Electronic Supplementary Material (ESI) for Environmental Science: Nano.

Supporting information for

Nanoelicitors with prolonged retention and sustained release to produce beneficial compounds in wine

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S1. MeJ quantification by UV-Vis spectroscopy

MeJ ketone group strongly absorbs in the UV region near λ = 291 nm and its ester group absorbs at λ = 214 nm (Figure S1a).[1] We selected the former absorption band for the calibration curves. Taking into account the low solubility of MeJ, we carried out two calibration curves: (1) 100-800 ppm in ultrapure water (Figure S1b, green dots) and (2) 100-2000 ppm ultrapure water:ethanol (50:50, Figure S1b, blue dots). The fitting parameters for each curves are:

$$Abs = 1.73 \cdot 10^{-4}\,[MeJ] + 0.0078 \quad R^2 = 0.99 \qquad (1)$$

$$Abs = 2.07 \cdot 10^{-4}[MeJ] - 0.0028 \quad R^2 = 0.99 \qquad (2)$$

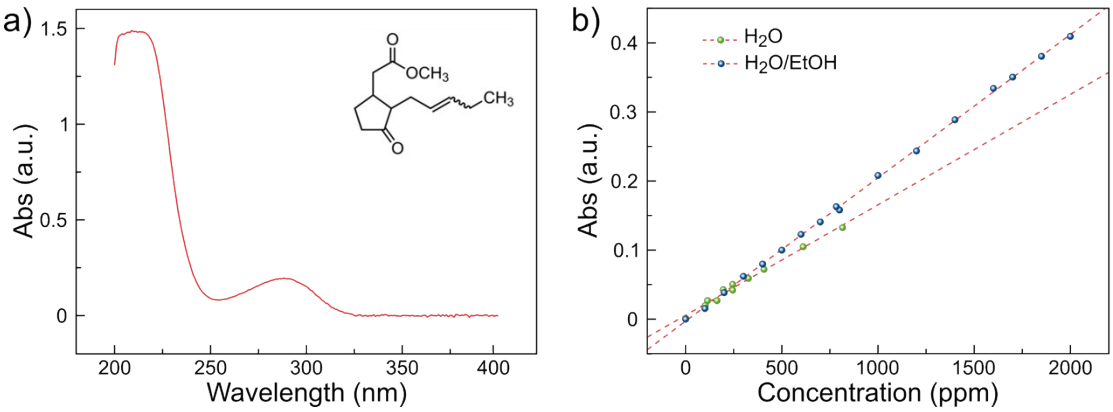

Fig. S1 UV-Vis spectrum (a) and calibration curve (b) of methyl jasmonate in H_2O (green dots) and H_2O/EtOH (1:1, blue dots). Dashed lines represent the best fits of the experimental data according to equation 1 for H_2O and equation 2 for H_2O/EtOH.

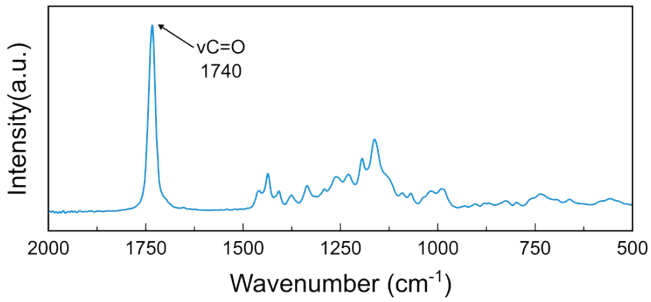

Fig. S2 FTIR spectrum of MeJ showing the most intense absorption band at 1740 cm^{-1} corresponding to carbonyl (ketone) groups.[2]

