# ELECTRONIC SUPPORTING INFORMATION

## ESI-MS reveals preferential complex formation of carbohydrates with *Z*- sinapinic acid compared with the *E*-isomer.

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**E-3,5-di(methoxy-d3)-4-hydroxycinnamic acid preparation.**

The synthesis of deuterium labeled *trans*-sinapinic acid E-3,5-di(methoxy-d3)-4-hydroxycinnamic acid (ESA-d6) was based on the method described by Yamauchi *et al*.[1,2] After methanol-d4 (3 mL) was placed in the flask, sodium (276 mg) was added and dissolved. 3,5-Dibromo-4-hydroxybenzaldehyde (336 mg) and 1-methyl imidazole (1.5 mL) were added to the solution. After heating the mixture at 130 °C for 5 min without cap to evaporate excess of methanol-d4, copper (II) chloride (113 mg) was added and connected to a Dimroth condenser. The reaction was continued for 1 h and then cooled down to room temperature. The reaction mixture was acidified to pH=3 using hydrochloric acid, and subsequently extracted with ethyl acetate. The organic layer was washed with brine (salt saturated aqueous solution) and dried with anhydrous sodium sulfate. The solvent was removed at reduced pressure to obtain 3,5-di(methoxy-d3)-4-hydroxybenzaldehyde (318 mg, yield 82 %). This 3,5-di(methoxy-d3)aldehyde (200 mg) was condensed with malonic acid (133 mg) in pyridine (1 mL) with small amount of piperidine (1 drop) at 70°C for 5 h. The reaction mixture was acidified to pH=3 with hydrochloric acid, and subsequently extracted with ethyl acetate. The organic layer was washed with brine, and dried with anhydrous sodium sulfate. The solvent was removed at reduced pressure and the reaction product was purified by recrystallization using acetone and hexane to obtain ESA-d6 (105 mg, yield 46 %). Melting point = 185.5 $^{o}$C. $^{1}$H-NMR (500 MHz; acetone-d6; tetramethylsilane (TMS) as internal standard: chemical shift values reported in ppm; coupling constants (*J*) given in Hertz) δ (ppm): 6.40 (d, *J* = 15.9 Hz, 1H, HCα), 7.01 (s, 2H, HC(2) and HC(6)) and 7.58 (d, *J* = 15.8 Hz, 1H, HCβ). High resolution MS (HRMS) data were acquired in negative ion mode: calculated *m/z* value for $[M-H]^-$ with M = $C_{11}H_6D_6O_5$ : 229.0989; experimental *m/z*: 229.0999; HRMS/MS data were acquired in negative ion mode (CID, voltage: 15 V): precursor ion with *m/z* 229.0999 (25%), product ions with *m/z* 211.0575 (100%), *m/z* 193.0148 (27%), *m/z* 185.1070 (12%), *m/z* 150.0312 (39%), *m/z* 149.0244 (23%), *m/z* 137.0552 (4%), *m/z* 121.0275 (2%), and *m/z* 93.0331 (1%).

(1) K. Yamauchi, S. Yasuda, and K. Fukushima, *J. Agric. Food Chem.*, 2002, **50**, 3222.

(2) K. Yamauchi, S. Yasuda, K. Hamada, Y. Tsutsumi and K. Fukushima, *Planta*, 2003, **216**, 496.

**Molecular Modeling.**

The ground state geometry of ZSA, $[ZSA-H]^-$, ESA, $[ESA-H]^-$, Glc, $[Glc-H]^-$, Frc, $[Frc-H]^-$, F5, $[F5-H]^-$, M5, $[M5-H]^-$, M6, $[M6-H]^-$, M7, $[M7-H]^-$, βCD and $[\beta CD-H]^-$, including three 3,5,dimethoxy-rotamers for each acid isomer and several $[carbohydrate-H]^-$ isomers for each carbohydrate with different location of the deprotonated hydroxyl ($^-$O-C) moiety were fully optimized without imposing any symmetry constraints by *ab initio* and semiempirical methods. For *ab initio* DFT calculations, we used the hybrid gradient-corrected exchange functional combined with the gradient-corrected correlation functional, commonly known as B3LYP, which has been shown to be quite reliable for geometries. The standardized 6-311G(d,p) basis set was used for geometry optimization. We denote our B3LYP calculations by B3LYP/6-311G(d,p). For single point calculations the standarized 6-311++G(d,p) basis set was used at B3LYP theory level (B3LYP/6-311++G(d,p)//B3LYP/6-311G(d,p). All the *ab initio* calculations were carried out using Gaussian 09.[3,4]

The quantitative structure–activity relationship (QSAR) properties (Tables S1 and S2) and molecular orbitals (highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), Tables S1 and S2 were obtained with the package implemenented in the HyperChem program, after conducting a single point calculation on a geometry optimized molecule structure, by using the semiempirical parametrized PM3 method as implemented in HyperChem version 8.0.10 for Windows [5,6] (Restricted Hartree-Fock (RHF) formalism; total charge: 0 and -1 for neutral and anionic species, respectively; multiplicity: 1; convergence limit: 1e-008; iteration limit: 50; accelerate convergence: on; CI method: none; Polak-Ribiere algorithm; RMS gradient: 0.006 kcal/(Å mol); in vacuo).

The ground-state geometry of dimeric structures (i.e., Scheme 2c-d) were calculated by using the semiempirical parametrized PM3 method as implemented in HyperChem version 8.08 for Windows [5,6] (RHF formalism; total charge: 0; spin multiplicity: 1; convergence limit: 1e-008; iteration limit: 50; accelerate convergence: on; CI method: none; Polak-Ribiere algorithm; RMS gradient: 0.006 kcal/(Å mol); in vacuo).

(3) M.L. Salum, S.L. Giudicessi, T. Schmidt De León, S.A. Camperi and R. Erra-Balsells, *J Mass Spectrom.*, 2017, **52**, 182.

(4) Gaussian 09, Revision A.02, M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery, Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, O. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, and D.J. Fox, Gaussian, Inc., Wallingford CT, 2009.

(5) M.L. Salum, L.M. Itovich and R. Erra-Balsells, *J. Mass Spectrom.*, 2013, **48**, 1160.

(6) HyperChem 8.0.10 for Windows, HyperCube Inc., Ontario, 2010.

**Table S1.** Molecular modeling. HOMO and LUMO energy and QSAR properties for ESA and ZSA

| | Compound | HOMO Energy (eV) | LUMO Energy (eV) | Δ* Energy (eV) | Dipolar moment (Debye) | Hydration Energy (kcal/mol) | LogP | Surface area (aprox.) ($Å^2$) | Surface area (Grid) ($Å^2$) | Volume ($Å^3$) | Polarizability ($Å^3$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | ESA | -9.245 | -1.015 | 8.230 | 5.2 | -15.9 | -1.6 | 411.2 | 421.9 | 669.4 | 22.1 |
| 2 | ESAp** | -8.891 | -0.862 | 8.029 | 2.4 | -13.7 | -1.6 | 402.9 | 421.2 | 664.2 | 22.1 |
| 3 | ESAps*** | -8.795 | -0.887 | 7.908 | 0.9 | -14.3 | -1.6 | 409.5 | 421.6 | 665.7 | 22.1 |
| 4 | $[ESA-H]^-$ | -4.548 | 2.484 | 7.032 | 20.0 | -8.9 | -0.2 | 409.7 | 416.8 | 660.8 | 21.6 |
| 5 | $[ESAp-H]^-$** | -4.519 | 2.640 | 7.159 | 20.7 | -8.4 | -0.2 | 404.2 | 415.9 | 655.2 | 21.6 |
| 6 | $[ESAps-H]^-$*** | -4.555 | 2.653 | 7.208 | 18.5 | -8.9 | -0.2 | 410.7 | 417.9 | 656.7 | 21.6 |
| 7 | ZSA | -9.095 | -0.601 | 8.494 | 1.9 | -12.8 | -1.6 | 371.8 | 410.3 | 657.5 | 22.1 |
| 8 | ZSAp** | -8.961 | -0.560 | 8.401 | 2.6 | -12.5 | -1.6 | 368.1 | 412.6 | 654.3 | 22.1 |
| 9 | ZSAps*** | -8.773 | -0.527 | 8.246 | 1.9 | -12.7 | -1.6 | 369.9 | 409.7 | 651.8 | 22.1 |
| 10 | $[ZSA-H]^-$ | -5.097 | 3.100 | 8.197 | 12,2 | -9.9 | -0.2 | 375.6 | 406.7 | 643.9 | 21.6 |
| 11 | $[ZSAp-H]^-$** | -4.983 | 3.123 | 8.106 | 11.2 | -10.0 | -0.2 | 374.7 | 404.5 | 644.6 | 21.6 |
| 12 | $[ZSAps-H]^-$*** | -4.936 | 3.155 | 8.091 | 11.7 | -10.1 | -0.2 | 376.5 | 408.7 | 643.7 | 21.6 |

