

SUPPORTING INFORMATION

Furanolysis with menthofuran: A new depolymerization method for analyzing condensed tannins

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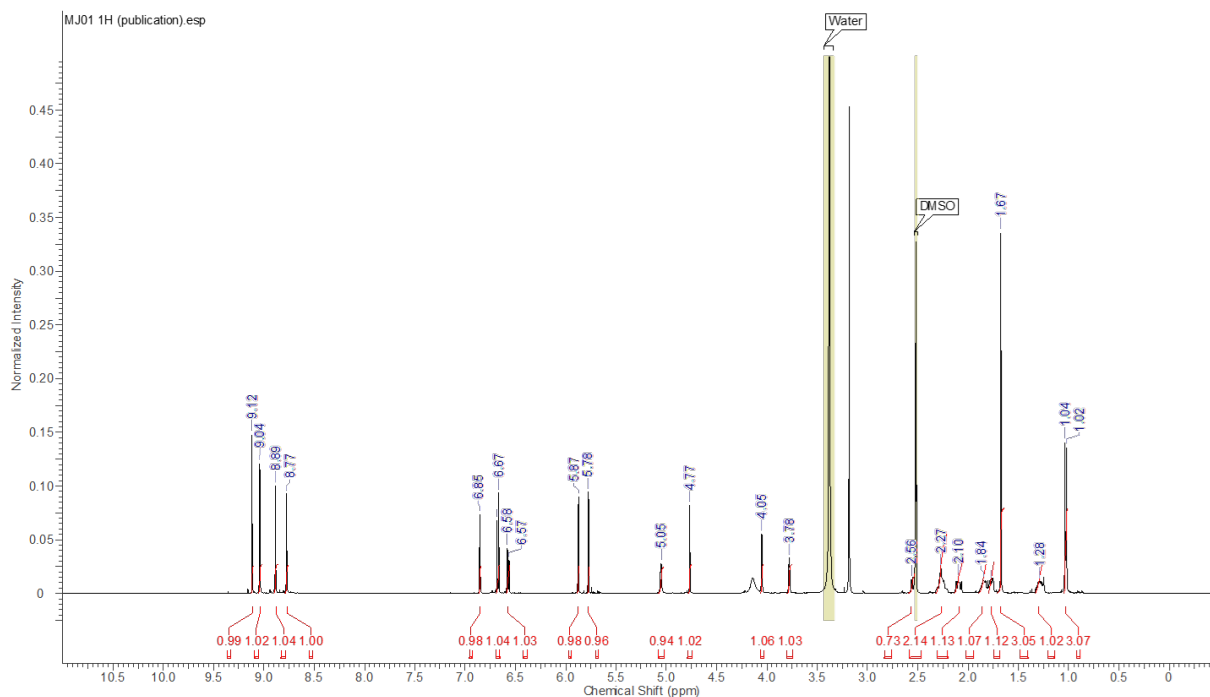


Figure S1

¹H NMR chemical shifts of epicatechin-(4→5)-menthofuran.

