

Supporting Information

Terpenoid Oligomers of Dammar Resin

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Contents: FIA/ESI mass spectra of five triterpenoid standard compounds (lupeol, lupenone, betulin, betulinic acid, hydroxydammarone and oleanolic acid) and tandem mass spectra of relevant m/z values

The FIA/ESI mass spectra of five triterpenoid standard compounds (lupeol, lupenone, betulin, betulinic acid, hydroxydammarone and oleanolic acid) are reported in Figure S1.

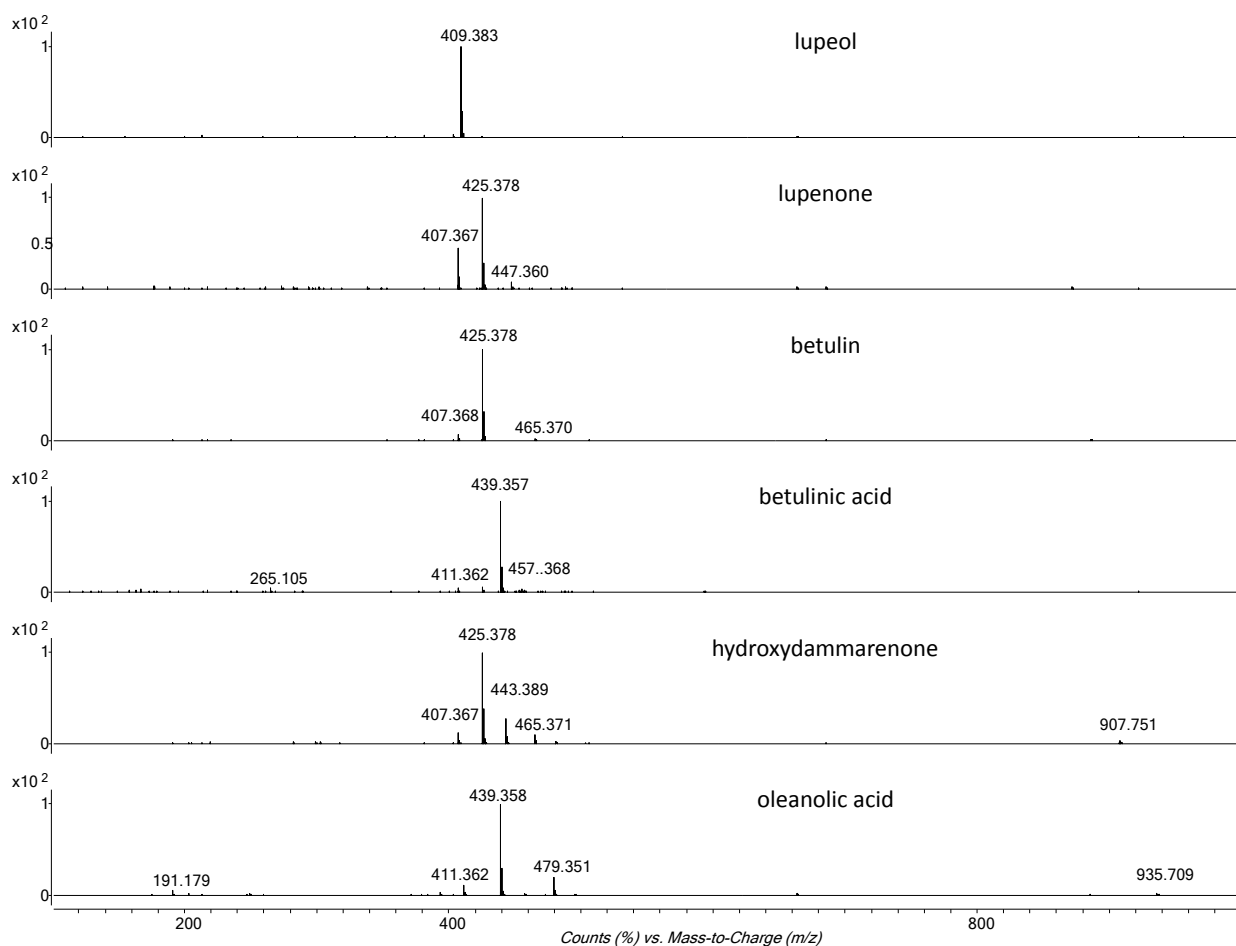
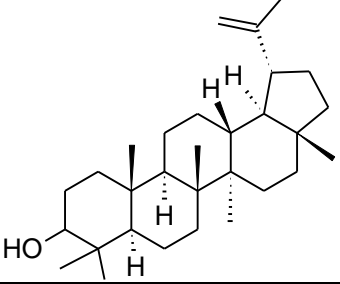
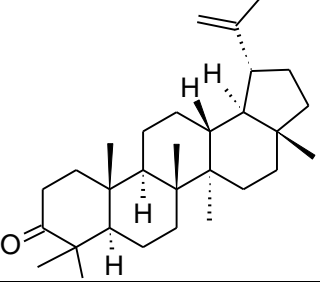
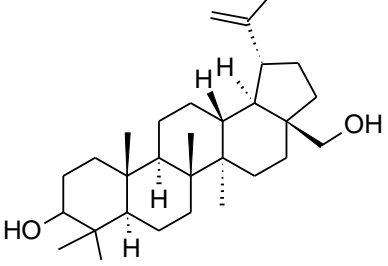
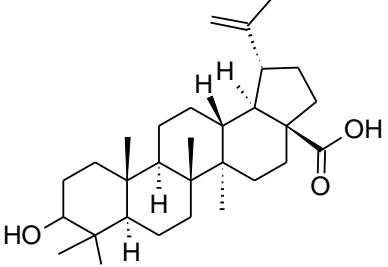
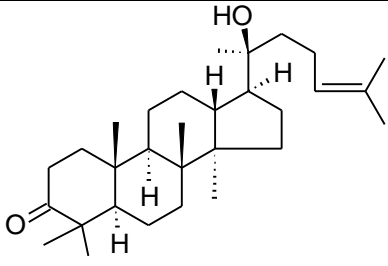
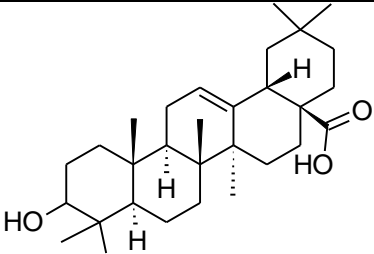