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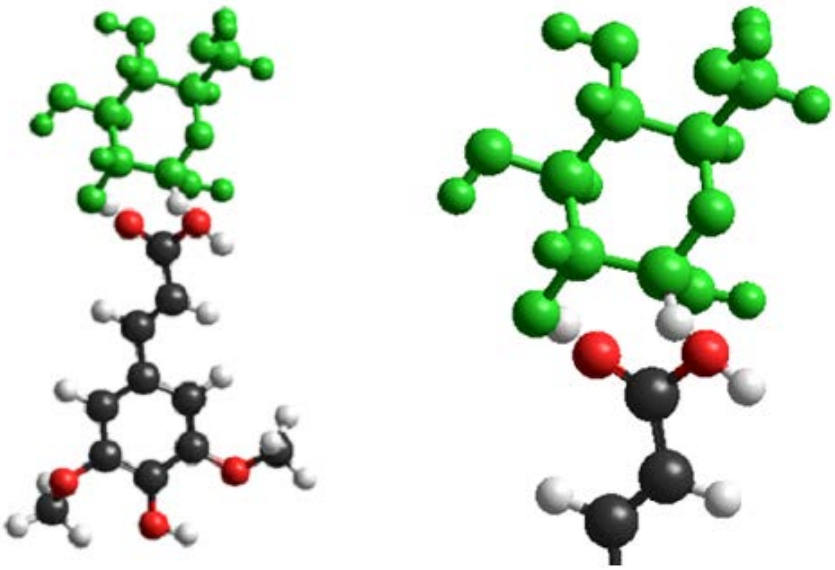
* Δ = [LUMO-HOMO]; **p, planar structure: both O-CH3 bond in the same plane than aromatic ring. *** ps, planar structure and symmetric position of the CH3O-substituents, symmetry element perpendicular to the aromatic ring plane.

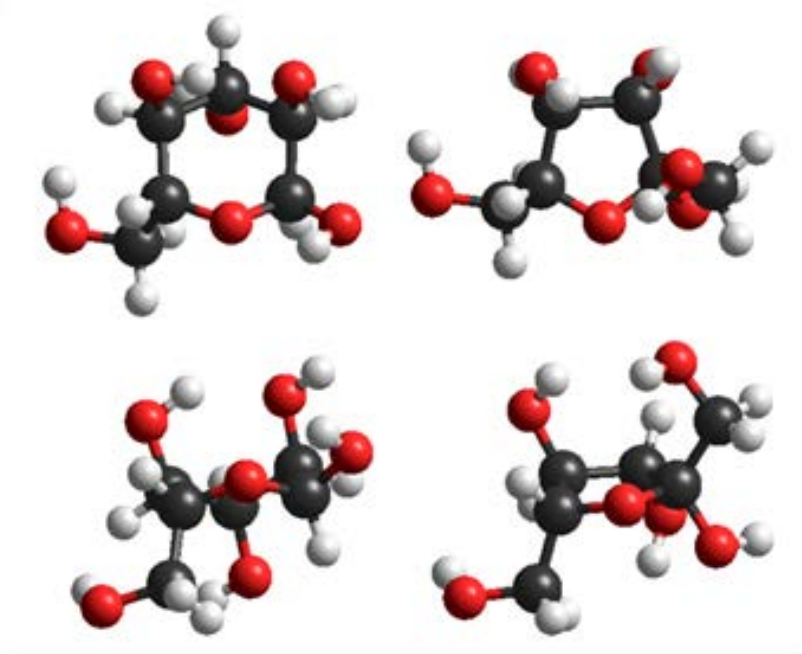
**Table S2.** Molecular modeling. HOMO and LUMO energy and QSAR properties for carbohydrates studied.

| | Compound | HOMO Energy (eV) | LUMO Energy (eV) | Δ* Energy (eV) | Dipolar moment (Debye) | Hydration Energy (kcal/mol) | LogP | Surface area (aprox.) (Å$^2$) | Surface area (Grid) (Å$^2$) | Volume (Å$^3$) | Polarizability (Å$^3$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Glu | -10.602 | 2.084 | 12.686 | 1.5 | -22.4 | -1.8 | 235.7 | 318.7 | 489.9 | 14.8 |
| 2 | Fruc | -10.930 | 1.862 | 12.792 | 1.5 | -23.2 | -1.8 | 267.9 | 325.1 | 504.8 | 14.8 |
| 4 | M5 | -10.390 | 1.271 | 11.661 | 10.3 | -69.5 | -6.6 | 794.4 | 1021.5 | 1914.6 | 68.5 |
| 3 | F5 | -10.822 | 1.050 | 11.872 | 3.5 | -62.9 | -4.6 | 705.1 | 905.5 | 1801.5 | 68.5 |
| 5 | M6 | -10.423 | 1.239 | 11.662 | 11.2 | -81.1 | -7.8 | 923.9 | 1203.9 | 2268.6 | 81.9 |
| 6 | M7 | -10.264 | 1.374 | 11.638 | 10.2 | -93.9 | -9.1 | 1083.4 | 1379.9 | 2636.3 | 95.4 |
| 7 | βCD | -10.604 | 1.362 | 11.966 | 5.6 | -76.8 | -8.5 | 907.7 | 1175.2 | 2423.3 | 93.9 |
| 8 | **[Glu-H]$^-$** | | | | | | | | | | |
| | GluA2** | -4.252 | 6.401 | 10.653 | 6.4 | -20.5 | <0.1 | 238.4 | 312.1 | 475.9 | 14.4 |
| | GluA3** | -3.485 | 6.383 | 9.868 | 5.9 | -20.3 | | 240.2 | 313.6 | 480.2 | |
| | GluA4** | -4.044 | 6.462 | 10.506 | 4.8 | -21.4 | | 242.4 | 312.8 | 476.0 | |
| | GluA6** | -3.748 | 6.310 | 10.058 | 6.9 | -19.9 | | 225.9 | 308.9 | 474.4 | |
| 9 | **[Fruc-H]$^-$** | | | | | | | | | | |
| | FrucA1** | -3.814 | 6.206 | 10.020 | 6.5 | -19.9 | 0.5 | 260.4 | 319.1 | 485.9 | 14.4 |
| | FrucA2** | -4.490 | 6.613 | 11.103 | 4.5 | -21.1 | | 264.1 | 318.9 | 489.1 | |
| | FrucA3** | -4.174 | 6.559 | 10.733 | 4.6 | -20.8 | | 265.7 | 318.7 | 488.0 | |
| | FrucA4** | -4.325 | 6.416 | 10.741 | 5.5 | -20.9 | | 255.2 | 313.4 | 479.0 | |
| | FrucA6** | -3.156 | 5.610 | 8.766 | 9.8 | -19.3 | | 259.5 | 319.7 | 484.1 | |
| 10 | **[F5-H]$^-$** | | | | | | | | | | |
| | F5A33*** | -4.929 | 3.285 | 8.214 | 13.6 | -61.8 | -2.8 | 705.2 | 898.6 | 1787.1 | 68.1 |
| | F5A34*** | -5.021 | 3.306 | 8.327 | 16.5 | -61.3 | | 705.7 | 896.2 | 1790.6 | |
| | F5A36*** | -4.807 | 3.099 | 7.906 | 18.6 | -58.4 | | 677.9 | 895.1 | 1782.8 | |
| | F5A16*** | -5.229 | 3.324 | 8.553 | 11.4 | -61.8 | | 670.9 | 873.2 | 1744.9 | |
| | F5A12*** | -4.417 | 2.752 | 7.169 | 22.9 | -61.8 | | 709.1 | 901.4 | 1788.9 | |
| | F5A13*** | -4.425 | 2.887 | 7.312 | 19.4 | -60.3 | | 688.9 | 895.0 | 1782.7 | |
| | F5A53*** | -5.702 | 3.371 | 9.073 | 6.9 | -61.7 | | 678.9 | 890.9 | 1769.4 | |
| 11 | **[M5-H]$^-$** | | | | | | | | | | |
| | M5A32*** | -4.014 | 3.143 | 7.157 | 7.6 | -68.2 | | 801.9 | 1020.5 | 1904.4 | 68.1 |
| | M5A33*** | -4.741 | 3.080 | 7.821 | 9.9 | -67.8 | | 773.6 | 1010.9 | 1897.8 | |
| | M5A36*** | -4.397 | 2.975 | 7.372 | 14.5 | -65.4 | | 768.1 | 1017.9 | 1889.5 | |
| | M5A11*** | -4.239 | 2.366 | 6.505 | 47.5 | -67.1 | | 795.7 | 1019.9 | 1903.5 | |
| | M5A12*** | -4.326 | 2.267 | 6.593 | 46.9 | -67.0 | | 769.1 | 1017.0 | 1885.9 | |
| 12 | **[M6-H]$^-$** | | | | | | | | | | |
| | M6A32*** | -4.800 | 2.495 | 7.295 | 24.7 | -78.9 | -6.0 | 915.6 | 1194.7 | 2257.6 | 81.5 |
| | M6A33*** | -4.649 | 2.468 | 7.117 | 22.4 | -79.6 | | 910.6 | 1195.3 | 2251.5 | |
| | M6A36*** | -3.972 | 2.687 | 6.659 | 14.6 | -78.7 | | 917.9 | 1199.4 | 2246.9 | |
| | M6A11*** | -4.183 | 2.082 | 6.265 | 55.1 | -78.8 | | 926.5 | 1198.3 | 2251.8 | |
| | M6A12*** | -4.839 | 2.211 | 7.050 | 46.7 | -77.3 | | 884.5 | 1172.1 | 2224.2 | |
| | M6A16*** | -3.423 | 2.111 | 5.534 | 53.6 | -78.8 | | 925.1 | 1196.1 | 2249.8 | |
| 13 | **[M7-H]$^-$** | | | | | | | | | | |
| | M7A42*** | -4.123 | 2.633 | 6.756 | 13.1 | -89.2 | -6.9 | 1086.1 | 1374.3 | 2611.9 | 99.3 |
| | M7A46*** | -4.138 | 2.793 | 6.931 | 12.2 | -86.9 | | 1057.9 | 1362.8 | 2594.4 | |
| | M7A11*** | -4.473 | 2.419 | 6.892 | 43.8 | -87.5 | | 1066.4 | 1361.4 | 2601.5 | |
| 14 | **[βCD-H]$^-$** | | | | | | | | | | |
| | bCDA2** | -5.854 | 2.929 | 8.783 | 15.0 | -74.2 | -6.8 | 833.7 | 1132.2 | 2377.9 | 93.5 |
| | bCDA6** | -4.542 | 2.655 | 7.197 | 19.5 | -75.0 | | 886.1 | 1146.7 | 2378.3 | |

