1.22 ± 0.10	0.28 ± 0.02	0.34 ± 0.03	0.92 ± 0.07	0.60 ± 0.05	1.04 ± 0.08
118	(*E*)-Sabinene hydrate	1103	1099	91	-	-	-	-	0.12 ± 0.01	-	0.08 ± 0.01
119	*n*-Nonanal	1105	1107	95	0.27 ± 0.02	0.60 ± 0.05	0.19 ± 0.02	0.74 ± 0.06	0.68 ± 0.05	0.35 ± 0.03	0.64 ± 0.05
120	Phenethyl alcohol	1111	1113	93	-	-	-	-	-	0.02 ± 0.00	-
121	1,3,8-p-Menthatriene	1113	1106	91	0.23 ± 0.02	0.10 ± 0.01	0.09 ± 0.01	0.23 ± 0.02	0.09 ± 0.01	0.06 ± 0.01	0.15 ± 0.01
122	Fenchyl alcohol	1121	1123	92	0.25 ± 0.02	0.08 ± 0.01	0.17 ± 0.01	0.12 ± 0.01	0.36 ± 0.03	0.17 ± 0.01	0.43 ± 0.03
123	Dihydrocitronellal	1126	1125	89	-	-	-	-	-	0.05 ± 0.00	-
124	endo-Fenchol	1127	1119	89	-	-	-	-	-	-	0.11 ± 0.01
125	(*E*)-Pinene hydrate	1128	1121	92	-	-	-	-	0.33 ± 0.03	0.09 ± 0.01	0.37 ± 0.03
126	(4E,6Z)-Allo-ocimene	1129	1128	91	0.51 ± 0.04	0.43 ± 0.03	0.31 ± 0.02	0.22 ± 0.02	-	-	-
127	2-Vinyl anisole	1130	1135	90	0.18 ± 0.01	-	0.07 ± 0.01	0.11 ± 0.01	-	-	-

Table 1s (*continued*)

