Electronic Supplementary Material (ESI) for Photochemical & Photobiological Sciences.

Electronic Supplementary Information

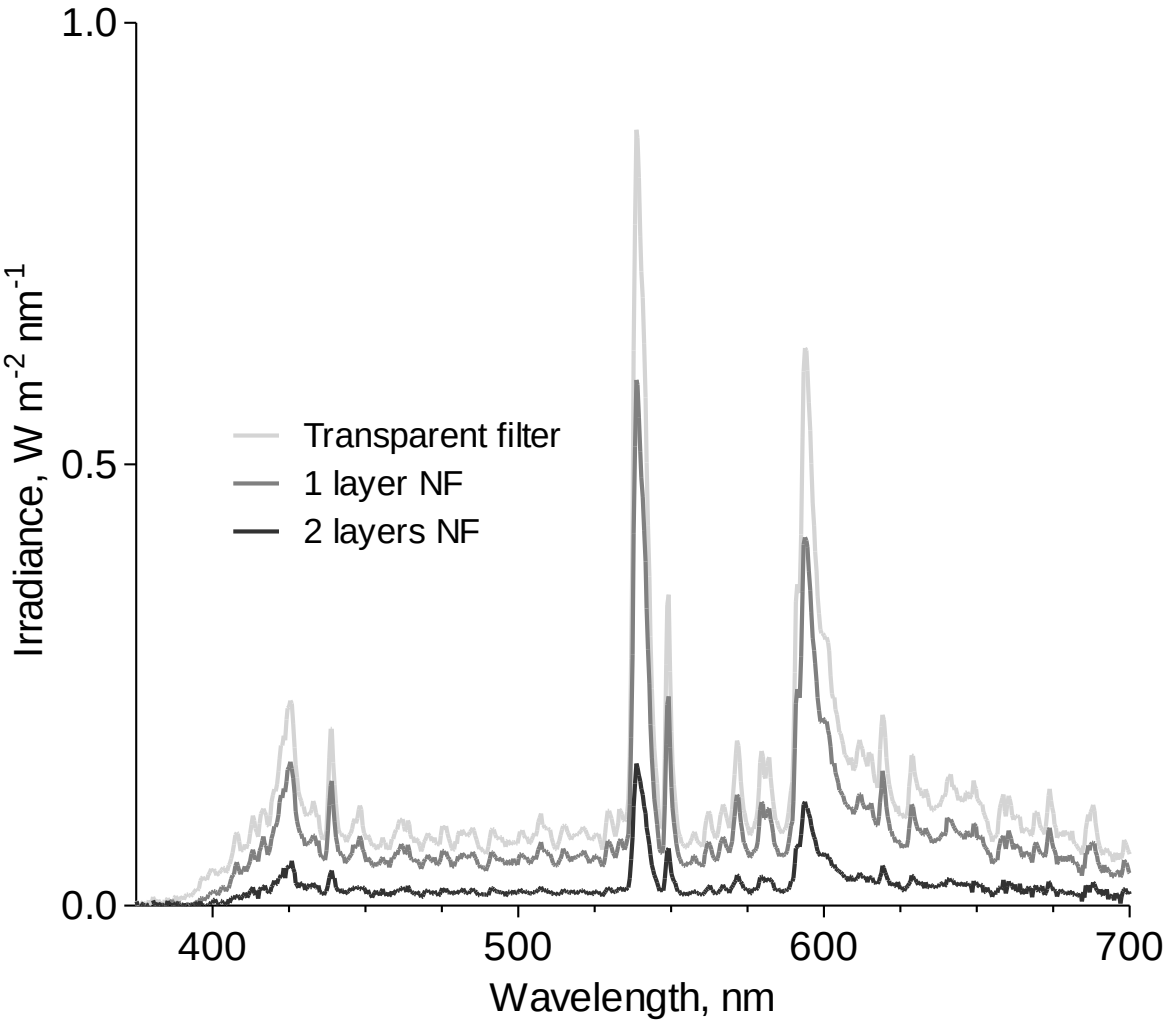

Figure S1: Emission spectra of growth light used for cultivation of sunflowers. In order to generate different light conditions, plants were grown under different combinations of neutral filter foils. Light of HQI lamps was damped with either a transparent filter (bright grey line, 210 µmol m^{-2} s^{-1}), one layer (grey line, 145 µmol m^{-2} s^{-1}) or two layers (black line, 40 µmol m^{-2} s^{-1}) of neutral filter (NF) foil.

