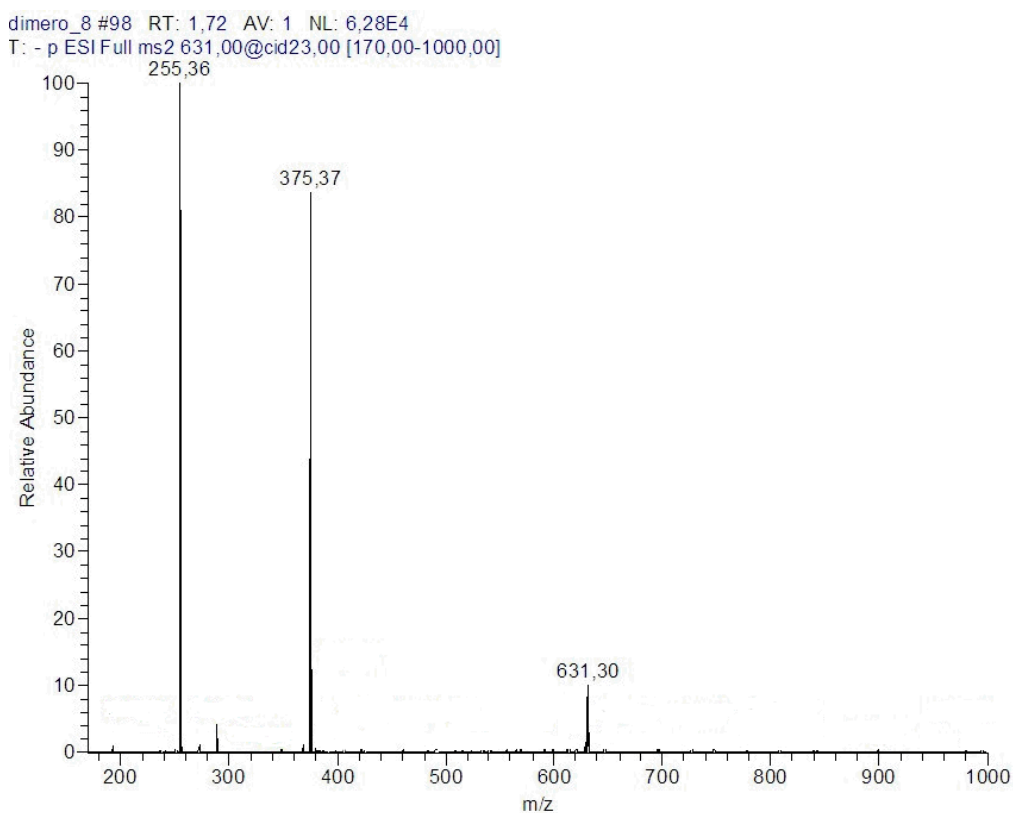


SUPPLEMENTARY INFORMATION

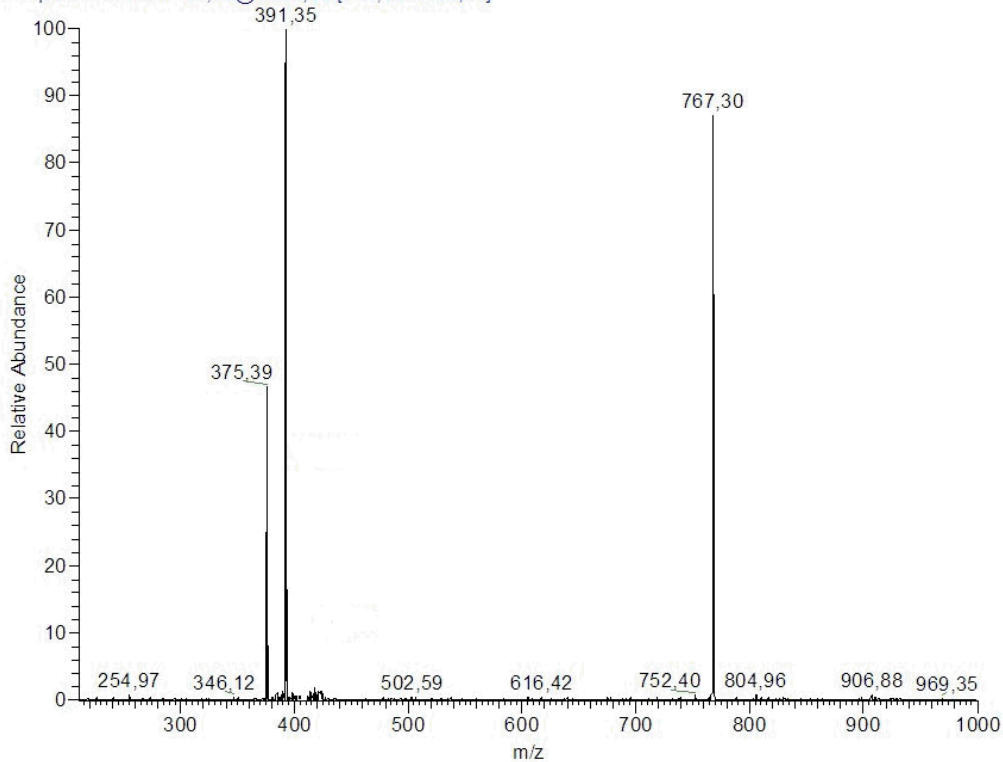
ESI mass spectra were obtained using a LCQ Duo (ThermoQuest, San Jose, CA, USA), in negative-ion mode, by introducing a 1:1 mixture of two selected bile acids dissolved in methanol (concentration of bile acids 10^{-3} M). Instrumental parameters: capillary voltage -10 V, spray voltage 4.50 kV, capillary temperature of 150 °C, mass scan range was from m/z 100 to 1000 amu, for 30000 ms scan time; N_2 was used as sheath gas. MS/MS mass spectra of hetero proton-bound dimers were performed upon isolation of $[BA_1 \cdots H \cdots BA_2]^-$ ionic species and CID fragmentation by application of