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**Comprehensive qualitative and quantitative analysis of
flavonoids in dandelion (*Taraxacum officinale*) flowers and
food products**

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1 **Comprehensive qualitative and quantitative analysis**
2 **of flavonoids in dandelion (*Taraxacum officinale*)**
3 **flowers and food products**

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ABSTRACT

Taraxacum officinale, a cosmopolitan perennial, is widely used as edible, forage, honey and medicinal plant. Unsurprisingly, detailed LC-QTOF-MS profiling of flower extract revealed the presence of several flavonoid signals most likely lacking literature confirmation. Targeted isolation, including DoE planning based extraction, led to the isolation of 11 flavonoids, of which three were new (**16**, **18** and **33**). Their structures were established by the use of NMR technique. Both biflavones (**16** and **18**) were structured from two luteolin molecules, linked by a C-C bond through IB (C-6') and IIA (C-6'' or C-8'') rings. Novel flavonolignan (**33**) composed of tricin and unusual, containing a carboxyl function, lignan moiety. The contents of 28 flavonoids (glycosides, aglycones, biflavones and flavonolignans) was determined, based on LC-MS/MS method, in raw flowers and dandelion syrups and tincture. Multivariate analyses showed the separation of spring and autumn flowers and a high diversity of food products, and helped identify metabolites correlated with the samples.

KEYWORDS: dandelion, flavonoids, biflavones, flavonolignans, NMR, UHPLC-MS/MS

INTRODUCTION

The genus *Taraxacum*, commonly known as dandelion, is one of the better-known and commonly used by humans representatives of Asteraceae plant family. *Taraxacum officinale* F.H.Wigg. (common dandelion) is a yellow-flowering herbaceous plant native to temperate climates, usually spreading in pastures and wasteland.¹ Over the centuries, common dandelion and other local *Taraxacum* species (e.g. *T. mongolicum* and *T. coreanum*) have been used in the European, Chinese and North American folk medicines as a remedy in the treatment of various ailments, such as liver and digestive disorders, diabetes, skin inflammations, arthritic and rheumatic diseases.² Nowadays, the whole plant (including root, leaves, and flowers) has “generally recognized as safe” status approved by U.S. Food and Drug Administration, and is commonly processed into different edible products – salads, teas, tinctures, syrups, jellies, cakes, wines, honeys and coffee substitutes.³ In addition, *T. officinale* herb is a Pharmacopeial material that is approved for use as an herbal supplement, in the form of tincture and tea preparations, by European Medicines Agency.^{4,5}

Taraxacum herb extracts (water and alcoholic) have been shown to exert a wide range of in vitro and in vivo biological actions, such as antioxidant, anti-inflammatory, anticarcinogenic, anti-hyperglycemic, anti-thrombotic, antimicrobial, antiviral, and hepatoprotective, in a number of scientific studies.^{5–11} Polyphenols, mainly hydroxycinnamic acids and flavonoids, as well as terpenoids and sesquiterpene lactones have been found as major bioactive metabolites of dandelion plant material.^{12,13} Albeit, despite the generally well-recognized chemical profile of dandelion herb and flowers, new metabolites (or metabolites not yet reported in the taxon) are occasionally documented, as exemplified by the recently characterized flavonoids of *T. mongolicum* or *T. officinale* fruits.^{14,15} In addition, despite the fairly widespread use

of dandelion herb, the amount of detailed research devoted to the quantitative content of bioactive metabolites (beyond colorimetric measurement of total polyphenols and flavonoids) seems to be negligible and insufficient.^{15–20} It should be noted that the vast majority of quantitative works on dandelion herb flavonoids include only a few major components (such as quercetin and luteolin and their glycosides) in a single analysis.^{16–20}

The work is phytochemically exploratory, with several specific objectives, including detailed HR-QTOF-MS qualitative analysis of *Taraxaci Flos*, targeted isolation and identification of flavonoid oligomers and flavonolignans, and measurement of the quantitative content of nearly 30 flavonoid compounds in raw plant material (spring and autumn flowers) and food products based on dandelion flowers (syrups and tincture).

MATERIALS AND METHODS

Plant Material. Dandelion flowers were collected from a natural site in southeastern Poland (Kazimierski Landscape Park, 51.378605 N, 22.072647 E) in 2021 (October), 2022 (April and October) and 2023 (April). Plant material was preserved by freeze-drying, then was finely ground with electric mill and sieved (1 mm), and finally stored at 4 °C until use. A voucher specimens are deposited in our laboratory. In addition, three different commercially available dandelion flower-based syrups (syrup I (48% flower decoction), II (60% flower decoction) and III (40% flower decoction), purchased on the Polish market in May 2023) and a handmade ethanol flower tincture (formulation according to the medicinal plant textbooks^{21–23}) were used in the study. Detailed information on syrup compositions and a description of the tincture preparation are given in the Supplementary Materials (Descriptions S1-S2).

Instruments and Materials. ¹H- and ¹³C-NMR spectra (including one- and two-dimensional) were recorded on a Bruker Avance III HD Ascend-500 spectrometer (Bruker BioSpin, Rheinstetten, Germany), equipped with 3 mm broad-band inverse (BBI) probe. HRESIMS spectra, exact masses of compounds, MS/MS fragmentation patterns, and molecular formulas were obtained using a Bruker Impact II HD (Bruker, Billerica, MA, USA) quadrupole time-of-flight (Q-TOF) mass spectrometer coupled with a Thermo Scientific Ultimate 3000 RS chromatographic system. HPLC separations towards extract fractionation and compounds isolation were performed with a Dionex (Sunnyvale, CA, USA) system equipped with a photodiode array detector PDA-100 and fraction collector FC 204 (Gilson, Middleton, WI, USA) using a Sephadex LH-20 (Merck, Warsaw, Poland) column (80 × 2.8 cm i.d.) and reversed-phase (RP) HPLC columns (Atlantis T3, 250 × 19 mm, 10 µm, and 250 × 10 mm, 5 µm, Waters, Milford, MA, USA; and Cosmosil πNAP, 250 × 10 mm, 5 µm, Nacalai Tesque Inc., Kyoto,

Japan). Quantitative UHPLC analyses were performed using a Waters ACQUITY chromatographic system equipped with PDA and Xevo TQ-S micro Triple Quadrupole (TQD) mass detector and RP column (BEH C18, 100 × 2.1 mm, 1.7 μm, Waters). Plant material, extracts and isolated compounds were dried using Gamma 2–16 LSC freeze dryer (Christ, Osterode am Harz, Germany).