n.	Compound	LRI_{ex}	LRI_{lib}	Similarity %	Oils				Flours		Flour by-product
					Oil 1	Oil 2	Oil 3	Oil 4	Flour 1	Flour 2	
128	2'-Methylacetophenone	1136	1136	89	0.10 ± 0.01	0.01 ± 0.00	0.05 ± 0.00	0.01 ± 0.00	0.04 ± 0.00	0.09 ± 0.01	0.08 ± 0.01
129	(*Z*)-p-Mentha-2,8-dien-1-ol	1138	1138	91	0.10 ± 0.01	0.44 ± 0.04	0.08 ± 0.01	0.08 ± 0.01	0.29 ± 0.02	0.40 ± 0.03	0.19 ± 0.02
130	Neo-allo-ocimene	1139	1139	92	0.36 ± 0.03	0.22 ± 0.02	0.19 ± 0.02	0.19 ± 0.02	0.01 ± 0.00	0.12 ± 0.01	-
131	(*E*)-Pinocarveol	1143	1141	95	0.33 ± 0.03	0.18 ± 0.01	0.05 ± 0.00	0.05 ± 0.00	0.30 ± 0.02	0.09 ± 0.01	0.85 ± 0.07
132	Camphor	1150	1149	88	0.29 ± 0.02	0.36 ± 0.03	0.05 ± 0.00	0.13 ± 0.01	0.22 ± 0.02	0.11 ± 0.01	1.00 ± 0.08
133	(2*E*, 6Z)-Nonadienal	1151	1155	88	0.09 ± 0.01	0.12 ± 0.01	0.05 ± 0.00	0.10 ± 0.01	0.01 ± 0.00	0.01 ± 0.00	0.19 ± 0.02
134	Tetrahydrolavandulyl	1155	1162	89	-	-	-	-	-	0.09 ± 0.01	0.08 ± 0.01
135	β-Pinene oxide	1156	1156	89	0.03 ± 0.00	0.31 ± 0.02	-	-	0.03 ± 0.00	-	-
136	Camphene hydrate	1157	1156	94	0.03 ± 0.00	0.22 ± 0.02	0.05 ± 0.00	0.08 ± 0.01	0.16 ± 0.01	0.20 ± 0.02	0.29 ± 0.02
137	(2*E*)-Nonenal	1160	1163	97	0.02 ± 0.00	0.29 ± 0.02	0.06 ± 0.00	0.13 ± 0.01	1.05 ± 0.08	0.25 ± 0.02	0.20 ± 0.02
138	(*E*)-Pinocamphone	1163	1160	89	0.07 ± 0.01	0.22 ± 0.02	0.01 ± 0.00	0.01 ± 0.00	0.22 ± 0.02	0.23 ± 0.02	0.16 ± 0.01
139	Pinocarvone	1164	1164	92	0.11 ± 0.01	0.23 ± 0.02	0.07 ± 0.01	0.09 ± 0.01	0.20 ± 0.02	0.05 ± 0.00	0.34 ± 0.03
140	Isomenthone	1167	1166	91	-	-	-	-	0.07 ± 0.01	-	-
141	(2*E*)-Nonenol	1169	1170	88	-	-	-	-	0.03 ± 0.00	-	-
142	Nonanol	1173	1176	90	0.03 ± 0.00	0.10 ± 0.01	0.06 ± 0.00	0.14 ± 0.01	0.16 ± 0.01	0.60 ± 0.05	0.18 ± 0.01
143	Borneol	1175	1173	91	0.13 ± 0.01	0.06 ± 0.00	0.07 ± 0.01	0.10 ± 0.01	0.40 ± 0.03	0.22 ± 0.02	0.70 ± 0.06
144	*n*-Octanoic acid	1176	1192	94	-	0.43 ± 0.03	-	-	-	-	-
145	(*Z*)-Pinocamphone	1178	1176	95	0.03 ± 0.00	0.22 ± 0.02	0.01 ± 0.00	0.59 ± 0.05	0.32 ± 0.03	0.03 ± 0.00	0.05 ± 0.00
146	1,8-menthadien-4-ol	1181	1174	91	0.58 ± 0.05	2.59 ± 0.21	0.26 ± 0.02	-	2.16 ± 0.17	0.19 ± 0.02	0.47 ± 0.04
147	Terpinen-4-ol	1183	1184	91	0.10 ± 0.01	0.37 ± 0.03	0.07 ± 0.01	0.06 ± 0.00	0.32 ± 0.03	0.01 ± 0.00	-
148	Heptyl vinyl ketone	1184	1179	92	-	-	-	0.16 ± 0.01	-	0.17 ± 0.01	-
149	p-Cymen-8-ol	1188	1189	95	0.16 ± 0.01	0.75 ± 0.06	0.06 ± 0.00	0.19 ± 0.02	0.54 ± 0.04	0.04 ± 0.00	0.55 ± 0.04
150	Octyl methyl ketone	1192	1196	92	-	-	-	-	0.08 ± 0.01	-	-
151	Dodec-1-ene	1193	1191	92	-	0.06 ± 0.00	0.03 ± 0.00	0.07 ± 0.01	-	0.60 ± 0.05	-
152	Hexyl butyrate	1195	1195	89	0.05 ± 0.00	0.06 ± 0.00	-	-	-	-	0.16 ± 0.01
153	α-Terpineol	1197	1195	94	0.11 ± 0.01	0.43 ± 0.03	0.07 ± 0.01	0.11 ± 0.01	0.39 ± 0.03	0.16 ± 0.01	0.45 ± 0.04
154	*n*-Dodecane	1199	1200	95	0.52 ± 0.04	0.27 ± 0.02	0.05 ± 0.00	0.11 ± 0.01	0.71 ± 0.06	1.92 ± 0.15	0.02 ± 0.00
155	1,6-Dihydrocarveol	1201	1203	91	-	0.10 ± 0.01	-	-	0.03 ± 0.00	-	-
156	2-Decanol	1203	1211	88	-	-	-	-	-	0.04 ± 0.00	-
157	(2Z)-Dodecene	1205	1205	88	-	-	-	-	0.01 ± 0.00	-	-
158	*n*-Decanal	1206	1208	94	0.06 ± 0.00	0.21 ± 0.02	0.08 ± 0.01	0.07 ± 0.01	0.12 ± 0.01	0.12 ± 0.01	0.28 ± 0.02
159	Verbenone	1210	1208	96	0.05 ± 0.00	0.14 ± 0.01	0.09 ± 0.01	0.05 ± 0.00	0.08 ± 0.01	0.20 ± 0.02	0.11 ± 0.01
160	(2*E*,4*E*)-Nonadienal	1217	1218	90	0.03 ± 0.00	0.11 ± 0.01	0.04 ± 0.00	0.06 ± 0.00	0.07 ± 0.01	0.22 ± 0.02	0.03 ± 0.00
161	(*E*)-Carveol	1222	1213	89	0.04 ± 0.00	0.06 ± 0.00	0.02 ± 0.00	0.03 ± 0.00	0.08 ± 0.01	0.06 ± 0.01	0.20 ± 0.02
162	2,4-Nonadien-1-ol	1225	1224	90	-	-	-	-	-	0.05 ± 0.00	-
163	(*Z*)-p-Mentha-1(7),8-dien-2-ol	1233	1230	91	-	-	-	-	-	0.05 ± 0.00	0.03 ± 0.00
164	endo-Fenchyl acetate	1234	1221	92	0.04 ± 0.00	0.11 ± 0.01	0.04 ± 0.00	0.04 ± 0.00	0.05 ± 0.00	0.24 ± 0.02	0.18 ± 0.01
165	Carvone	1246	1246	93	0.02 ± 0.00	0.12 ± 0.01	0.04 ± 0.00	0.03 ± 0.00	0.04 ± 0.00	0.17 ± 0.01	0.09 ± 0.01
166	γ-Octalactone	1253	1263	96	-	-	-	-	-	0.15 ± 0.01	-
167	(*Z*)-Anethole	1255	1253	90	0.04 ± 0.00	0.09 ± 0.01	0.08 ± 0.01	0.04 ± 0.00	0.03 ± 0.00	0.07 ± 0.01	0.21 ± 0.02
168	(2*E*)-Decenal	1263	1265	91	-	0.09 ± 0.01	-	-	0.02 ± 0.00	0.08 ± 0.01	0.03 ± 0.00
169	1,2,3,4-Tetrahydro-6-methyl-naphthalene	1268	1261	89	-	-	-	-	-	-	0.07 ± 0.01
170	*n*-Nonanoic acid	1270	1289	94	-	0.45 ± 0.04	-	-	0.08 ± 0.01	0.14 ± 0.01	0.01 ± 0.00

Table 1s (*continued*)

