Supplementary Material (ESI) for Green Chemistry

The same and not the same. Similarities and differences in the resolution of *trans*-chrysanthemic acid of industrial origin by the enantiomers of some *threo*-1-aryl-2-dimethylamino-1,3-propanediols.

Goffredo Rosini,*[a] Claudia Ayoub,[b] Valerio Borzatta,[b] Emanuela Marotta,[a] Andrea Mazzanti,[a] and Paolo Righi[a]

[a] *Dipartimento di Chimica Organica "A. Mangini", Alma Mater Studiorum – Università di Bologna, Viale del Risorgimento 4, - 40136 Bologna, Italy. Fax: +39 051 20 93654; Tel:+39 051 20 93640; E-mail:goffredo.rosini@unibo.it*

[b] *Endura SpA, Viale Pietramellara 5, 40131 Bologna, Italy.*

Electronic Supporting Information (ESI)

Characterisation data of the salts

(1*R*,3*R*)-(+)-*trans*-ChA•(1*R*,2*R*)-(–)-MTDP, unsolvated (–)-*n* salt

(1*R*,2*R*)-1,3-dihydroxy-*N*,*N*-dimethyl-1-[4-(methylthio)phenyl]propan-2-aminium (1*R*,3*R*)-2,2-dimethyl-3-(2-methylprop-1-enyl)cyclopropanecarboxylate: mp 138-140 °C; $[\alpha]_D$ –10.7 (*c* 0.986, $CHCl_3$); ν_{max} (KBr)/cm^{-1} 3254, 2915, 1576, 1424; δ_H (300 MHz) 1.08 (s, 3H), 1.22 (s, 3H), 1.30 (d, 1H, *J* 5.32), 1.68 (s, 6H), 1.94 (dd, 1H, *J* 7.75, *J* 5.37), 2.44 (s, 3H), 2.73 (s, 6H), 2.92 (m, 1H), 3.33 (dd, 1Ha, *J* 12.89, *J* 5.47), 3.57 (dd, 1Hb, *J* 12.89, *J* 3.16), 4.67 (d, 1H, *J* 10.31), 4.86 (d, 1H, *J* 8.18), 7.18 (d, 2H, 8.82), 7.28 (d, 2H, J_1 8.82), 7.36 (bs, 3H); δ_C (75 MHz) 16.24, 19.10, 21.33, 23.06, 26.16, 27.92, 32.34, 37.56, 42.08, 58.36, 71.10, 71.51, 122.79, 127.46, 128.20, 134.90, 138.64, 139.21 and 179.60. Mass: (ES+) 242 (M^++1), 243 (M^++2); (ES-) 167 (M^--1, 168 (M^-). Elemental analysis: calculated for $C_{22}H_{35}NO_4S$: %C 64.51, %H 8.61; %N 3.42; found: %C 64.59, %H 8.67, %N 3.37.

X-Ray crystal structure: $C_{12}H_{20}NO_2S \cdot C_{10}H_{15}O_2$; M_r 409.58; monoclinic; $P2_1$; a = 9.9940(5), b = 7.8004(4), c = 15.8597(8) Å; V = 1186.68(10) $Å^3$; Z = 2; $\mu(Mo_{K\alpha})$ = 0.161 mm^{-1}; T = 293 K; 10410 reflections collected; 4144 independent reflections; R_{int} = 0.022; $R[F^2 > 2\sigma(F^2)]$ = 0.0528.

(1*R*,3*R*)-(+)-*trans*-ChA•(1*R*,2*R*)-(–)-MTDP, methanol solvated (–)-*n* salt

(1*R*,2*R*)-1,3-dihydroxy-*N*,*N*-dimethyl-1-[4-(methylthio)phenyl]propan-2-aminium (1*R*,3*R*)-2,2-dimethyl-3-(2-methylprop-1-enyl)cyclopropanecarboxylate, methanol solvated form: mp 138-140 °C; $[\alpha]_D$ –10.7 (c 0.986, $CHCl_3$); ν_{max} (KBr)/cm^{-1} 3254, 2915, 1576, 1424; δ_H (300 MHz) 1.09 (s, 3H), 1.23 (s, 3H), 1.32 (dd, 1H, *J* 5.37, J_2 1.78), 1.69 (s, 6H), 1.94 (dd, 1H, *J* 7.75, *J*