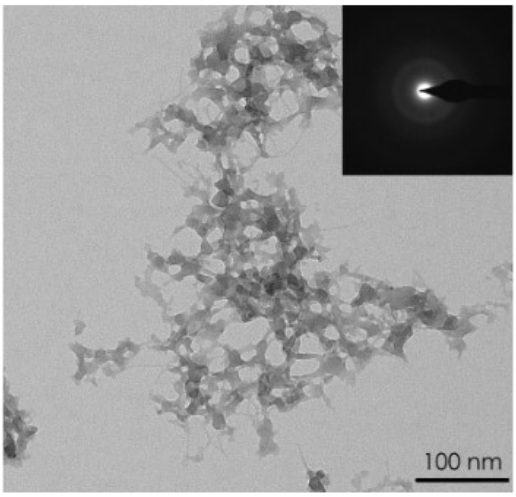

Fig. S3 TEM micrograph of nano-MeJ. The nanoparticles shows the same morphology than control ACP nanoparticles.[3] The amorphous nature of the particles is confirmed by the lack of diffraction spots in the selected-area electron diffraction (SAED) pattern (inset).

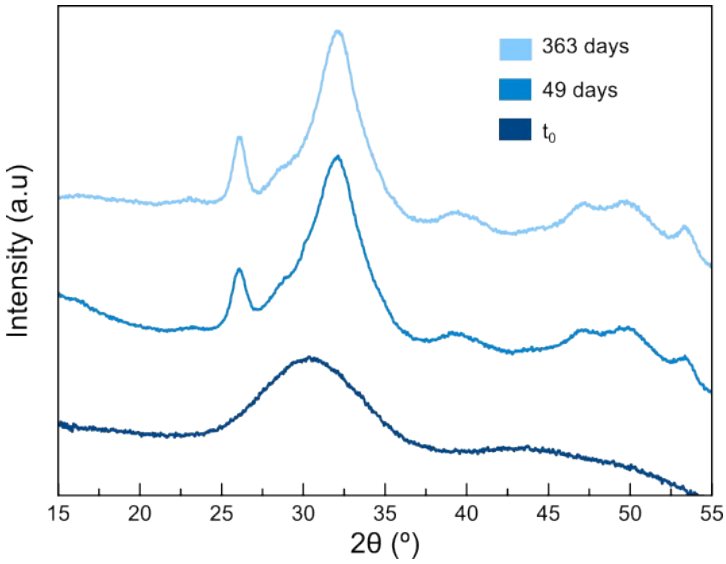

Fig. S4 XRD patterns of nano-MeJ sample freeze-dried at time 0, 49 and after 363 days. XRD patterns after 49 and 363 days of storage show two broad Bragg peaks at around 26º and 32º (2θ) ascribed to hydroxyapatite (HA, ASTM card file No 09-432).

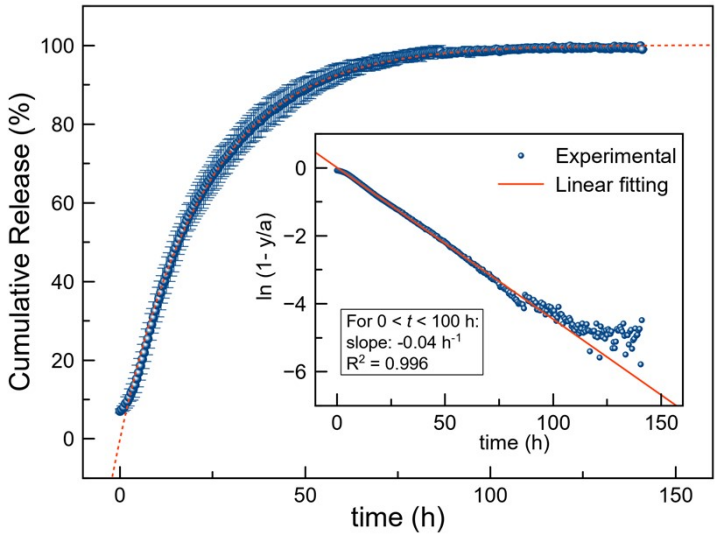

Fig. S5 MeJ release profile from nano-MeJ in ultrapure water. Dashed line represents the best fits of the experimental data to the first order equation: $y(t) = a*(1-e^{-kt})$, being the rate constant, k = 0.05 h^{-1}. The inset shows the linearized experimental data (symbols) and the first order equation (line).