n.	Compound	LRI_{ex}	LRI_{lib}	Similarity %	Oils				Flours		Flour by-product
					Oil 1	Oil 2	Oil 3	Oil 4	Flour 1	Flour 2	
171	Dipentyl ketone	1271	1273	91	0.01 ± 0.00	-	-	0.06 ± 0.00	0.11 ± 0.01	0.48 ± 0.04	0.16 ± 0.01
172	2-Decen-1-ol	1272	1270	88	-	0.04 ± 0.00	-	-	0.01 ± 0.00	0.05 ± 0.00	-
173	Bornyl acetate	1286	1285	90	-	-	-	-	0.05 ± 0.00	0.08 ± 0.01	0.04 ± 0.00
174	Pentyl hexanoate	1287	1287	93	0.01 ± 0.00	-	-	0.12 ± 0.01	0.15 ± 0.01	0.50 ± 0.04	-
175	(*E*)-Anethole	1290	1288	98	1.20 ± 0.10	-	-	-	0.17 ± 0.01	0.01 ± 0.00	6.06 ± 0.48
176	*n*-Tridecane	1299	1300	95	-	2.01 ± 0.16	-	-	6.96 ± 0.56	2.08 ± 0.17	2.64 ± 0.21
177	*n*-Undecanal	1307	1309	91	-	0.02 ± 0.00	-	-	-	0.01 ± 0.00	0.01 ± 0.00
178	4-Vinyl guaiacol	1312	1309	89	-	0.04 ± 0.00	-	-	0.02 ± 0.00	0.38 ± 0.03	0.07 ± 0.01
179	Dihydro citronellol acetate	1324	1319	88	-	0.07 ± 0.01	-	-	0.05 ± 0.00	0.06 ± 0.01	0.01 ± 0.00
180	α-Cubebene	1350	1347	92	-	-	-	-	-	0.15 ± 0.01	0.09 ± 0.01
181	γ-Nonalactone	1361	1362	94	-	0.39 ± 0.03	-	0.05 ± 0.00	0.15 ± 0.01	3.43 ± 0.27	0.01 ± 0.00
182	Isoledene	1368	1372	91	-	-	-	-	-	-	0.04 ± 0.00
183	2-Butyl-2-octen-1-al	1372	1369	96	0.09 ± 0.01	0.14 ± 0.01	0.12 ± 0.01	0.08 ± 0.01	0.03 ± 0.00	1.25 ± 0.10	0.02 ± 0.00
184	α-Ylangene	1372	1371	90	0.10 ± 0.01	0.10 ± 0.01	0.08 ± 0.01	0.07 ± 0.01	0.48 ± 0.04	0.16 ± 0.01	0.71 ± 0.06
185	α-Copaene	1373	1375	89	0.04 ± 0.00	0.14 ± 0.01	0.04 ± 0.00	0.01 ± 0.00	0.16 ± 0.01	0.43 ± 0.03	0.32 ± 0.03
186	Hexyl hexanoate	1385	1390	92	0.02 ± 0.00	0.02 ± 0.00	0.06 ± 0.00	0.12 ± 0.01	0.01 ± 0.00	1.21 ± 0.10	0.15 ± 0.01
187	7-epi-Sesquithujene	1388	1387	92	0.03 ± 0.00	0.03 ± 0.00	-	-	0.02 ± 0.00	0.03 ± 0.00	0.08 ± 0.01
188	1-Tetradecene	1392	1392	90	-	-	-	-	0.03 ± 0.00	0.09 ± 0.01	0.01 ± 0.00
189	Sativene	1396	1394	91	-	-	-	-	-	0.04 ± 0.00	0.05 ± 0.00
190	*n*-Tetradecane	1400	1400	97	0.05 ± 0.00	0.05 ± 0.00	0.01 ± 0.00	0.02 ± 0.00	0.59 ± 0.05	1.09 ± 0.09	0.41 ± 0.03
191	Sesquithujene	1403	1410	89	-	0.04 ± 0.00	-	-	0.08 ± 0.01	0.17 ± 0.01	-
192	α-Funebrene	1405	1403	94	0.02 ± 0.00	-	-	-	-	-	0.16 ± 0.01
193	(*Z*)-Caryophyllene	1409	1415	88	0.15 ± 0.01	0.35 ± 0.03	0.15 ± 0.01	0.04 ± 0.00	0.65 ± 0.05	0.30 ± 0.02	1.18 ± 0.09
194	α-Gurjunene	1410	1406	92	0.08 ± 0.01	0.10 ± 0.01	0.04 ± 0.00	0.02 ± 0.00	0.15 ± 0.01	0.08 ± 0.01	0.07 ± 0.01
195	β-Maaliene	1412	1415	89	0.03 ± 0.00	-	-	-	-	-	0.23 ± 0.02
196	(*Z*)-α-Bergamotene	1415	1416	96	0.11 ± 0.01	0.24 ± 0.02	0.09 ± 0.01	0.03 ± 0.00	0.47 ± 0.04	0.07 ± 0.01	0.77 ± 0.06
197	α-Santalene	1423	1418	91	0.07 ± 0.01	0.18 ± 0.01	0.04 ± 0.00	0.02 ± 0.00	0.29 ± 0.02	0.03 ± 0.00	0.08 ± 0.01
198	(*E*)-Caryophyllene	1424	1424	96	3.36 ± 0.27	5.65 ± 0.45	4.02 ± 0.32	0.86 ± 0.07	12.29 ± 0.98	1.84 ± 0.15	16.02 ± 1.28
199	β-Ylangene	1433	1422	91	0.13 ± 0.01	0.26 ± 0.02	0.20 ± 0.02	0.04 ± 0.00	0.25 ± 0.02	0.02 ± 0.00	0.34 ± 0.03
200	(E)-α-Bergamotene	1435	1432	96	0.66 ± 0.05	1.27 ± 0.10	0.51 ± 0.04	0.17 ± 0.01	2.84 ± 0.23	0.75 ± 0.06	3.66 ± 0.29
201	α-Guaiene	1439	1438	91	0.02 ± 0.00	0.03 ± 0.00	0.02 ± 0.00	0.04 ± 0.00	0.09 ± 0.01	0.24 ± 0.02	0.20 ± 0.02
202	Aromadendrene	1443	1438	90	0.02 ± 0.00	0.03 ± 0.00	0.06 ± 0.00	-	0.05 ± 0.00	-	0.19 ± 0.02
203	Geranylacetone	1445	1442	92	-	-	-	-	-	0.02 ± 0.00	0.01 ± 0.00
204	Guaia-6,9-diene	1447	1441	91	0.02 ± 0.00	0.03 ± 0.00	0.01 ± 0.00	0.02 ± 0.00	0.06 ± 0.01	0.03 ± 0.00	0.23 ± 0.02
205	(*E*)-β-Farnesene	1454	1452	96	0.32 ± 0.03	0.66 ± 0.05	0.14 ± 0.01	0.04 ± 0.00	1.65 ± 0.13	0.11 ± 0.01	2.81 ± 0.23
206	Alloaromadendrene	1456	1458	91	-	-	-	-	-	-	0.07 ± 0.01
207	α-Humulene	1459	1454	97	1.13 ± 0.09	1.97 ± 0.16	1.16 ± 0.09	0.26 ± 0.02	4.88 ± 0.39	0.97 ± 0.08	7.27 ± 0.58
208	9-epi-(*E*)-Caryophyllene	1464	1464	88	0.33 ± 0.03	0.36 ± 0.03	0.36 ± 0.03	0.15 ± 0.01	0.98 ± 0.08	0.50 ± 0.04	1.88 ± 0.15
209	β-Acoradiene	1469	1467	89	-	0.03 ± 0.00	-	-	0.03 ± 0.00	0.01 ± 0.00	0.02 ± 0.00
210	Drima-7,9(11)-diene	1475	1473	92	0.04 ± 0.00	-	0.02 ± 0.00	-	0.04 ± 0.00	0.01 ± 0.00	0.12 ± 0.01
211	Germacrene D	1478	1480	92	-	0.11 ± 0.01	-	-	0.06 ± 0.01	0.03 ± 0.00	-
212	γ-Muurolene	1479	1478	89	-	-	-	-	0.07 ± 0.01	-	-
213	γ-Gurjunene	1480	1476	88	0.07 ± 0.01	-	0.04 ± 0.00	-	-	-	-