normalized collision energies from 10 to 25 % of the instrument maximum. The samples were injected into the spectrometer by a syringe pump at a constant flow rate of $8 \mu\text{L}/\text{min}$. The experiments and the related MS/MS mass spectra were repeated two times and the results reported in the Tables are the average of these experiments.

1) MS/MS mass spectrum of the proton-bound dimer formed by mixing lithocholic and palmitic acid. Lithocholate anion (m/z 375) palmitate anion (m/z 255)



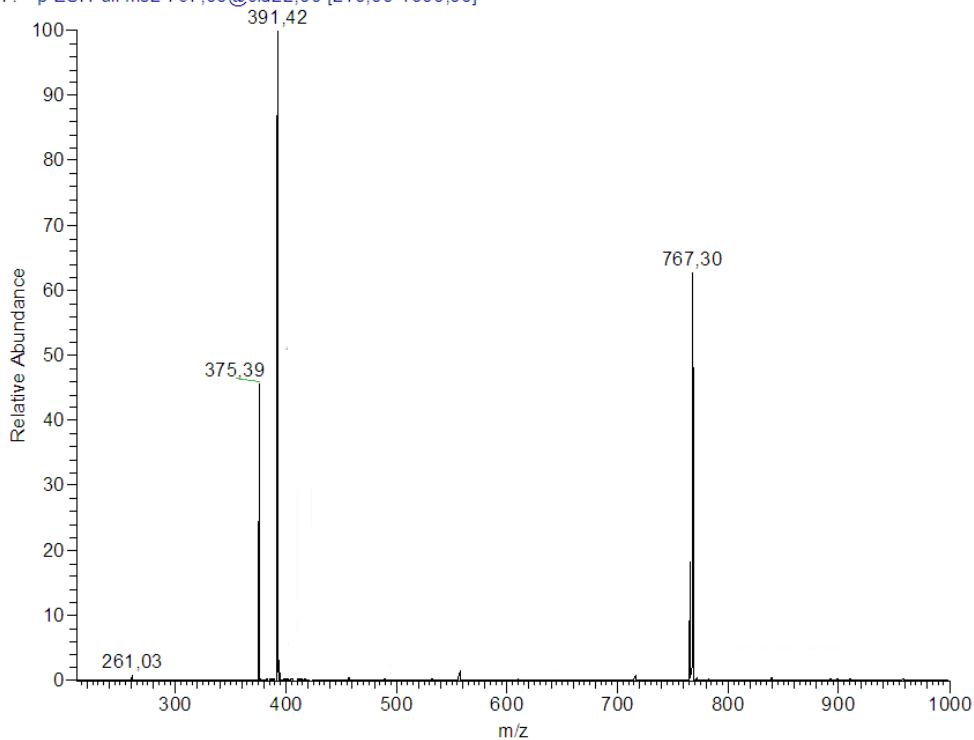
2) MS/MS mass spectrum of the proton-bound dimer formed by mixing lithocholic and ursodeoxycholic acid. Lithocholate anion (m/z 375) ursodeoxycholate anion (m/z 391)