5.49), 2.46 (s, 3H), 2.76 (s, 6H), 2.91-3.02 (m, 1H), 3.33 (dd, 1Ha, *J* 12.93, *J* 6.22), 3.38 (s, 3H), 3.52 (dd, 1Hb, *J* 12.70, *J* 3.04), 4.68 (d, 1H, *J* 10.05), 4.87 (d, 1H, *J* 5.27), 5.41 (broad s, 4H), 7.19 (d, 2H, *J* 8.82), 7.29 (d, 2H, *J* 8.82) ; δ_C (75 MHz) 15.49, 18.32, 20.59, 22.30, 25.40, 27.13, 31.59, 36.94, 41.34, 50.13, 57.58, 70.30, 70.82, 71.51, 122.05, 126.44, 127.47, 134.19, 137.82, 138.53, 178.90. Mass spectra: (EI +70 eV, temperature of probe = 20°C, pre-vacuum 10^{-3} mbar, source vacuum = 10^{-7} mbar, source temeperature = 210 °C) persistent signals at 32, 31, 30, 29, 28, 15, 14 *m/e* tipical for methanol are observed togheter with the signals of the fragmentation tipical for chrysanthemic acid: 168 (MP), 153, 123 (bp), 107, 81 m/e. Electron Spray MS: (ES+) 242 (M^++1), 243 (M^++2); (ES-) 167 (M^--1, 168 (M^-). Elemental analysis: calculated for $C_{23}H_{39}NO_5S$: %C 62.55, %H 8.90, %N 3.17; found: %C 62.72, %H 8.85, %N 3.11.

X-Ray crystal structure: $C_{12}H_{20}NO_2S \cdot C_{10}H_{15}O_2 \cdot CH_4O$; M_r 441.61; orthorhombic; $P2_12_12_1$; a = 7.1563(10), b = 13.1156(15), c = 27.469(3) Å; V = 2578.2(5) Å^3; Z = 4; $\mu(Mo_{K\alpha})$ = 0.156 ; T = 293 K; 33557 reflections collected; 7508 independent reflections; R_{int} = 0.030; $R[F^2 > 2\sigma(F^2)]$ = 0.0470.

The dextrorotating enantiomer of unsolvated *n* salt as well as of methanol solvated *n* salt were obtained by reacting (1S,2S)-(+)-MTDP with racemic *trans*-ChA or from enriched mixtures of (1*S*,3*S*)-(–)-ChA in *i*-Pr_2O. IR, ^{1}H NMR, ^{13}C NMR, mass spectroscopic data and elemental analyses proved to be consistent for the structure of unsolvated **(1*S*,3*S*)-(-)-*trans*-ChA•(1*S*,2*S*)-(+)-MTDP** and of its methanol solvated pseudopolymorphic form.

(1*S*,3*S*)-(–)-*trans*-ChA•(1*R*,2*R*)-(–)-MTDP, (–)-*p* salt:

(1*R*,2*R*)-1,3-dihydroxy-*N*,*N*-dimethyl-1-[4-(methylthio)phenyl]propan-2-aminium (1*S*,3*S*)-2,2-dimethyl-3-(2-methylprop-1-enyl)cyclopropanecarboxylate: mp 77.5-78.5 °C from toluene/*n*-hexane; $[\alpha]_D$ –34.1 (*c* 1.000, $CHCl_3$); ν_{max} (KBr)/cm^{-1} 3291, 3076, 2981, 2920, 1573, 1453, 1418, 1381; δ_H (300 MHz) 1.08 (s, 3H, CH_3), 1.23 (s, 3H), 1.31 (d, 1H, *J* 5.39), 1.68 (s, 6H), 1.94 (dd, 1H, *J* 7.75, *J* 5.37), 2.45 (s, 3H), 2.71 (s, 6H), 2.86-2.99 (m, 1H), 3.29 (dd, 1Ha, *J* 12.50, *J* 5.47), 3.60 (dd, 1Hb, *J* 12.50, *J* 3.16), 4.63 (d, 1H, *J* 9.62), 4.87 (d, 1H, *J* 7.93), 7.18 (d, 2H, *J* 8.82), 7.28 (d, 2H, *J* 8.82), 7.25 (bs, 3H); δ_C (75 MHz) 15.59, 18.39, 20.66, 22.35, 25.45, 27.34, 31.80, 36.72, 41.41, 57.76, 70.38, 71.05, 122.05, 126.51, 127.47, 134.29, 137.94, 138.51 and 178.66. Elemental analysis: calculated for $C_{22}H_{35}NO_4S$: %C 64.51, %H 8.61; %N 3.42; found: %C 64.42, %H 8.58, %N 3.32.