Extraction and Isolation of Flavonoids. The powdered plant material (750 g) was defatted with *n*-hexane (6 L) over 10 h using Soxlet apparatus. The residue (600 g) was twice extracted with 90% methanol (MeOH) (2 × 6 L) at 65 °C and 180 rpm for 55 min (Innova 44R shaker, Eppendorf, Hamburg, Germany), based on the optimization results of Design of Experiment (DoE) design (Description S3, Tables S1–S4, Fig. S1–S2). The raw extract (E1) was filtered and concentrated under reduced pressure, followed by liquid-liquid extraction with ethyl acetate (3 × 1 L). After evaporation of the solvent, the residue was suspended in 50% *t*-BuOH (v/v) and freeze-dried, yielding 10.4 g of flavonoid extract (E2). The E2 was further fractionated on a Sephadex LH-20 (Merck) column (100 × 2.8 cm), which was eluted with 95% MeOH (v/v) at a flow rate of 2.4 mL/min. The separation was under the control of HPLC-UV_{350nm} detection and additionally monitored by LC-MS analyses. The seven pooled fractions (A–G) were collected, concentrated, and freeze-dried to give 1.23 g of fraction A, 0.95 g of fraction B, 1.21 g of fraction C, 483 mg of fraction D, 51 mg of fraction E, 49 mg of fraction F, and 31 mg of fraction G. Fractions promising with new metabolites, including A, and D–G, were further separated to individual compounds using reverse-phase HPLC (Dionex HPLC-PDA system). Fraction A was chromatographed in 3 steps using Atlantis T3 (250 × 19 mm, Waters; gradient 20–55% of acetonitrile (MeCN), flow rate 7 mL/min, temperature 30 °C) and Cosmosil πNAP (Nacalai Tesque Inc.; gradient 25–30% of MeCN, flow rate 3.5 mL/min, temperature 30 °C; and gradient 60–64% of

MeOH, flow rate 3 mL/min, temperature 25 °C) columns. Fractions D-G were purified using Atlantis T3 (250 × 10 mm, Waters; gradient 26–29% of MeCN, flow rate 3 mL/min, temperature 25 °C) column. Aforementioned chromatographic methods resulted in 11 pure flavonoid metabolites, including compound **16** (17 mg) was recovered from fraction E, compound **18** (14 mg) from fraction G, and compound **33** (9 mg) from fraction A.

Liquid Chromatography High-Resolution Mass Spectrometric Analysis. HR-MS/MS data were obtained using a Bruker Impact II HD Q-TOF mass spectrometer coupled with a Ultimate 3000 RS (Thermo Scientific) UHPLC system. The MS operated in electrospray ionization and both polarity modes, with the following settings: mass scan range 50–1400 *m/z*; capillary voltage 4.0 kV (ESI+) or 3.0 kV (ESI–); nebulizer and drying gas (N₂) 2.0 bar and 10 L/min, respectively; dry gas temperature 220 °C. The MS/MS spectra were registered using a collision energy (CE) of 50 eV with stepping between 50–125% of CE. The acquired data were calibrated internally with sodium formate (10 mM solution in 50% 2-propanol) which was injected to the ion source before the sample analysis. Data were processed using DataAnalysis 4.4 software (Bruker). Chromatographic separation was carried out on an HSS C18 column (100 × 2.1 mm, 1.7 μm, Waters) equipped with a pre-column. A 28 min linear gradient (10→35%) of acetonitrile–water (both acidified with 0.1% formic acid), with a flow rate of 0.4 mL/min, was applied. The column was held at 45 °C. Injection volume was 2 μL.

NMR Measurements. 1D and 2D NMR spectra were recorded on Bruker Avance III HD Ascend-500 spectrometer (Bruker BioSpin, Rheinstetten, Germany) equipped with 5 mm broad-band inverse (BBI) probe. The ¹H and ¹³C NMR spectra (at 500 and 125 MHz, respectively) were measured in DMSO-*d*₆ at 30 °C. Chemical shifts are given on

the δ scale. Data processing was performed with the Topspin software (version 3.5pl2, Bruker BioSpin).

Quantitative UHPLC Analysis of Flavonoids. For plant material (autumn 2021-spring 2023), a 250 mg of ground flowers were extracted twice (2×4 mL) using 80% MeOH in two steps: I – thermo-shaking (20 min, 60 °C, 800 rpm; Thermomixer, Eppendorf), and II – ultrasonic bath (10 min, 40 °C, 35 kHz). After centrifugation (10 min, 5 °C, $12,000 \times g$), the supernatants were combined and dried in a thermo-block (40 °C) under N_2 and re-dissolved in 2 mL of 80% MeOH. Samples of syrups (4 mL) and tincture (15 mL after concentration to 3 mL) were purified using SPE technique (Oasis HLB 500 mg column (Waters)). Polar components were eluted with 2% MeOH, while flavonoids using 95% MeOH (containing 1% ammonia). Purified samples were dried similarly to the extracts and re-dissolved in 1 mL of 80% MeOH. All samples were stored at -20 °C until analysis. Five independent extracts were prepared for ground flowers and four purified samples for syrups and tincture. Prior to analyses, the samples were appropriately diluted with 80% MeOH and filtered (0.22 μ m).

Quantitative UHPLC-MS/MS (Waters) measurements were based on multiple reaction monitoring (MRM) detection mode and external calibration for the 16 reference flavonoid substances. Detailed information regarding detection: capillary voltage, precursor→fragment ions' transitions, and collision energy is shown in Table S6; while calibration parameters are placed in Table S7. The general chromatographic separation conditions were as follows: column BEH C18 (100 $\times$ 2.1 mm, 1.7 μ m, Waters), column temperature 45 °C, a 14 min linear gradient (15→35%) of acetonitrile–water (both acidified with 0.1% formic acid), flow rate of 0.4 mL/min, and injection volume 2 μ L. The MS detector was operated in positive ion mode with the following settings: capillary voltage (3.1 kV), source and desolvation gas temperatures (150 °C

and 450 °C, respectively), and cone and desolvation gas flow rates (100 and 900 L/h, respectively). Data acquisition and processing were performed using Waters MassLynx 4.1 software.

Due to the co-elution and high similarity of compounds **18** and **19**, their sum content was calculated using the standard curve for compound **19**; and due to the lack of analytical standards available for most of the detected flavonolignans (compounds **29-30**, **32**, **34-43**) and their common feature (tricin as a flavone aglycone), their content was given based on the calibration curve for compound **24**. Quantitative results in flowers are given in mg/g (or µg/g) of dry material, and in syrups and tincture in µg/mL (or ng/mL).

Chemical Data of Compounds 16, 18 and 33. Flavonoid **16** (taraxabiluteolin A): amorphous yellow solid; UV (MeOH) $\lambda_{\max}$ 254.7, 344.7 nm; C₃₀H₁₈O₁₂; HR-QTOF-MS [M+H]⁺ *m/z* 571.0881 (calcd. for C₃₀H₁₉O₁₂, error -1.8 ppm); MS/MS *m/z* 419.0778, 153.0195, 445.0560; for ¹H and ¹³C NMR data see Table 2.

Flavonoid **18** (taraxabiluteolin B): amorphous yellow solid; UV (MeOH) $\lambda_{\max}$ 256.7, 344.7 nm; C₃₀H₁₈O₁₂; HR-QTOF-MS [M+H]⁺ *m/z* 571.0885 (calcd. for C₃₀H₁₉O₁₂, error -2.5 ppm); MS/MS *m/z* 419.0778, 445.0562; for ¹H and ¹³C NMR data see Table 2.

Flavonoid **33** (taraxalignan A): amorphous yellow solid; UV (MeOH) $\lambda_{\max}$ 270.7, 322.7 nm; C₂₇H₂₂O₁₁; HR-QTOF-MS [M+H]⁺ *m/z* 525.1399 (calcd. for C₂₇H₂₅O₁₁, error -1.5 ppm); MS/MS *m/z* 331.0826, 284.0693, 255.0664; for ¹H and ¹³C NMR data see Table 2.