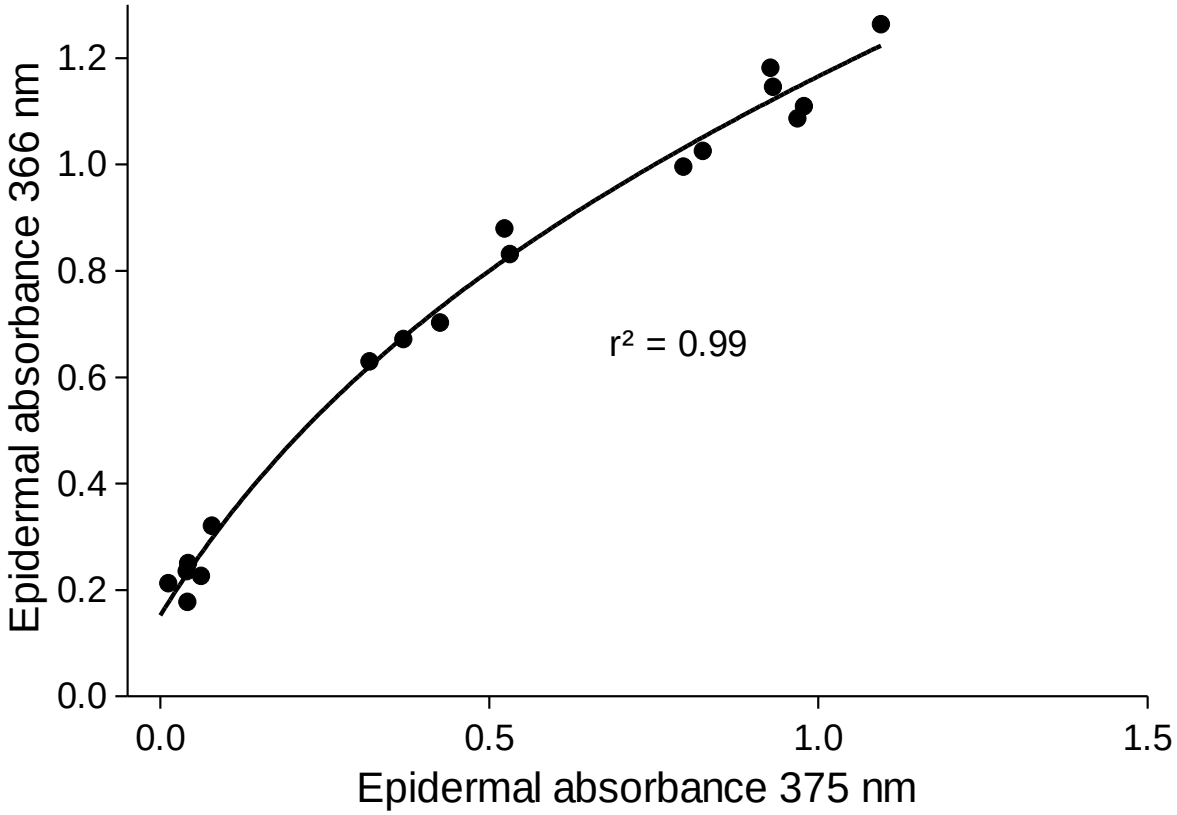

Figure S2: Calibration function for converting epidermal absorbance at 375 nm to epidermal absorbance at 366 nm. 18 Leaf samples were measured using a Xenon-PAM-chlorophyll fluorometer and a combination of UV-A- and Mini-PAM fluorometer for determination of UV-A transmittance at 366 nm and 375 nm, respectively. The curve fit was $f(x) = 1.047 + x / (0.6347 + x) + 0.3727x + 0.1523$. Epidermal absorbance was calculated following the equation $A=-\log$ (Transmittance).