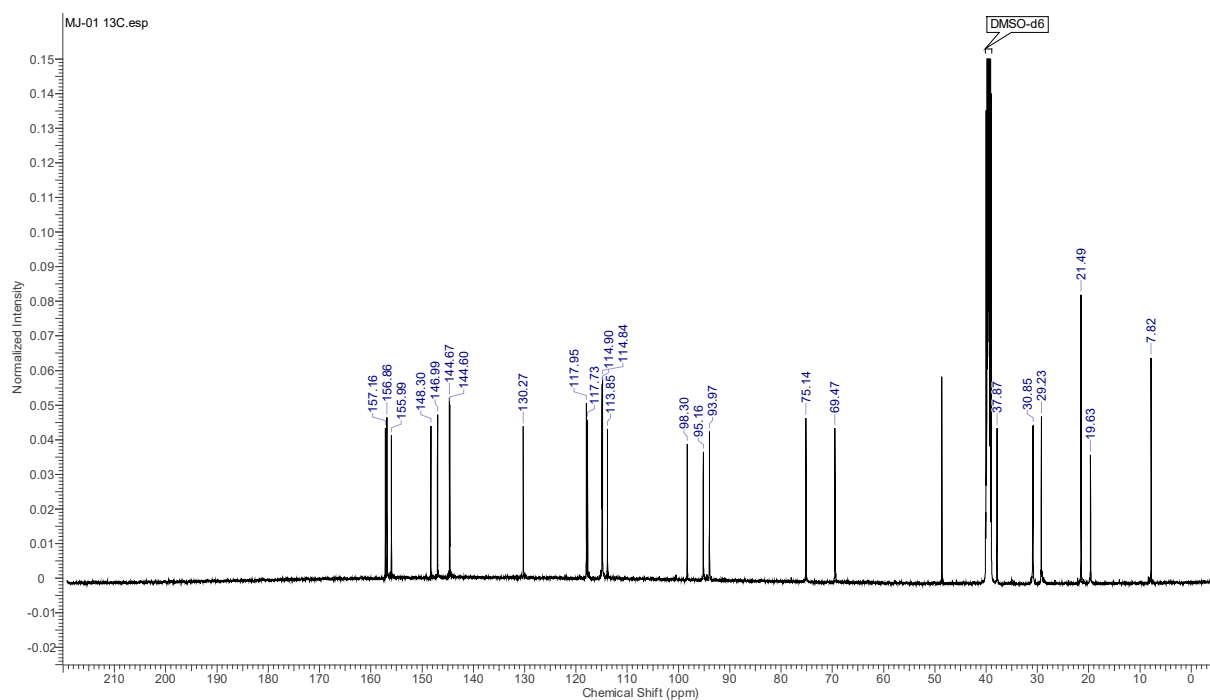


Figure S2

¹³C NMR chemical shifts of epicatechin-(4→5)-menthofuran.

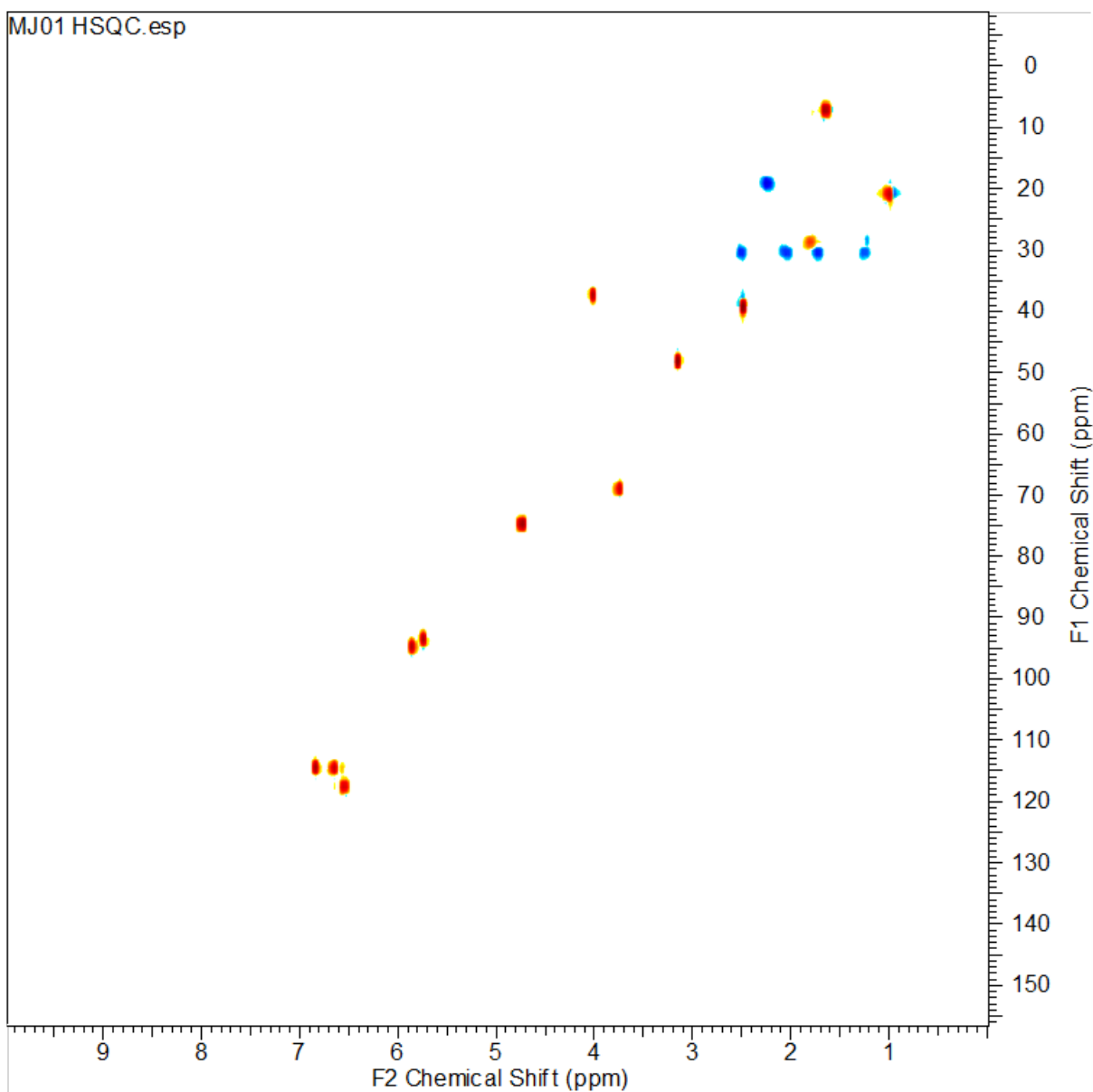


Figure S3

HSQC spectrum of epicatechin-(4→5)-menthofuran.

