

Table S4 MS spectra of each compound in references

Name	MS spectrum in references	MS spectrum in this study
22R-hydroxycholesterol ^[1-2]	A RT: 18.76 min NL: 3.90E+007 22(R)-hydroxycholesterol MW: 402.71, TMS derivative MW: 474.89	22(R)-hydroxycholesterol
22R-26-dihydroxycholesterol ^[1]	B RT: 21.56 min NL: 1.03E+007 22(R),26-dihydroxycholesterol MW: 418.36, TMS derivative MW: 490.54	22(R),26-dihydroxycholesterol
22-hydroxy-26-aminocholesterol ^[1, 3]	C RT: 7.679 min NL: 1.00E+004 22(R)-hydroxy-26(S)-aminocholesterol MW: 417.36 +H⁺: 418.36	22(R)-hydroxy-26(S)-aminocholesterol
Verazine ^[1,3]	D RT: 7.736 min NL: 6.00E+004 verazine MW: 397.36 +H⁺: 398.36	verazine

[1] Zhou, C., Yang, Y., Tian, J., Wu, Y., An, F., Li, C., Zhang, Y. (2022), 22R- but not 22S-hydroxycholesterol is recruited for diosgenin biosynthesis. *Plant J.* 109: 940–951.

[2]Kou, C., Liu, J., Yin, X., He, D., Liu, J., Hua, X., Ma, R., Sun, W., Xue, Z., Ma, P. (2024) Efficient heterologous biosynthesis of verazine, a metabolic precursor of the anti-cancer drug cyclopamine. *Plant Commun.* 5: 100831.

[3] Augustin, M.M., Shukla, A.K., Starks, C.M. Linna Han, M., Holland, C.K., Kutchan, T.M. (2017) Biosynthesis of Veratrum californicum specialty chemicals in Camelina sativa seed. *Plant Biotechnol Rep.* 11: 29–41.