Comparative Ascaroside Profiling of Caenorhabditis Exometabolomes

Reveals Species-Specific (ω) and (ω – 2)-Hydroxylation

Downstream of Peroxisomal β-Oxidation.

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Figure S1a. Extracted ion chromatograms for the K1 fragment ion at m/z 130.1 [C₆H₁₄OSi]^{+•} from GC-EIMS analysis of TMS-derivatized crude nematode exometabolome extracts.



Figure S1b. Extracted ion chromatograms for the K1 fragment ion at m/z 130.1 [C₆H₁₄OSi]^{+•} from GC-EIMS analysis of TMS-derivatized crude nematode exometabolome extracts.



Figure S1c. Extracted ion chromatograms for the K1 fragment ion at m/z 130.1 [C₆H₁₄OSi]^{+•} from GC-EIMS analysis of TMS-derivatized crude nematode exometabolome extracts.



Figure S1d. Extracted ion chromatograms for the K1 fragment ion at m/z 130.1 [C₆H₁₄OSi]^{+•} from GC-EIMS analysis of TMS-derivatized crude nematode exometabolome extracts.



Figure S1e. Extracted ion chromatograms for the K1 fragment ion at m/z 130.1 [C₆H₁₄OSi]^{+•} from GC-EIMS analysis of TMS-derivatized crude nematode exometabolome extracts.







Figure S1g. Extracted ion chromatograms for the K1 fragment ion at 130.1 $[C_6H_{14}OSi]^{+\bullet}$ from GC-EIMS analysis of TMS-derivatized crude nematode exometabolome extracts.



Figure S2: Electron ionization mass spectra of TMS derivatized (A) asc-7OH-C9 (**11**) from *C*. *nigoni* and *C. afra*; and (B) asc- β OH-C9 (**3**, n = 4, bhas#10) from *Panagrellus redivivus*.



Figure S3: GC-EIMS extracted ion traces (EICs) for the ascaroside-derived K1 fragment at m/z 130.1 [C₆H₁₄OSi]^{+•} for the crude *C. nigoni* exometabolome extract and ascaroside containing fractions obtained by chromatography on C18 using a stepwise gradient of aqueous methanol as eluent.





Figure S4: ¹H NMR spectra (400 MHz, CD₃OD) of RP-C₁₈-SPE fractions of the *C. nigoni* exometabolome extract.

Figure S5. Section of the dqf-COSY spectrum of the *C. nigoni* exometabolome fraction SPE40 showing signals corresponding to indole-3-acetic acid (IAA, auxin) and anthranilic acid.



Figure S6: Determination of diastereomeric excess (*de* >99%) of *threo*-18a and *erythro*-18b by ¹H NMR spectroscopy (400 MHz, CDCl₃).



Figure S7a: Assignment of (7R,8R)-threo configuration for the natural asc-7OH- Δ C9 (10) isolated from *C. nigoni* by comparison of ¹H NMR spectra with those of synthetic standards (10a and 10b).



Figure S7b: Assignment of (7R,8R)-threo configuration for the natural asc-7OH- Δ C9 (10) isolated from *C. nigoni* by comparison of ¹H NMR spectra with those of synthetic standards (10a and 10b).



Figure S8: Chemical correlation of *threo*-asc-7OH- Δ C9 (**10**) and asc-9OH- Δ C9 (**12**) from *C*. *nigoni* with synthetic standards of *threo*-asc-7OH- Δ C9 (**10a**), *erythro*-asc-7OH- Δ C9 (**10b**), and asc-9OH- Δ C9 (**12**) using GC-EIMS extracted ion chromatograms for the J1 fragment ions at *m/z* 433.2 [C₁₉H₄₁O₅Si₃]⁺.



Figure S9: Chemical correlation of *threo*-asc-7OH-C9 (**11a**) from *C. nigoni* with synthetic standards obtained by Pd/C-catalyzed hydrogenation of *threo*-asc-7OH- Δ C9 (**10a**) and *erythro*-asc-7OH- Δ C9 (**10b**) using GC-EIMS extracted ion chromatograms for the J2 fragment ions at *m*/*z* 317.2 [C₁₅H₃₃O₃Si₂]⁺.



