Supporting Information

Ionic liquids and fragrances – Direct isolation of orange essential oil

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1. General

All chemicals unless otherwise stated were purchased from commercial suppliers and used without further purification. *N*-Methylimidazole was distilled from KOH prior to use. Ionic liquids **1** and **2** were prepared according to literature procedures, and analytical data were in accordance with literature.[1,2] [C_2mim]OAc **3** was purchased from Iolitec (Heilbronn, Germany) in >95% purity. All ionic liquids were dried for 24 h at 80 °C and 0.01 mbar with stirring before use and were stored under argon.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 200 at 200 and 50 MHz, resp., using the solvent peak as reference.

GC–MS analyses were conducted on a VOYAGER Quadrupol (Thermo Finnigan) directly interfaced to a GC 8000 TOP gas chromatograph using a BGB-5 (30 m × 0.32 mm i.d., 1.0 µm film thickness) cross-bonded dimethyl polysiloxane capillary column. The oven temperature program was 40 °C (3 min)//10 °C/min//280 °C (3 min). Source and transfer line temperatures were set at 200 and 280 °C, resp.

2. Experimental Procedure

[1] J. Dupont, C. S. Consorti, P. A. Z. Suarez and R. F. de Souza, *Org. Synth.* 2003, **79**, 236.
[2] H. Zhang, J. Wu, J. Zhang and J. He, *Macromolecules* 2005, **38**, 8272.

Dissolution: A 100 mL round-bottom flask is charged with 35 g of [C_4mim]OAc **3** and dried under high vacuum (0.1 mbar, 50 °C) with stirring for 30 min. 15 g orange peel in pieces (finely grated on a conventional kitchen rasp) were added, and the flask sealed with a stopper and secured with a clamp. The mixture was stirred for 1 h at 60 °C (oil bath temperature) with efficent stirring until the biomass was mostly dissolved.

Isolation of Essential Oil: The crude mass was subjected to a Kugelrohr oven and a mixture of water and limonene was distilled at ~ 60-65 °C and 12/15 mbar (efficient cooling with ice/NaCl was required). The distillate was separated between water and dichloromethane, the organic layer dried over Na_2SO_4, filtered, and the solvent removed under reduced pressure.

Recovery of Ionic Liquid: The remaining residue after dissolution was diluted with 200 mL of H_2O to precipitate the biopolymers. The suspension was filtered over silica, and the filtrate evaporated. The remaining volatiles were removed under reduced pressure (0.1 mbar, stirring, 80 °C) to give [C_4mim]OAc **3** as a dark brown liquid in quantitative yield. The obtained ionic liquid was pure according to ^{1}H NMR spectroscopy.
For further purification, the ionic liquid was re-dissolved in 100 mL of H_2O and refluxed with an excess of charcoal for 2 h. The suspension was filtered over silica, and the filtrate evaporated. The remaining volatiles were removed under reduced pressure (0.1 mbar, stirring, 80 °C) to give [C_4mim]OAc **3** as a colourless liquid in 90% yield.

Fig. S1. GC-MS chromatogram of isolated orange oil

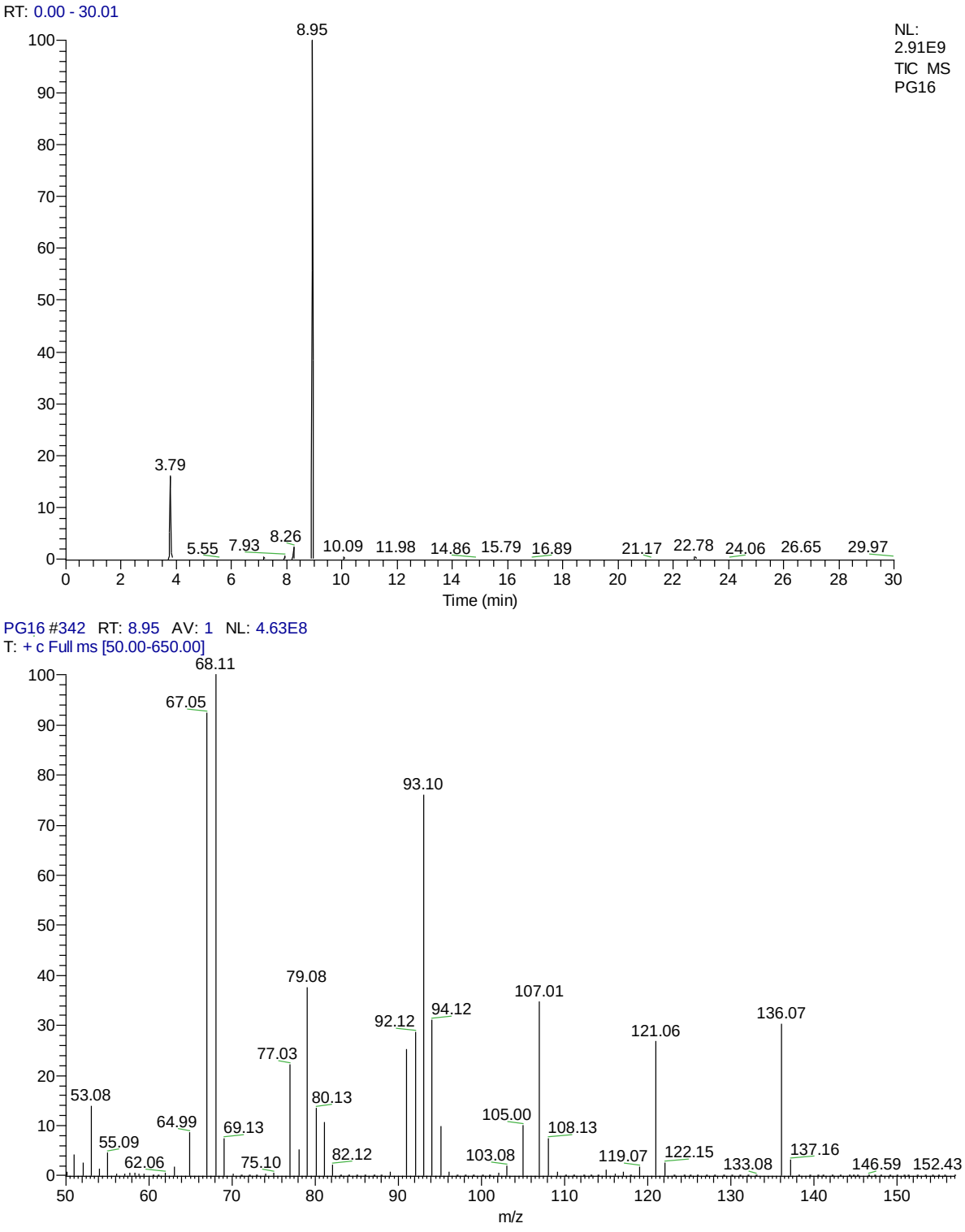

Fig. S2. NMR spectra of pure and recovered ionic liquid [C_2mim]OAc 3