Table 1s (*continued*)

n.	Compound	LRI_{ex}	LRI_{lib}	Similarity %	Oils				Flours		Flour by-product
					Oil 1	Oil 2	Oil 3	Oil 4	Flour 1	Flour 2	
214	α-Curcumene	1482	1480	91	0.10 ± 0.01	0.16 ± 0.01	0.06 ± 0.00	0.03 ± 0.00	0.39 ± 0.03	0.12 ± 0.01	1.00 ± 0.08
215	γ-Amorphene	1483	1490	90	-	-	-	-	-	-	0.09 ± 0.01
216	Selina-4,11-diene	1484	1476	92	0.14 ± 0.01	0.28 ± 0.02	0.13 ± 0.01	0.03 ± 0.00	0.08 ± 0.01	0.13 ± 0.01	0.20 ± 0.02
217	Aristolochene	1489	1490	90	-	-	-	-	0.30 ± 0.02	0.01 ± 0.00	1.73 ± 0.14
218	(Z)-β-Guaiene	1490	1498	88	-	0.01 ± 0.00	-	-	-	0.07 ± 0.01	0.01 ± 0.00
219	β-Selinene	1493	1492	95	0.40 ± 0.03	0.48 ± 0.04	0.26 ± 0.02	0.08 ± 0.01	1.26 ± 0.10	0.21 ± 0.02	2.56 ± 0.20
220	Valencene	1496	1492	93	0.09 ± 0.01	0.13 ± 0.01	0.06 ± 0.00	0.02 ± 0.00	0.35 ± 0.03	0.61 ± 0.05	0.55 ± 0.04
221	α-Selinene	1501	1501	95	0.22 ± 0.02	0.44 ± 0.04	0.18 ± 0.01	0.05 ± 0.00	1.49 ± 0.12	0.88 ± 0.07	2.60 ± 0.21
222	(*E*,*E*)-α-Farnesene	1503	1504	89	-	0.06 ± 0.00	-	-	0.09 ± 0.01	-	0.01 ± 0.00
223	α-Bulnesene	1506	1505	90	-	-	-	-	-	-	0.09 ± 0.01
224	β-Himachalene	1512	1503	88	-	-	-	-	-	-	0.08 ± 0.01
225	β-Bisabolene	1513	1508	95	0.05 ± 0.00	0.09 ± 0.01	-	-	0.41 ± 0.03	0.02 ± 0.00	0.32 ± 0.03
226	γ-Cadinene	1516	1512	90	0.03 ± 0.00	0.04 ± 0.00	-	-	0.13 ± 0.01		0.13 ± 0.01
227	Pseudowiddrene	1518	1510	90	-	-	-	-	-	0.23 ± 0.02	0.14 ± 0.01
228	δ-Cadinene	1523	1518	91	-	-	-	-	0.12 ± 0.01	0.02 ± 0.00	0.06 ± 0.01
229	7-epi-α-Selinene	1525	1518	92	0.09 ± 0.01	0.14 ± 0.01	0.05 ± 0.00	0.02 ± 0.00	0.13 ± 0.01	0.04 ± 0.00	1.04 ± 0.08
230	2(4H)-Benzofuranone, 5,6,7,7a-tetrahydro-4,4,7a-trimethyl-	1534	1532	89	-	-	-	-	-	0.28 ± 0.02	-
231	γ-Cuprenene	1536	1530	89	0.04 ± 0.00	0.07 ± 0.01	0.02 ± 0.00	-	0.48 ± 0.04	-	-
232	Selina-4(15),7(11)-diene	1538	1540	89	0.10 ± 0.01	-	0.07 ± 0.01	0.02 ± 0.00	0.69 ± 0.06	0.13 ± 0.01	1.25 ± 0.10
233	Selina-3,7(11)-diene	1540	1546	91	0.08 ± 0.01	0.13 ± 0.01	0.05 ± 0.00	-	0.60 ± 0.05	0.12 ± 0.01	1.06 ± 0.08
234	4a,5-Dimethyl-3-(prop-1-en-2-yl)-1,2,3,4,4a,5,6,7-octahydronaphthalen-1-ol	1553	1552	91	-	-	-	-	-	0.06 ± 0.01	0.12 ± 0.01
235	Italicene epoxide	1554	1546	92	0.03 ± 0.00	0.06 ± 0.00	-	-	0.21 ± 0.02	0.05 ± 0.00	0.11 ± 0.01
236	(*E*)-Nerolidol	1562	1561	90		0.07 ± 0.01	-	-	0.09 ± 0.01	0.17 ± 0.01	0.38 ± 0.03
237	epi-Longipinanol	1564	1558	91	0.02 ± 0.00	-	-	-	0.04 ± 0.00	0.12 ± 0.01	-
238	Hexyl octanoate	1581	1583	90		-	-	-		0.14 ± 0.01	-
239	Caryophyllene oxide	1587	1587	95	0.11 ± 0.01	0.56 ± 0.04	0.10 ± 0.01	0.08 ± 0.01	1.03 ± 0.08	0.39 ± 0.03	1.61 ± 0.13
240	*n*-Hexadecane	1600	1600	91	-	-	-	-	-	0.22 ± 0.02	-
241	Humulene epoxide II	1615	1613	94	0.03 ± 0.00	0.16 ± 0.01	0.03 ± 0.00	0.02 ± 0.00	0.25 ± 0.02	0.09 ± 0.01	0.60 ± 0.05
242	Isopropyl laurate	1625	1625	90	-	-	-	-	-	-	0.08 ± 0.01
243	Junenol	1627	1619	88	-	-	-	-	0.01 ± 0.00	-	-
244	epi-γ-Eudesmol	1630	1624	89	-	-	-	-	-	-	0.20 ± 0.02
245	Allo-aromandendrene epoxide	1640	1644	89	-	0.04 ± 0.00	-	-	0.24 ± 0.02	0.05 ± 0.00	0.37 ± 0.03
246	Humulenol-II	1642	1650	90	0.04 ± 0.00	0.05 ± 0.00	0.02 ± 0.00	0.01 ± 0.00	0.04 ± 0.00	-	-
247	Caryophylla-4(12),8(13)-dien-5-beta-ol	1644	1642	90	0.05 ± 0.00	0.05 ± 0.00	0.04 ± 0.00	0.03 ± 0.00	0.66 ± 0.05	0.21 ± 0.02	0.81 ± 0.06
248	14-Hydroxy-9-epi-(E)-caryophyllene	1677	1671	89	0.09 ± 0.01	0.11 ± 0.01	0.06 ± 0.00	0.03 ± 0.00	0.82 ± 0.07	0.03 ± 0.00	0.06 ± 0.01
249	Germacra-4(15),5,10(14)-trien-1-alpha-ol	1689	1683	90	0.03 ± 0.00	-	-	-	0.25 ± 0.02	-	0.37 ± 0.03
250	*n*-Heptadecane	1700	1700	95	-	-	-	-	0.01 ± 0.00	0.05 ± 0.00	0.05 ± 0.00
251	*n*-Octadecane	1800	1800	92	-	-	-	-	-	0.02 ± 0.00	-
252	Phytone	1841	1841	92	-	0.02 ± 0.00	-	-	0.05 ± 0.00	0.07 ± 0.01	0.06 ± 0.01
253	Methyl hexadecanoate	1925	1925	94	-	-	-	-	0.01 ± 0.00	0.03 ± 0.00	-