Figure S10: Confirmation of the structure assignment of natural asc-9OH- Δ C9 (12) from *C. nigoni* by comparison of the ¹H NMR spectra of an isolated mixture of asc-9OH- Δ C9 (12) and *threo*-asc-9OH-C9 (11a) with those of isolated *threo*-asc-9OH-C9 (11a) and synthetic asc-9OH- Δ C9 (12).



Figure S11: Extracted ion chromatograms of GC-EIMS screening for the ascaroside specific K1 fragment ion signal at m/z 130.1 $[C_6H_{14}OSi]^{+\bullet}$ for (A) the *C. nigoni* (JU1422) exometabolome extract and (B) the *C. afra* (JU1286) exometabolome extract.



Figure S12: Total ion chromatograms of HPLC-ESI-(–)-MS/MS precursor ion screens for m/z73.1 [C₃H₅O₂]⁻ for (A) the *C. nigoni* (JU1422) exometabolome extract and (B) the *C. afra* (JU1286) exometabolome extract.



Figure 13a: Male response of *C. nigoni*; Wilcoxon Matched-Pairs Signed Rank Test; control vs. 1 μ M ascaroside #3 derivative; Male Response: **** p < 0.0001, ** p = 0.0052, * p = 0.0266, n \geq 13.



Figure 13b: Female response of *C. nigoni*; Wilcoxon Matched-Pairs Signed Rank Test; control vs. 1 μ M ascaroside #3 derivative; Female Response: n.s. (p > 0.05), n ≥10.





Figure S14: ¹H NMR spectrum of synthetic (*R*)-Methyl 2-(4-methoxybenzyloxy)propanoate (15) in CDCl₃.



Figure S15: ¹³C NMR spectrum of synthetic (*R*)-Methyl 2-(4-methoxybenzyloxy) propanoate (15) in CDCl₃.







Figure S17: ¹³C NMR spectrum of synthetic (*R*)-2-(4-Methoxybenzyloxy)propanal (16) in CDCl₃.



Figure S18: ¹H NMR spectrum of synthetic (2*R*,3*R*)*-threo*-3-Hydroxy-2-(4-methoxybenzyloxy)-7-octene (**17**) in CDCl₃.



Figure S19: ¹³C NMR spectrum of synthetic (2*R*,3*R*)-*threo*-3-Hydroxy-2-(4-methoxybenzyloxy)-7-octene (17) in CDCl₃.



Figure S20: HSQC spectrum of synthetic (2*R*,3*R*)-*threo*-3-Hydroxy-2-(4-methoxybenzyloxy)-7-octene (17) in CDCl₃.



Figure S21: ¹H NMR spectrum of synthetic (2*R*,3*R*)-threo-3-Benzoyloxy-2-(4-methoxybenzyloxy)-7-octene (18a) in CDCl₃.



Figure S22: ¹³C NMR spectrum of synthetic (2*R*,3*R*)-*threo*-3-Benzoyloxy-2-(4-methoxybenzyloxy)-7-octene (18a) in CDCl₃.



Figure S23: ¹H NMR spectrum of synthetic (2*R*,3*S*)-*erythro*-3-Benzoyloxy-2-(4-methoxybenzyloxy)-7-octene (18b) in CDCl₃.



Figure S24: ¹³C NMR spectrum of synthetic (2*R*,3*S*)-*erythro*-3-Benzoyloxy-2-(4-methoxybenzyloxy)-7-octene (18b) in CDCl₃.

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Figure S25: ¹H NMR spectrum of synthetic (7*R*,8*R*,2*E*)-*threo*-Ethyl 7-benzoyloxy-8-(4-methoxybenzyloxy)-2-nonenoate (19a) in CDCl₃.



Figure S26: ¹³C NMR spectrum of synthetic (7*R*,8*R*,2*E*)-*threo*-Ethyl 7-benzoyloxy-8-(4-methoxybenzyloxy)-2-nonenoate (19a) in CDCl₃.



Figure S27: HSQC spectrum of synthetic (7*R*,8*R*,2*E*)-*threo*-Ethyl 7-benzoyloxy-8-(4-methoxybenzyloxy)-2-nonenoate (19a) in CDCl₃.