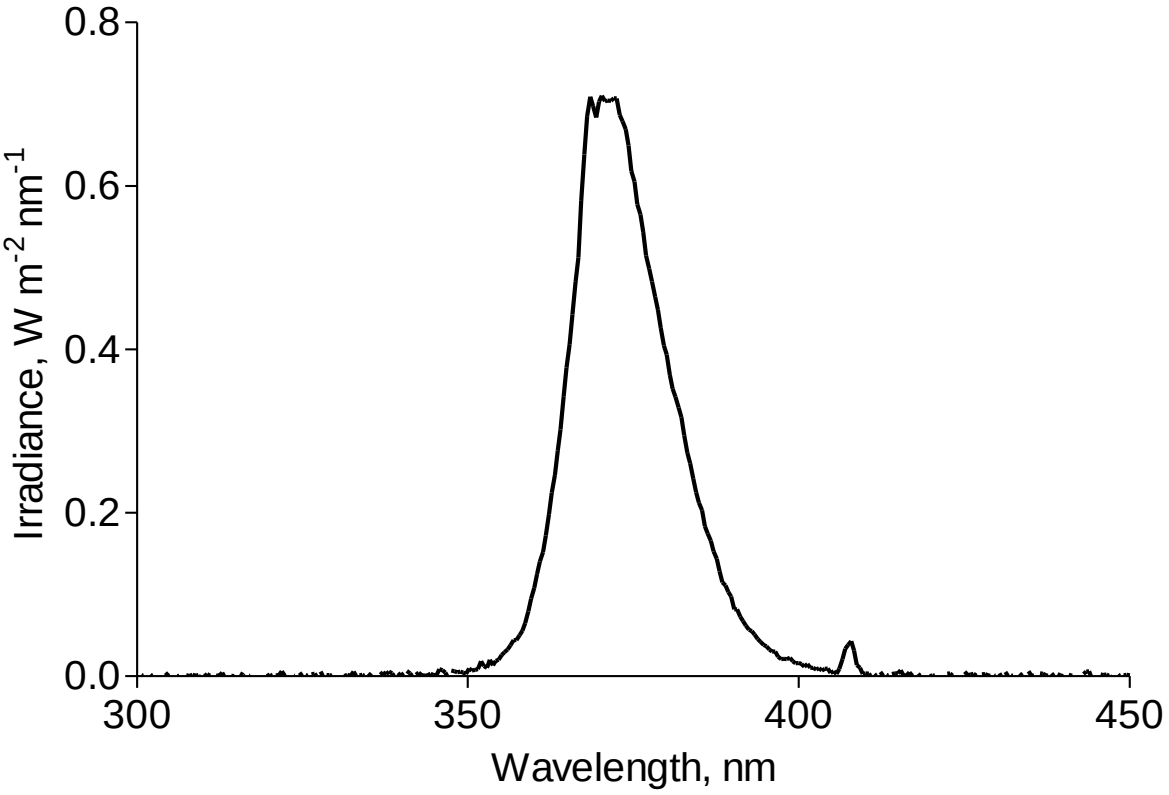

Figure S3: Emission spectrum of the UV-A tubes used in the photoinhibition experiment with a total output of 25.7 W m^{-2}. UV-A tubes were covered with a polyester filter foil to assure exclusion of UV-B.