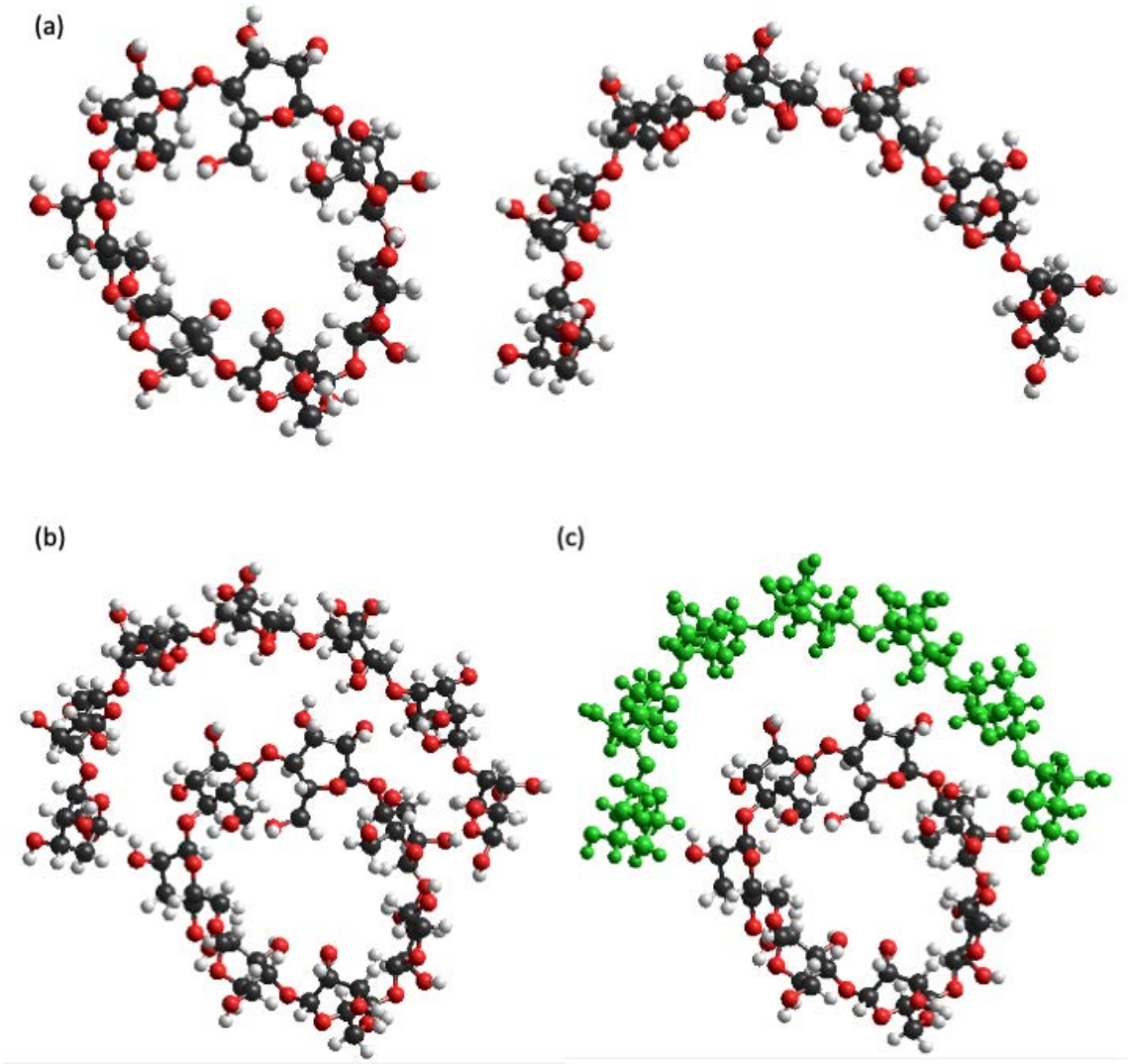
*Δ=LUMO-HOMO. **CarbAz: z is the molecule position of the C-OH group whose H is removed. *** CarbAxz: x is the molecule position of the monosaccharide moiety in the total Carb molecule structure; z is the position in the monosaccharide moiety of the C-OH group whose H is removed.



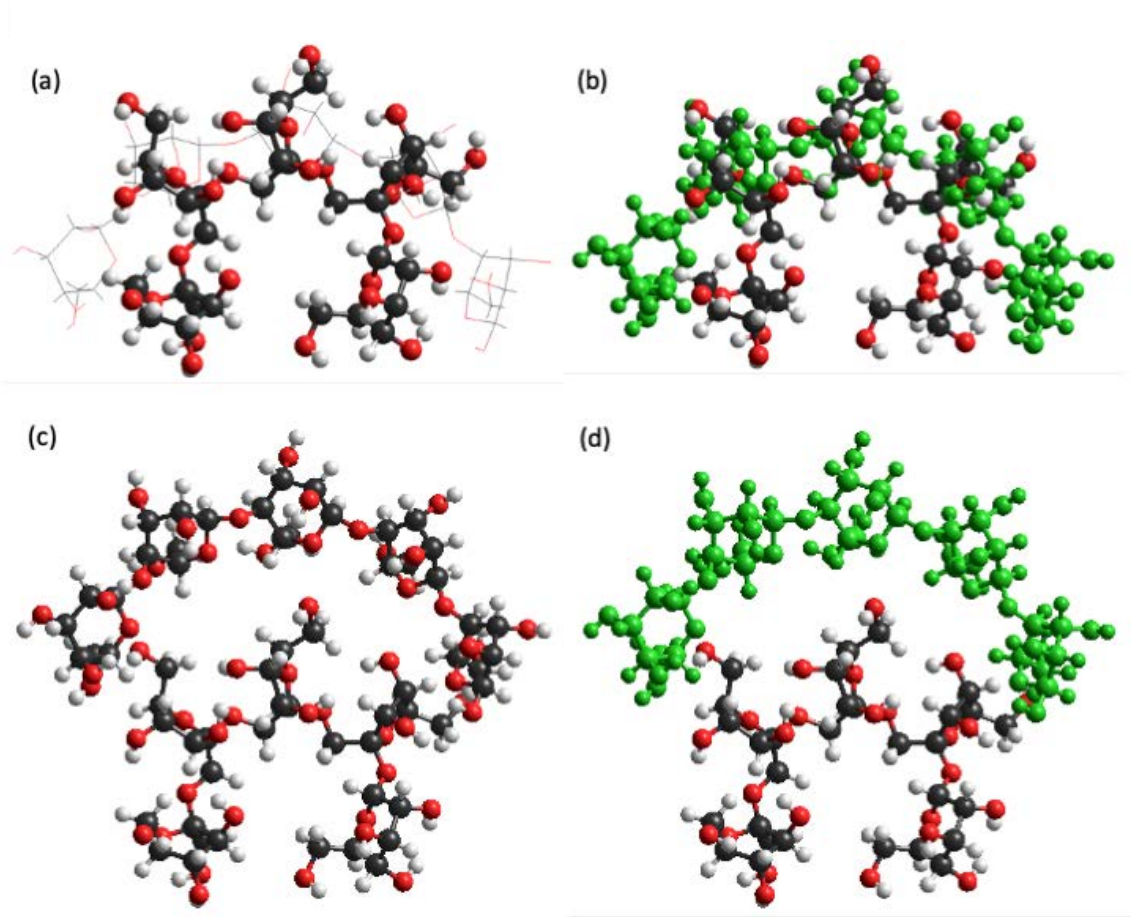
**Scheme S1.** (A) Additional details for Scheme 2 (c) included in main text: (left) ESA+Glc 1:1 complex. Glc in green except the two H atoms involved in the H bridges between ESA and Glc; (right) enhances view of the H bridges interaction region.