Figure S28: ¹H NMR spectrum of synthetic (7*S*,8*R*,2*E*)-*erythro*-Ethyl 7-benzoyloxy-8-(4-methoxybenzyloxy)-2-nonenoate (**19b**) in CDCl₃.

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Figure S29: ¹³C NMR spectrum of synthetic (7*S*,8*R*,2*E*)-*erythro*-Ethyl 7-benzoyloxy-8-(4-methoxybenzyloxy)-2-nonenoate (**19b**) in CDCl₃.



Figure S30: HSQC NMR spectrum of synthetic (*7S*,8*R*,2*E*)-*erythro*-Ethyl 7-benzoyloxy-8-(4-methoxybenzyloxy)-2-nonenoate (**19b**) in CDCl₃.



Figure S31: ¹H NMR spectrum of synthetic (7*R*,8*R*,2*E*)-*threo*-Ethyl 7-benzoyloxy-8-hydroxy-2-nonenoate (20a) in CDCl₃.



Figure S32: ¹³C NMR spectrum of synthetic (7*R*,8*R*,2*E*)-*threo*-Ethyl 7-benzoyloxy-8-hydroxy-2-nonenoate (20a) in CDCl₃.



Figure S33: HSQC spectrum of synthetic (7*R*,8*R*,2*E*)-*threo*-Ethyl 7-benzoyloxy-8-hydroxy-2-nonenoate (20a) in CDCl₃.



Figure S34: dqf-COSY spectrum of synthetic (7*R*,8*R*,2*E*)-*threo*-Ethyl 7-benzoyloxy-8-hydroxy-2-nonenoate (20a) in CDCl₃.



Figure S35: ¹H NMR spectrum of synthetic (7*S*,8*R*,2*E*)-*erythro*-Ethyl 7-benzoyloxy-8-hydroxy-2-nonenoate (20b) in CDCl₃.



Figure S36: ¹³C NMR spectrum of synthetic (7*S*,8*R*,2*E*)-*erythro*-Ethyl 7-benzoyloxy-8-hydroxy-2-nonenoate (20b) in CDCl₃.



Figure S37: HSQC spectrum of synthetic (7*S*,8*R*,2*E*)-*erythro*-Ethyl 7-benzoyloxy-8-hydroxy-2-nonenoate (20b) in CDCl₃.





Figure S39: ¹H NMR spectrum of synthetic (7*R*,8*R*,2*E*)-*threo*-Ethyl 7-benzoyloxy-8-[(2,4-di-*O*-benzoyl-3,6-dideoxy- α -L-*arabino*-hexopyranosyl)oxy]-2-nonenoate (**22a**) in CDCl₃.



Figure S40: ¹³C NMR spectrum of synthetic (7*R*,8*R*,2*E*)-*threo*-Ethyl 7-benzoyloxy-8-[(2,4-di-*O*-benzoyl-3,6-dideoxy- α -L-*arabino*-hexopyranosyl)oxy]-2-nonenoate (**22a**) in CDCl₃.



Figure S41: HSQC spectrum of synthetic (7*R*,8*R*,2*E*)-*threo*-Ethyl 7-benzoyloxy-8-[(2,4-di-*O*-benzoyl-3,6-dideoxy- α -L-*arabino*-hexopyranosyl)oxy]-2-nonenoate (**22a**) in CDCl₃.



Figure S42: dqf-COSY spectrum of synthetic (7*R*,8*R*,2*E*)-*threo*-Ethyl 7-benzoyloxy-8-[(2,4-di-*O*-benzoyl-3,6-dideoxy- α -L-*arabino*-hexopyranosyl)oxy]-2-nonenoate (**22a**) in CDCl₃.

Figure S43: ¹H NMR spectrum of synthetic (7*S*,8*R*,2*E*)-*erythro*-Ethyl 7-benzoyloxy-8-[(2,4-di-*O*-benzoyl-3,6-dideoxy- α -L-*arabino*-hexopyranosyl)oxy]-2-nonenoate (**22b**) in CDCl₃.