RESULTS AND DISCUSSION

Phytochemical HR-MS Analysis of Dandelion Flower Flavonoids. Detailed phytochemical profiling of the dandelion flavonoid extract was carried out using ESI-QTOF-MS analysis, in-house dandelion metabolite database, online plant metabolite databases (such as COCONUT, LOTUS and PubChem) and literature. Flavonoids predominated among the more than 40 compounds described; in addition, several hydroxycinnamic acids, taraxinic acid glucoside and a phenolic spermine derivative were found (Table 1 and Fig. 1). Among the flavonoids already described in the genus *Taraxacum* were luteolin, chrysoeriol, tricin, apigenin, apometzgerin, three luteolin glucosides, calquiquelignan D and E, and salcolin A and B (Table S5). Preliminary identification of more than 20 other flavonoid signals (with UV absorption spectra typical of these compounds) showed the presence of 9 flavone oligomers (di- and trimers; compounds 15-16, 18-19 and 10-12, 17, 23) and 14 different lignan derivatives of tricin (compounds 29-30, 32-43). Due to identification difficulties and residual literature data on the occurrence of such metabolites in *Taraxacum* (Table S5),^{15,24} a decision was made to perform targeted isolation and further identification based on spectroscopic data.

Targeted Isolation and Structure Elucidation of Flavonoids. In order to maximize the yield of signals belonging to the flavonoids of interest (flavone oligomers and flavonolignans), DoE planning was used to perform flower extraction. The optimization was a two-step process and included the influence of key parameters, such as various solvents (MeOH, acetone and ethyl acetate/MeOH), concentrations (50–90% v/v), time (20–60 min), and temperature (40–65 °C) on the extraction yield and intensity levels of six LC-MS flavonoid signals (flavonolignans (m/z 497, 525 and 527) and biflavone (m/z 571)) (Table S1 and S3). According to Fig. S1, both parameters tested in step 1

214 had a significant impact on the recorded responses, except for the LC-MS m/z 525
215 signal, and the largest effects were obtained for the type of extraction solvent. In step
216 2, significant effects were observed mainly for extraction time on the yield and levels
217 of LC-MS signals m/z 571 and 527 (Fig. S2). Finally, according to response
218 optimization models (Table S2 and S4, Description S3), the maximum responses were
219 provided by the following extraction conditions: solvent 90% MeOH, time 53 min and
220 temperature 65 °C; and with their application, a preparative scale extraction was
221 carried out. Subsequently, the flavonoid extract E2 was separated from the crude
222 extract E1, by liquid-liquid extraction (water-ethyl acetate), and was the base material
223 for targeted isolation of selected flavonoid signals. Fractionation and isolation were
224 carried out using chromatographic techniques, including Sephadex LH-20 molecular
225 sieving (Fig. S3-S4) and various reversed-phase (C-18) HPLC methods. Thus, the
226 multistep purification process led to the isolation of 11 compounds (15-16, 18-19, 24,
227 26-28, 33, 40-41; Table 1), and their structures (Fig. 2) were determined with the aid
228 of NMR technique and literature data. Unfortunately, many minor metabolites,
229 including trimeric flavones and flavonolignans, could not be isolated in sufficient
230 quantity to allow their identification. Eight of the 11 isolates turned out to be already
231 described plant flavonoids, five of which have annotations of occurrence in the genus
232 *Taraxacum* (compounds 15, 24, 26-28; Table 1), while dicranolomin, 7"-
233 methoxycalquiquelignan D and E are reported for the first time in this taxon. On the
234 other hand, three compounds (**16**, **18** and **33**, Table 1) have not been reported to date.
235 Compound **16** was obtained as yellow amorphous powder. Its negative HRESIMS
236 spectrum showed deprotonated molecule at m/z 569.0723 $[M-H]^-$, corresponding to the
237 molecular formula of $C_{30}H_{17}O_{12}$. In the MS/MS spectrum the two fragment ions were
238 observed: m/z 417.0556 and 283.0208 (Table S5). The UV spectrum exhibited maxima

at 255 and 354 nm, which is the typical characteristic of flavonoid derivatives. The ^{13}C NMR spectrum showed 30 signals, including two conjugated ketonic carbons (δ_{C} 181.1 and 181.8), and 28 aromatic/olefinic carbons (δ_{C} 93.2–165.9) (Table 2). Moreover, the presence of ten aromatic methine groups was indicated by the ^1H -NMR and HSQC spectral data. The above information fits two flavone aglycone molecules linked together; and matching of 1D NMR signals, with the aid of 2D NMR data, showed that we were dealing with two luteolin molecules. Connection location between them (C-6'–C-8'') was revealed by an HMBC spectrum, which showed the H→C correlations between H-5' (δ_{H} 6.82, s) and C8'' (δ_{C} 107.1), and H-6'' (δ_{H} 6.31, s) and C-6' (δ_{C} 122.9) (Fig. 3); as well as by the exclusive presence of singlet methine protons in ring IB (H-2' and H-5') and IIA (H-6''). Thus, the structure of **16** was elucidated as the new 6',8''-biluteolin, and the proposed trivial name is taraxabiluteolin A.

Compound **18** was obtained as yellow amorphous powder, and showed great similarity to **16** regarding HRESIMS (m/z 569.0718, $[\text{M}-\text{H}]^-$) and UV (254 and 342 nm) data. The same was observed for the ^1H - and ^{13}C -NMR data (10 methine protons and 30 carbon signals, Table 2), the exact match of which translated into two luteolin molecules linked together. The way they were connected (C-6'–C-6'') was deduced from the H→C correlation on the HMBC spectrum: H-5' (δ_{H} 6.74, s) and C6'' (δ_{C} 111.8); as well as by the exclusive presence of singlet methine protons in rings IB (H-2' and H-5') and IIA (H-8'') (Table 2). Thus, the structure of **18** was elucidated as the new 6',6''-biluteolin, and the proposed trivial name is taraxabiluteolin B.

Compound **33** was obtained as yellow amorphous powder. Its negative HRESIMS spectrum showed deprotonated molecule at m/z 523.1241 $[\text{M}-\text{H}]^-$, corresponding to the molecular formula of $\text{C}_{27}\text{H}_{23}\text{O}_{11}$. In the MS/MS spectrum the fragment ions at m/z 314.0370, 329.0601 and 299.0137 (Table S5), corresponding to the presence of

264 methylated flavone, were observed. The UV spectrum exhibited maxima at 271 and
265 325 nm, which is the typical characteristic of flavonoid derivative with a substituted B
266 ring. The ^{13}C NMR spectrum contained 27 signals, including a carboxylic carbon (δ_{C}
267 194.0), conjugated ketonic carbon (δ_{C} 181.6), a 20 aromatic/olefinic carbons (δ_{C} 94.3–
268 162.6), methine carbon (δ_{C} 83.2), oxygenated methylene carbon (δ_{C} 62.4), and three
269 methoxy carbons (δ_{C} 55.5 and double 56.2) (Table 2). The presence of tricin fragment
270 was specifically indicated by five aromatic methine (δ_{H} 6.22 (H-6), 6.56 (H-8), 7.02 (H-
271 3), and 7.31 (H-2',6')) and two methoxy (δ_{H} 3.87 (H-3',5'-OCH₃)) proton signals. The
272 seven remaining ^1H NMR signals were matched, with the aid of 2D NMR data, to the
273 3-hydroxy-2-(4-hydroxy-3-methoxyphenyl) propanoic acid, which was linked to the
274 tricin via an ether bond C4'-O-C8" (Fig. 3). Finally, a novel compound **33** received the
275 trivial name taraxalignan A. To the best of our knowledge, this is the first study
276 demonstrating such a lignan fragment in combination with a flavonoid molecule, thus
277 our results expands the architectural complexity of the flavonolignan group.
278 NMR spectra (including ^1H and ^{13}C NMR, HSQC, HMBC, ^1H - ^1H COSY, and ROESY)
279 for the three novel compounds (**16**, **18** and **33**) are included in the Supplementary
280 Materials (Fig. S5-S22).