**Scheme S1.** (B) Optimized molecule geometry comparison for Glc (left) and Frc (right). Molecule views from two different planes (upper row, view from ceiling plane; bottom row, view from plane perpendicular to ceiling).

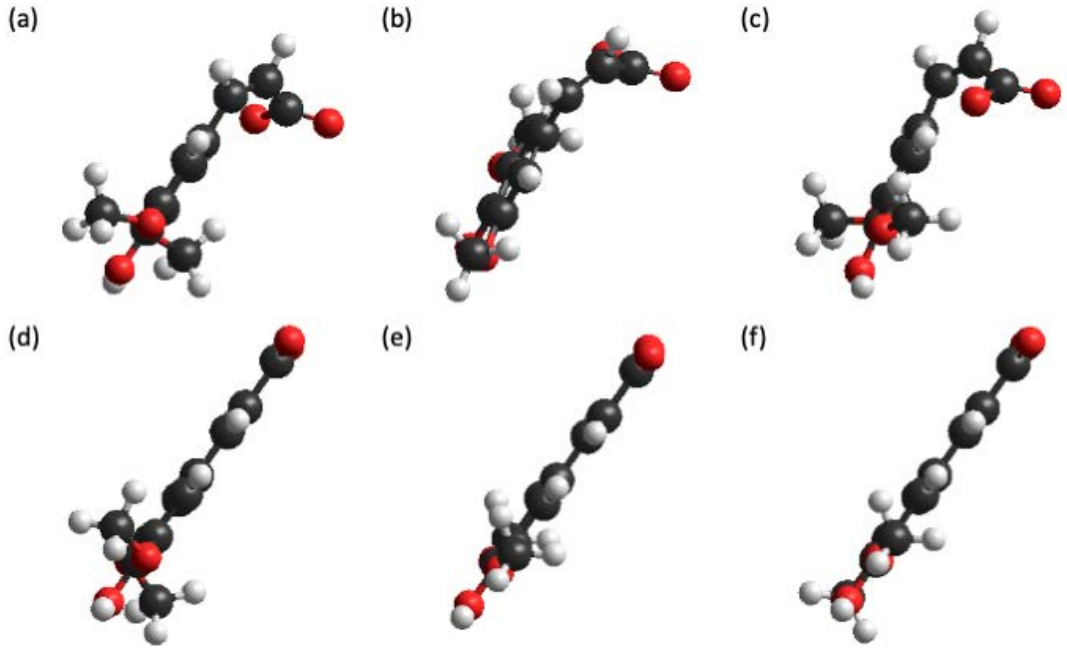



**Scheme S1.** (C) Optimized molecule geometry comparison for βCD and M7. (a) βCD (left) and M7 (right); (b) M7 (top) and βCD (bottom); (c) idem (b) with M7 in green.

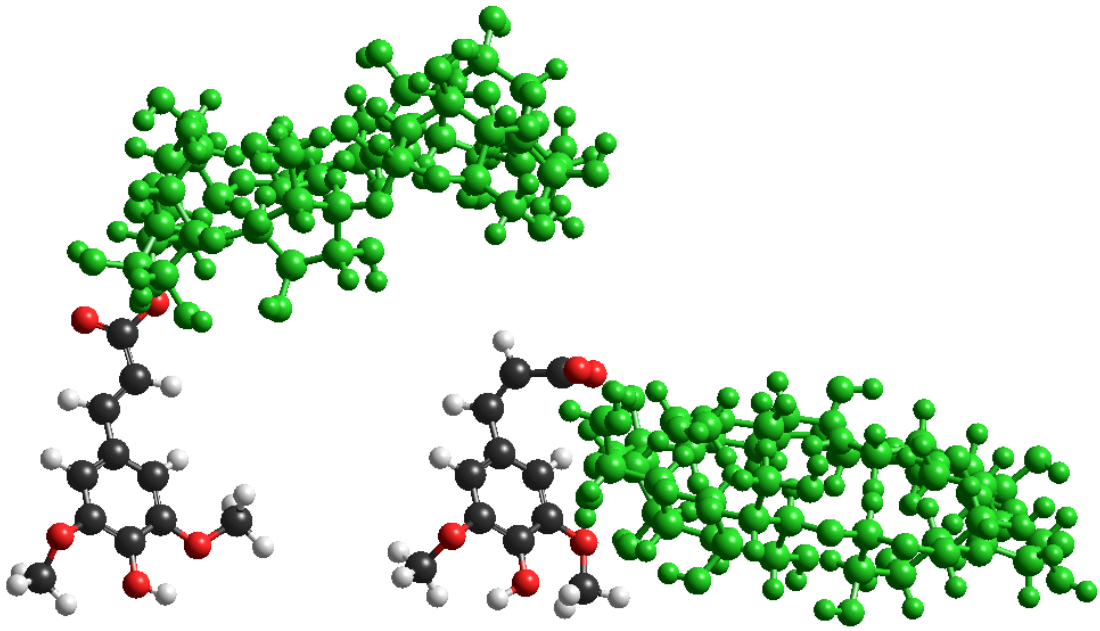



**Scheme S1.** (D) Optimized molecule geometry comparison for F5 and M5: (a) Artificial in silico superposition of molecules F5 (sticks and ball) and M5 (sticks); (b) Artificial in silico superposition of molecules F5 (sticks and ball) and M5 (sticks and balls in green); (c) M5 (top) and F5 (bottom) and (d) M5 (top) and F5, M5 in green.

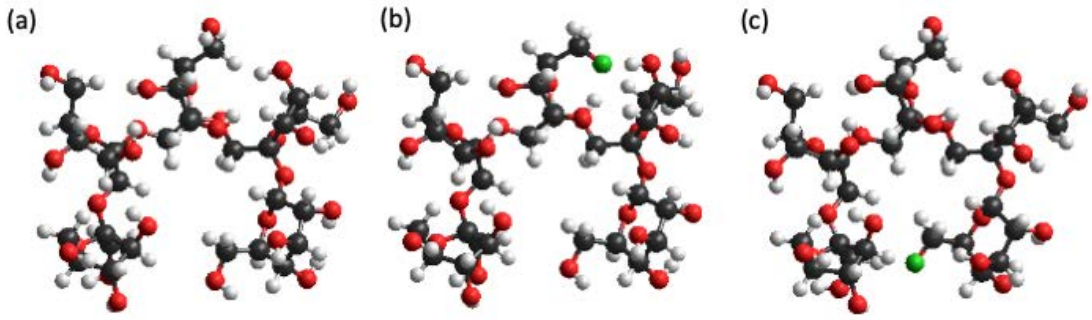
**Scheme S1.** (A) Additional details for Scheme 2 (c) included in main text: (left) ESA+Glc 1:1 complex. Glc in green except the two H atoms involved in the H bridges between ESA and Glc; (right) enhances view of the H bridges interaction region. (B) Optimized molecule geometry comparison for Glc (left) and Frc (right). Molecule views from two different planes (upper row, view from ceiling plane; bottom row, view from plane perpendicular to ceiling). (C) Optimized molecule geometry comparison for βCD and M7. (a) βCD (left) and M7 (right); (b) M7 (top) and βCD (bottom); (c) idem (b) with M7 in green. (D) Optimized molecule geometry comparison for F5 and M5: (a) Artificial on silico superposition of molecules F5 (sticks and ball) and M5 (sticks); (b) Artificial on silico superposition of molecules F5 (sticks and ball) and M5 (sticks and balls in green); (c) M5 (top) and F5 (bottom) and (d) M5 (top) and F5, M5 in green.