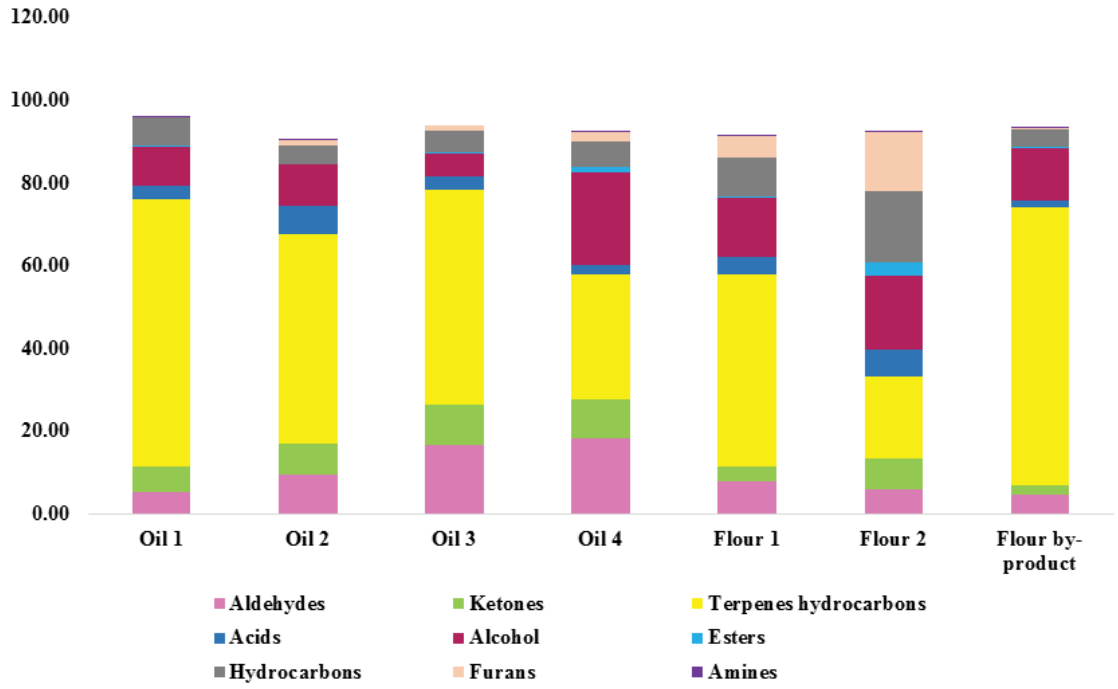

Figure 1s: Contribution of each group of volatile fraction in the hempseed products investigated

Table 2s: Analysis of unsaponificable fraction in hemp seed oils espressed in area % ± SD as measurement acquired by GC-FID analysis.