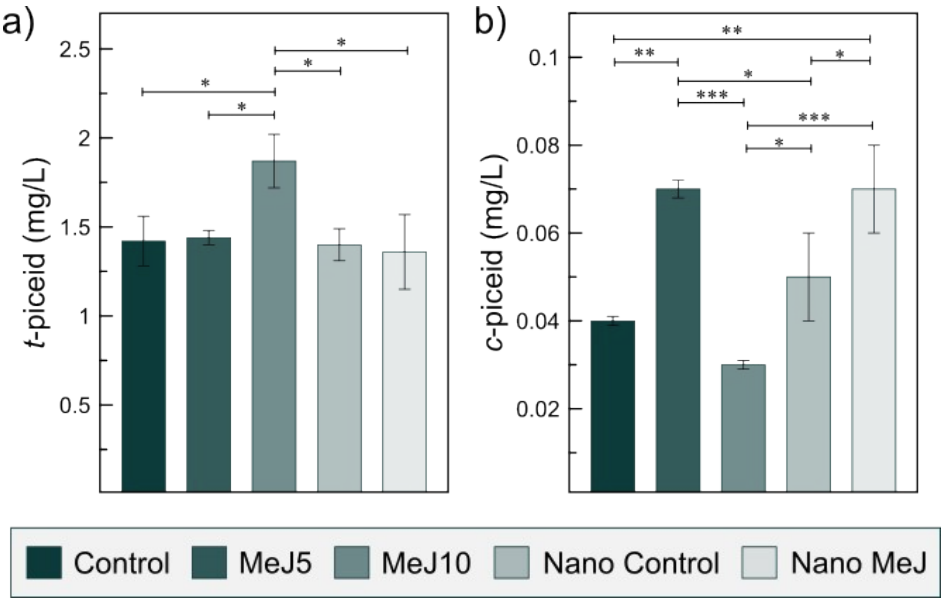

Fig. S6 (a) *t*-piceid and **(b)** *c*-piceid concentration (mg L^{-1}) in wines from grapes treated with MeJ (5 mM, MeJ5, and 10 mM, MeJ10) and nano-MeJ with a total concentration of 1 mM. Results of grapes treated with ACP nanoparticles (nano-Control) and non-treated grapes (control) are also shown. Data are expressed as mean with their corresponding standard deviation as error bars. Statistically significant differences between measurements are marked with * (P-value < 0.05), ** (P-value < 0.01) or *** (P-value < 0.001).

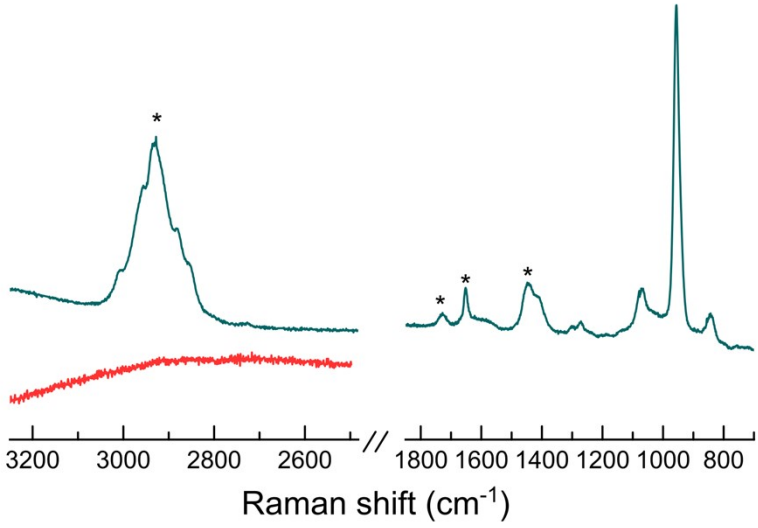

Fig. S7 Raman spectroscopy of 10 mM MeJ (red spectrum) and NanoMeJ (blue spectrum) after 24 hours at 50°C. Asterisks indicate the presence of MeJ.