**Scheme S2**. Optimized molecule geometry comparison for $[ZSA\text{-}H]^-$ (top) and $[ESA\text{-}H]^-$ (bottom) rotamers whose QSAR and HOMO properties are included in Table S1. Details according to nomenclature in Table S1: $[ZSA\text{-}H]^-$ (top), left to right: $[ZSA\text{-}H]^-$, $[ZSAp\text{-}H]^-$ and $[ZSAps\text{-}H]^-$; $[ESA\text{-}H]^-$ (bottom), left to right: $[ESA\text{-}H]^-$, $[ESAp\text{-}H]^-$ and $[ESAps\text{-}H]^-$.



**Scheme S3.** Optimized molecule geometry comparison for $[ESA-H]^-$ (left) and $[ZSA-H]^-$ (right) complexes with βCD, $[ESA+βCD-H]^-$ and $[ZSA+βCD-H]^-$. βCD in green.




**Scheme S4.** Optimized molecule geometry comparison for F5 (a) and $[F5\text{-}H]^-$ (b and c), whose QSAR and HOMO properties are included in Table S2. Details according to nomenclature in Table S2: F5 (neutral molecule, a), $[F5\text{-}H]^-$ (anion in general): F5A36 (b), F5A16 (c), In the anionic species the deprotonated oxygen is indicated in green. The distortion of the molecule geometry allows a special stabilization because of the hydrogen bond formed involving this oxo-ion and a proton belonging to an HO group spatially located nearby, at an atom-atom distance < 2 Å (Angstrom).

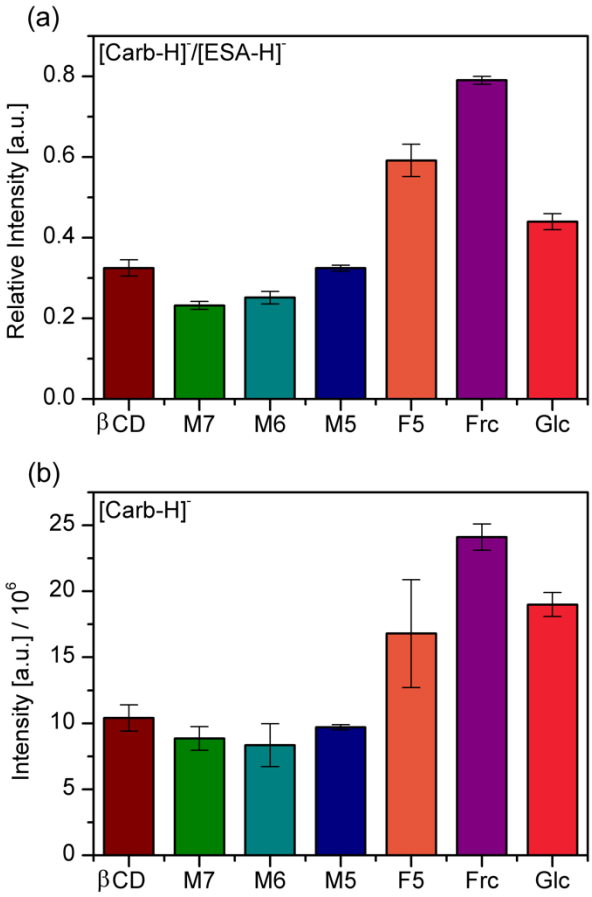



**Figure S1.** (a) Intensity of $[Carb\text{-}H]^-$ peak relative to $[ESA\text{-}H]^-$ ($[Carb\text{-}H]^-$ / $[ESA\text{-}H]^-$) and (b) absolute intensity of [Carb-H]- peak for each Carb studied. Carb 15 uM and ESA 5 uM in water: MeOH 7:3. ESA used as external calibrant (reference).

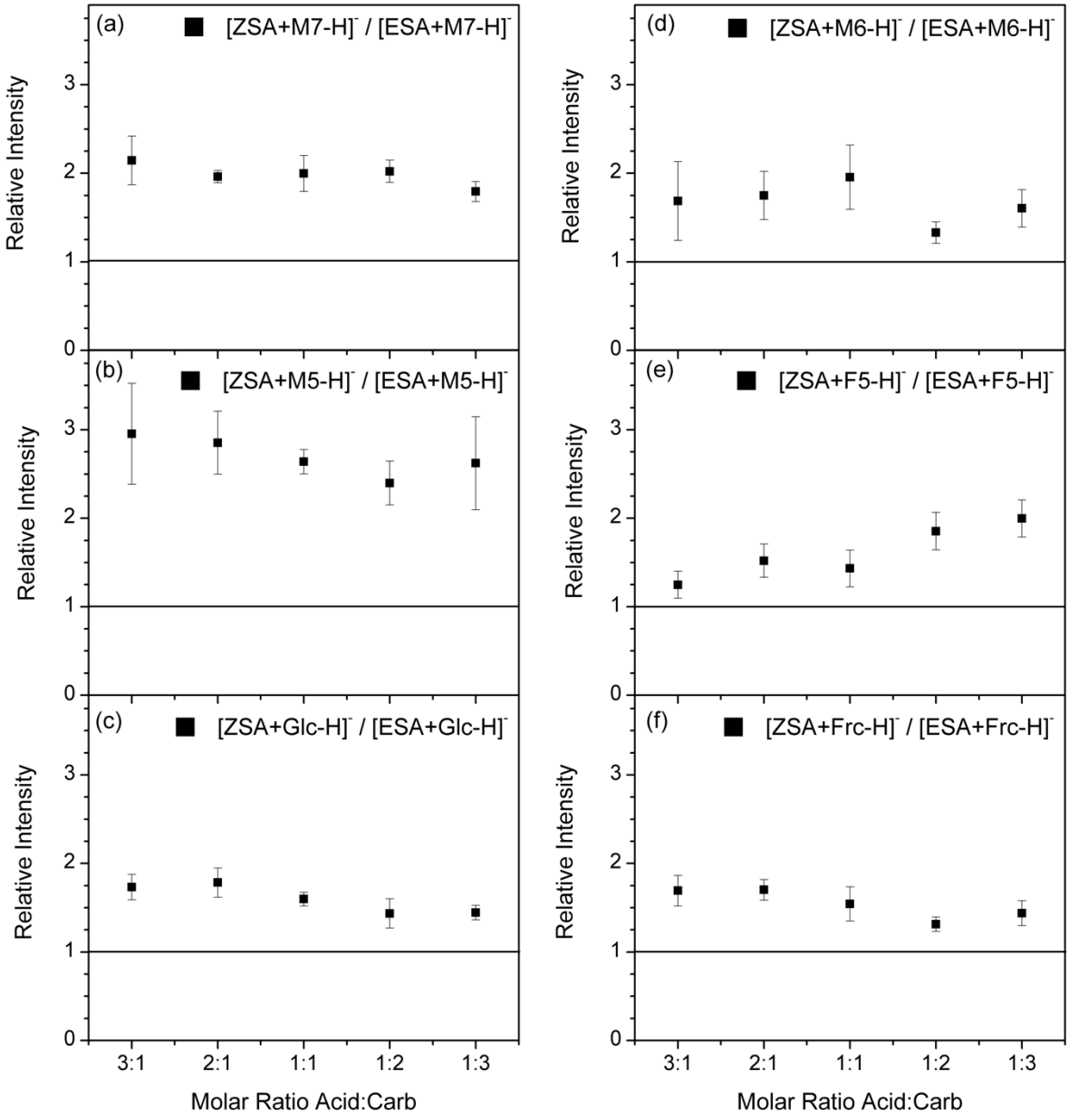



**Figure S2.** Intensity of the $[ZSA+Carb-H]^-$ peak relative to $[ESA+Carb-H]^-$, ($[ZSA+Carb-H]^-$ / $[ESA+Carb-H]^-$), for different Acid:Carb molar ratios. Acid concentration 5 μM in all the experiments. Carbohydrate (Carb) studied: (a) M7, (b) M5, (c) Glc, (d) M6, (e) F5 and (f) Frc.

