Supplementary material

Table a. High resolution MS data of the six pentacyclic triterpenes found in *Olea europaea* in both ESI-QTOF MS and APCI-QTOF MS detectors.

	Compound	t_r (min)	MS mode	*m/z* experimental	Pseudo-molecular formula	m/z theoretical	Error (ppm)	mSigma value	Pseudo-molecular ions* and other signals
ESI-QTOF	Maslinic acid	1.5	-	471.3491	$C_{30}H_{47}O_4$	471.3474	-3.5	11.3	471.3491 $[M-H]^-$ (100); 539.3357 $[M-H+NaHCO_2]^-$ (5.5)
			+	473.3630	$C_{30}H_{49}O_4$	473.3631	0.2	80.4	495.3488 $[M+Na]^+$ (100); 409.3456 $[M + H - H_2O - COOH]^+$ (99.6); 490.3936 $[M+NH_4]^+$ (7.7); 473.3630 $[M+H]^+$ (4.9)
	Betulinic acid	2.4	-	455.3550	$C_{30}H_{47}O_3$	455.3525	-2.5	27.8	455.3550 $[M-H]^-$ (100); 523.3408 $[M-H+NaHCO_2]^-$ (2.8)
			+	457.3686	$C_{30}H_{49}O_3$	457.3682	-0.9	30.3	457.3686 $[M+H]^+$ (100); 479.3621 $[M+Na]^+$ (97.8); 439.3528 $[M+H-H_2O]^+$ (60.7); 495.3596 $[M+K]^+$ (5.1)
	Oleanolic acid	2.8	-	455.3534	$C_{30}H_{47}O_3$	455.3525	-1.9	36.7	455.3534 $[M-H]^-$ (100); 523.3386 $[M-H+NaHCO_2]^-$ (3.7)
			+	457.3669	$C_{30}H_{49}O_3$	457.3682	2.8	39.2	439.3532 $[M+H-H_2O]^+$ (100); 479.3617 $[M+Na]^+$ (63.8); 495.3599 $[M+K]^+$ (31.8); 457.3669 $[M+H]^+$ (4.8)
	Ursolic acid	3.1	-	455.3532	$C_{30}H_{47}O_3$	455.3525	-1.5	79.3	455.3532 $[M-H]^-$ (100); 523.3420 $[M-H+NaHCO_2]^-$ (4.4)
			+	457.3670	$C_{30}H_{49}O_3$	457.3682	2.5	167.7	479.3622 $[M+Na]^+$ (100); 439.3550 $[M+H-H_2O]^+$ (98.5); 495.3278 $[M+K]^+$ (28); 457.3670 $[M+H]$+ (21.2)
	Erythrodiol	4.8	+	443.3879	$C_{30}H_{51}O_2$	443.3889	2.3	24.4	425.3769 $[M+H-H_2O]^+$ (100); 465.3699 $[M+Na]^+$ (94.5); 443.3879 $[M+H]^+$ (18.5); 407.3672 $[M + H - 2\ H_2O]^+$(5.5)
	Uvaol	5.1	+	443.3876	$C_{30}H_{51}O_2$	443.3889	2.9	21.2	465.3703 $[M+Na]^+$ (100); 425.3773 $[M+H-H_2O]^+$ (53.8); 443.3876 $[M+H]^+$ (32.8); 407.3679 $[M + H - 2\ H_2O]^+$(5.5)