Figure S44: ¹³C NMR spectrum of synthetic (7*S*,8*R*,2*E*)-*erythro*-Ethyl 7-benzoyloxy-8-[(2,4-di-*O*-benzoyl-3,6-dideoxy- α -L-*arabino*-hexopyranosyl)oxy]-2-nonenoate (**22b**) in CDCl₃.



Figure S45: HSQC spectrum of synthetic (7*S*,8*R*,2*E*)-*erythro*-Ethyl 7-benzoyloxy-8-[(2,4-di-*O*-benzoyl-3,6-dideoxy- α -L-*arabino*-hexopyranosyl)oxy]-2-nonenoate (**22b**) in CDCl₃.



Figure S46: dqf-COSY spectrum of synthetic (7*S*,8*R*,2*E*)-*erythro*-Ethyl 7-benzoyloxy-8-[(2,4-di-*O*-benzoyl-3,6-dideoxy- α -L-*arabino*-hexopyranosyl)oxy]-2-nonenoate (**22b**) in CDCl₃.

Figure S47: ¹H NMR spectrum of synthetic (7R,8R,2E)-*threo*-8-[(3',6'-Dideoxy- α -L-*arabino*-hexopyranosyl)oxy]-7-hydroxy-2-nonenoic acid ((7R,8R)-*threo*-asc-7OH- Δ C9, (7R,8R)-*threo*-**10a**) in CD₃OD.



Figure S48: ¹³C NMR spectrum of synthetic (7*R*,8*R*,2*E*)-*threo*-8-[(3',6'-Dideoxy- α -L-*arabino*-hexopyranosyl)oxy]-7-hydroxy-2-nonenoic acid ((7*R*,8*R*)-*threo*-asc-7OH- Δ C9, (7*R*,8*R*)-*threo*-10a) in CD₃OD.



Figure S49: HSQC spectrum of synthetic (7R,8R,2E)-*threo*-8-[(3',6'-Dideoxy- α -L-*arabino*-hexopyranosyl)oxy]-7-hydroxy-2-nonenoic acid ((7R,8R)-*threo*-asc-7OH- Δ C9, (7R,8R)-*threo*-**10a**) in CD₃OD.



Figure S50: dqf-COSY spectrum of synthetic (7R,8R,2E)-*threo*-8-[(3',6'-Dideoxy- α -L-*arabino*-hexopyranosyl)oxy]-7-hydroxy-2-nonenoic acid ((7R,8R)-*threo*-asc-7OH- Δ C9, (7R,8R)-*threo*-**10a**) in CD₃OD.





Figure S51: ¹H NMR spectrum of synthetic $2-((6R)-6-((R)-1-[(3,6-dideoxy-\alpha-L-$ *arabino*-hexopyranosyl)oxy]ethyl)tetrahydro-2H-pyran-2-yl)acetic acid (**23a**) in CD₃OD.

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Figure S52: ¹³C NMR spectrum of synthetic 2-((6R)-6-((R)-1-[(3,6-dideoxy- α -L-*arabino*-hexopyranosyl)oxy]ethyl)tetrahydro-2H-pyran-2-yl)acetic acid (**23a**) in CD₃OD.



Figure S53: dqf-COSY spectrum of synthetic $2-((6R)-6-((R)-1-[(3,6-dideoxy-\alpha-L-$ *arabino*-hexopyranosyl)oxy]ethyl)tetrahydro-2H-pyran-2-yl)acetic acid (**23a**) in CD₃OD.



Figure S54: HMQC spectrum of synthetic $2-((6R)-6-((R)-1-[(3,6-dideoxy-\alpha-L-$ *arabino*-hexopyranosyl)oxy]ethyl)tetrahydro-2H-pyran-2-yl)acetic acid (**23a**) in CD₃OD.

Figure S55: ¹H NMR spectrum of synthetic (7*S*,8*R*,2*E*)-*erythro*-8-[(3',6'-Dideoxy- α -L-*arabino*-hexopyranosyl)oxy]-7-hydroxy-2-nonenoic acid ((7*S*,8*R*)-*erythro*-asc-7OH- Δ C9, (7*S*,8*R*)-*erythro*-**10b**) in CD₃OD.