dimero_7 #193-279 RT: 3,39-4,90 AV: 87 NL: 9,92E5
T: - p ESI Full ms2 767,00@cid22,00 [210,00-1000,00]

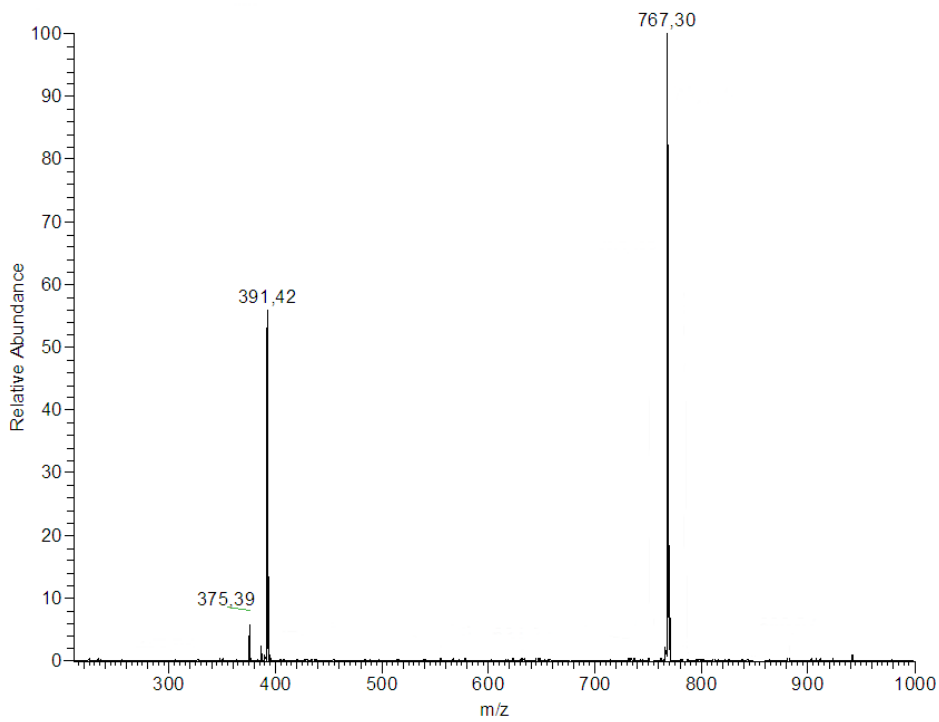


3) MS/MS mass spectrum of the proton-bound dimer formed by mixing lithocholic and chenodeoxycholic acid. Lithocholate anion (m/z 375) chenodeoxycholate anion (m/z 391)