n.	Compound	LRI_{ex}	LRI_{lib}	Similarity %	Oils			
					Oil 1	Oil 2	Oil 3	Oil 4
1	Styrene	897	891	90	0.05 ± 0.00	0.02 ± 0.00	0.02 ± 0.00	0.05 ± 0.00
2	Diethylene glycol, 2TMS derivative	1243	1238	94	0.02 ± 0.00	0.01 ± 0.00	0.02 ± 0.00	0.01 ± 0.00
3	Glycerol, 3TMS derivative	1274	1284	92	0.14 ± 0.01	0.84 ± 0.05	0.01 ± 0.00	0.12 ± 0.01
4	Butanedioic acid, 2TMS derivative	1315	1321	91	0.01 ± 0.00	0.01 ± 0.00	0.01 ± 0.00	0.01 ± 0.00
5	(*E*)-Caryophyllene	1421	1424	89	0.08 ± 0.00	0.03 ± 0.00	0.09 ± 0.00	0.02 ± 0.00
6	(*E*)-α-Bergamotene	1434	1432	93	0.04 ± 0.00	0.01 ± 0.00	0.02 ± 0.00	0.01 ± 0.00
7	(*E*)-β-Farnesene	1454	1452	92	0.03 ± 0.00	0.04 ± 0.00	0.01 ± 0.00	0.01 ± 0.00
8	α-Humulene	1457	1454	91	0.03 ± 0.00	0.01 ± 0.00	0.04 ± 0.00	0.01 ± 0.00
9	9-epi-(*E*)-Caryophyllene	1462	1464	88	0.02 ± 0.00	0.02 ± 0.00	0.01 ± 0.00	0.02 ± 0.00
10	Selinene beta	1490	1492	89	0.02 ± 0.00	0.02 ± 0.00	0.03 ± 0.00	0.02 ± 0.00
11	BHT	1505	1503	96	0.85 ± 0.05	0.61 ± 0.04	0.42 ± 0.02	0.99 ± 0.06
12	Caryophyllene oxide	1585	1587	97	0.12 ± 0.01	0.03 ± 0.00	0.11 ± 0.00	0.06 ± 0.00
13	*n*-Hexadecene	1593	1593	92	0.02 ± 0.00	0.01 ± 0.00	0.01 ± 0.00	0.02 ± 0.00
14	Humulene epoxide II	1613	1613	90	0.04 ± 0.00	0.01 ± 0.00	0.03 ± 0.00	0.01 ± 0.00
15	Phytone	1843	1841	93	0.04 ± 0.00	0.01 ± 0.00	0.03 ± 0.00	0.03 ± 0.00
16	Methyl hexadecanoate	1927	1925	91	0.04 ± 0.00	0.01 ± 0.00	0.01 ± 0.00	0.02 ± 0.00
17	Palmitelaidic acid 1TMS	2022	2020	89	0.03 ± 0.00	0.02 ± 0.00	0.02 ± 0.00	0.02 ± 0.00
18	Palmitic Acid, TMS derivative	2045	2041	96	3.00 ± 0.18	4.16 ± 0.25	3.91 ± 0.23	2.56 ± 0.15
19	Methyl linoleate	2093	2090	91	0.21 ± 0.01	0.01 ± 0.00	0.02 ± 0.00	0.03 ± 0.00
20	Methyl oleate	2100	2098	91	0.15 ± 0.01	0.01 ± 0.00	0.01 ± 0.00	0.01 ± 0.00
21	1-Octadecanol, TMS derivative	2155	2152	93	0.05 ± 0.00	0.04 ± 0.00	0.03 ± 0.00	0.03 ± 0.00
22	Phytol, TMS derivative	2171	2180	96	2.63 ± 0.16	1.59 ± 0.10	1.88 ± 0.11	2.29 ± 0.14
23	Trimethylsilyl linoleate	2210	2205	97	27.30 ± 1.64	38.14 ± 2.29	35.81 ± 2.15	27.89 ± 1.67
24	Trimethylsilyl oleate	2216	2213	95	16.26 ± 0.98	21.98 ± 1.32	19.11 ± 1.15	14.25 ± 0.86
25	Vaccenic acid, trimethylsilyl ester	2221	2213	91	0.41 ± 0.02	0.64 ± 0.04	0.60 ± 0.04	0.37 ± 0.02
26	Trimethylsilyl stearate	2242	2238	97	1.40 ± 0.08	2.32 ± 0.14	1.96 ± 0.12	1.22 ± 0.07
27	13-Eicosenoic acid, (Z)-, TMS derivative	2412	2410	91	0.13 ± 0.01	0.24 ± 0.01	0.24 ± 0.01	0.08 ± 0.00
28	Arachidic acid, TMS derivative	2440	2447	92	0.30 ± 0.02	0.51 ± 0.03	0.53 ± 0.03	0.27 ± 0.02
29	*n*-Pentacosane	2500	2500	91	0.02 ± 0.00	0.01 ± 0.00	0.02 ± 0.00	0.02 ± 0.00
30	Docosanol, TMS derivative	2548	2542	90	0.05 ± 0.00	0.02 ± 0.00	0.02 ± 0.00	0.03 ± 0.00
31	Behenic acid, TMS derivative	2638	2644	96	0.14 ± 0.01	0.19 ± 0.01	0.21 ± 0.01	0.10 ± 0.01
32	*n*-Heptacosane	2700	2700	97	0.12 ± 0.01	0.04 ± 0.00	0.08 ± 0.00	0.07 ± 0.00
33	Tetracosanol, O-TMS	2744	2741	96	0.17 ± 0.01	0.05 ± 0.00	0.10 ± 0.01	0.10 ± 0.01
34	*n*-Octacosane	2800	2800	89	0.03 ± 0.00	0.02 ± 0.00	0.01 ± 0.00	0.02 ± 0.00
35	Squalene	2813	2810	94	0.36 ± 0.02	0.20 ± 0.01	0.18 ± 0.01	0.24 ± 0.01
36	Tetracosanoic acid, trimethylsilyl ester	2836	2838	89	0.05 ± 0.00	0.08 ± 0.00	0.05 ± 0.00	0.03 ± 0.00
37	1-Pentacosanol, TMS derivative	2842	2836	93	0.03 ± 0.00	0.01 ± 0.00	0.02 ± 0.00	0.01 ± 0.00
38	δ-Tocopherol, TMS derivative	2893	2900	92	0.06 ± 0.00	0.07 ± 0.00	0.05 ± 0.00	0.06 ± 0.00
39	*n*-Nonacosane	2900	2900	96	0.69 ± 0.04	0.21 ± 0.01	0.50 ± 0.03	0.30 ± 0.02

Table 2s (*continued*)

