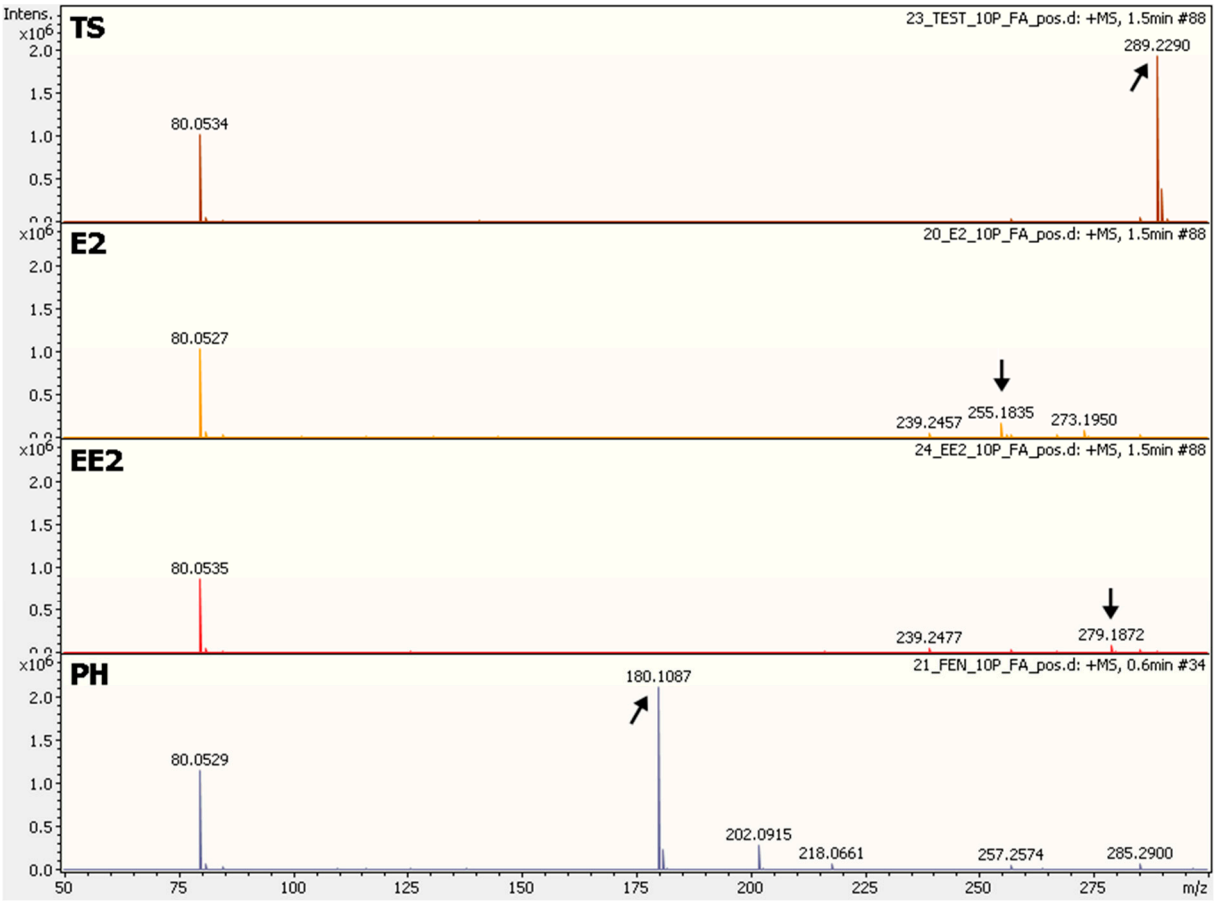

Figure S1. ESI ionization yield of the standards and their CID-fragmentation. ESI-qTOF MS1 spectra of a 10 µM solution of testosterone (TS), 17β-estradiol (E2), 17α-ethinylestradiol (EE2) and phenacetin (PH) in methanol with 0.1 % formic acid; in a uniform scale. Arrows indicate peaks characteristic of TS (m/z 289.23, MH^+), E2 (m/z 255.18, MH^+-H_2O), EE2 (m/z 279.18, MH^+-H_2O) and PH (m/z 180.11, MH^+). ESI source parameters: direct injection at 200 µl/h, capillary voltage 4500 V, nebulizer 0.4 bar, dry gas 4 l/min, dry temperature 180 °C.