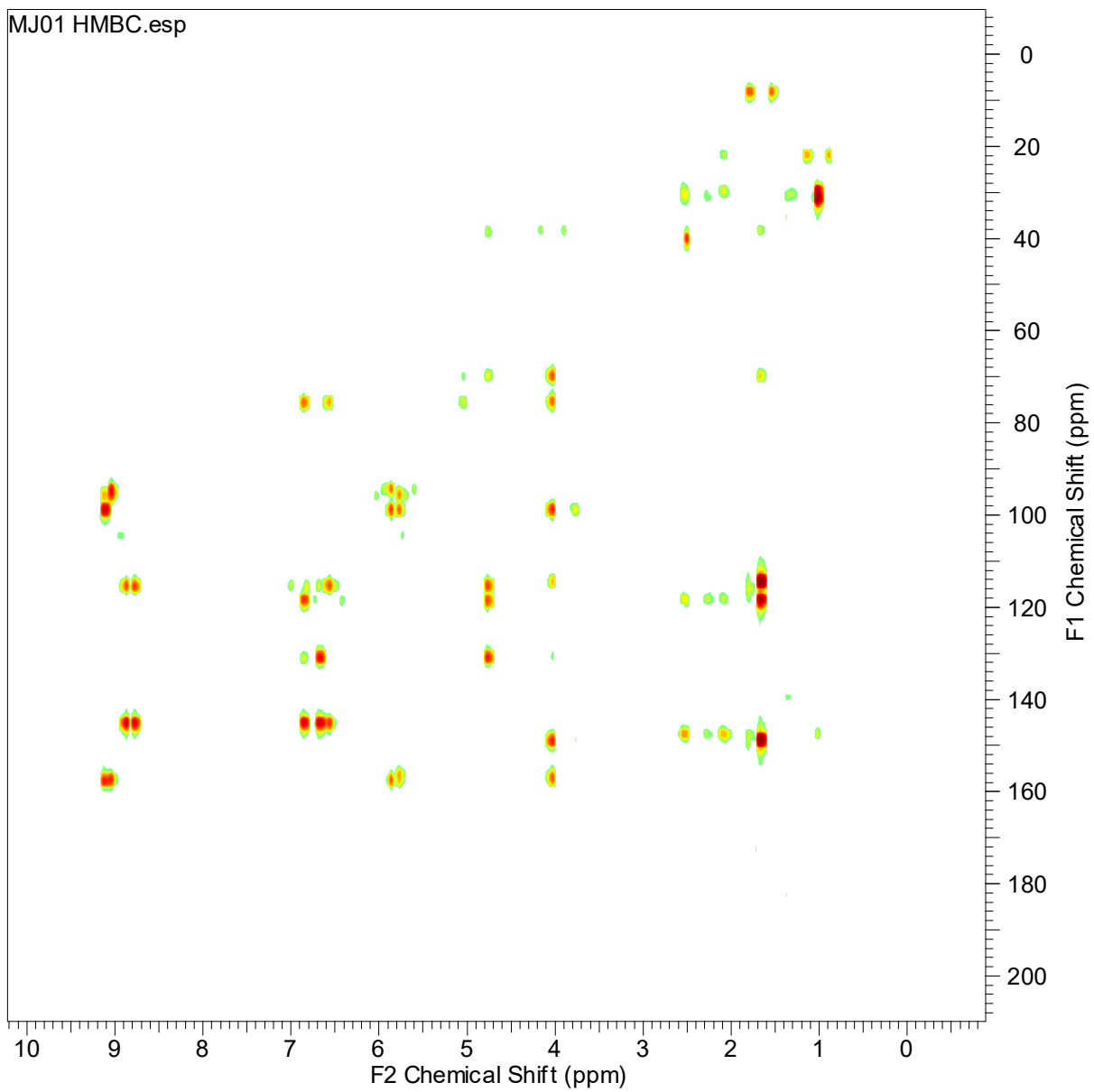


Figure S4

HMBC spectrum of epicatechin-(4→5)-menthofuran.