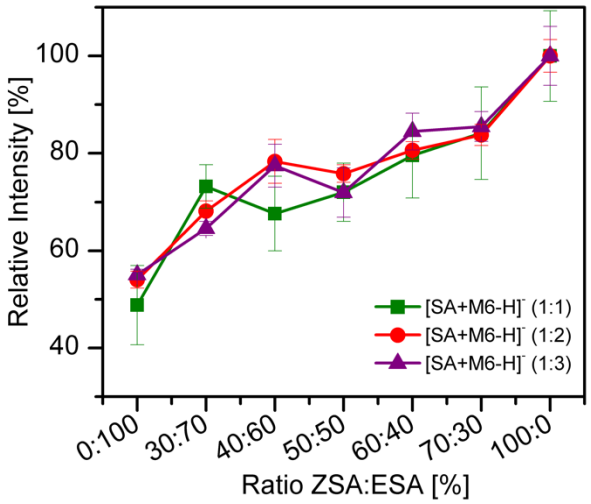
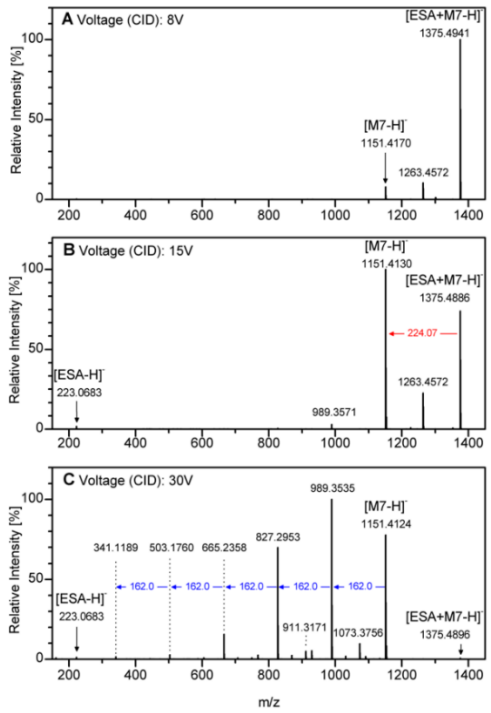
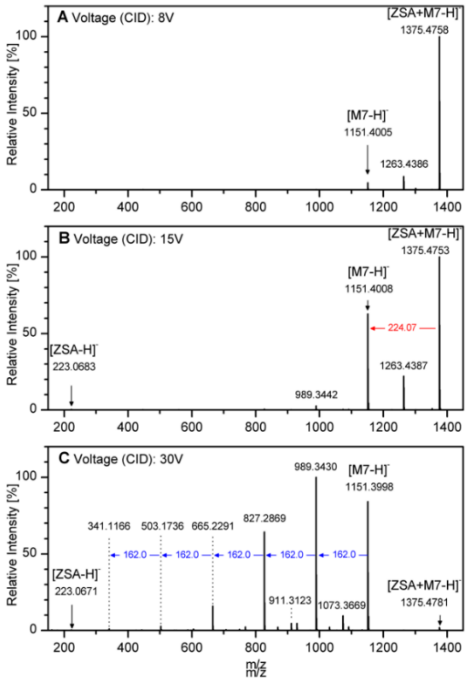


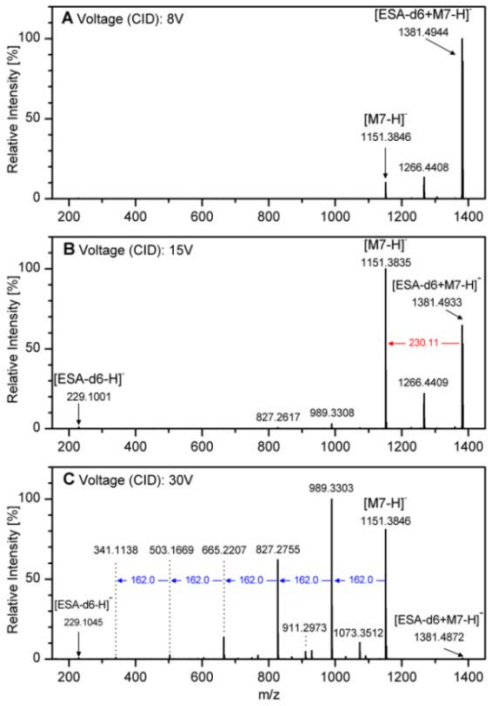

**Figure S3.** Competitive titration curves for Carb: M6. $[Acid+M6-H]^-$ peak intensity relative to $[ZSA+M6-H]^-$ peak intensity at ZSA:ESA 100:0%, ($[Acid+M6-H]^-$ / $[ZSA+M6-H]^-$), vs ZSA:ESA % ratio. Acid:M6 (■) 1:1, (●) 1:2 y (▲) 1:3 mol/mol; Acid = ZSA+ESA from ZSA:ESA 0:100% to 100:0%.




– MS/MS spectra. Precursor ion $[ESA+M7-H]^-$. CID voltage, 8V (A), 15V (B) and 30V (C ).

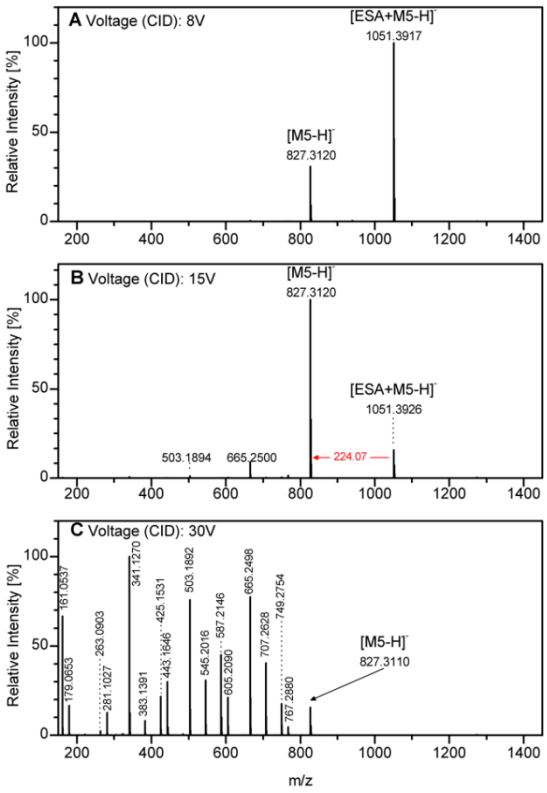



– MS/MS spectra. Precursor ion $[ZSA+M7-H]^-$. CID voltage, 8V (A), 15V (B) and 30V (C ).

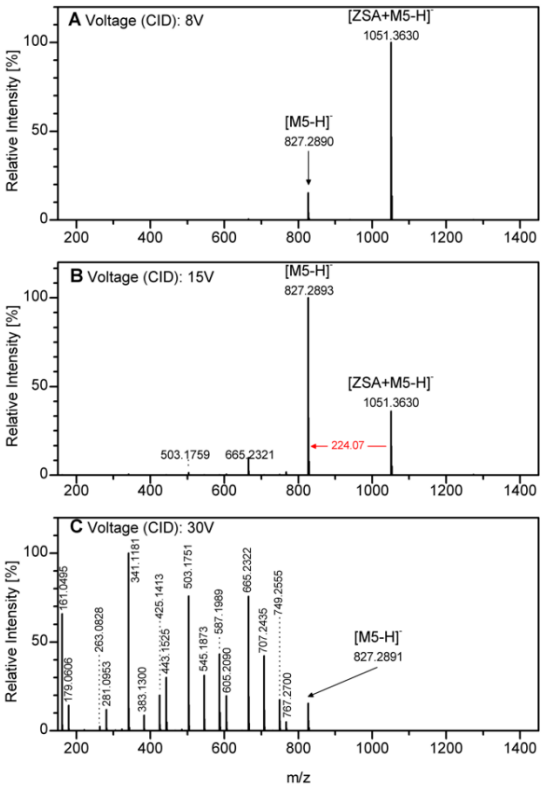



– MS/MS spectra. Precursor ion $[ESA-d6+M7-H]^-$. CID voltage, 8V (A), 15V (B) and 30V (C ).