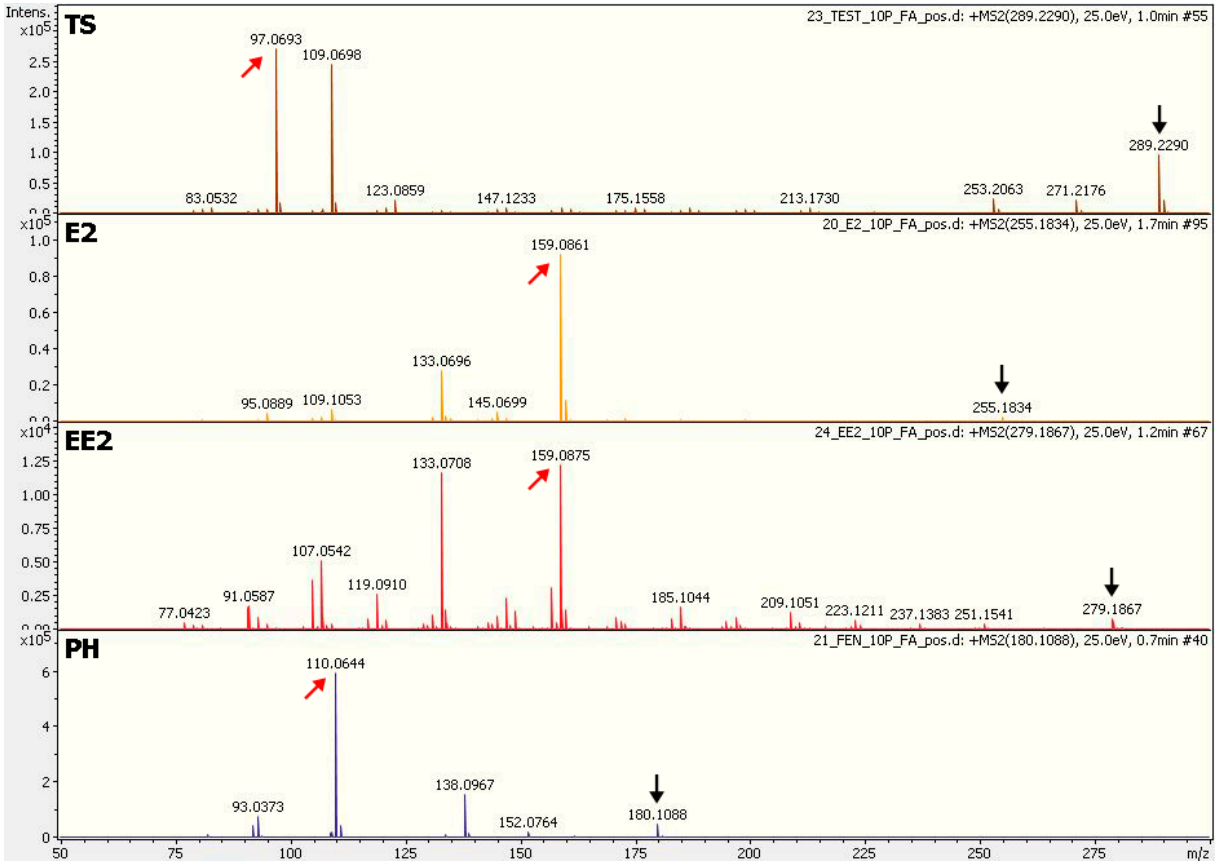

Figure S2. CID fragmentation of the standards. ESI-qTOF MS2 spectra of a 10 µM solution of testosterone (TS), 17β-estradiol (E2), 17α-ethinylestradiol (EE2) and phenacetin (PH) in methanol with 0.1 % formic acid. Black arrows indicate precursor peaks, red arrows indicate most intensive fragment peak used for confirmation. ESI source parameters: direct injection at 200 µl/h, capillary voltage 4500 V, nebulizer 0.4 bar, dry gas 4 l/min, dry temperature 180 °C, collision energy 25 eV

Scheme S1: Methodological steps of the study with the composition of the samples used in each method of analysis and a summary of the main findings.