High Resolution Mass Result

Analysis Info

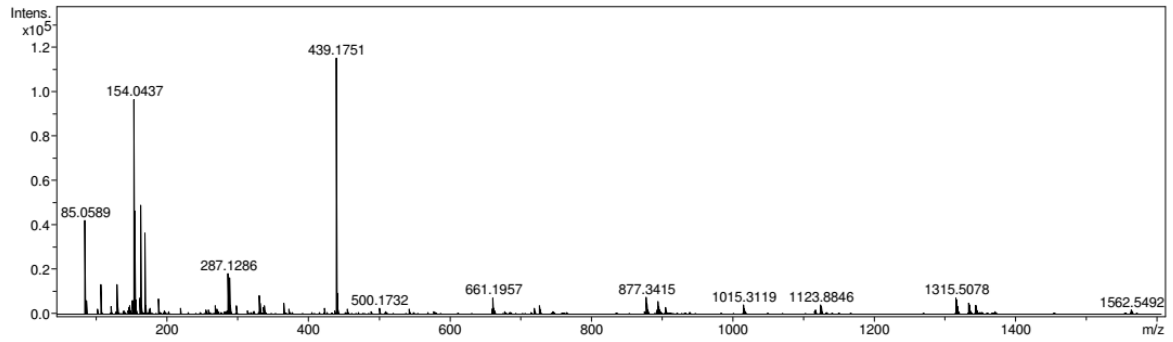
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Instrument / Ser# micrOTOF-Q II 10300

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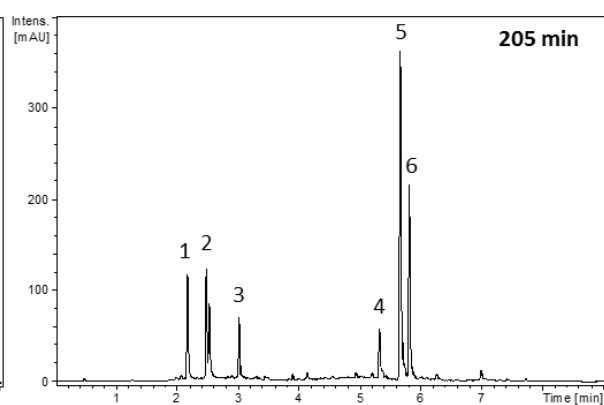
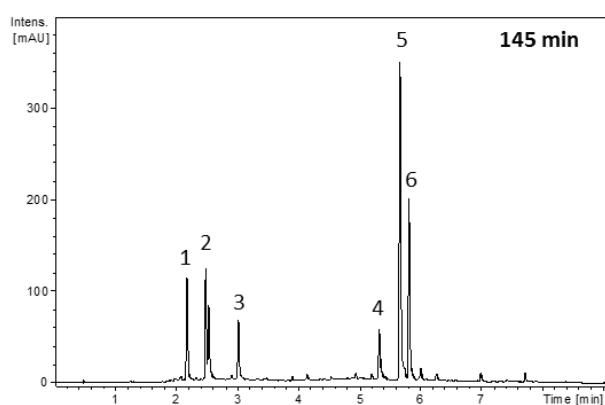
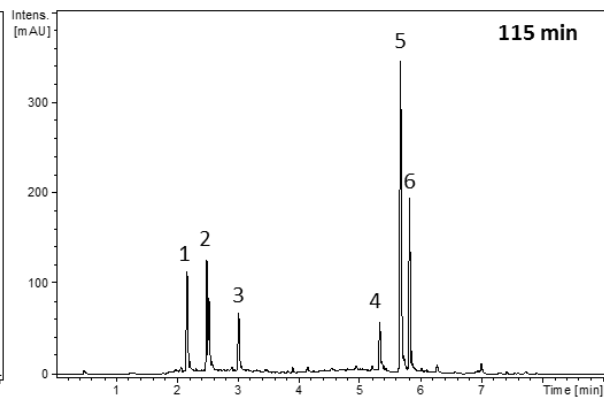
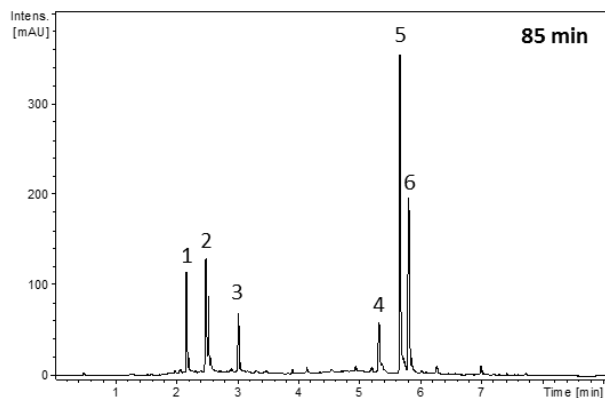
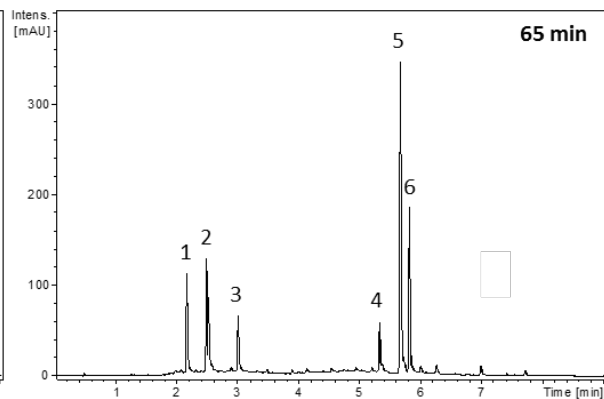
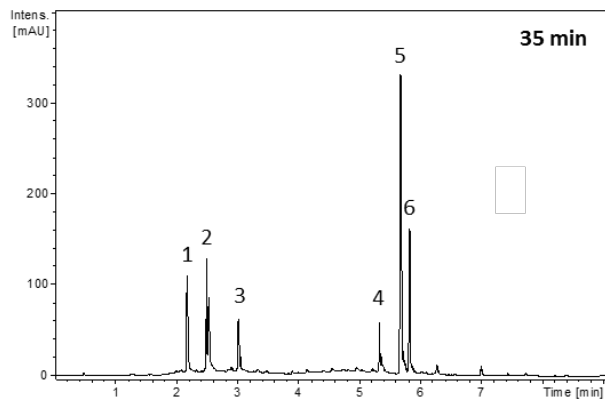
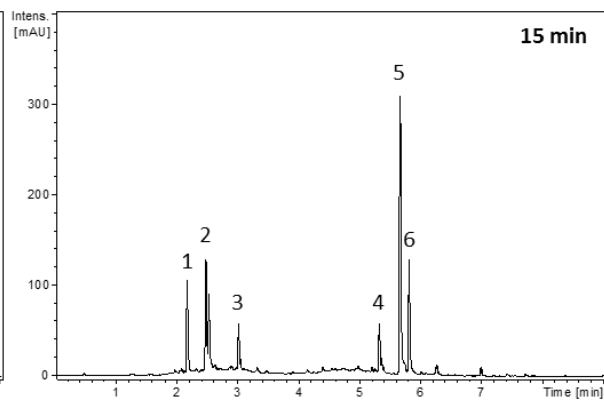
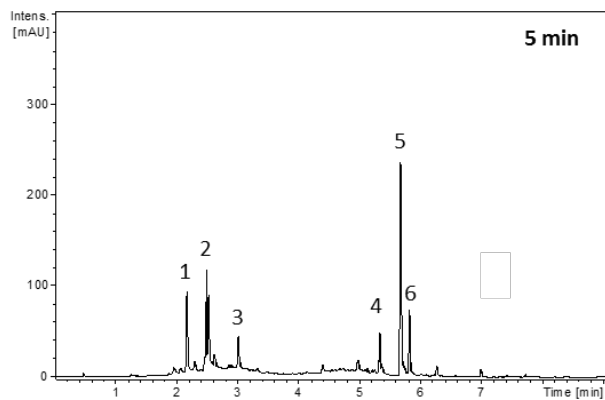
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Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	rdB	e ⁻ Conf	N-Rule
439.1751	1	C ₂₅ H ₂₇ O ₇	100.00	439.1751	0.1	0.1	12.5	even	ok
	2	C ₃₂ H ₂₃ O ₂	0.29	439.1693	-5.8	-13.3	21.5	even	ok

