Supporting Information

Quantification of Whisky Congeners by $^1$H NMR Spectroscopy

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Figure S1. $^1$H NMR spectra of seven compounds previously not characterised by Kew et al (2019). 1 - vanillin; 2 - vanillic acid; 3 – scopoletin; 4 – iso-amyl acetate; 5 – lactose; 6 – sucrose; 7 – maltose. The inset contains aromatic regions of the spectra for compounds 1-3.
Table S1. $^1$H NMR parameters of additional compounds profiled in Scotch Whisky by NMR, which were not characterised in Kew et al (2019), including $^1$H chemical shifts, $J$ coupling constants, multiplicity (m), group, and number of protons. For lactose, sucrose and maltose only the key signals used in the profiling are listed.

| Compound          | $\delta(^1$H)/ ppm | $J$ / Hz | Multiplicity | Group | Number of protons | Compound          | $^1$H / ppm | Multiplicity |
|-------------------|---------------------|----------|--------------|-------|-------------------|-------------------|-------------|--------------|
| Vanillin          | 3.89                | -        | s            | CH$_3$| 3                 | Lactose          | 3.26        | t            |
|                   | 7.05                | 8.01     | d            | CH    | 1                 |                   | 3.90        | d            |
|                   | 7.50                | 1.85     | d            | CH    | 1                 |                   | 4.42        | d            |
|                   | 7.54                | 8.20, 1.88| dd          | CH    | 1                 |                   | 4.62        | d            |
|                   | 9.72                | -        | s            | CH    | 1                 |                   | 5.19        | d            |
| Vanillic Acid     | 3.89                | -        | s            | CH$_3$| 3                 | Sucrose           | 3.44        | t            |
|                   | 6.93                | 8.20     | d            | CH    | 1                 |                   | 3.52        | dd           |
|                   | 7.54                | 8.07, 2.0| dd          | CH    | 1                 |                   | 4.30        | t            |
|                   | 7.56                | 2.02     | d            | CH    | 1                 |                   | 4.18        | d            |
|                   |                     |          |              |       |                   |                   | 5.39        | d            |
| Scopoletin        | 3.91                | -        | s            | CH$_3$| 3                 | Maltose           | 3.95        | t            |
|                   | 6.33                | 9.41     | d            | CH    | 1                 |                   | 4.60        | d            |
|                   | 6.92                | -        | s            | CH    | 1                 |                   | 5.19        | d            |
|                   | 7.22                | -        | s            | CH    | 1                 |                   | 5.32        | t            |
|                   | 7.99                | 9.48     | d            | CH    | 1                 |                   |             |              |
| Iso-Amyl Acetate  | 0.90                | 6.61     | d            | CH$_3$| 6                 |                   |             |              |
|                   | 1.52                | 6.82     | q            | CH$_2$| 2                 |                   |             |              |
|                   | 1.66                | 6.79     | m            | CH    | 2                 |                   |             |              |
|                   | 2.07                | -        | s            | CH$_3$| 3                 |                   |             |              |
|                   | 4.12                | 6.80     | t            | CH$_2$| 2                 |                   |             |              |
Table S2. Composition of model mixtures used for testing of the quantification protocol. Concentrations are given in mM.