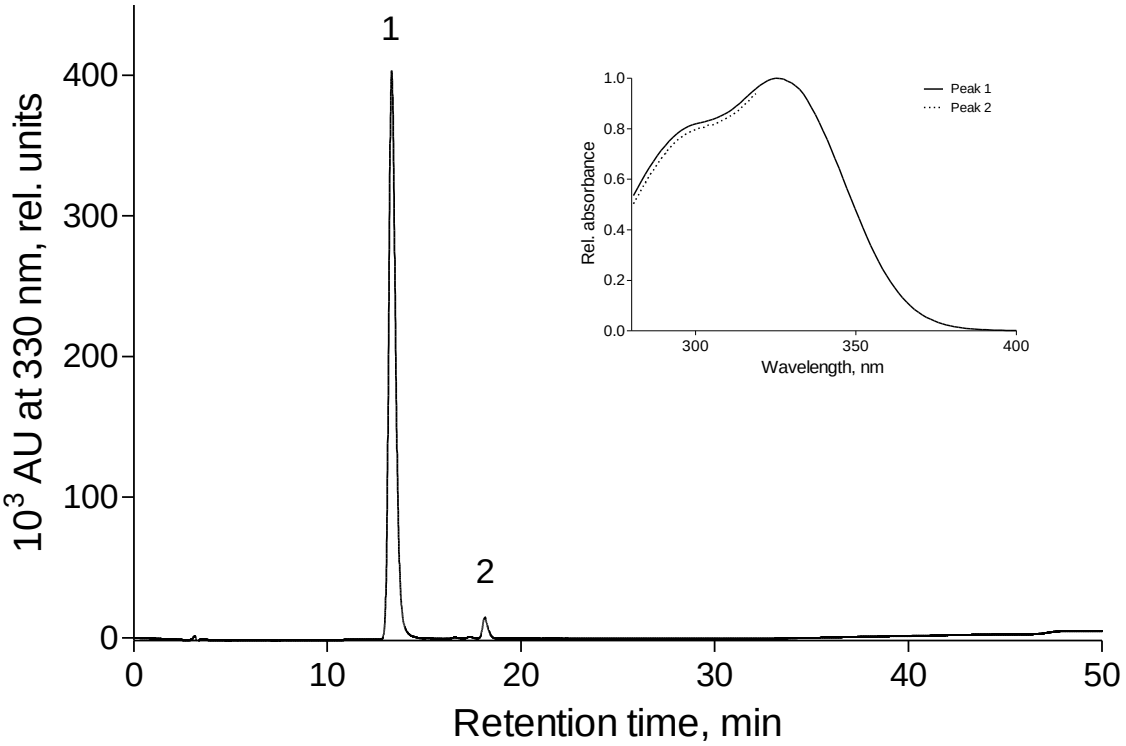

Figure S4: Chromatogram of the CGA standard solution used for calibrating the HPLC system before sample analysis. 1.4177 mg CGA standard were diluted in 25 mL 50 % MeOH with 1 % HCl. The inset shows the corresponding normalized online UV absorbance spectra of the two peaks, both of which were taken into account for calibration.