Figure S1. FIA/ESI mass spectra of the CH₂Cl₂- MeOH solutions of five triterpenoid standards

All the detected peaks correspond to singly charged ions. Possible assignments for the main peaks observed in the FIA/ESI mass spectra are reported in Table 1.

Table S1. Possible Assignments for the Main Peaks Observed in the FIA/ESI Mass Spectra of the CH₂Cl₂- MeOH Solutions of Five Triterpenoid Standards

compound (molecular formula)	molecular structure	assignment	m/z	theoretical m/z	mass accuracy (ppm)
lupeol (C ₃₀ H ₅₀ O)		[C ₃₀ H ₅₀ O - H ₂ O+H] ⁺	409.383	409.3834	-1.0
lupenone (C ₃₀ H ₄₈ O)		[C ₃₀ H ₄₈ O - H ₂ O+H] ⁺ [C ₃₀ H ₄₈ O + H] ⁺ [C ₃₀ H ₄₈ O+ Na] ⁺	407.367 425.378 447.360	407.3672 425.3783 447.3602	-0.5 -0.7 -0.6
betulin (C ₃₀ H ₅₀ O ₂)		[C ₃₀ H ₅₀ O ₂ - 2H ₂ O+H] ⁺ [C ₃₀ H ₅₀ O ₂ - H ₂ O+H] ⁺ [C ₃₀ H ₅₀ O ₂ + H] ⁺ [C ₃₀ H ₅₀ O ₂ + Na] ⁺	407.368 425.378 443.388 465.370	407.3672 425.3783 443.3884 465.3703	-2.0 -0.7 -0.9 -0.6
betulinic acid (C ₃₀ H ₄₈ O ₃)		[C ₃₀ H ₄₈ O ₃ - COOH] ⁺ [C ₃₀ H ₄₈ O ₃ - H ₂ O+H] ⁺ [C ₃₀ H ₄₈ O ₃ + H] ⁺ [C ₃₀ H ₄₈ O ₃ + Na] ⁺	411.362 439.358 457.368 479.349	411.3626 439.3576 457.3682 479.3501	-1.4 0.9 -0.4 -2.3
hydroxy- dammarenone (C ₃₀ H ₅₀ O ₂)		[C ₃₀ H ₅₀ O ₂ - 2H ₂ O+H] ⁺ [C ₃₀ H ₅₀ O ₂ - H ₂ O+H] ⁺ [C ₃₀ H ₅₀ O ₂ + H] ⁺ [C ₃₀ H ₅₀ O ₂ + Na] ⁺ [C ₆₀ H ₁₀₀ O ₄ + Na] ⁺	407.367 425.378 443.389 465.370 907.751	407.3672 425.3778 443.3884 465.3703 907.7519	-0.5 -0.7 1.3 -0.6 1.0