| Mixture number (overlap)* | 1(1) | 2(3) | 3(5) | 4(2) | 5(2) | 6(1) | 7(1) | 8(5) | 9(1) | 10(3) | 11(2) | 12(1) | 13(2) | 14(2) | 15(5) | 16(1) | 17(4) | 18(4) |
|---------------------------|------|------|------|------|------|------|------|------|------|-------|-------|-------|-------|-------|-------|-------|-------|
| **Gallic Acid**           |      |      |      |      |      |      |      | 0.0105| 0.0105| 0.0070 | 0.0035 | 0.0035 |       |       |       |       |       |
| **Vanillin**              |      |      |      |      |      |      |      |       |       |       |       |       | 0.0042 |       |       |       |       |       |
| **Vanillic Acid**         |      |      |      |      |      |      |      |       |       |       |       |       | 0.0038 |       |       |       |       |       |
| **Syringaldehyde**        | 0.0097| 0.0097| 0.0065| 0.0065| 0.0032| 0.0034|       |       |       |       |       |       |       |       |       |       |       |       |
| **Syringic Acid**         | 0.0061| 0.0061| 0.0061| 0.0061| 0.0031| 0.0029|       |       |       |       |       |       |       |       |       |       |       |       |
| **Scopoletin**            |      |      |      |      |      |      |      |       |       |       |       |       | 0.0030 |       |       |       |       |       |
| **HMF**                   | 0.0184| 0.0138| 0.0138| 0.0055| 0.0049|       |       |       |       |       |       |       |       |       |       |       |       |       |
| **Ethyl Acetate**         | 1.14 | 1.14 |      |      | 0.455 | 1.14 | 1.11 |       |       |       |       |       |       |       |       |       |       |       |
| **Methanol**              | 0.94 |      |      |      | 0.312 |      |      |       |       |       |       |       |       |       |       |       |       |       |
| **n-Propanol**            | 1.67 | 1.67 | 1.66 | 1.66 | 0.664 |      |      |       |       |       |       |       |       |       |       |       |       |       |
| **iso-Butanol**           | 1.35 | 1.35 | 1.35 |      | 0.539 |      |      |       |       |       |       |       |       |       |       |       |       |       |
| **iso-Amyl Acetate**      | 0.0767| 0.0767| 0.0762|      | 0.0307| 0.0572| 0.193|       |       |       |       |       |       |       |       |       |       |       |
| **n-Butanol**             | 0.0675| 0.0675|      |      | 0.0227|       |      |       |       |       |       |       |       |       |       |       |       |       |
| **2-Methylbutanol**       | 1.13 | 1.13 | 1.13 | 0.57 | 0.566 | 4.53 | 0.564| 0.0227|       |       |       |       |       |       |       |       |       |       |
| **3-Methylbutanol**       | 1.13 | 1.13 | 0.57 | 1.13 | 1.13 | 0.565 | 4.52 | 0.452 |       |       |       |       |       |       |       |       |       |       |
| **Furfural**              |      |      |      |      |       | 0.104| 0.104| 0.0417|       |       |       |       |       |       |       |       |       |       |

*Mixture Overlap | 19(5) | 20(5) | 21(4) |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| **Glucose**             | 0.455 | 0.455 |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| **Fructose**            | 0.423 | 0.423 |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| **Lactose**             | 0.415 | 0.0415| 0.0094|       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| **Sucrose**             | 0.457 | 0.0457| 0.0094|       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| **Maltose**             | 0.426 | 0.0426| 0.0094|       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |

*Numbers 1-5 given in parenthesis indicate severity of the overlap. 1 - no overlap, 5 - severe overlap.
Table S3. Comparison of the nominal and NMR derived concentrations of whisky congeners in 21 model mixtures