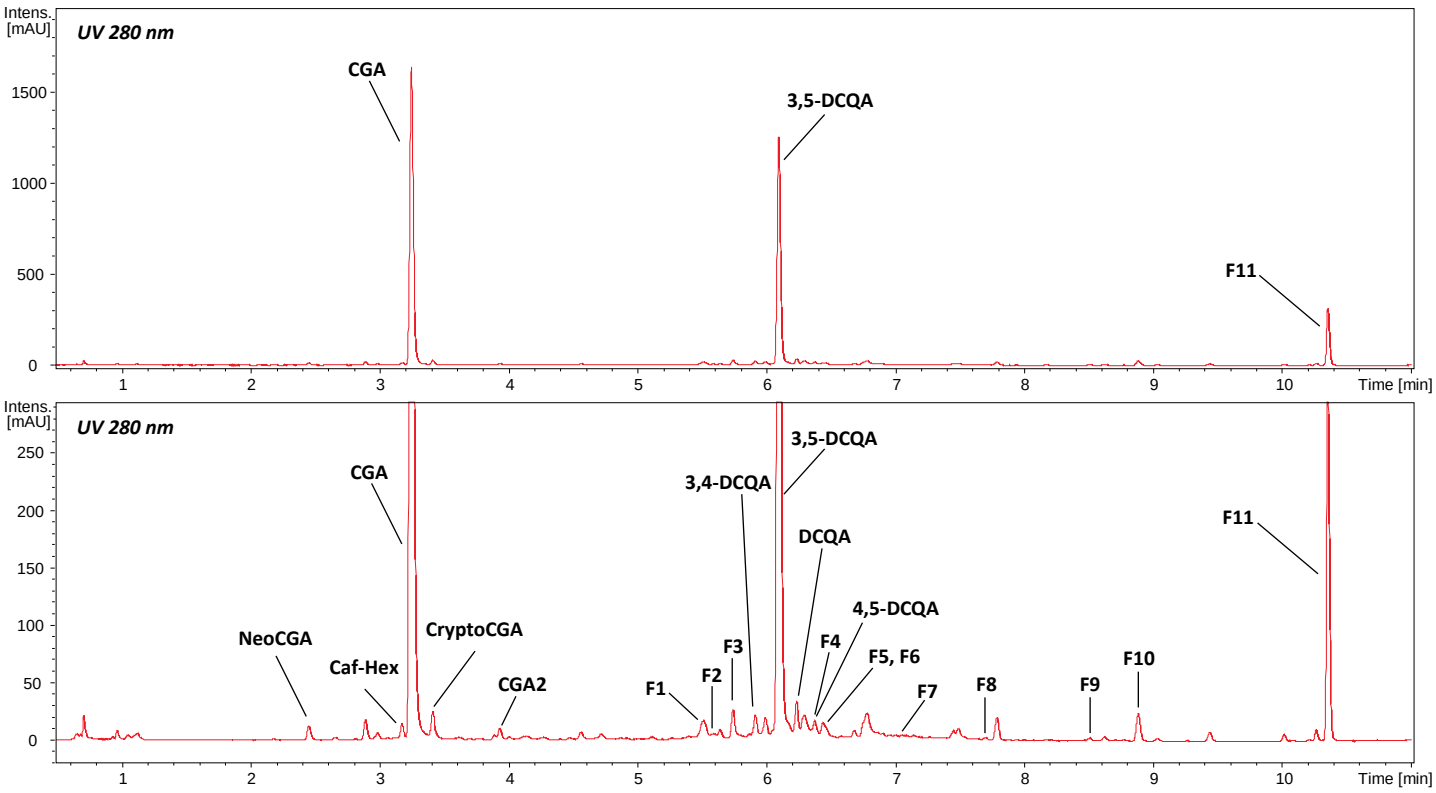

Figure S5: Annotation of semi-polar polyphenolic compounds in leaves of *Helianthus annuus* L. cv. Peredovick. HPLC-PDA chromatograms (280 nm; normal and expanded scale) of concentrated methanolic extracts. Polyphenolic compounds, including chlorogenic acids (CGA, DCQA) and flavonoid derivatives (F), were identified using HPLC-PDA-ESI-QTOF-MS/MS. The MS/MS fragmentation patterns in positive ionization mode and compound annotations are provided in Table S1.