Analytical Approach No.	Purpose	Assay	Enzymes Present	Tested Perfumes	Internal Standard	Separation / Product Detection	Results
1	A pilot experiment	CYP19 activity	CYP19, CYPOR	Samples 1-10	-	TLC / H_2SO_4	CYP19 activity assay developed.
2	Determination of perfume components impact on the chromatographic column; estimation of CYP19 activity inhibition by the Samples.				Phenacetin	HPLC / UV-VIS	No deterioration of the chromatographic column observed for any of the Samples; inhibitory effect estimated for Samples 1-3.
3	Quantification of CYP19 activity inhibition by the Samples.				Phenacetin, EE2	HPLC / MS	Inhibitory effect quantified for all Samples.
4	Comparison of CYP19 activity inhibition by the UV exposed and unaffected Samples.			Samples 3 (h.i.e.) and 6 (l.i.e.) after UV exposure	Phenacetin, EE2	HPLC / MS	Inhibitory effect of the Sample 6 (l.i.e.) enhanced after UV irradiation, while was unaffected for Sample 3 (h.i.e.).
5	Determination whether CYP19 or CYPOR is affected by the Sample components.	CYPOR activity	CYPOR	Sample 3 (h.i.e.)	-	- / UV-VIS	CYP19 was the enzyme affected by the Sample.

Abbreviations: CYP19 - aromatase; CYPOR - NADPH:cytochrome P450 oxidoreductase ; TLC - Thin Layer Chromatography; HPLC - High-Performance Liquid Chromatography; UV-VIS - ultraviolet-visible spectroscopy; MS - Mass Spectrometry; EE2 - 17α-ethinylestradiol ; h.i.e. - highest inhibitory effect; l.i.e. - lowest inhibitory effect.

Methods S1. qTOF MS Acquisition Method Parameters

- Ion Polarity: Positive
- Mass Range: 50 to 1300 m/z
- Spectra Rate: 4 Hz

1/ Mode

- Save Spectra: Line and Profile Spectra
- Absolute Threshold: 25 cts.
- Peak Summation Width: 3 pts.

2/ Source

- End Plate Offset: 500 V
- Capillary: 4500 V
- Nebulizer: 1.8 Bar
- Dry Gas: 8.0 l/min
- Dry Temp: 220 °C

3/ Tune

- Transfer
  - Funnel 1 RF: 150.0 Vpp
  - isCID Energy: 0.0 eV
  - Multipole RF: 50.0 Vpp
- Quadrupole
  - Ion Energy: 4.0 eV
  - Low Mass: 60.0 m/z
- Collision Cell

- Collision Energy: 7.0 eV
- Collision RF: 300 Vpp
- Transfer Time: 80.0 µs
- Pre Pulse Storage: 5.0 µs

4/ MS/MS

Auto MS/MS

- No. of Precursors: 3
- Absolute Threshold: 400 cts.
- Active Exclusion
  - Exclude after: 3 Spectra
  - Release after: 0.30 min
  - Reconsider Precursor, if Current Intens. / Previous Intens.: 5.0
- Smart Exclusion: 2×
- Precursor Ion List: Include
  - Mass Range:
    - 180.06-180.16
    - 255.13-255.23
    - 279.14-279.24
    - 289.18-289.28

Preferences

- no preferences

CID

- Isolation + Fragmentation List

Type	Mass	Width	Collision	Charge State
Base	500.0000	5.00	25.00	1

Acquisition

- MS/MS
  - Low: 10000 cts, 8 Hz
  - High: 100000 cts, 8 Hz