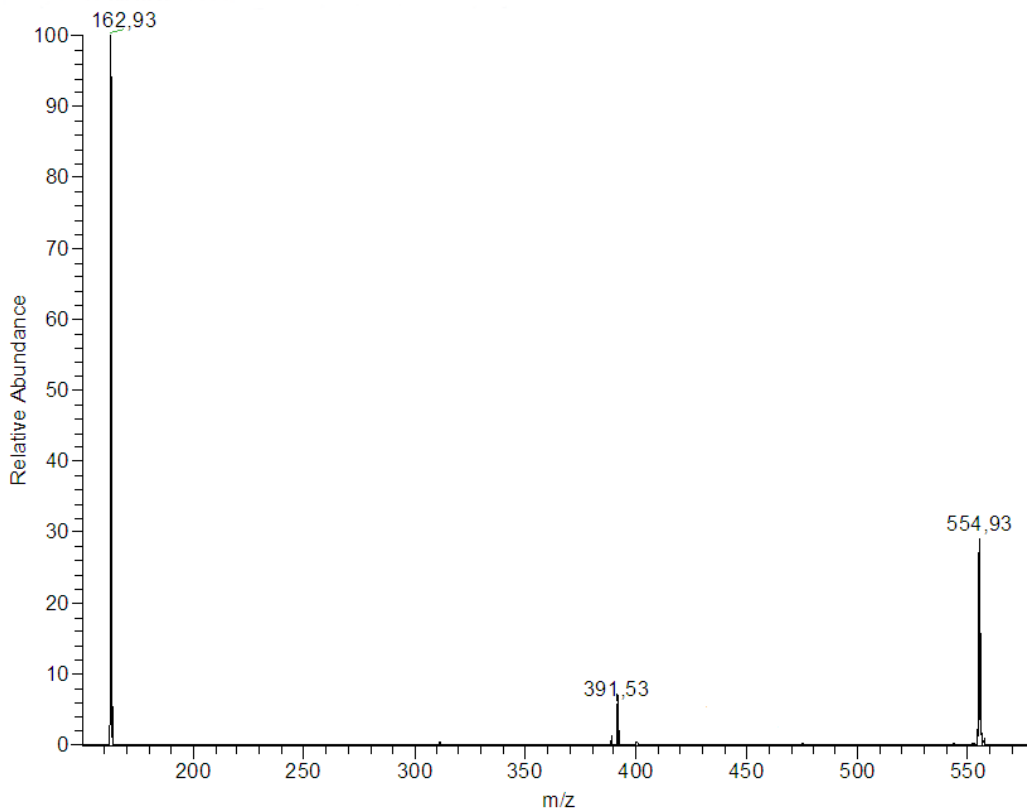
dimero_15 #96 RT: 1,70 AV: 1 NL: 1,33E6
T: - p ESI Full ms2 767,00@cid22,00 [210,00-1000,00]



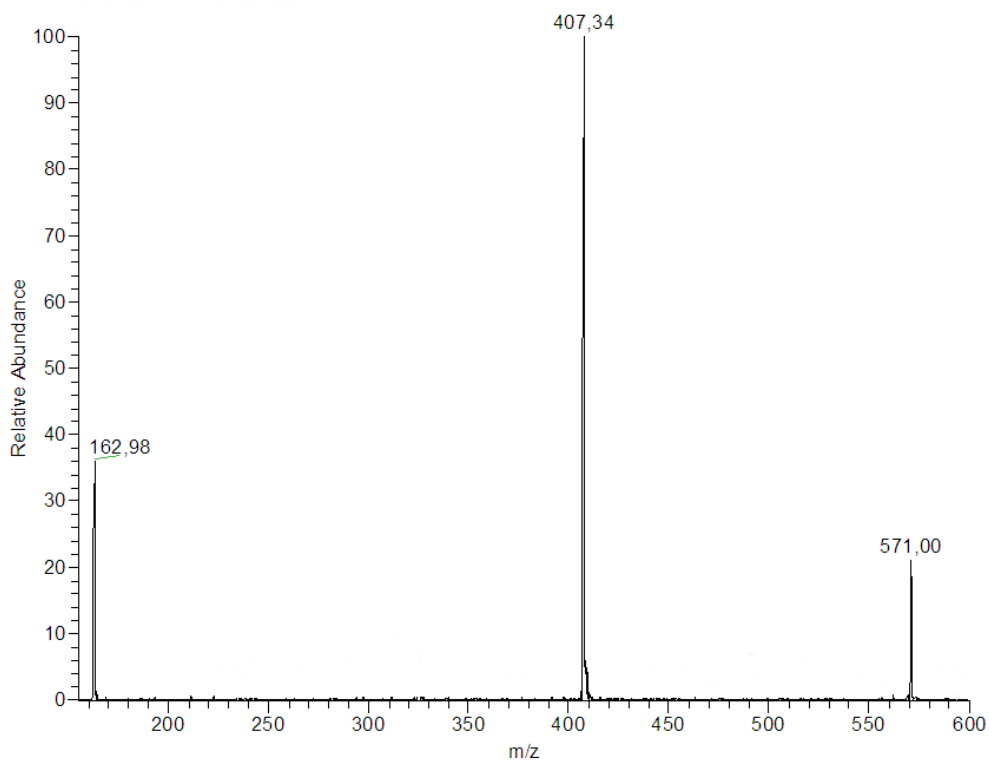
4) MS/MS mass spectrum of the proton-bound dimer formed by mixing lithocholic and deoxycholic acid. Lithocholate anion (m/z 375) deoxycholate anion (m/z 391)