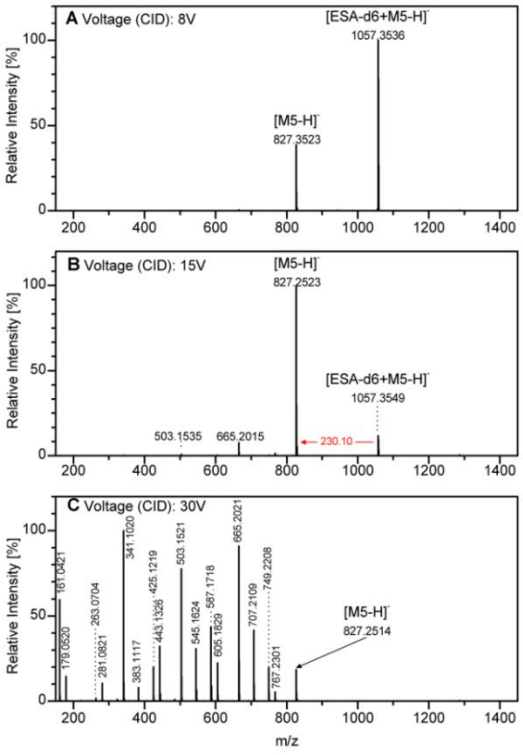
**Figure S4.** MS/MS spectra. Precursor ions: $[ESA+M7-H]^-$ (top, left), $[ZSA+M7-H]^-$ (top, right) and $[ESA- d6+M7-H]^-$ (bottom, left). CID voltage, 8V, 15V and 30V. Acid:M7 1:3 mol/mol; water:MeOH 7:3.




– MS/MS spectra. Precursor ion $[ESA+M5-H]^-$. CID voltage, 8V (A), 15V (B) and 30V (C ).

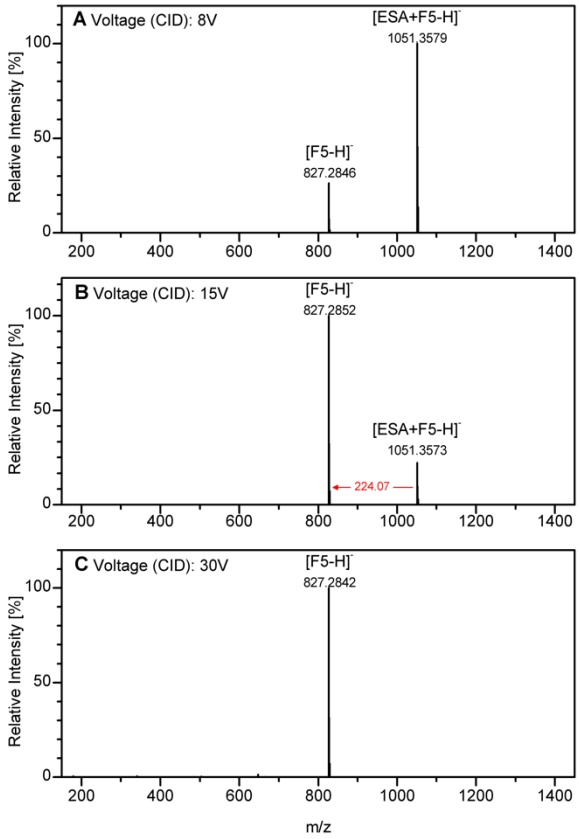



– MS/MS spectra. Precursor ion $[ZSA+M5-H]^-$. CID voltage, 8V (A), 15V (B) and 30V (C ).

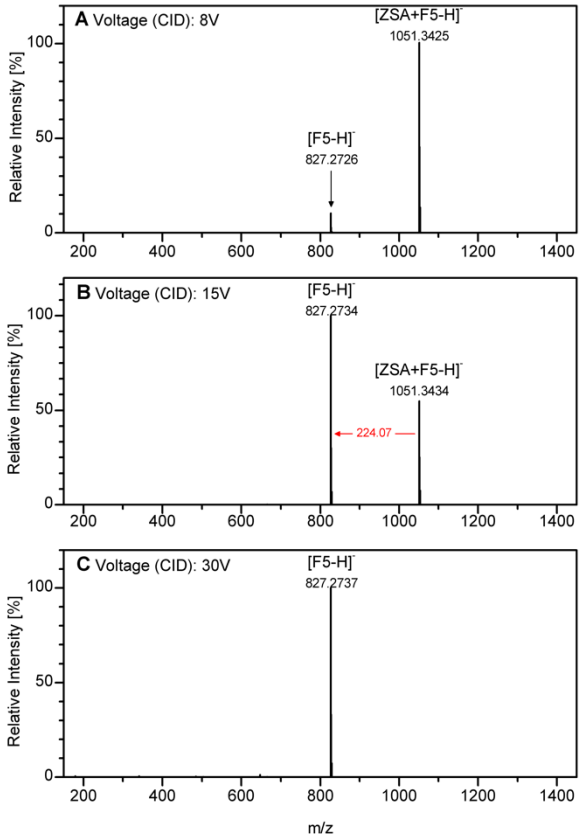



– MS/MS spectra. Precursor ion $[ESA-d6+M5-H]^-$. CID voltage, 8V (A), 15V (B) and 30V (C ).

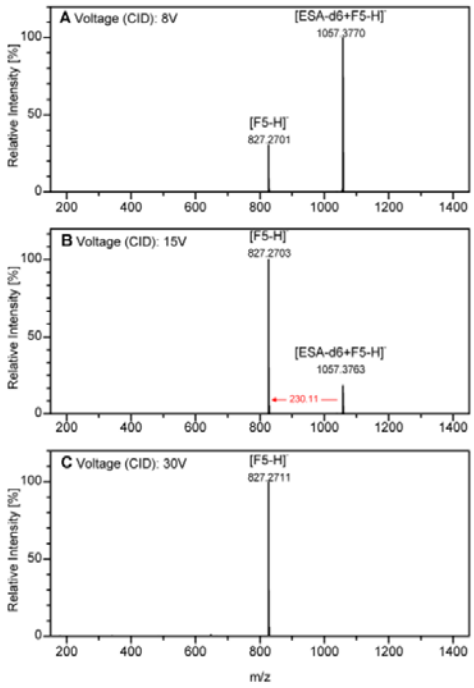
**Figure S5.** MS/MS spectra. Precursor ions: $[ESA+M5-H]^-$ (top, left), $[ZSA+M5-H]^-$ (top, right) and $[ESA- d6+M5-H]^-$ (bottom, left). CID voltage, 8V, 15V and 30V. Acid:M5 1:3 mol/mol; water:MeOH 7:3.




– MS/MS spectra. Precursor ion $[ESA+F5-H]^-$. CID voltage, 8V (A), 15V (B) and 30V (C).




– MS/MS spectra. Precursor ion $[ZSA+F5-H]^-$. CID voltage, 8V (A), 15V (B) and 30V (C ).




– MS/MS spectra. Precursor ion $[ESA-d6+F5-H]^-$. CID voltage, 8V (A), 15V (B) and 30V (C ).

**Figure S6.** MS/MS spectra. Precursor ions: $[ESA+F5-H]^-$ (top, left), $[ZSA+F5-H]^-$ (top, right) and $[ESA- d6+F5-H]^-$ (bottom, left). CID voltage, 8V, 15V and 30V. Acid:F5 1:3 mol/mol; water:MeOH 7:3.

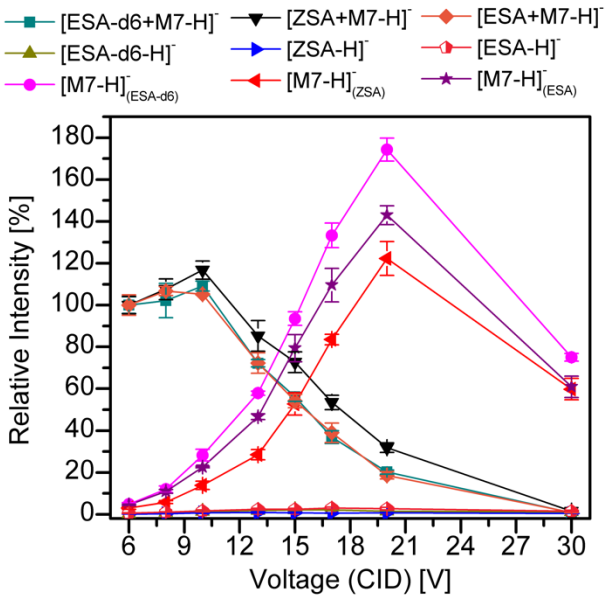



**Figure S7**. MS/MS (CID) experiments. Intensity of the species [Acid+M7-H]⁻. [Acid-H]⁻ and [M7-H]⁻ detected at different voltages relative to the value obtained at the lowest voltage (6V), Precursor ions [ESA-d6+M7-H]⁻ (■), [ESA+M7-H]⁻ (♦) and [ZSA+M7-H]⁻ (▼). Acid:M7 1:3 mol/mol; water:MeOH 7:3.