n.	Compound	LRI_{ex}	LRI_{lib}	Similarity %	Oils			
					Oil 1	Oil 2	Oil 3	Oil 4
40	1-Hexacosanol, TBDMS derivative	2942	2940	91	0.43 ± 0.03	0.13 ± 0.01	0.24 ± 0.01	0.18 ± 0.01
41	γ-Tocopherol, TMS derivative	2990	2989	90	0.02 ± 0.00	0.13 ± 0.01	0.12 ± 0.01	0.02 ± 0.00
42	*n*-Triacontane	3000	3000	92	0.04 ± 0.00	0.01 ± 0.00	0.02 ± 0.00	0.01 ± 0.00
43	*n*-Hentriacontane	3100	3100	92	0.18 ± 0.01	0.06 ± 0.00	0.13 ± 0.01	0.09 ± 0.01
44	24-methylene-cholesterol, trimethylsilyl ether	3234	3225	89	0.14 ± 0.01	0.12 ± 0.01	0.15 ± 0.01	0.18 ± 0.01
45	Campesterol, TMS derivative	3242	3233	91	4.70 ± 0.28	2.88 ± 0.17	3.57 ± 0.21	5.18 ± 0.31
46	Stigmasterol trimethylsilyl ether	3269	3274	95	1.04 ± 0.06	0.60 ± 0.04	0.76 ± 0.05	1.09 ± 0.07
47	Clerosterol, trimethylsilyl ether	3314	3308	91	0.22 ± 0.01	0.14 ± 0.01	0.08 ± 0.00	0.28 ± 0.02
48	β-Sitosterol trimethylsilyl ether	3335	3343	96	25.24 ± 1.51	15.06 ± 0.9	19.04 ± 1.14	27.68 ± 1.66
49	δ-5-avenasterol, trimethylsilyl ether	3347	3338	95	3.46 ± 0.21	2.51 ± 0.15	2.70± 0.16	4.35 ± 0.26
50	β-Amyrin trimethylsilyl ether	3352	3359	89	0.22 ± 0.01	0.09 ± 0.01	0.17 ± 0.01	0.14 ± 0.01
51	Parkeol, trimethylsilyl ether	3362	3370	91	0.68 ± 0.04	0.43 ± 0.03	0.42 ± 0.03	0.87 ± 0.05
52	Isofucosterol, O-TMS	3371	3363	89	0.36 ± 0.02	0.27 ± 0.02	0.20 ± 0.01	0.42 ± 0.03
53	δ-7-Stigmastenol, trimethylsilyl ether	3394	3401	90	0.27 ± 0.02	0.15 ± 0.01	0.20 ± 0.01	0.23 ± 0.01
54	Cycloartenol, trimethylsilyl ether	3400	3407	91	1.90 ± 0.11	1.10 ± 0.07	1.11 ± 0.07	1.89 ± 0.11
55	δ-7-avenasterol, trimethylsilyl ether	3421	3421	92	0.26 ± 0.02	0.19 ± 0.01	0.21 ± 0.01	0.31 ± 0.02
56	24-methylene-cycloartanol, trimethylsilyl ether	3457	3465	93	0.52 ± 0.03	0.29 ± 0.02	0.31 ± 0.02	0.51 ± 0.03
57	Citrostadienol, trimethylsilyl ether	3496	3492	91	0.82 ± 0.05	0.48 ± 0.03	0.60 ± 0.04	0.90 ± 0.05

Table 3s: Phenol and cannabinoid contents (mg/L ± standard deviation) in hemp seed-based food products.

n.	Compound	λ nm	$[M+H]^+$	$[M-H]^-$	Oils				Flours		Flour by-product
					Oil 1	Oil 2	Oil 3	Oil 4	Flour 1	Flour 2	
1+2	Citric acid + Malic acid	190	-	191/133	n.q.	n.q.	n.q.	-	n.q	n.q	n.q
3	Trigonelline	190	138	-	n.q.	n.q.	n.q.	-	n.q	n.q	n.q
4	Dihydroxybenzoic acid hexoside	206, 307	-	315	0.50 ± 0.02	-	-	-	42.93 ± 1.18	44.99 ± 1.47	21.26 ± 0.24
5	Hydroxytyrosol hexoside	217,307	-	315	1.16 ± 0.04	-	-	-	51.23 ± 3.93	8.42 ± 0.44	37.97 ± 1.42
6	Medioresinol	278, 307	-	387	n.q.	n.q.	n.q.	-	n.q	n.q	n.q
7	Benzoic acid	283	-	121	2.43 ± 0.05	-	3.69 ± 0.00	-	20.44 ± 0.08	24.30 ± 1.53	13.76 ± 1.24
8	N-trans-caffeoyloctopamine	216, 292, 315	-	314	-	-	-	-	13.30 ± 0.16	13.97 ± 0.85	13.67 ± 0.11
9	Luteolin hexoside	308	-	447	-	-	-	-	4.93 ± 0.04	5.87 ± 0.19	8.03 ± 0.22
10	Luteolin glucuronide	297, 337	463	461	-	-	-	-	9.29 ± 0.28	9.99 ± 0.09	12.46 ± 0.04
11	N-caffeoyltyramine dimer hydroxy derivate	218, 290, 325	615	613	-	-	-	-	6.08 ± 0.40	5.77 ± 0.08	20.25 ± 0.09
12	N-trans-caffeoyl tyramine	230, 295, 319	300	298	-	-	-	-	140.23 ± 2.25	149.04 ± 0.86	270.24 ± 8.62
13+14	Cannabisin A + Cannabisin B	253, 313, 332	-/597	593/595	-	-	-	-	97.49 ± 2.49	97.70 ± 3.15	159.65 ± 3.39
15	N-trans-coumaroyltyramine	221, 258, 288	284	282	-	-	-	-	13.15± 0.05	13.24 ± 0.08	23.64 ± 0.16
16	Cannabisin H isomer 1	285, 323	506	508	-	-	-	-	13.55 ± 0.03	14.03 ± 0.06	21.29 ± 0.21
17	Cannabisin H isomer 2	286, 323	506	508	-	-	-	-	9.59 ± 0.07	9.84 ± 0.15	12.83 ± 0.28
18	N-trans-Feruloyl tyramine	220, 290, 317	314	312	2.55 ± 0.00	2.48 ± 0.00	2.57 ± 0.00	-	29.83 ± 0.14	29.75 ± 0.12	53.05 ± 0.11
19	3-demethyl cannabisin G	280, 326	611	609	-	-	-	-	13.91 ± 0.05	14.64 ± 0.09	21.11 ± 0.04
20	Cannabisin C	249, 290, 324	611	609	-	-	-	-	27.64 ± 0.13	27.83 ± 0.24	44.89 ± 0.12
21	Cannabisin C isomer	254, 284, 316	611	609	-	-	-	-	12.74 ± 0.07	12.93 ± 0.07	19.11 ± 0.04

