Biomimetically relevant self-condensations of C_5 units derived from lysine

A contribution from:

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SUPPORTING INFORMATION
Acetylation of 6 into compounds 6A and 6B:

[A]: oil, $\delta_C$ (100 MHz; CDCl$_3$) 193.0 (HC=O), 169.1 (CH$_3$CO), 150.3 (C-5), 140.9 (C-6), 91.7 (C2), 71.7 (C-8a), 40.5 (C-4a), 28.5, 27.2, 24.1, 20.9, 20.8 (CH$_3$).

[B]: crystals, $\delta_C$ (100 MHz; CDCl$_3$) 193.0 (HC=O), 168.9 (CH$_3$CO), 149.4 (C-5), 140.9 (C-6), 94.2 (C2), 76.8 (C-8a), 40.2 (C-4a), 30.1, 27.3, 27.2, 20.9, 20.8 (CH$_3$).
Crystal structure determinations

Single colourless crystals of 8, 10, 18 were recrystallised from cyclohexane, ethylic ether, cyclohexane/ethyl acetate (7:3) respectively, and glued on top of a thin silica rod and X-ray data were collected on an Enraf-Nonius kappaCCD diffractometer at room temperature using graphite monochromatized Mo-Kα radiation (λ = 0.7107 Å).

Each crystal was positioned at 31 mm from the CCD and the Bragg peaks were measured using a ϕ-and-ω-scan-strategy optimized by the COLLECT suite once the cell parameters were derived by DENZO (HKL2000 suite) from a preliminary ϕ-scan. The counting time employed was 10 s (20 s for compound 10) per degree of oscillation. Data reduction including a multiscan absorption correction was carried out using the Scalepack (HKL2000). The structures were solved by direct methods and by subsequent difference Fourier syntheses and refined by full matrix least squares on F² using the SHELX-97 suite. Anisotropic thermal parameters were used for all non-hydrogen atoms whereas hydrogen atoms, located from difference Fourier maps, were refined as a riding model with Uiso = 1.2Ueq of the parent atom (1.5 for the O–H hydrogen atoms).

Crystal data of compound 8, C₁₀H₁₂O₃. Mr = 180.20. Monoclinic, space group P 2₁/c, Z = 4, a = 6.627(1), b = 12.282(3), c = 10.388(2) Å, β = 96.38(5)°, V = 908.7(3)Å³, ρ(calc)=1.317g.cm⁻³, μ=0.097mm⁻¹. 13337 reflections were collected and subsequently merged to 1646 unique reflections with an Rint of 0.0189. The final refinement of 119 parameters converged to final R and wR indices R1 = 0.073 and wR2 = 0.197 for 1166 reflections with I > 2σ(I) and R1 = 0.096 and wR2 = 0.219 for all hkl data.

Crystal data of compound 10. C₁₀H₁₆O₄. Mr = 200.23. Triclinic, space group P -1, Z = 2, a = 6.280(3), b = 7.095(3), c = 11.413(5) Å, α = 97.531(5), β = 102.847(8), γ = 101.348(6)°, V = 477.9(4)Å³, ρ(calc)=1.391g.cm⁻³, μ=0.107mm⁻¹. 2432 reflections were collected and subsequently merged to 1098 unique reflections with an Rint of 0.0410. The final refinement of 128 parameters converged to final R and wR indices R1 = 0.073 and wR2 = 0.184 for 817 reflections with I > 2σ(I) and R1 = 0.096 and wR2 = 0.205 for all hkl data.

Crystal data of compound 18. C₁₀H₁₂O₂. Mr = 164.20. Monoclinic, space group P 2₁/n, Z = 4, a = 7.160(4), b = 13.956(5), c = 8.879(4) Å, β = 101.312(5)°, V = 870.0(7)Å³, ρ(calc)=1.254g.cm⁻³, μ=0.086mm⁻¹. 11473 reflections were collected and subsequently merged to 1701 unique reflections with an Rint of 0.0236. The final refinement of 109 parameters converged to final R and wR indices R1 = 0.047 and wR2 = 0.114 for 1204 reflections with I > 2σ(I) and R1 = 0.071 and wR2 = 0.129 for all hkl data.

CCDC 753047 (compound 8), 753048 (compound 10), and 753049 (compound 18) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.


Supplementary Material (ESI) for Organic and Biomolecular Chemistry
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(E)-2-(3,3-diethoxypropyl)-7,7-diethoxyhept-2-enal

14

ppm (f1)
\((E)\)-2-(3,3-diethoxypropyl)-7,7-diethoxyhept-2- enal
(E)-2-(5,5-diethoxypentylidene)pentanediial

COSY
(E)-2-(5,5-diethoxypentylidene)pentanedioic acid

NOE
(E)-2-(3,3-diethoxypropyl)hept-2-enedial
(E)-2-(3,3-dithoxypropyl)hept-2-enedial
(E)-hept-3-ene-1,3,7-tricarbaldehyde

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(E)-hept-3-ene-1,3,7-tricarboxaldehyde
(E)-hept-3-ene-1,3,7-tricarbaldehyde

HSQC
(E)-hept-3-ene-1,3,7-tricarbaldehyde

HMOCQ
(E)-hept-3-ene-1,3,7-tricarbaldahyde

NOE
(1E,5E)-cycloocta-1,5-diene-1,5-dicarboxaldehyde
(1E,5E)-cycloocta-1,5-diene-1,5-dicarbaldehyde
2-oxo-3,4,4a,7,8,8a-hexahydro-2H-chromene-3-carboxaldehyde
2-oxo-3,4,4a,7,8,8a-hexahydro-2H-chromene-6-carboxaldehyde.