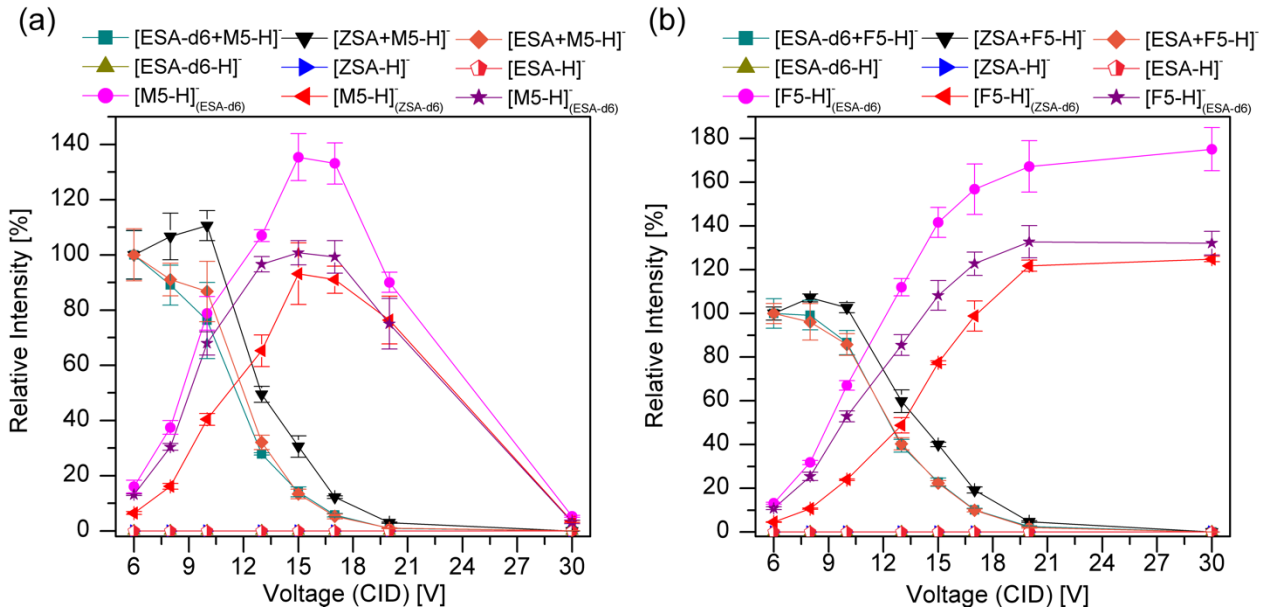



**Figure S8**. MS/MS (CID) experiments. Intensity of the species [Acid+Carb-H]⁻. [Acid-H]⁻ and [Carb-H]⁻ detected at different voltages relative to the value obtained at the lowest voltage (6V), Precursor ions: (a) left [ESA-d6+M5-H]⁻ (■), [ESA+M5-H]⁻ (♦) and [ZSA+M5-H]⁻ (▼); (b) right [ESA-d6+F5-H]⁻ (■), [ESA+F5-H]⁻ (♦) and [ZSA+F5-H]⁻ (▼). Acid:Carb 1:3 mol/mol; water:MeOH 7:3.

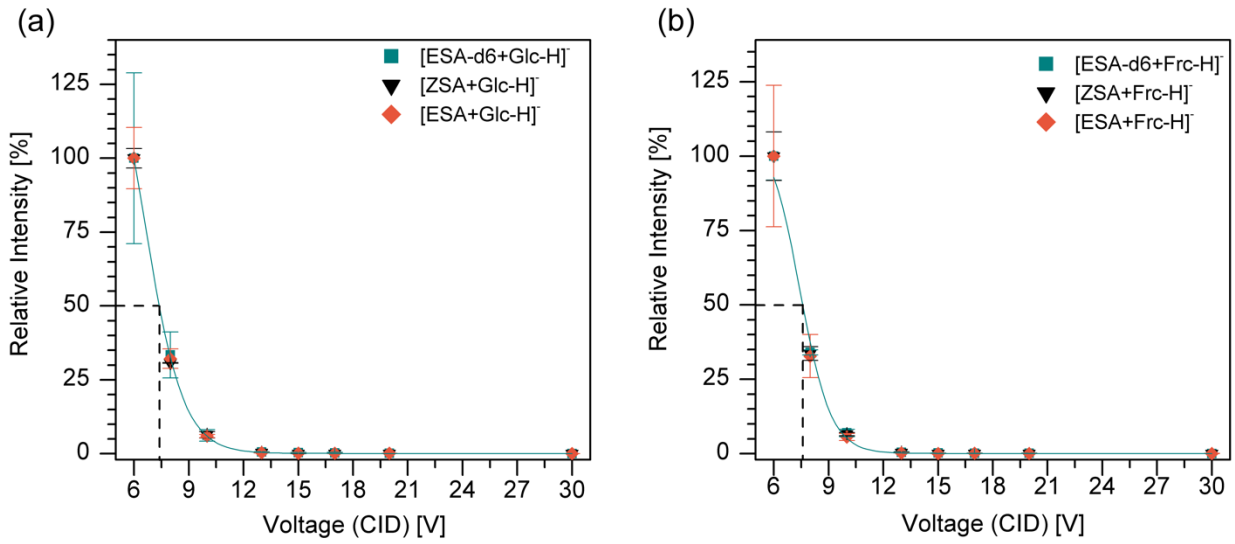



**Figure S9.** MS/MS (CID) experiments. Intensity of the species [Acid+Carb-H]⁻ detected at different voltages relative to the value obtained at the lowest voltage (6V), fitted curves. Precursor ions: (i) left [ESA-d6+Glc-H]⁻ (■), [ESA+Glc-H]⁻ (♦) and [ZSA+Glc-H]⁻ (▼); (ii) right [ESA-d6+Frc-H]⁻ (■), [ESA+Frc-H]⁻ (♦) and [ZSA+Frc-H]⁻ (▼). Acid:Carb 1:3 mol/mol; water:MeOH 7:3.

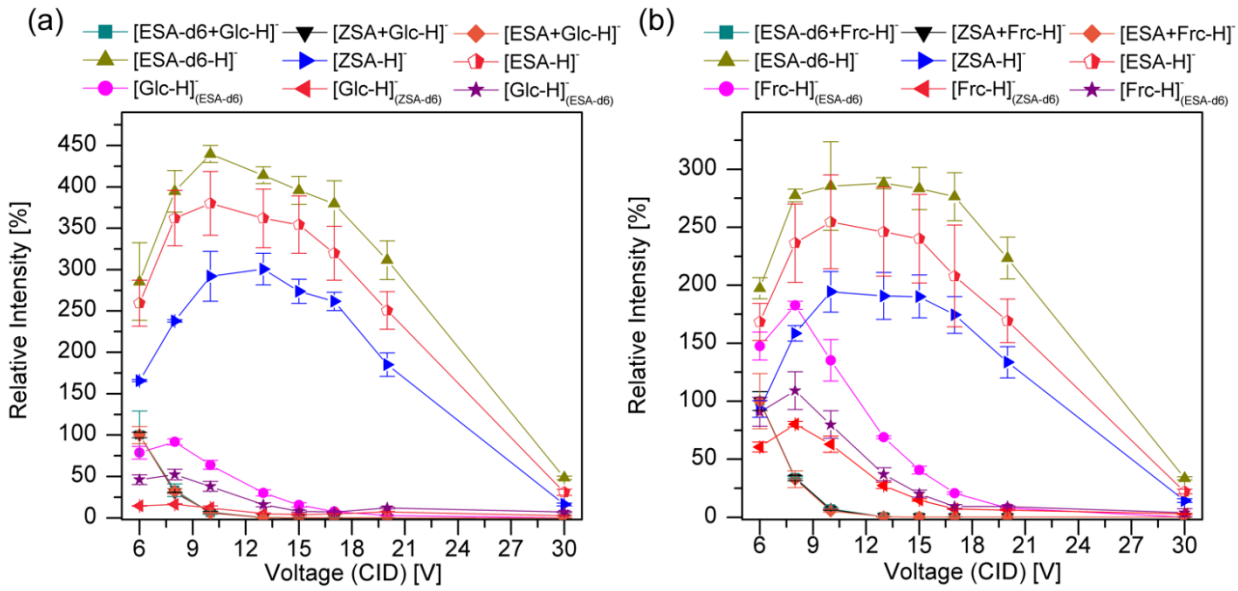



**Figure S10.** MS/MS (CID) experiments. Intensity of the species [Acid+Carb-H]⁻. [Acid-H]⁻ and [Carb-H]⁻ detected at different voltages relative to the value obtained at the lowest voltage (6V), Precursor ions: (i) left [ESA-d6+Glc-H]⁻ (■), [ESA+Glc-H]⁻ (♦) and [ZSA+Glc-H]⁻ (▼); (ii) right [ESA-d6+Frc-H]⁻ (■), [ESA+Frc-H]⁻ (♦) and [ZSA+Frc-H]⁻ (▼); Acid:Carb 1:3 mol/mol; water:MeOH 7:3.