Figure S56: ¹³C NMR spectrum of synthetic (7*S*,8*R*,2*E*)-*erythro*-8-[(3',6'-Dideoxy- α -L-*arabino*-hexopyranosyl)oxy]-7-hydroxy-2-nonenoic acid ((7*S*,8*R*)-*erythro*-asc-7OH- Δ C9, (7*S*,8*R*)-*erythro*-**10b**) in CD₃OD.



Figure S57: HSQC spectrum of synthetic (7*S*,8*R*,2*E*)-*erythro*-8-[(3',6'-Dideoxy- α -L-*arabino*-hexopyranosyl)oxy]-7-hydroxy-2-nonenoic acid ((7*S*,8*R*)-*erythro*-asc-7OH- Δ C9, (7*S*,8*R*)-*erythro*-**10b**) in CD₃OD.



Figure S58: dqf-COSY spectrum of synthetic (7*S*,8*R*,2*E*)-*erythro*-8-[(3',6'-Dideoxy- α -L-*arabino*-hexopyranosyl)oxy]-7-hydroxy-2-nonenoic acid ((7*S*,8*R*)-*erythro*-asc-7OH- Δ C9, (7*S*,8*R*)-*erythro*-**10b**) in CD₃OD.



~3.75 ~3.66 ~3.52 -4.66 -2.53 -2.47 -2.44 -2.44 -2.39 -2.39 71.96 71.93 71.80 -1.58 -1.42 1.22 1.15 3.31 -1800 -1700 -1600 -1500 -1400 -1300 -1200 -1100 -1000 -900 -800 -700 -600 -500 -400 -300 -200 -100 -0 **1**.0-I 2.0 2.0 1.0 2.0 2.0 0.84 0.74 0.64 2.9<u>4</u> 2.9<u>4</u> 1.0-] 1.0-1.7-3.3---100 3.0 f1 (ppm) .5 5.0 4.5 4.0 3.5 2.5 2.0 1.5 1.0 0.5

Figure S59: ¹H NMR spectrum of synthetic $2-((6S)-6-((R)-1-[(3,6-dideoxy-\alpha-L-$ *arabino*-hexopyranosyl)oxy]ethyl)tetrahydro-2H-pyran-2-yl)acetic acid (**23b**) in CD₃OD.

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Figure S60: ¹³C NMR spectrum of synthetic 2-((6*S*)-6-((*R*)-1-[(3,6-dideoxy- α -L-*arabino*-hexopyranosyl)oxy]ethyl)tetrahydro-2H-pyran-2-yl)acetic acid (**23b**) in CD₃OD.



Figure S61: dqf-COSY spectrum of synthetic $2-((6S)-6-((R)-1-[(3,6-dideoxy-\alpha-L-$ *arabino*-hexopyranosyl)oxy]ethyl)tetrahydro-2H-pyran-2-yl)acetic acid (**23b**) in CD₃OD.



Figure S62: HMQC spectrum of synthetic $2-((6S)-6-((R)-1-[(3,6-dideoxy-\alpha-L-$ *arabino*-hexopyranosyl)oxy]ethyl)tetrahydro-2H-pyran-2-yl)acetic acid (**23b**) in CD₃OD.



Figure S63: ¹H NMR spectrum of synthetic (7*S*)-7-*tert*-Butyldimethylsilyloxy-6-hydroxy-1-octene (25) in CDCl₃.


Figure S64: ¹³C NMR spectrum of synthetic (7*S*)-7-*tert*-Butyldimethylsilyloxy-6-hydroxy-1-octene (25) in CDCl₃.



Figure S65: ¹H NMR spectrum of synthetic (2*E*,8*S*)-Ethyl 9-*tert*-butyldimethylsilyloxy-8-hydroxy-2-nonenoate (26) in CDCl₃.



Figure S66: ¹³C NMR spectrum of synthetic (2*E*,8*S*)-Ethyl 9-*tert*-butyldimethylsilyloxy-8-hydroxy-2-nonenoate (26) in CDCl₃.



Figure S67: HMQC spectrum of synthetic (2E,8S)-Ethyl 9-tert-butyldimethylsilyloxy-8-hydroxy-2-nonenoate (26) in CDCl₃.