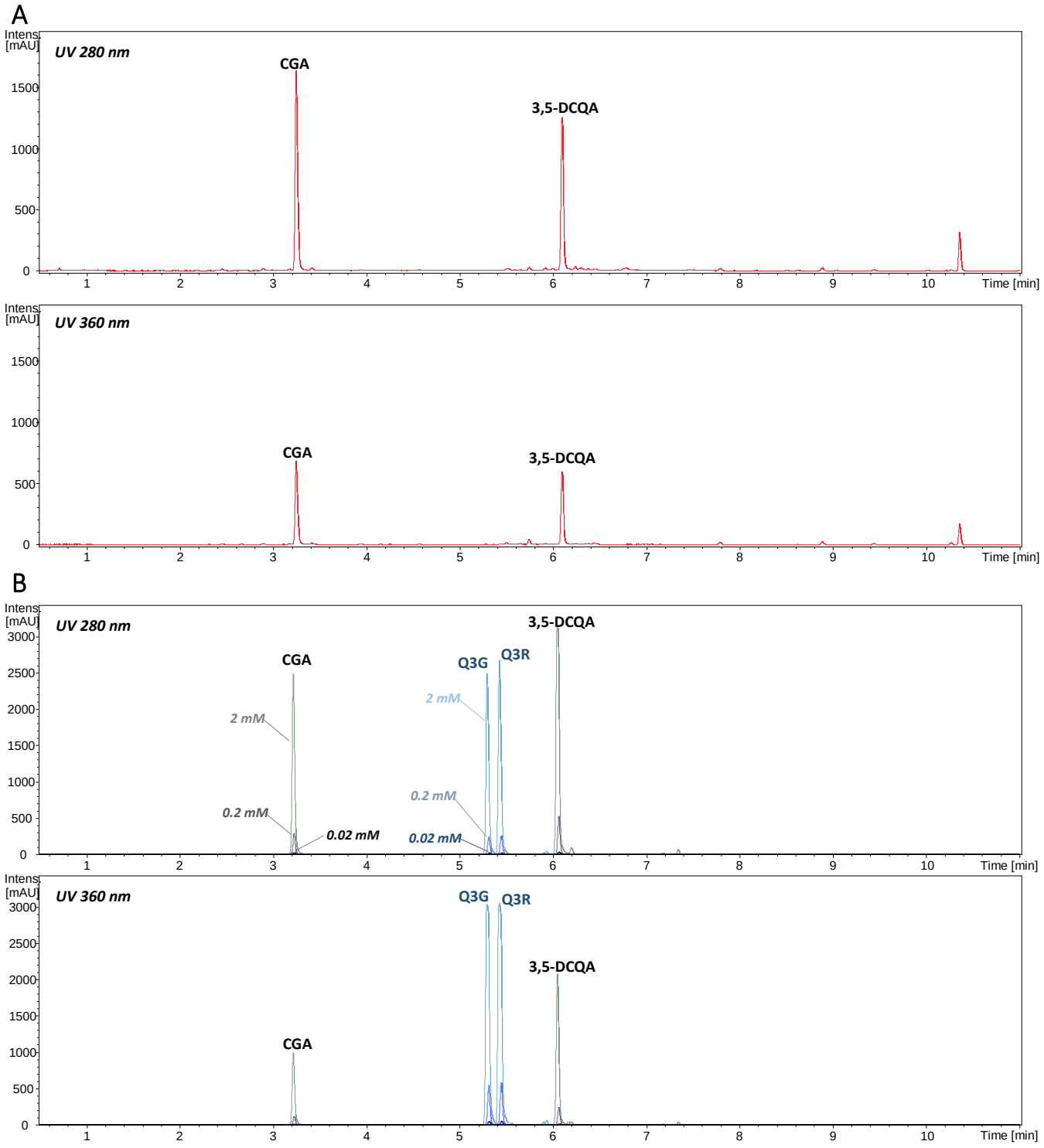

Figure S6: Caffeoyl quinic acids are the most predominant UV-absorbing semi-polar polyphenolic compounds in leaves of *Helianthus annuus* L. cv. Peredovick. A. HPLC-PDA chromatograms of a highly concentrated leaf methanolic extract at 280 and 360 nm, the latter corresponding to the maxima absorption wavelength of flavonoids. B. HPLC-PDA chromatograms showing the absorption at 280 and 360 nm of authentic standards representative for the major caffeoyl quinic acids and tentative flavonoids detected in sunflower leaves. All four authentic standards were analyzed at three different concentrations: 0.02, 0.2 and 2 mM. CGA: chlorogenic acid; 3,5-DCQA: 3,5-di-*O*-caffeoyl quinic acid; Q3G: quercetin 3-*O*-galactoside; Q3R: quercetin 3-*O*-rutinoside.