| Compound          | Number of compounds in the mixture | Profiled successfully by $^1$H NMR | No of >10% deviations from the nominal value | Average relative difference from the nominal concentration$^b$ ± stdev (%) |
|-------------------|-----------------------------------|------------------------------------|---------------------------------------------|--------------------------------------------------------------------------|
| Gallic acid       | 5                                 | 5                                  | 0                                           | 4.5 ± 3.6                                                                |
| Vanillin          | 1                                 | 1                                  | 0                                           | 5.1 ± 0.0                                                                |
| Vanillic acid     | 1                                 | 1                                  | 0                                           | 6.3 ± 0.0                                                                |
| Syringaldehyde    | 6                                 | 6                                  | 0                                           | 4.6 ± 4.2                                                                |
| Syringic acid     | 6                                 | 6                                  | 0                                           | 5.5 ± 3.7                                                                |
| Scopoletin        | 1                                 | 1                                  | 0                                           | 2.7 ± 0.0                                                                |
| HMF               | 5                                 | 5                                  | 0                                           | 3.4 ± 3.5                                                                |
| Ethyl acetate     | 5                                 | 5                                  | 0                                           | 4.9 ± 2.9                                                                |
| Methanol          | 2                                 | 2                                  | 0                                           | 10.2 ± 0.5                                                               |
| n-Propanol        | 5                                 | 5                                  | 0                                           | 5.2 ± 2.9                                                                |
| iso-Butanol       | 4                                 | 4                                  | 0                                           | 2.2 ± 2.2                                                                |
| iso-Amyl acetate  | 6                                 | 6                                  | 4                                           | 23.5 ± 19.8                                                              |
| n-Butanol         | 5                                 | 5                                  | 2                                           | 16.2 ± 9.5                                                               |
| 2-Methylbutanol   | 7                                 | 7                                  | 0                                           | 4.5 ± 2.8                                                                |
| 3-Methylbutanol   | 8                                 | 8                                  | 0                                           | 5.7 ± 3.6                                                                |
| Furfural          | 4                                 | 4                                  | 0                                           | 3.7 ± 2.9                                                                |
| Glucose           | 2                                 | 2                                  | 0                                           | 10.6 ± 0.2                                                               |
| Fructose          | 2                                 | 2                                  | 0                                           | 1.5 ± 1.2                                                                |
| Lactose           | 3                                 | 3                                  | 0                                           | 5.7 ± 1.4                                                                |
| Sucrose           | 3                                 | 3                                  | 0                                           | 7.9 ± 1.9                                                                |
| Maltose           | 3                                 | 3                                  | 0                                           | 6.2 ± 0.2                                                                |

$^a$Average difference from nominal concentration expressed in % deviations include results that deviated >10% for the nominal concentration.

$^b$Average % Diff = $\frac{1}{n} \left( \sum_{i=1}^{n} \left( \frac{NMR_i - Nominal_i}{Nominal_i} \times 100 - 100 \right) \right) \pm \sigma_{%Diff}$


Table S4. Handle peaks for individual compounds.

| Compound               | $^1$H$/\text{ppm}$ | Hydrogen type | Multiplicity |
|-----------------------|---------------------|---------------|--------------|
| Gallic Acid           | 7.10                | CH            | singlet      |
| Vanillin              | 7.50                | CH            | doublet      |
| Vanillic Acid         | 6.93                | CH            | doublet      |
| Syringaldehyde        | 7.30                | CH            | singlet      |
| Syringic Acid         | 7.32                | CH            | singlet      |
| Scopoletin            | 6.33                | CH            | doublet      |
| Hydroxymethylfurfural | 7.54                | CH            | doublet      |
| Ethyl Acetate         | 4.13                | CH$_2$        | quartet      |
| Methanol              | 3.35                | CH$_3$        | singlet      |
| n-Propanol            | 1.54                | CH$_2$        | sextet       |
| iso-Butanol           | 3.35                | CH$_2$        | doublet      |
| iso-Amyl Acetate      | 4.12                | CH$_2$        | triplet      |
| n-Butanol             | 1.52                | CH$_2$        | pentet       |
| 2-Methylbutanol       | 3.36                | CH$_2$        | higher order multiplet |
| 3-Methylbutanol       | 1.66                | CH            | septet       |
| Furfural              | 7.93                | CH            | doublet of triplets |
| Glucose               | 5.19                | CH            | doublet      |
| Fructose              | 4.08                | CH$_3$        | overlapping multiplets |
| Lactose               | 4.42                | CH            | doublet      |
| Sucrose               | 5.39                | CH            | doublet      |
| Maltose               | 5.32                | CH            | triplet      |
Figure S2. Profiling of the three regions of $^1$H NMR spectra of Scotch Whisky. Red box – higher alcohols, green box – carbohydrates, blue box – aromatics.