281 **Quantitation of Flavonoids in Plant Material and Food Products.** UHPLC-MS/MS
282 technique was successfully used to quantify the content of nearly 30 flavonoid
283 compounds in raw dandelion material and food products in this study. A 16 major
284 flavonoids, including flavone aglycones and bi-flavones (compounds 14, 20-22, 26 and
285 15-16, 19, respectively; Table 1), flavone glycosides (3, 5, 8) and lignan derivatives of
286 tricin (24-25, 27-28, 33) were used for calibration. Detailed information on MRM
287 detection and calibration parameters for standard substances used is included in
288 Tables S6-S7. Quantitative data (Table 3) were further used to identify changes in the

chemical composition of flowers from different seasons, as well as similarities/differences between the food products analyzed.

Autumn and spring flowers were characterized by similar content of total flavonoids (4.7-4.9 mg/g), with the exception of autumn 2022 material (3.7 mg/g). The contribution of the specified flavonoid groups was similar in all samples: major input from aglycones (51-55%) and glycosides (37-41%), and minor from flavonolignans (6-8%) and biflavones (0.8-1.5%). In contrast, much greater flower diversity has been recorded in terms of individual compounds, as much as for 19 flavonoids the differences between results exceeded 35%. As can be seen in Table 3, the most important flavonoids of dandelion flowers include: luteolin (14) > luteolin-7-O-glc (3) ≥ luteolin-3'-O-glc (8) > chrysoeriol (21) > calquiquelignan E (27). Despite the relatively widespread use of dandelion aerial parts, there are only a few available studies reporting the quantitative flavonoid profile of herb (leaves and flowers), and they include only a few metabolites in the analysis (mainly quercetin and luteolin and their glycosidic derivatives). Interestingly, the reported levels of flavonoids are very broad, for example luteolin (1-83 mg/g of extract) and luteolin-7-O-hexoside (1.4-110 mg/g of extract), most likely influenced by both the variability of the plant material and the research methodology used.¹⁶⁻¹⁹ In addition, in one of our previous papers on dandelion herb, we used a simplified analytical method (UHPLC-UV and calibration for luteolin) to quantify about 25 flavonoids in several different fruit extracts¹⁵, while the current quantitative work is the first based on LC-MS/MS technique and calibration for all major flavonoid compounds.

Then, multivariate statistical methods²⁵ were used for graphically illustrating seasonal variation in flowers and plant material-flavonoid relationships. The PCA (nearly 90% variability encompassed by PC1-3 components, Fig. S23A) and HCA (Euclidean

distance and Ward's algorithm) analyses highlighted the great distinctness of spring and autumn flowers, as well as a greater variation in spring material (separation of spring flowers 2022 and 2023 along PC2) compared to autumn samples was observed (Fig. 4A-B). Nonetheless, the separation of autumn flowers from the two harvest years was later evident along PC3 (Fig. S23B). The PCA biplots (Fig. 4C and S23C) and heat map (Fig. 4B) confirmed the seasonal clustering of the flowers with respect to chemical composition, and among the positive correlations recorded were: autumn 2021 – compounds 5, 24 and 27; autumn 2022 – compounds 21 and 40-43; spring 2022 – compounds 15, 18+19, 22, 25-26, 28, 33 and 37-39; spring 2023 – compounds 3, 8, 14, 16 and 20. The current work is the first to attempt to identify seasonal phytochemical variation in dandelion flowers.

The quantitative flavonoid analysis of dandelion food products revealed their high variability (6.5-30.9 $\mu\text{g/mL}$ of total flavonoids, Table 3), and they were generally arranged in the following order: syrup I $\geq$ tincture > syrup II > syrup III. The proportion of the specified flavonoid groups in the samples was also heterogeneous: glycosides (70% of total flavonoids) and aglycones (27%) predominated in syrup I, while in syrups II-III the proportion was reversed (aglycones – about 70% and glycosides – about 25%), similarly, aglycones (83%) definitely predominated in the tincture, but flavonolignans (11%) were second. In each product, total biflavones were a minor fraction (less than 2% of total flavonoids), but in the tincture (0.35 $\mu\text{g/mL}$) their level was several times (3-15) higher than those in syrups (0.02–0.1 $\mu\text{g/mL}$) (Table 3). Surprisingly, the three commercial syrups differed significantly in their quantitative flavonoid profile, which, in addition, was not simply related to the manufacturer's declared dandelion decoction content (syrups I-III – 48%, 60% and 40%, respectively). According to Table 3, the distinguishing feature for syrup III was the lowest recorded

concentrations of all flavonoids, for syrup I the highest levels of the three luteolin glycosides, and for the tincture the highest concentrations of most other compounds (aglycones, biflavones and flavonolignans). It can be noted that the number of publications devoted to quantitative chemical analysis of dandelion food products, like flowers, is negligible. Overall, the flavonoid levels in commercial syrups, especially I-II, are in fairly close agreement with the result obtained for the handmade syrup (22 μg luteolin eq/mL) in the paper by Majewski et al. 2022.¹¹ On the other hand, our alcoholic flower tincture (85 g/1000 mL) had a significantly higher flavonoid content (269 $\mu\text{g/g}$ dw) compared to herb tincture (50 g/500 mL, 90 $\mu\text{g/g}$ dw) developed by Epure et al. 2023.²⁰

Subsequently, multivariate statistical methods were used to graphically illustrate the differences/similarities between dandelion food products. The results of PCA (95% variability covered by the first two components, Fig. S24) and HCA (Ward's algorithm and Euclidean distance) analyses confirmed the high variability of the products (separate grouping of samples, Fig. 4D-E). Similarly, the PCA-biplots (Fig. 4F and S24) and heat map (Fig. 4E) confirmed the sample clustering with respect to chemical composition, which was previously highlighted at the level of Table 3 (e.g., the positive correlation of syrup I with glycosides, as well as tincture with flavone aglycones).

Dandelion is a well-known useful plant with many documented biological properties. HR-QTOF-MS/MS analysis of the flower extract of this plant revealed the presence of numerous flavonoids, among which were well-known and bioactive metabolites such as luteolin and its glycosides, chrysoeriol, tricetin, apigenin. In addition, more than 20 other flavonoid compounds were detected, including several oligomers and more than a dozen flavonolignans (lignan derivatives of tricetin). Targeted isolation of metabolites using extraction optimized by DoE planning and various chromatographic methods led

364 to the isolation of 11 metabolites whose chemical structures were determined by
365 spectroscopic data. Among them were four biflavones, including philonotisflavone
366 (previously reported in the taxon) and dicranolomin (reported for the first time in the
367 taxon), as well as two new compounds, 6',8''-biluteolin (**16**) and 6',6''-biluteolin (**18**).
368 On the other hand, among the seven flavonolignans isolated, there was one new
369 compound, taraxalignan A (**33**), as well as six already described metabolites, except
370 that two methoxycalquiquelignan derivatives (40-41) have not yet been reported in the
371 *Taraxacum*. The quantitative content of more than 30 flavonoids was determined,
372 based on UHPLC-ESI-MS/MS analysis, in raw flowers and dandelion food products.
373 Comparative and chemometric analysis (including PCA, HCA and PLS-DA) using
374 quantitative flavonoid data showed seasonal clustering of flower samples (spring vs.
375 autumn), with compounds 27, 24, 34, 29, 35, 16, 5, 32 and 25 among the traits with
376 the greatest impact. A similar approach for food products (three commercial syrups
377 and a handmade tincture) showed their high variation in phytochemical composition.
378 Our work is the first such comprehensive study of flavonoids in dandelion flowers, and
379 fills many phytochemical knowledge gaps for this plant and the food products made
380 from it.