oleanolic acid ($C_{30}H_{48}O_3$) 	$[C_{30}H_{48}O_3 - COOH]^+$	411.362	411.3626	-1.4
	$[C_{30}H_{48}O_3 - H_2O + H]^+$	439.357	439.3576	-1.3
	$[C_{30}H_{48}O_3 + H]^+$	457.368	457.3682	-0.4
	$[C_{30}H_{48}O_3 + Na]^+$	479.350	479.3501	-0.2
	$[C_{60}H_{96}O_6 + Na]^+$	935.709	935.7104	-1.5

The mixture of hydroxydammarone and oleanolic acid (Figure S2) shows the same peaks as those observed when the triterpenoids were analysed separately, plus one ion at m/z 931.731 which is consistent with the sodiated form of a species of molecular formula $C_{60}H_{98}O_5$ (theoretical m/z 931.7301, mass accuracy 1.0 ppm)

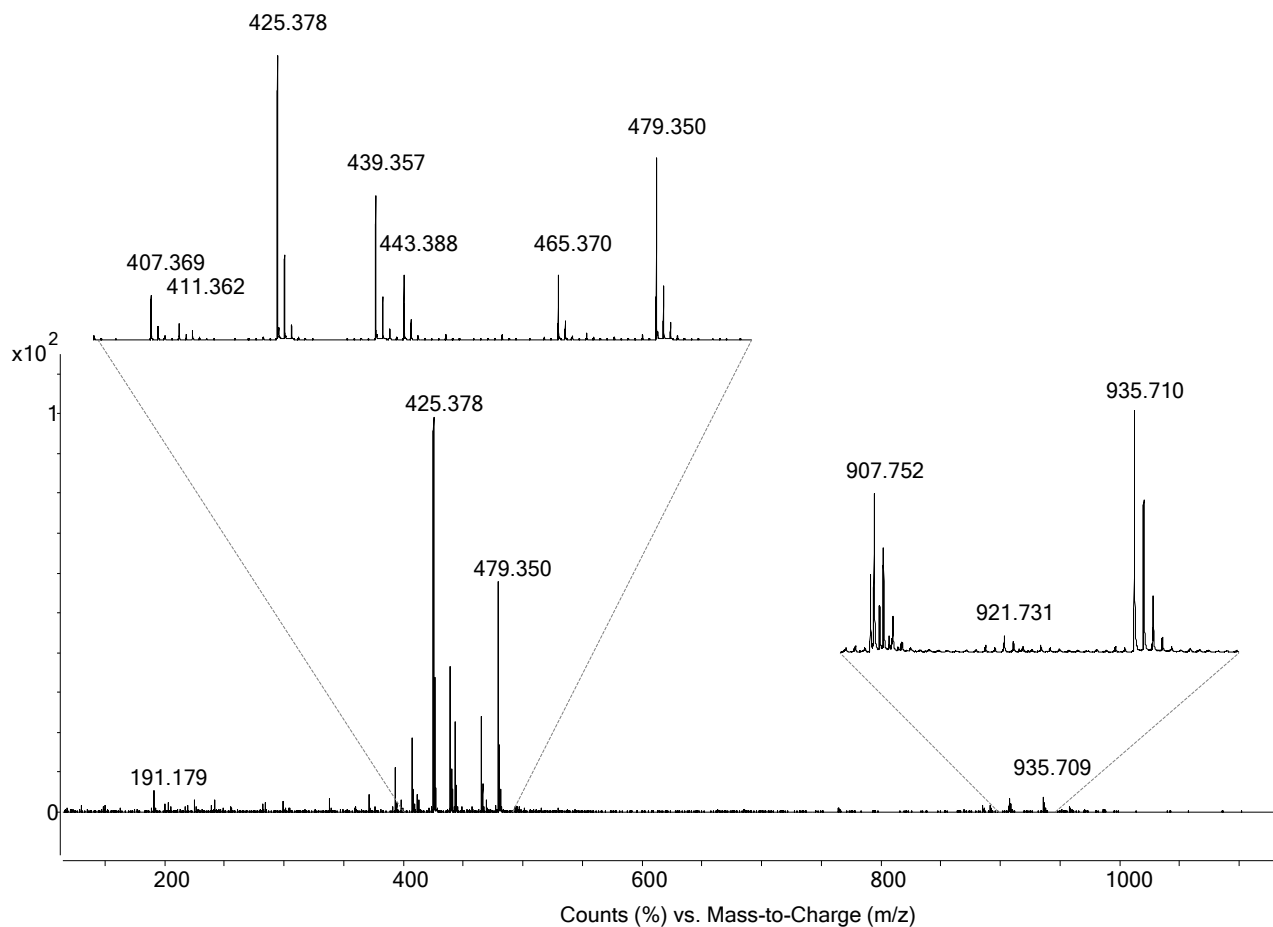


Figure S2. FIA/ESI mass spectrum of the CH_2Cl_2 - MeOH solution of a mixture of hydroxydammarenone and oleanolic acid