			Positive ion mode					Aglycone (flavonoids)			
Polyphenol	**Abbreviation** (Fig. S5)	**Rt** *(min)*	**Precursor** *(m/z)*	**Fragments** *(m/z)*	**Annotation**	**Molecular formula**	**Monoiso-topic mass**	**Tentative aglycone**	**Molecular formula**	**Monoisotopic mass**	**Reference**
1	NeoCGA	2.46	355.1008	163.03, 145.02, 135.04	*trans*-5-*O*-Caffeoyl quinic acid (Neochlorogenic acid)	$C_{16}H_{18}O_9$	354.0951	--	--	--	Authentic standard. Confirmed by MS/MS and Rt.
2	Caf-Hex	3.19	343.1015	325.09, 307.08, 181.04, 163.03, 145.02, 135.04	Caffeoyl-hexoside	$C_{15}H_{18}O_9$	342.298	--	--	--	Not available.
3	CGA	3.25	355.1028	337.09, 163.03, 145.02, 135.04	3-*O*-Caffeoyl quinic acid (Chlorogenic acid)	$C_{16}H_{18}O_9$	354.0951	--	--	--	Authentic standard. Confirmed by MS/MS and Rt.
4	CryptoCGA	3.41	355.1026	163.03, 135.04	4-*O*-Caffeoylquinic acid (Cryptochlorogenic acid)	$C_{16}H_{18}O_9$	354.0951	--	--	--	Authentic standard. Confirmed by MS/MS and Rt.
5	CGA2	3.96	355.1026	163.03, 145.02, 135.04	*O*-Caffeoyl quinic acid	$C_{16}H_{18}O_9$	354.0951	--	--	--	Authentic standard. Confirmed by MS/MS.
6	F1	5.52	641.1793	495.11, 333.06, **318.03**	Pentahydroxy-methoxyflavone-hexoside-deoxyhexoside	$C_{28}H_{32}O_{17}$	640.1639	Flavonol	$C_{15}H_{10}O_8$	318.0376	Not available.
7	F2	5.6	465.0952	**303.04**	Pentahydroxyflavone-hexoside	$C_{21}H_{20}O_{12}$	464.0955	Quercetin	$C_{15}H_{10}O_7$	302.0427	Schilling et al., 1981; 1983; 1987
8	F3	5.74	495.1154	333.06, **318.03**	Pentahydroxy-methoxyflavone-hexoside	$C_{22}H_{22}O_{13}$	494.106	Flavonol	$C_{15}H_{10}O_8$	318.0376	Not available.
9	3,4-DCQA	5.92	517.1346	499.12, 163.03	3,4-Di-*O*-Caffeoyl quinic acid	$C_{25}H_{24}O_{12}$	516.1268	--	--	--	Authentic standard. Confirmed by MS/MS and Rt.
10	3,5-DCQA	6.11	517.1337	499.12, 319.08, 163.03, 145.02, 135.04	3,5-Di-*O*-Caffeoyl quinic acid	$C_{25}H_{24}O_{12}$	516.1268	--	--	--	Authentic standard. Confirmed by MS/MS and Rt.
11	DCQA	6.24	517.1347	499.12, 163.03, 145.02, 135.04	Di-*O*-Caffeoyl quinic acid	$C_{25}H_{24}O_{12}$	516.1268	--	--	--	Authentic standard. Peak 2 (Fig. 2).
12	F4	6.36	551.1089	**303.05**	Pentahydroxyflavone-malonyl-hexoside	$C_{24}H_{22}O_{15}$	550.0959	Quercetin	$C_{15}H_{10}O_7$	302.0427	Schilling et al., 1981; 1983; 1987
13	4,5-DCQA	6.38	517.1344	499.12, 163.03	4,5-Di-*O*-Caffeoyl quinic acid	$C_{25}H_{24}O_{12}$	516.1268	--	--	--	Authentic standard. Confirmed by MS/MS and Rt.
14	F5	6.42	581.1203	333.06, **318.03**	Pentahydroxy-methoxyflavone-malonyl-hexoside	$C_{25}H_{24}O_{16}$	580.1064	Flavonol	$C_{15}H_{10}O_8$	318.0376	Not available
15	F6	6.49	565.1192	479.11, 317.06, **302.04**	Tetrahydroxy-methoxyflavone-malonyl-hexoside	$C_{25}H_{24}O_{15}$	564.1115	Quercetin	$C_{15}H_{10}O_7$	302.0427	Schilling et al., 1981; 1983; 1987