381

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SUPPORTING INFORMATION

Supplementary Materials include Descriptions S1-S3, Tables S1-S7 and Figures S1-S24. The material is available free of charge via Internet at [http:// pubs.acs.org](http://pubs.acs.org).

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Table 1. UHPLC-HR-QTOF-MS/MS characterization of metabolites detected in dandelion flower flavonoid extract.

No	RT (min)	UV λ_{max} (nm)	Observed $[M+H]^+$, m/z	Formula	Error (ppm)	MS/MS fragments	Identity
1	1.69	323, 295sh	163.0393/181.0498	C ₉ H ₉ O ₄	-1.2	89.0384, 117.0336, 136.0516	caffeic acid*
2	2.73	308	147.0445/165.0547	C ₉ H ₇ O ₂	-0.6	-	coumaric acid*
3	3.78	254, 336	449.1084	C ₂₁ H ₂₁ O ₁₁	-1.1	287.0564	luteolin-7-O-glucoside*
4	4.83	326, 295sh	499.1241/517.1351	C ₂₅ H ₂₅ O ₁₂	-1.4	163.0397	3,5-di-caffeoylquinic acid*
5	5.55	267, 337	449.1086	C ₂₁ H ₂₁ O ₁₁	-1.8	287.0555	luteolin-4'-O-glucoside*
6	6.36	326, 295sh	499.1241/517.1348	C ₂₅ H ₂₅ O ₁₂	-1.5	163.0395	di-caffeoylquinic acid
7	6.59	250, 269, 345	463.1240	C ₂₂ H ₂₃ O ₁₁	-1.1	301.0712	chrysoeriol-O-hexoside
8	6.84	267, 340	449.1083	C ₂₁ H ₂₁ O ₁₁	-0.9	287.0558	luteolin-3'-O-glucoside*
9	7.01	-	442.2071 $[M+NH_4]^+$	C ₂₁ H ₃₂ NO ₉	0.0	171.1172, 217.1227	taraxinic acid-1-O-glucoside*
10	8.49	254, 341	855.1186	C ₄₅ H ₂₇ O ₁₈	0.7	285.0400, 419.0771, 703.1097	flavonoid (tri-luteolin)
11	8.98	254, 344	855.1187	C ₄₅ H ₂₇ O ₁₈	0.6	285.0401, 153.0188, 703.1081	flavonoid (tri-luteolin)
12	9.31	256, 344	855.1183	C ₄₅ H ₂₇ O ₁₈	1.0	285.0403, 153.0186, 703.1076	flavonoid (tri-luteolin)
13	9.80	327, 295sh	513.1395/531.1500	C ₂₆ H ₂₇ O ₁₂	-0.5	163.0395	caffeoyl-feruloylquinic acid
14	10.16	252, 346	287.0557	C ₁₅ H ₁₁ O ₆	-2.3	153.0188, 135.0446	luteolin*
15	11.85	253, 341	571.0882	C ₃₀ H ₁₉ O ₁₂	-1.9	419.0775, 153.0192, 285.0389	philonotisflavone#
16	12.53	254, 344	571.0881	C ₃₀ H ₁₉ O ₁₂	-1.8	419.0778, 153.0195, 445.0560	taraxabiluteolin A#
17	13.23	254, 341	855.1200	C ₄₅ H ₂₇ O ₁₈	-0.9	153.0186, 551.0983, 703.1094	flavonoid (tri-luteolin)
18	13.66	254, 342	571.0885	C ₃₀ H ₁₉ O ₁₂	-2.5	419.0778, 445.0562	taraxabiluteolin B#
19	13.68	254, 340	571.0887	C ₃₀ H ₁₉ O ₁₂	-2.6	419.0778, 445.0563	dicranolomin#
20	14.09	265, 338	271.0609	C ₁₅ H ₁₁ O ₅	-3.1	153.0183	apigenin*
21	15.52	250, 269, 346	301.0710	C ₁₆ H ₁₃ O ₆	-1.0	258.0529, 286.0478	chrysoeriol*
22	15.67	250, 269, 351	331.0816	C ₁₇ H ₁₅ O ₇	-1.1	315.0501, 203.0338	tricin*
23	16.25	255, 342	853.1036	C ₄₅ H ₂₅ O ₁₈	-0.1	153.0188, 269.0439, 497.0499	flavonoid oligomer
24	17.34	268, 339	497.1441	C ₂₆ H ₂₅ O ₁₀	0.2	331.0815, 315.0503	calquiquelignan D#
25	18.00	269, 339	527.1550	C ₂₇ H ₂₇ O ₁₁	-0.5	331.0824, 315.0506	salcolin B#
26	18.12	268, 330	331.0816	C ₁₇ H ₁₅ O ₇	-1.0	315.0507, 270.0528	apometzgerin*
27	18.74	268, 337	497.1447	C ₂₆ H ₂₅ O ₁₀	-0.9	331.0818, 315.0504	calquiquelignan E#
28	19.58	269, 337	527.1549	C ₂₇ H ₂₇ O ₁₁	-0.2	331.0822, 315.0507	salcolin A#
29	20.25	269, 342	675.2076	C ₃₆ H ₃₅ O ₁₃	-0.5	331.0820, 315.0510, 270.0533	flavonolignan (tricin derivative)
30	20.69	270, 337	495.1286	C ₂₆ H ₂₃ O ₁₀	-2.0	284.0687, 331.0821, 255.0661	flavonolignan (tricin derivative)
31	20.86	297, 310	787.3688	C ₄₅ H ₅₅ O ₁₂	-1.9	147.0444, 204.1030, 641.3354	N-coumaroyl-spermine derivative
32	21.16	269, 341	705.2183	C ₃₇ H ₃₇ O ₁₄	-0.7	331.0830, 315.0512	flavonolignan (tricin derivative)
33	21.46	270, 321	525.1399	C ₂₇ H ₂₅ O ₁₁	-1.5	331.0826, 284.0693, 255.0664	taraxalignan A#
34	21.51	269, 340	675.2080	C ₃₆ H ₃₅ O ₁₃	-1.2	331.0822, 315.0511	flavonolignan (tricin derivative)
35	22.03	269, 340	675.2079	C ₃₆ H ₃₅ O ₁₃	-1.0	331.0823, 315.0512	flavonolignan (tricin derivative)

36	22.35	268, 339	479.0979	C ₂₅ H ₁₉ O ₁₀	-1.4	257.0456, 435.1101, 287.0557	flavonoid
37	22.56	269, 341	705.2185	C ₃₇ H ₃₇ O ₁₄	-1.1	331.0830, 315.0512	flavonolignan (tricin derivative)
38	23.14	269, 341	705.2186	C ₃₇ H ₃₇ O ₁₄	-1.1	331.0832, 315.0513	flavonolignan (tricin derivative)
39	23.89	269, 341	495.1299	C ₂₆ H ₂₃ O ₁₀	-2.8	287.0560, 315.0509	flavonolignan (tricin derivative)
40	24.03	268, 340	511.1614	C ₂₇ H ₂₇ O ₁₀	-3.0	331.0828, 315.0513	7"-methoxycalquiquelignan D#
41	24.58	268, 339	511.1610	C ₂₇ H ₂₇ O ₁₀	-2.2	331.0826, 315.0515	7"-methoxycalquiquelignan E#
42	25.10	269, 340	541.1715	C ₂₈ H ₂₉ O ₁₁	-1.9	331.0821, 315.0509	flavonolignan (methoxysalcolin B)
43	25.13	269, 339	541.1713	C ₂₈ H ₂₉ O ₁₁	-1.7	331.0822, 315.0507	flavonolignan (methoxysalcolin A)

* the identity of the compound was confirmed by comparison with reference substance; # compound was isolated and identified in this study

Table 2. ^1H and ^{13}C NMR data for new flavonoid compounds **16**, **18** and **33** (in $\text{DMSO}-d_6$).