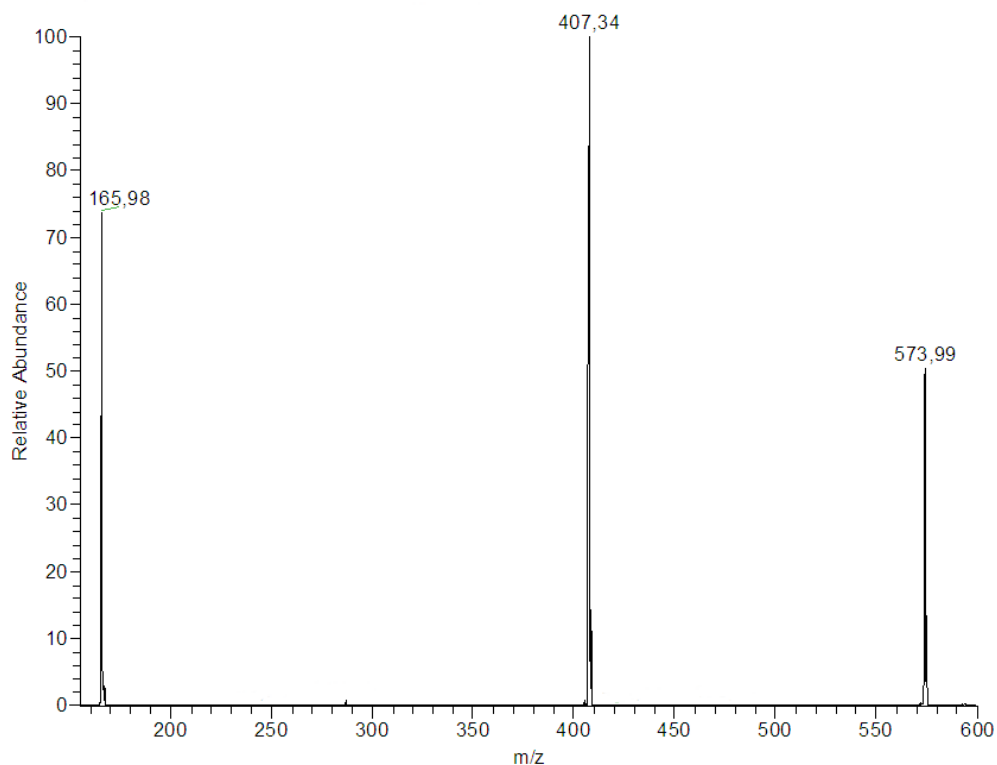
5) MS/MS mass spectrum of the proton-bound dimer formed by mixing ursodeoxycholic and 2,4,6-trimethylbenzoic acid. Ursodeoxycholate anion (m/z 391), 2,4,6-trimethylbenzoic anion (m/z 163)



6) MS/MS mass spectrum of the proton-bound dimer formed by mixing cholic and 2,4,6-trimethylbenzoic acid. Chololate anion (m/z 407), 2,4,6-trimethylbenzoic anion (m/z 163)



7) MS/MS mass spectrum of the proton-bound dimer formed by mixing phocaecholic and 4-nitrobenzoic acid. Phocaecholate anion (m/z 407), 4-nitrobenzoic anion (m/z 166)



8) MS/MS mass spectrum of the proton-bound dimer formed by mixing 3-keto-cholanic and 3,7-diketo-cholanic acids. 3-Keto-cholate anion (m/z 373) 3,7-diketo-cholate anion (m/z 387).