16	F7	7.04	549.1216	463.14, 301.07, **286.04**	Trihydroxy-methoxyflavone-malonyl-hexoside	$C_{25}H_{24}O_{14}$	548.1166	Kaempferol / Luteolin	$C_{15}H_{10}O_6$	286.0477	Schilling et al., 1981; Rieseberg et al., 1987
17	F8	7.71	317.0656	**302.04**	Tetrahydroxy-methoxyflavone	$C_{16}H_{12}O_7$	316.0583	Quercetin	$C_{15}H_{10}O_7$	302.0427	Schilling et al., 1981; 1983; 1987
18	F9	8.5	301.0708	**286.04**	Trihydroxy-methoxyflavone	$C_{16}H_{12}O_6$	300.0634	Kaempferol / Luteolin	$C_{15}H_{10}O_6$	286.0477	Schilling et al., 1981; Rieseberg et al., 1987
19	F10	8.88	361.0921	346.04, 331.04, **316.02**	Trihydroxy-trimethoxyflavone	$C_{18}H_{17}O_8$	361.0923	Flavonol	$C_{15}H_{10}O_8$	318.0376	Not available
20	F11	10.33	345.0969	330.07, 315.05, **300.06**	Dihydroxy-trimethoxyflavone	$C_{18}H_{16}O_7$	344.0896	Quercetin	$C_{15}H_{10}O_7$	302.0427	Schilling et al., 1981; 1983; 1987

Table S1: Annotation of semi-polar polyphenolic compounds in leaves of *Helianthus annuus* L. cv. Peredovick. Polyphenolic compounds, including caffeoyl quinic acids (CGA, DCQA) and flavonoid derivatives (F), were identified by HPLC-PDA-ESI-QTOF-MS/MS analysis of concentrated methanolic extracts (Fig. S5). Using authentic standards, the caffeoyl quinic acids were annotated and confirmed based on their UV/visible absorption spectra and their MS fragmentation patterns. The annotations of flavonoid derivatives were based on their UV/visible absorption and analysis of their MS fragmentation patterns using the MetaboScape 3.0 SR1 software (Bruker Daltonik GmbH, Germany) and the FlavonoidSearch system (Akimoto et al., 2017). Most of the annotated flavonoids consisted on methoxylated flavones, as their product ion MS/MS spectra yielded evidence for fragments arising from the neutral loss of methyl radicals (15.02 amu), which is typical for methoxylated flavones (Schmidt et al., 2011). The MS fragmentation patterns of non-annotated UV-absorbing peaks already suggest that these may consist on additional methoxylated flavones and caffeoyl-derivatives as well, due to the identification of fragments at *m/z* 163.03 which are distinctive of caffeic acid. Rt: retention time; *m/z*: mass to charge ratio.

References:

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