Table 3s (*continued*)

n.	Compound	λ nm	$[M+H]^+$	$[M-H]^-$	Oils				Flours		Flour by-product
					Oil 1	Oil 2	Oil 3	Oil 4	Flour 1	Flour 2	
22	N-caffeoyltyramine dimer	221, 254, 284, 317	611	609	-	-	-	-	14.64 ± 0.24	14.58 ± 0.31	23.25 ± 0.08
23	N-caffeoyltyramine/ N-caffeoyloctopanine dimer	270, 323, 391	613	611	-	-	-	-	5.78 ± 0.25	5.71 ± 0.25	7.86 ± 0.41
24	Cannabisin D	221,285, 335	625	623	-	-	-	-	15.85 ± 0.23	10.11 ± 0.18	28.09 ± 0.04
25	Cannabisin G	287, 321	625	623	-	-	-	-	21.14 ± 0.08	21.13 ± 0.27	35.00 ± 0.08
26	3'3-demethyl grossamide	285, 320	597	595	-	-	-	-	7.04 ± 0.02	7.48 ± 0.34	10.58 ± 0.04
27	Cannabisin E	220, 282, 312	-	641	-	-	-	-	14.91 ± 0.05	15.19 ± 0.08	24.17 ± 0.06
28	Grossamide K	223, 295	492	490	-	-	-	-	49.57 ± 0.23	53.12 ± 0.27	86.42 ± 0.19
29	Unnamed condensed tri-lignanamide 1	221, 294	894	892	-	-	-	-	23.40 ± 0.12	27.38 ± 1.87	40.01 ± 0.11
30	3,3'-demethyl-heliotropamide	220, 280, 320	-	595	-	-	-	-	21.10 ± 0.05	20.11 ± 2.05	34.83 ± 0.07
31	Cannabisin M	284, 316	597	595	-	-	-	-	28.59 ± 0.16	28.94 ± 0.14	45.52 ± 0.07
32	Cannabisin Q	284, 315	597	595	-	-	-	-	17.43 ± 0.03	17.40 ± 0.12	26.57 ± 0.36
33	Unnamed condensed tri-lignanamide 2	220, 282, 325	895	893	-	-	-	-	9.84 ± 0.18	9.84 ± 0.04	15.42 ± 0.40
34	N-caffeoyltyramine dimer 1	283, 320	597	595	-	-	-	-	16.24 ± 0.25	16.39 ± 0.06	25.41 ± 0.34
35	N-caffeoyltyramine dimer 2	220, 274, 320	593	591	-	-	-	-	9.64 ± 0.03	9.72 ± 0.04	13.31 ± 0.35
36	Isocannabisin N	282, 322	611	609	-	-	-	-	10.74 ± 0.03	10.62 ± 0.07	24.13 ± 0.08
37	Cannabisin F	288, 319	625	623	-	-	-	-	28.99 ± 0.12	28.09 ± 0.14	58.90 ± 0.16
38	Grossamide	221, 287, 317	625	623	-	-	-	-	27.57 ± 0.12	26.88 ± 0.14	51.50 ± 0.10
39	Cannabisin O	222, 288, 314	934	936	-	-	-	-	22.28 ±0.09	22.75 ± 0.13	27.75 ± 0.05

Table 3s (*continued*)

n.	Compound	λ nm	$[M+H]^+$	$[M-H]^-$	Oils				Flours		Flour by-product
					Oil 1	Oil 2	Oil 3	Oil 4	Flour 1	Flour 2	
40	Unnamed lignanamide	222, 283, 315	-	589	-	-	-	-	11.68 ± 0.20	12.17 ± 0.17	13.23 ± 0.32
41	Dihydrocannabinol	277	313	311	1.27 ± 0.01	1.51 ± 0.03	1.10 ± 0.01	1.03 ± 0.01	1.03 ± 0.01	1.07 ± 0.01	-
	Total phenol				**7.91**	**3.99**	**7.35**	**1.03**	**862.75**	**839.92**	**1345.16**
42	Cannabielsoic acid A (CBEA-A)	222, 292	375	373	21.74 ± 0.11	18.07 ± 0.25	12.19 ± 0.15	4.92 ± 0.24	8.43 ± 0.07	9.60 ± 0.20	3.66 ± 0.08
43	Cannabielsoic acid B (CBEA-B)	221, 271	375	373	12.08 ± 0.34	5.71 ± 0.07	4.78 ± 0.27	2.66 ± 0.05	7.02 ± 0.08	7.51 ± 0.03	-
44	Cannabitriolic acid (CBTA)	221, 277	-	389	1.14 ± 0.01	3.04 ± 0.06	1.65 ± 0.07	1.33 ± 0.03	-	-	-
45	Cannabidivarinic acid (CBDVA)	221, 303	331	329	35.58 ± 0.23	83.23 ± 0.54	66.02 ± 0.22	35.86 ± 0.12	160.15 ± 1.16	135.09 ± 0.98	29.15 ± 0.13
46	Cannabidivarin (CBDV)	225, 275	287	-	24.40 ± 0.11	68.05 ± 0.52	56.67 ± 0.27	30.79 ± 0.22	130.01 ± 0.93	112.05 ± 1.08	25.81 ± 0.05
47	Cannabielsoic acid (CBEA)	221, 272	375	373	27.02 ± 0.28	125.45 ± 0.13	55.74 ± 0.44	25.63 ± 0.70	110.42 ± 0.61	111.58 ± 0.62	7.50 ± 0.05
48	6,7-Epoxy-CBGA	221, 276	-	375	1.39 ± 0.02	21.25 ± 0.34	3.54 ± 0.09	2.80 ± 0.12	3.08 ± 0.02	2.71 ± 0.11	1.36 ± 0.01
49	CBDA-C4	221, 279	345	343	2.14 ± 0.03	2.55 ± 0.04	2.46 ± 0.06	2.01 ± 0.02	4.38 ± 0.02	3.98 ± 0.10	2.26 ± 0.04
50	Cannabidiolic acid (CBDA)	223, 268, 307	359	357	124.75 ± 1.63	37.60 ± 0.55	10.89 ± 0.85	21.54 ± 0.02	43.18 ± 0.32	45.59 ± 0.43	20.36 ± 0.06
51	Cannabidiol (CBD)	214, 274	315	-	22.14 ± 0.13	4.72 ± 0.06	33.03 ± 0.09	6.05 ± 0.19	18.13 ± 0.16	16.84 ± 0.15	4.81 ± 0.05
52	Cannabigerolic acid (CBGA)	221, 304	-	359	2.60 ± 0.12	7.54 ± 0.21	4.88 ± 0.04	1.54 ± 0.02	2.39 ± 0.05	2.94 ± 0.06	1.68 ± 0.05
	Total cannabinoid				**274.99**	**377.20**	**348.86**	**135.14**	**488.21**	**448.96**	**96.59**