Figure S5

HMRS spectrum of epicatechin-(4→5)-menthofuran.



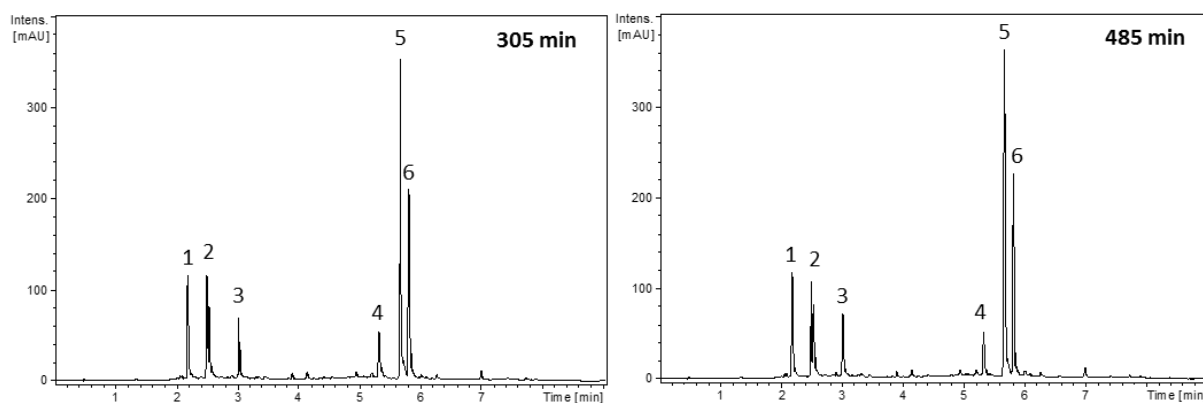


Figure S6

UV chromatograms (280 nm) of the grape seed extract depolymerization products obtained with menthofuran at all the reaction time performed (i.e., 5 min, 15 min, 35 min, 65 min, 85 min, 115 min, 145 min, 205 min, 305 min, and 485 min) for a single kinetic experiment out of three independent replicates. **1**: C (Retention Time (RT) 2.2 min; 291 m/z), **2**: EC (RT 2.5 min; 291 m/z), **3**: ECG (RT 3.0 min; 443 m/z), **4**: C-MF (RT 5.3 min; 439 m/z), **5**: EC-MF (RT 5.7 min; 439 m/z), **6**: ECG-MF (RT 5.9 min; 591 m/z). The peak areas measured for these six products are used to obtain Figure 2.