No	16 (taraxabiluteolin A)		18 (taraxabiluteolin B)		33 (taraxalignan A)	
	δ_{C}	δ_{H} (J in Hz)	δ_{C}	δ_{H} (J in Hz)	δ_{C}	δ_{H} (J in Hz)
2	165.9	-	166.1	-	162.6	-
3	106.2	5.97, s	105.9	5.99, s	104.8	6.99, s
4	181.1	-	181.3	-	181.6	-
5	161.2	-	161.3	-	161.3	-
6	98.7	6.08, d (2.1)	98.8	6.11, d (2.0)	99.3	6.18, br s
7	164.1	-	164.2	-	165.6	-
8	93.2	5.74, d (2.0)	93.4	5.97, d (2.0)	94.4	6.51, br s
9	157.2	-	157.4	-	157.5	-
10	103.2	-	103.4	-	103.3	-
1'	123.0	-	122.8	-	125.5	-
2'	115.9	7.29, s	115.6	7.22, s	104.2	7.30, s
3'	145.1	-	144.9	-	152.2	-
4'	148.3	-	148.1	-	139.3	-
5'	119.9	6.82, s	119.9	6.74, s	152.2	-
6'	122.9	-	123.8	-	104.2	7.30, s
3',5'-OMe	-	-	-	-	56.3	3.77, s
1''	-	-	-	-	139.3	-
2''	163.8	-	163.8	-	111.7	7.51, d (2.0)
3''	102.4	6.59, s	102.9	6.69, s	147.5	-
4''	181.8	-	181.7	-	152.2	-
5''	160.2	-	158.3	-	114.9	6.88, d (8.3)
6''	98.5	6.31, s	111.8	-	123.6	7.58, dd (8.3, 2.0)
7''	161.4	-	161.5	-	83.3	5.52, t (5.6)
8''	107.1	-	93.4	6.53, s	62.5	3.78, o 3.84, o
9''	153.8	-	156.0	-	194.0	-
10''	103.4	-	103.4	-	-	-
3''-OMe	-	-	-	-	55.6	3.81, s
1'''	121.3	-	121.4	-	-	-
2'''	113.6	7.04, d (2.3)	113.3	7.42, d (2.3)	-	-
3'''	145.7	-	145.8	-	-	-
4'''	149.8	-	149.9	-	-	-
5'''	115.6	6.76, d (8.3)	116.1	6.90, d (8.2)	-	-
6'''	118.6	7.02, dd (2.2, 8.3)	119.0	7.43, dd (2.3, 8.2)	-	-

Table 3. Flavonoid content of dandelion flowers and food products based on them (syrops and tincture) (mean $\pm$ SD). Compound numbering is consistent with Table 1.

No	Flowers				Food products			
	2021-Autumn	2022-Spring	2022-Autumn	2023-Spring	Syrup I (48% decoction)	Syrup II (60% decoction)	Syrup III (40% decoction)	Tincture (85 g/1000 mL)
$\mu\text{g/g}$ (flowers) or ng/mL food products								
5	213.41 $\pm$ 44.9a	10.15 $\pm$ 0.50b	8.74 $\pm$ 0.99b	11.45 $\pm$ 0.19b	211.84 $\pm$ 8.05a	59.52 $\pm$ 0.85c	68.76 $\pm$ 0.79b	76.96 $\pm$ 2.03b
15	35.79 $\pm$ 1.54c	64.08 $\pm$ 2.89a	37.23 $\pm$ 5.84bc	45.23 $\pm$ 7.85b	38.79 $\pm$ 1.88c	91.34 $\pm$ 5.23b	24.06 $\pm$ 2.39d	317.65 $\pm$ 3.88a
16	2.53 $\pm$ 0.18b	3.08 $\pm$ 0.11b	1.89 $\pm$ 0.15c	4.30 $\pm$ 0.57a	trace ^c	3.36 $\pm$ 0.11b	trace	11.96 $\pm$ 0.09a
18+19 ^a	1.65 $\pm$ 0.08b	2.84 $\pm$ 0.14b	1.67 $\pm$ 0.24b	1.95 $\pm$ 0.34a	trace	2.85 $\pm$ 0.35b	trace	15.68 $\pm$ 0.61a
20	10.48 $\pm$ 0.86a	8.88 $\pm$ 0.87b	7.06 $\pm$ 0.35c	10.75 $\pm$ 0.43a	24.25 $\pm$ 0.69c	53.71 $\pm$ 0.34b	17.25 $\pm$ 0.17d	158.70 $\pm$ 3.01a
26	8.85 $\pm$ 0.35b	12.85 $\pm$ 0.89a	6.32 $\pm$ 0.6c	9.66 $\pm$ 0.34b	294.98 $\pm$ 6.74c	312.59 $\pm$ 7.87b	60.59 $\pm$ 0.52d	577.92 $\pm$ 7.86a
29 ^b	1.17 $\pm$ 0.03a	0.98 $\pm$ 0.10b	1.08 $\pm$ 0.07ab	0.72 $\pm$ 0.02c	6.12 $\pm$ 0.19c	7.57 $\pm$ 0.30b	1.38 $\pm$ 0.02d	12.16 $\pm$ 0.07a
30 ^b	trace	trace	trace	trace	trace	trace	trace	trace
32 ^b	0.46 $\pm$ 0.02c	0.75 $\pm$ 0.06a	0.48 $\pm$ 0.02c	0.58 $\pm$ 0.03b	6.54 $\pm$ 0.20a	3.31 $\pm$ 0.06c	1.12 $\pm$ 0.01d	5.66 $\pm$ 0.05b
33	21.19 $\pm$ 0.64b	30.65 $\pm$ 6.26b	18.76 $\pm$ 1.17b	23.71 $\pm$ 1.94a	45.16 $\pm$ 0.82c	65.47 $\pm$ 2.14b	10.45 $\pm$ 0.57d	231.39 $\pm$ 1.12a
34 ^b	0.78 $\pm$ 0.02a	0.65 $\pm$ 0.05b	0.72 $\pm$ 0.05a	0.49 $\pm$ 0.02c	2.29 $\pm$ 0.09c	3.41 $\pm$ 0.12b	trace	8.01 $\pm$ 0.18a
35 ^b	0.86 $\pm$ 0.02a	0.73 $\pm$ 0.07b	0.81 $\pm$ 0.05ab	0.54 $\pm$ 0.02c	1.97 $\pm$ 0.07c	3.04 $\pm$ 0.08b	trace	9.76 $\pm$ 0.11a
36 ^b	trace	trace	trace	trace	trace	trace	trace	trace
37 ^b	0.31 $\pm$ 0.01c	0.51 $\pm$ 0.04a	0.32 $\pm$ 0.02c	0.37 $\pm$ 0.02b	2.42 $\pm$ 0.10b	1.59 $\pm$ 0.06c	trace	3.42 $\pm$ 0.06a
38 ^b	0.40 $\pm$ 0.01c	0.70 $\pm$ 0.06a	0.42 $\pm$ 0.03c	0.49 $\pm$ 0.03b	2.31 $\pm$ 0.09b	1.67 $\pm$ 0.03c	trace	5.48 $\pm$ 0.13a
39 ^b	4.91 $\pm$ 0.28c	7.64 $\pm$ 0.76a	6.23 $\pm$ 0.96b	5.24 $\pm$ 0.69bc	9.20 $\pm$ 0.21c	10.80 $\pm$ 0.42b	2.52 $\pm$ 0.03d	64.25 $\pm$ 0.28a
40 ^b	0.43 $\pm$ 0.02b	0.35 $\pm$ 0.06b	0.57 $\pm$ 0.09a	0.41 $\pm$ 0.03b	0.49 $\pm$ 0.01c	0.94 $\pm$ 0.04a	trace	0.72 $\pm$ 0.06b
41 ^b	0.55 $\pm$ 0.03ab	0.45 $\pm$ 0.09b	0.59 $\pm$ 0.09a	0.51 $\pm$ 0.04ab	0.69 $\pm$ 0.01c	1.35 $\pm$ 0.10a	trace	1.07 $\pm$ 0.08b
42+43 ^b	5.01 $\pm$ 0.25bc	4.76 $\pm$ 0.34c	6.78 $\pm$ 1.59a	6.35 $\pm$ 0.47ab	1.59 $\pm$ 0.03c	2.61 $\pm$ 0.22b	0.72 $\pm$ 0.12d	6.15 $\pm$ 0.16a
mg/g (flowers) or $\mu\text{g/mL}$ food products								
3	0.87 $\pm$ 0.05a	0.87 $\pm$ 0.05a	0.69 $\pm$ 0.04b	0.92 $\pm$ 0.12a	10.72 $\pm$ 0.38a	1.96 $\pm$ 0.05b	0.84 $\pm$ 0.01c	0.81 $\pm$ 0.03c
8	0.87 $\pm$ 0.05a	0.87 $\pm$ 0.05a	0.69 $\pm$ 0.04b	0.92 $\pm$ 0.12a	10.75 $\pm$ 0.39a	1.71 $\pm$ 0.04b	0.79 $\pm$ 0.01c	0.75 $\pm$ 0.02c
14	2.22 $\pm$ 0.08a	2.27 $\pm$ 0.20a	1.76 $\pm$ 0.06b	2.43 $\pm$ 0.12a	6.60 $\pm$ 0.07c	9.61 $\pm$ 0.16b	4.04 $\pm$ 0.03d	21.08 $\pm$ 0.33a
21	0.16 $\pm$ 0.00a	0.15 $\pm$ 0.02a	0.17 $\pm$ 0.02a	0.16 $\pm$ 0.00a	0.59 $\pm$ 0.01c	0.93 $\pm$ 0.01b	0.33 $\pm$ 0.00d	2.14 $\pm$ 0.03a
22	0.06 $\pm$ 0.00c	0.10 $\pm$ 0.01a	0.05 $\pm$ 0.00c	0.07 $\pm$ 0.01b	0.71 $\pm$ 0.01a	0.44 $\pm$ 0.00c	0.14 $\pm$ 0.00d	0.64 $\pm$ 0.01b