Figure S68: ¹H NMR spectrum of synthetic (2*E*,8*S*)-Ethyl 8-[(2,4-di-*O*-benzoyl-3,6-dideoxy-α-L-*arabino*-hexopyranosyl)oxy]-9-*tert*-butyldimethylsilyloxy-2-nonenoate (**27**) in CDCl₃.



Figure S69: ¹³C NMR spectrum of synthetic (2*E*,8*S*)-Ethyl 8-[(2,4-di-*O*-benzoyl-3,6-dideoxy- α -L-*arabino*-hexopyranosyl)oxy]-9-*tert*-butyldimethylsilyloxy-2-nonenoate (**27**) in CDCl₃.





Figure S70: dqf-COSY spectrum of synthetic (2*E*,8*S*)-Ethyl 8-[(2,4-di-*O*-benzoyl-3,6-dideoxy- α -L-*arabino*-hexopyranosyl)oxy]-9-*tert*-butyldimethylsilyloxy-2-nonenoate (**27**) in CDCl₃.



Figure S71: HMQC spectrum of synthetic (2*E*,8*S*)-Ethyl 8-[(2,4-di-*O*-benzoyl-3,6-dideoxy- α -L-*arabino*-hexopyranosyl)oxy]-9-*tert*-butyldimethylsilyloxy-2-nonenoate (**27**) in CDCl₃.



Figure S72: ¹H NMR spectrum of synthetic (2*E*,8*S*)-Ethyl 8-[(2,4-di-*O*-benzoyl-3,6-dideoxy- α -L-*arabino*-hexopyranosyl)oxy]-9-hydroxy-2-nonenoate (**28**) in CDCl₃.



Figure S73: ¹³C NMR spectrum of synthetic (2*E*,8*S*)-Ethyl 8-[(2,4-di-*O*-benzoyl-3,6-dideoxy- α -L-*arabino*-hexopyranosyl)oxy]-9-hydroxy-2-nonenoate (**28**) in CDCl₃.



Figure S74: dqf-COSY spectrum of synthetic (2*E*,8*S*)-Ethyl 8-[(2,4-di-*O*-benzoyl-3,6-dideoxy- α -L-*arabino*-hexopyranosyl)oxy]-9-hydroxy-2-nonenoate (**28**) in CDCl₃.



Figure S75: HMQC spectrum of synthetic (2*E*,8*S*)-Ethyl 8-[(2,4-di-*O*-benzoyl-3,6-dideoxy- α -L-*arabino*-hexopyranosyl)oxy]-9-hydroxy-2-nonenoate (**28**) in CD₃OD.

Figure S76: ¹H NMR spectrum of synthetic (2*E*,8*S*)-8-[(3,6-Dideoxy- α -L-*arabino*-hexopyranosyl)oxy]-9-hydroxy-2-nonenoic acid (asc-9OH- Δ C9) (**12**) in CD₃OD.





Figure S77: ¹³C NMR spectrum of synthetic (2*E*,8*S*)-8-[(3,6-Dideoxy- α -L-*arabino*-hexopyranosyl)oxy]-9-hydroxy-2-nonenoic acid (asc-9OH- Δ C9) (**12**) in CD₃OD.



Figure S78: dqf-COSY spectrum of synthetic (2*E*,8*S*)-8-[(3,6-Dideoxy- α -L-*arabino*-hexopyranosyl)oxy]-9-hydroxy-2-nonenoic acid (asc-9OH- Δ C9) (**12**) in CD₃OD.



Figure S79: HMQC spectrum of synthetic (2*E*,8*S*)-8-[(3,6-Dideoxy- α -L-*arabino*-hexopyranosyl)oxy]-9-hydroxy-2-nonenoic acid (asc-9OH- Δ C9) (**12**) in CD₃OD.



Figure S80: ¹H NMR spectrum of synthetic (7*S*)-7-[(3,6-Dideoxy-α-L-*arabino*-hexopyranosyl)oxy]oxocan-2-yl)-acetic acid (**29**) in CD₃OD.



Figure S81: ¹³C NMR spectrum of synthetic (7*S*)-7-[(3,6-Dideoxy-α-L-*arabino*-hexopyranosyl)oxy]oxocan-2-yl)-acetic acid (**29**) in CD₃OD.