Table S1

Protonated molecule, retention time and molar response relative to epicatechin of the procyanidin and prodelphinidin depolymerization products of this study.

	Protonated molecule [M + H] ⁺	Retention time (min)	Molar response relative to EC
Terminal units			
C	291	2.6 ^a / 2.2 ^b	1.0 ^{c,d}
EC	291	3.1 ^a / 2.5 ^b	1.0
ECG	443	3.8 ^a / 3.0 ^b	3.7 ^c
EGC	307	2.4 ^a / 2.0 ^b	0.24 ^c
EGCG	459	3.1 ^a / 2.5 ^b	3.0 ^c
Extension units (phloroglucinol)			
C-PG	415	2.2 ^a	1.1 ^d
EC-PG	415	2.3 ^a	1.1 ^{d,e}
ECG-PG	567	3.0 ^a	3.7 ^d
Extension units (2-mercaptoethanol)			
C-ME	367	3.2 ^a	1.0 ^f
EC-ME	367	3.6 ^a	1.0 ^e
ECG-ME	519	4.2 ^a	3.7 ^f
EGC-ME	383	3.0 ^a	0.24 ^f
EGCG-ME	535	3.4 ^a	3.0 ^f
Extension units (menthofuran)			
C-MF	439	5.2 ^b	1.0 ^f
EC-MF	439	5.6 ^b	1.0 ^e
ECG-MF	591	5.8 ^b	3.7 ^f
EGC-MF	455	5.0 ^b	0.24 ^f
EGCG-MF	607	5.3 ^b	3.0 ^f

Retention times determined with (a) the first gradient conditions given in the section Analytical method (UHPLC-DAD-MS system), (b) the second gradient conditions applied exclusively to menthofuran analyses.

Molar responses relative to EC (c) were determined by calibration with commercial standards, (d) were found in Kennedy and Jones³⁰, (e) were obtained by depolymerizing a procyanidin B2 sample with a large excess of nucleophile, (f) were assumed considering that the additional nucleophile moiety does not alter the molar response of the flavanol.