24	0.09 ± 0.00a	0.07 ± 0.01b	0.07 ± 0.00b	0.05 ± 0.00c	0.25 ± 0.01c	0.51 ± 0.01b	0.04 ± 0.00d	0.96 ± 0.02a
25	0.05 ± 0.00c	0.08 ± 0.01a	0.05 ± 0.00c	0.06 ± 0.00b	0.04 ± 0.00c	0.08 ± 0.00b	0.01 ± 0.00d	0.18 ± 0.01a
27	0.12 ± 0.00a	0.09 ± 0.01b	0.09 ± 0.01b	0.07 ± 0.00c	0.25 ± 0.01c	0.52 ± 0.01b	0.03 ± 0.00d	1.17 ± 0.01a
28	0.05 ± 0.00c	0.09 ± 0.01a	0.05 ± 0.00c	0.07 ± 0.01b	0.28 ± 0.00b	0.27 ± 0.01c	0.04 ± 0.00d	0.58 ± 0.01a
Total	4.78 ± 0.17a	4.74 ± 0.29a	3.73 ± 0.16b	4.87 ± 0.29a	30.85 ± 0.87a	16.66 ± 0.30b	6.45 ± 0.05c	29.81 ± 0.47a
Glycosides	1.95 (40.74%)	1.75 (37.00%)	1.40 (37.43%)	1.85 (37.97%)	21.68 (70.29%)	3.73 (22.41%)	1.70 (26.34%)	1.63 (5.47%)
Aglycones	2.45 (51.28%)	2.54 (53.57%)	1.99 (53.36%)	2.68 (55.05%)	8.22 (26.66%)	11.34 (68.08%)	4.59 (71.07%)	24.60 (82.52%)
Biflavones	0.04 (0.84%)	0.07 (1.48%)	0.04 (1.09%)	0.05 (1.06%)	0.04 (0.13%)	0.10 (0.59%)	0.02 (0.38%)	0.35 (1.16%)
Flavonolignans	0.34 (7.14%)	0.38 (7.95%)	0.30 (8.12%)	0.29 (5.93%)	0.90 (2.93%)	1.49 (8.92%)	0.14 (2.21%)	3.23 (10.85%)

^a – calculation based on the calibration for compd. 19; ^b – calculation based on the calibration for compd. 24; ^c – trace, value below lower limit of quantification of calibration curve. Mean values with the same letter in each row (separately for flowers and food products) are not significantly different (Tukey’s test, *p* < 0.05). Color code was generated using Microsoft Excel and indicates flavonoid levels in samples (separately for flowers and food products): (green (high) > white (medium) > red (low)).

Figure Captions:

Figure 1. UHPLC-CAD-HR-QTOF-MS analysis of dandelion flower flavonoid extract.

Peak numbering is consistent with Table 1.

Figure 2. Structures of 11 isolated and identified flavonoids from dandelion flowers.

Figure 3. Key COSY, HMBC and NOESY correlations for novel compound **16** (taraxabiluteolin A) and **33** (taraxalignan A) isolated from *Taraxaci Flos*.

Figure 4. Results of multivariate statistical analyses of dandelion flowers and food products: PCA scores plot of autumn (2021-2022) and spring (2022-2023) flowers (A); HCA dendrogram of autumn (2021-2022) and spring (2022-2023) flowers and heat map of flavonoids (B); PCA biplot of autumn (2021-2022) and spring (2022-2023) flowers and flavonoids (C); PCA scores plot of dandelion syrups (I-III) and handmade tincture (D); HCA dendrogram of dandelion syrups (I-III) and handmade tincture and heat map of flavonoids (E); PCA biplot of dandelion syrups (I-III) and handmade tincture and flavonoids (F).