Figure S82: dqf-COSY spectrum of synthetic (7*S*)-7-[(3,6-Dideoxy-α-L-*arabino*-hexopyranosyl)oxy]oxocan-2-yl)-acetic acid (**29**) in CD₃OD.



Figure S83: HMQC spectrum of synthetic (7*S*)-7-[(3,6-Dideoxy-α-L-*arabino*-hexopyranosyl)oxy]oxocan-2-yl)-acetic acid (**29**) in CD₃OD.







Figure S85: dqf-COSY spectrum of *C. nigoni* exometabolome fraction SPE40 in CD₃OD.



Figure S86: ¹H NMR spectrum of (7*R*,8*R*,2*E*)-*threo*-8-[(3',6'-Dideoxy- α -L-*arabino*-hexopyranosyl)oxy]-7-hydroxy-2-nonenoic acid (*threo*-asc-7OH- Δ C9, **10a**) isolated from the *C. nigoni* exometabolome (~275 µg) in CD₃OD.

Figure S87: dqf-COSY spectrum of (7*R*,8*R*,2*E*)-*threo*-8-[(3',6'-Dideoxy- α -L-*arabino*-hexopyranosyl)oxy]-7-hydroxy-2-nonenoic acid (*threo*-asc-7OH- Δ C9, **10a**) isolated from the *C. nigoni* exometabolome (~275 µg) in CD₃OD.



Figure S88: NOESY spectrum of (7R, 8R, 2E)-*threo*-8-[(3',6'-Dideoxy- α -L-*arabino*-hexopyranosyl)oxy]-7-hydroxy-2-nonenoic acid (*threo*-asc-7OH- Δ C9, **10a**) isolated from the *C. nigoni* exometabolome (~275 µg) in CD₃OD.



Figure S89: HSQC spectrum of (7R,8R,2E)-*threo*-8-[(3',6'-Dideoxy- α -L-*arabino*-hexopyranosyl)oxy]-7-hydroxy-2-nonenoic acid (*threo*-asc-7OH- Δ C9, **10a**) isolated from the *C. nigoni* exometabolome (~275 µg) in CD₃OD.





Figure S90: ¹H NMR spectrum of (7*R*,8*R*)-*threo*-8-[(3',6'-Dideoxy- α -L-*arabino*-hexopyranosyl)oxy]-7-hydroxynonanoic acid (*threo*-asc-7OH-C9, **11**) isolated from the *C. nigoni* exometabolome (~110 µg) in CD₃OD.

Figure S91: dqf-COSY spectrum of (7R,8R)-*threo*-8-[(3',6'-Dideoxy- α -L-*arabino*-hexopyranosyl)oxy]-7-hydroxynonanoic acid (*threo*-asc-7OH-C9, **11**) isolated from the *C. nigoni* exometabolome (~110 µg) in CD₃OD.





Figure S92: HSQC spectrum of (7R,8R)-*threo*-8-[(3',6'-Dideoxy- α -L-*arabino*-hexopyranosyl)oxy]-7-hydroxynonanoic acid (*threo*-asc-7OH-C9, **11**) isolated from the *C. nigoni* exometabolome (~110 µg) in CD₃OD.



Figure S93: ¹H NMR spectrum of (2*E*,8*S*)-8-[(3,6-Dideoxy- α -L-*arabino*-hexopyranosyl)oxy]-9-hydroxy-2-nonenoic acid (asc-9OH- Δ C9, **12**) isolated from the *C. nigoni* exometabolome (~130 µg) in CD₃OD.



Figure S94: dqf-COSY spectrum of (2*E*,8*S*)-8-[(3,6-Dideoxy- α -L-*arabino*-hexopyranosyl)oxy]-9-hydroxy-2-nonenoic acid (asc-9OH- Δ C9, **12**) isolated from the *C. nigoni* exometabolome (~130 µg) in CD₃OD.



Figure S95: HSQC spectrum of (2E,8S)-8-[(3,6-Dideoxy- α -L-*arabino*-hexopyranosyl)oxy]-9-hydroxy-2-nonenoic acid (asc-9OH- Δ C9, **12**) isolated from the *C. nigoni* exometabolome (~130 µg) in CD₃OD.