In order to investigate the structure of the species responsible for the signals at m/z 907.751, m/z 921.731 and m/z 935.709, MS/MS experiments were carried out, and relative tandem mass spectra are shown in Figure S3.

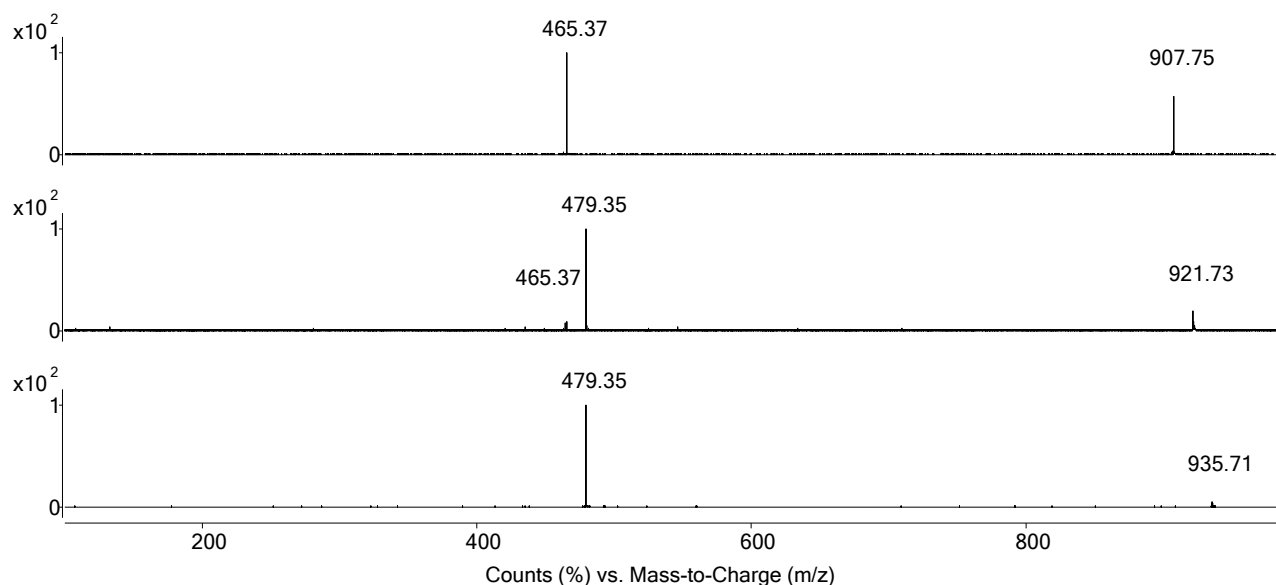


Figure S3. Tandem mass spectra of the ions at m/z 907.751, m/z 921.731 and m/z 935.709. The voltage used for CID was 30 V.

The spectra are dominated by signals that can be assigned to sodiated pseudomolecular ions of triterpenoids, and the difference between the precursor ion and the fragments is compatible with the neutral loss of a triterpenoid molecule. In particular, the ion at m/z 907.751 can be ascribed to the sodiated adduct of two hydroxydammarenone molecules, the ion at m/z 935.709 to the sodiated adduct of two oleanolic acid molecule, and the ion at m/z 921.731 to the sodiated adduct of a hydroxydammarenone and oleanolic acid molecule.