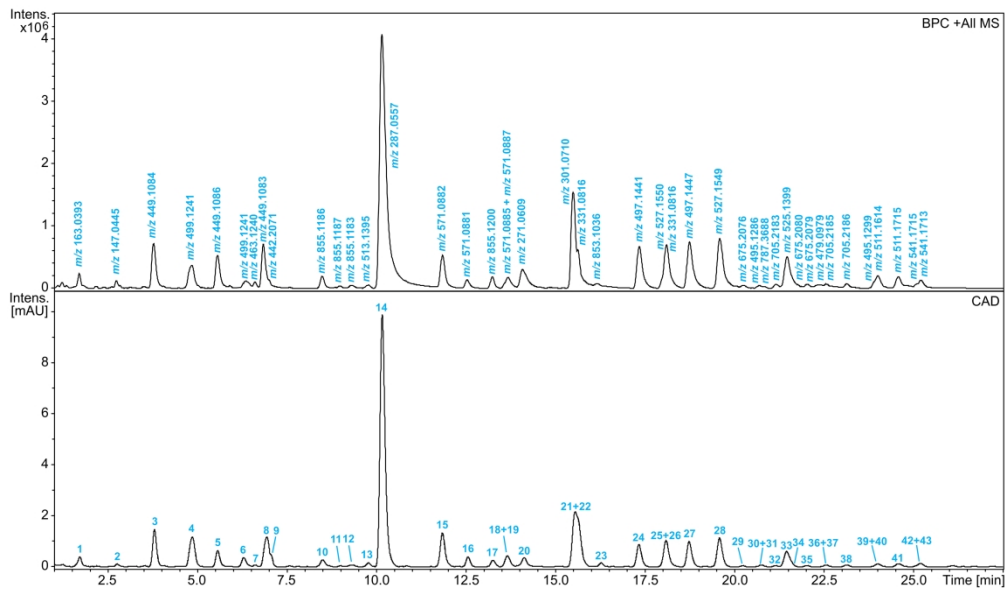


Figure 1. UHPLC-CAD-HR-QTOF-MS analysis of dandelion flower flavonoid extract. Peak numbering is consistent with Table 1.

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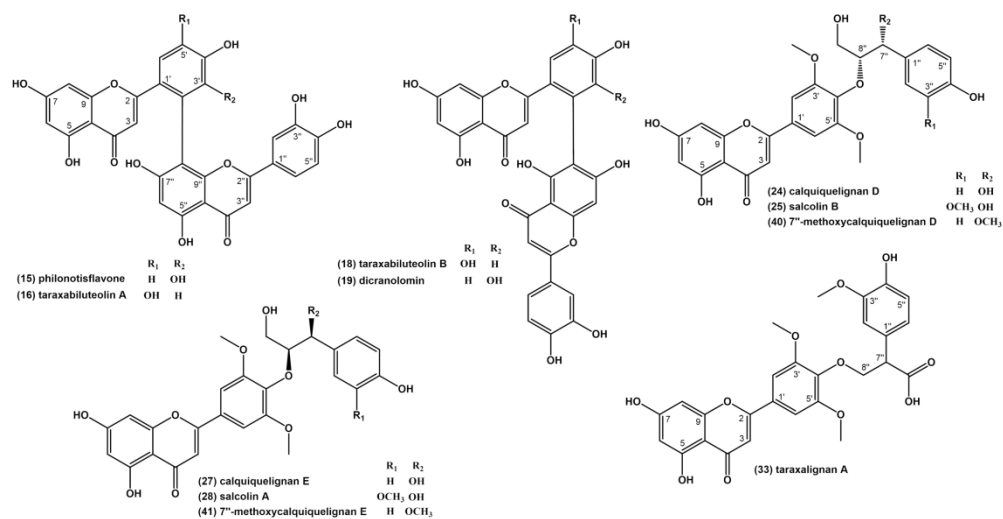


Figure 2. Structures of 11 isolated and identified flavonoids from dandelion flowers.

242x124mm (300 x 300 DPI)

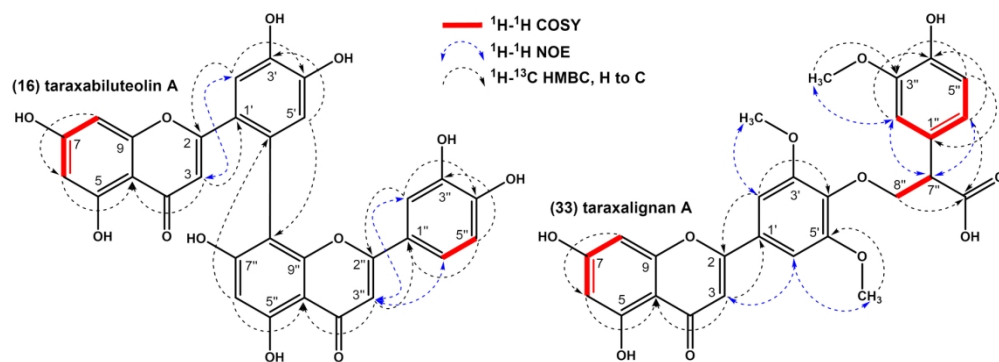


Figure 3. Key COSY, HMBC and NOESY correlations for novel compound 16 (taraxabiluteolin A) and 33 (taraxalignan A) isolated from Taraxaci Flos.

166x59mm (300 x 300 DPI)

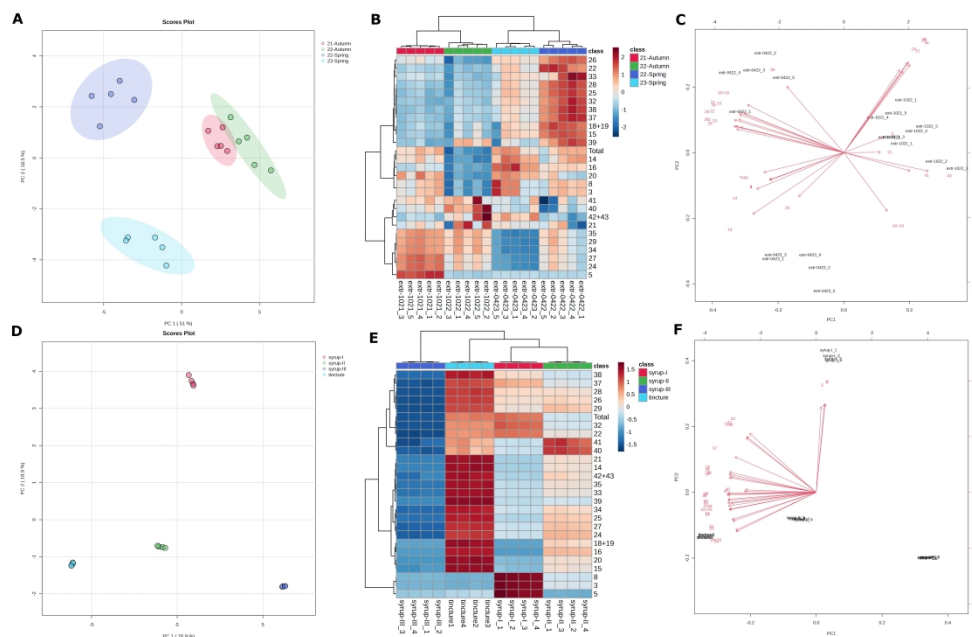


Figure 4. Results of multivariate statistical analyses of dandelion flowers and food products: PCA scores plot of autumn (2021-2022) and spring (2022-2023) flowers (A); HCA dendrogram of autumn (2021-2022) and spring (2022-2023) flowers and heat map of flavonoids (B); PCA biplot of autumn (2021-2022) and spring (2022-2023) flowers and flavonoids (C); PCA scores plot of dandelion syrups (I-III) and handmade tincture (D); HCA dendrogram of dandelion syrups (I-III) and handmade tincture and heat map of flavonoids (E); PCA biplot of dandelion syrups (I-III) and handmade tincture and flavonoids (F).

2469x1583mm (72 x 72 DPI)