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•••H•••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 μL/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)

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)
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. Cholate 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-cholic and 3,7-diketo-cholic acids. 3-Keto-cholate anion (m/z 373) 3,7-diketo-cholate anion (m/z 387).