	Compound	t_r (min)	MS mode	m/z experimental	Pseudo-molecular formula	m/z theoretical	Error (ppm)	i-FIT	Pseudo-molecular ions* and other signals
APCI-QTOF	Maslinic acid	1.5	-	471.3476	$C_{30}H_{47}O_4$	471.3474	0.4	28.1	471.3476 $[M-H]^-$ (100); 539.3330 $[M-H+NaHCO_2]^-$ (2.0)
			+	473.3628	$C_{30}H_{49}O_4$	473.3631	-0.6	35.9	409.3438 $[M-H_2O-COO]^+$ (100); 473.3628 $[M+H]^+$ (72.5); 437.3359 $[M+H-2H_2O]^+$ (61.8); 490.3752 $[M+NH_4]^+$ (14.6)
	Betulinic acid	2.4	-	455.3529	$C_{30}H_{47}O_3$	455.3525	0.9	43.1	455.3529 $[M-H]^-$ (100); 523.3370 $[M-H+NaHCO_2]^-$ (2.1)
			+	457.3683	$C_{30}H_{49}O_3$	457.3682	0.2	11.4	439.3559 $[M+H-H_2O]^+$ (100); 457.3683 $[M+H]^+$ (12.0)
	Oleanolic acid	2.8	-	455.3524	$C_{30}H_{47}O_3$	455.3525	-0.2	71.9	455.3524 $[M-H]^-$ (100)
			+	457.3679	$C_{30}H_{49}O_3$	457.3682	-0.7	79.1	439.3573 $[M+H-H_2O]^+$ (100); 411.3618 $[M+H-COOH]^+$ (7.0); 457.3679 $[M+H]^+$ (4.6)
	Ursolic acid	3.1	-	455.3525	$C_{30}H_{47}O_3$	455.3525	0.0	72.9	455.3525 $[M-H]^-$ (100)
			+	457.3669	$C_{30}H_{49}O_3$	457.3682	-2.8	68.1	439.3563 $[M+H-H_2O]^+$ (100); 411.3595 $[M+H-COOH]^+$ (28.9); 457.3669 $[M+H]^+$ (19.9)
	Erythrodiol	4.8	+	443.3893	$C_{30}H_{51}O_2$	443.3889	0.9	97.7	425.377 $[M+H-H_2O]^+$ (100); 407.3667 $[M+H-2H_2O]^+$ (41.4); 443.3893 $[M+H]^+$ (18.7)
	Uvaol	5.1	+	443.3889	$C_{30}H_{51}O_2$	443.3889	0	100.5	425.3773 $[M+H-H_2O]^+$ (100); 407.3669 $[M+H-2H_2O]^+$ (46.2); 443.3878 $[M+H]^+$ (44.0)

*Pseudo-molecular ions *m/z* signals are also included in this column to indicate their relative intensity.

Table b. ESI-IT MS signals produced by each analyte in both positive and negative polarities and MS/MS mode.

Compound	MS mode	Major *m/z* signals in MS	Major ion signal in MS	Precursor ions and fragments in MS/MS			Cut off energy	Amplitude (V)
Maslinic acid	-	471.3	$[M-H]^-$	**471.3**	423.3	393.4	130	1.25
	+	495.4	$[M+Na]^+$	**495.4**	451.3		137	0.8
Betulinic acid	-	455.4	$[M-H]^-$	**455.3**	407.3		126	1.3
	+	457.4	$[M+H]^+$	**479.4**	435.3		132	0.8
				457.4	439.2	411.3	126	0.8
				439.4	393.4	191.2	121	0.8
Oleanolic acid	-	455.4	$[M-H]^-$	**455.2**	407.3		126	1.25
	+	439.4	$[M+H-H_2O]^+$	**479.4**	435.3		132	0.8
				457.4	439.2	411.3	126	0.8
				439.4	191.2	393.4	121	0.8
Ursolic acid	-	455.4	$[M-H]^-$	**455.3**	407.3		126	1.25
	+	479.4	$[M+Na]^+$	**479.4**	435.3		132	0.8
				457.4	439.2	411.3	126	0.8
				439.4	191.2	393.4	121	0.8
Erythrodiol	+	425.4	$[M+H-H_2O]^+$	**465.4**	407.3		128	0.7
				425.4	191.2	407.3	117	0.7
				443.4	425.3	191.2	122	0.7
Uvaol	+	465.4	$[M+Na]^+$	**465.4**	407.3		128	0.7
				425.4	191.2	407.3	117	0.7
				443.4	425.3	191.2	122	0.7

In bold letter we indicate the precursor ion. Fragments appear in decreasing order of intensity in the MS/MS spectrum. In every case, width in MS/MS was set at 4 units of *m/z*.