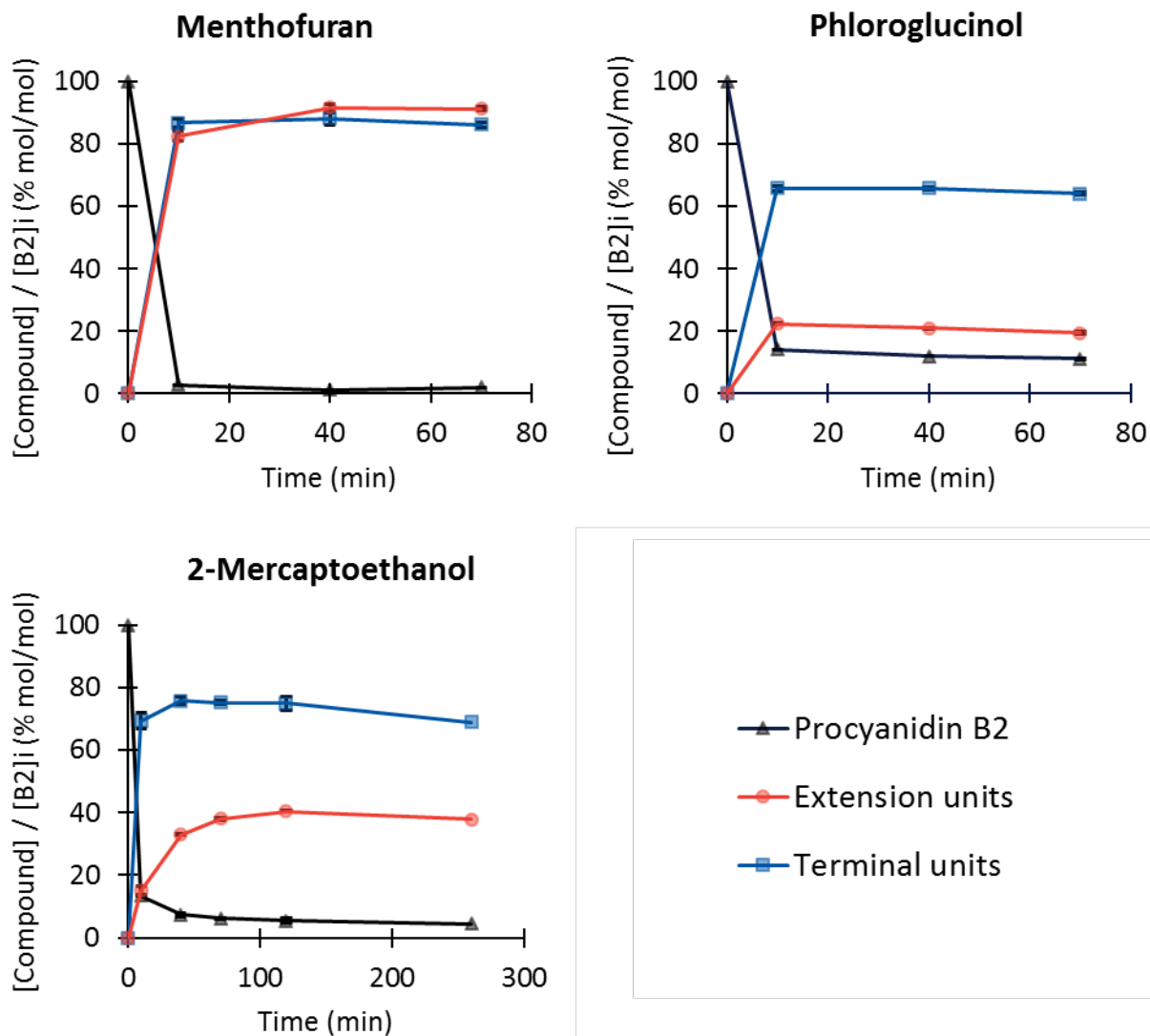


Figure S7

Kinetics of the depolymerization tests performed on procyanidin B2 with 1 molar equivalent of nucleophile including menthofuran, phloroglucinol, and 2-mercaptoethanol. Procyanidin B2 are represented by black triangles, extension units (EC-NU) by red circles, and terminal units (EC) by blue squares, all concentrations being normalized by the initial concentration of procyanidin B2. The same experimental data are used in Table 1.