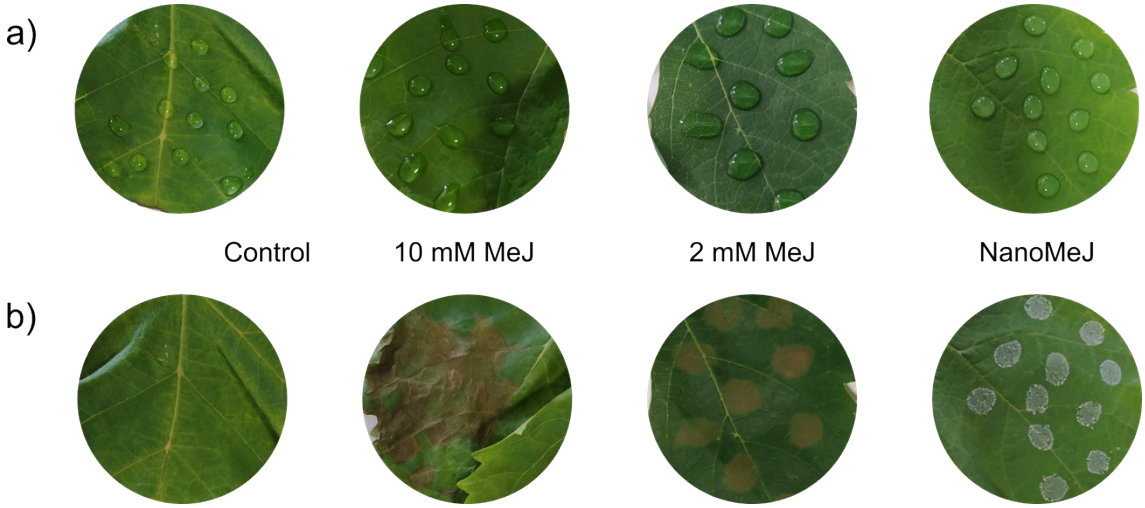

Fig. S8. Images of vineyards leaves treated with water (Control), MeJ solution (10 and 2 mM) and NanoMeJ (2 mM) at time zero (a) and after 24 hours (b).

Table S1. Chemical composition and ζ-potential of nano-MeJ and ACP nanoparticles (nano-Control). Data are expressed as mean ± standard deviation.

	Ca[a] (wt.%)	P[a] (wt.%)	K[a] (wt.%)	Ca/P[a]	ζ[b] (mV)	MeJ[c] (wt.%)
Nano-MeJ	18.02 ± 4.3	8.79 ± 1.3	0.27 ± 0.01	1.57 ± 0.13	-15.7 ± 0.6	6.15 ± 1.71
Nano-Control	14.7 ± 0.14	8.06 ± 0.1	0.46 ± 0.01	1.41 ± 0.03	-10.3 ± 0.7	-

[a] Analysed by ICP-OES. [b]Analysed by Litesizer 500. [c]Estimated by UV-Vis spectroscopy

Table S2. Enological parameters of the must from grapes under each treatment. Statistically significant differences between measurements are marked with ** (P-value < 0.01) whereas ns means no statistical differences.

	Control	Nano-Control	MeJ	Nano-MeJ	p
ºBaumé	12.9 ± 0.4	13.1 ± 0.2	12.8 ± 0.2	12.9 ± 0.4	ns
Total Acidity (g/L)	2.8 ± 0.2b	2.5 ± 0.1c	3.2 ± 0.2a	2.9 ± 0.1b	**
pH	3.9 ± 0.1	3.9 ± 0.1	3.8 ± 0.1	3.9 ± 0.1	ns

References

1 J. Islam, S. Phukan and P. Chattopadhyay, Development of a validated RP-HPLC/DAD method for the quantitative determination of methyl jasmonate in an insect repellent semi-solid formulation, *Heliyon*, 2019, **5**, e01775.

2 T. Sato, T. Kawara, K. Sakata and T. Fujisawa, Jasmonoid Synthesis from sci-4-Heptenoic Acid, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 505–508.

3 G. B. Ramírez-Rodríguez, G. Dal Sasso, F. J. Carmona, C. Miguel-Rojas, A. Pérez-de-Luque, N. Masciocchi, A. Guagliardi and J. M. Delgado-López, Engineering Biomimetic Calcium Phosphate Nanoparticles: A Green Synthesis of Slow-Release Multinutrient (NPK) Nanofertilizers, *ACS Appl. Bio Mater.*, 2020, **3**, 1344–1353.