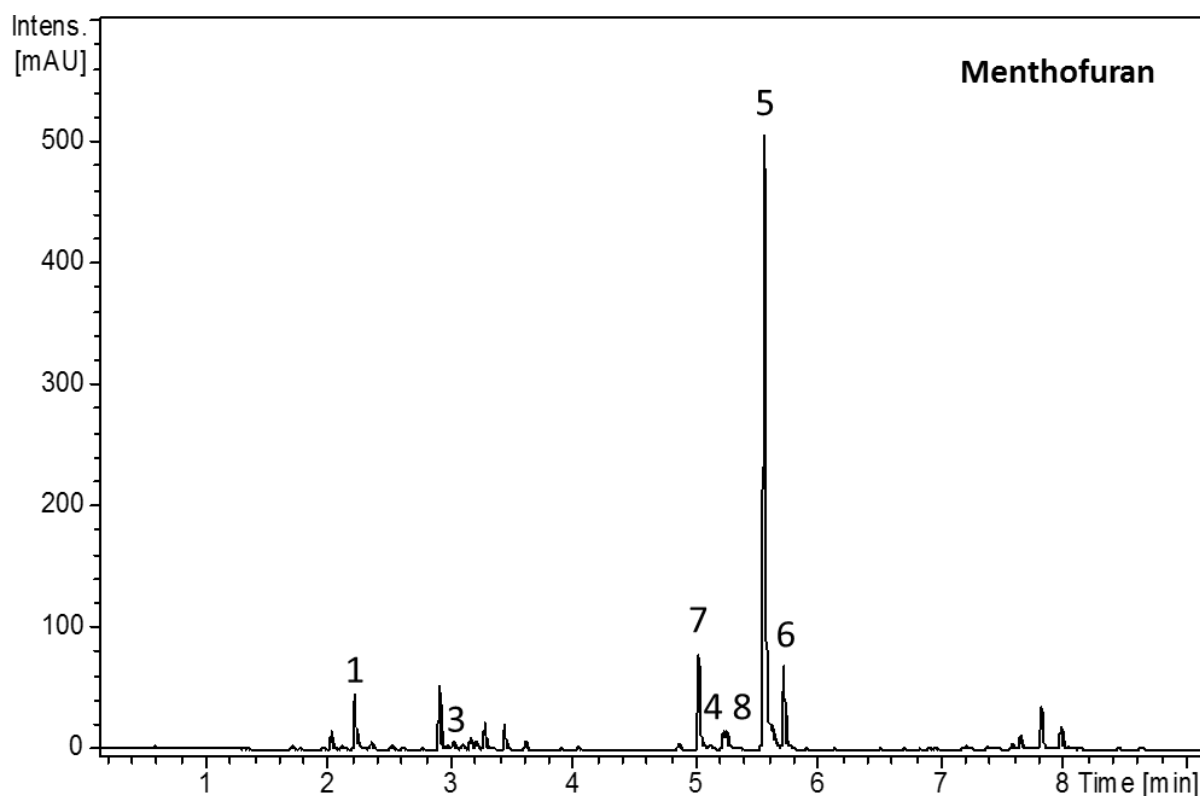


Figure S8

UV chromatogram (280 nm) of the grape pericarp depolymerization products obtained with menthofuran after 2h of reaction for a single characterization experiment out of three independent replicates. **1**: C (Retention Time (RT) 2.2 min; 291 m/z), **3**: ECG (RT 3.0 min; 443 m/z), **4**: C-MF (RT 5.2 min; 439 m/z), **5**: EC-MF (RT 5.6 min; 439 m/z), **6**: ECG-MF (RT 5.8 min; 591 m/z), **7**: EGC-MF (RT 5.0 min; 455 m/z), **8**: EGCG-MF (RT 5.3 min; 591 m/z). The peak areas measured for these seven products are used to obtain Figure 3.

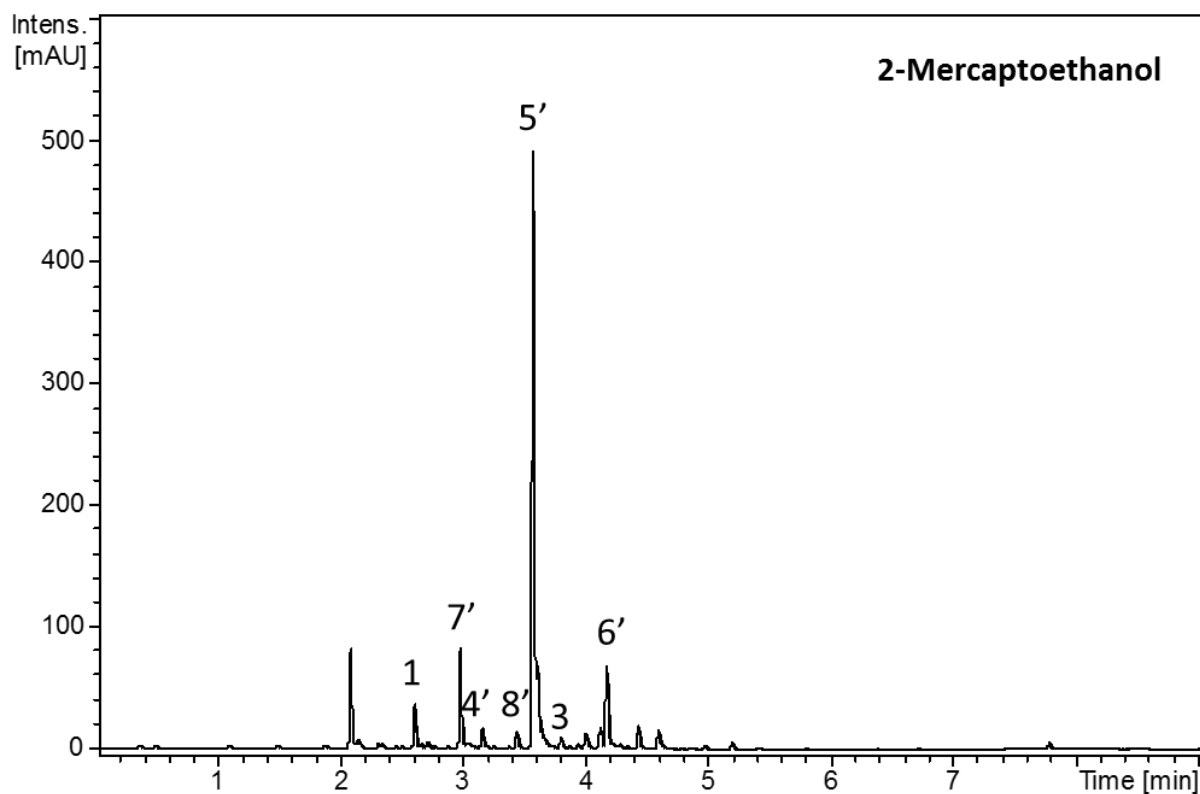


Figure S9

UV chromatograms (280 nm) of the grape pericarp depolymerization products obtained with 2-mercaptoethanol for a single characterization experiment out of three independent replicates. **1**: C (Retention Time (RT) 2.6 min; 291 m/z), **3**: ECG (RT 3.8 min; 443 m/z), **4'**: C-ME (RT 3.2 min; 367 m/z), **5'**: EC-ME (RT 3.6 min; 367 m/z), **6'**: ECG-ME (RT 4.2 min; 519 m/z), **7'**: EGC-ME (RT 3.0 min; 383 m/z), **8'**: EGCG-ME (RT 3.4 min; 535 m/z). The peak areas measured for these seven products are used to obtain Figure 3.