# Production process defects of Mixi beverage detected by neutral desorption-extractive electrospray ionization mass spectrometry

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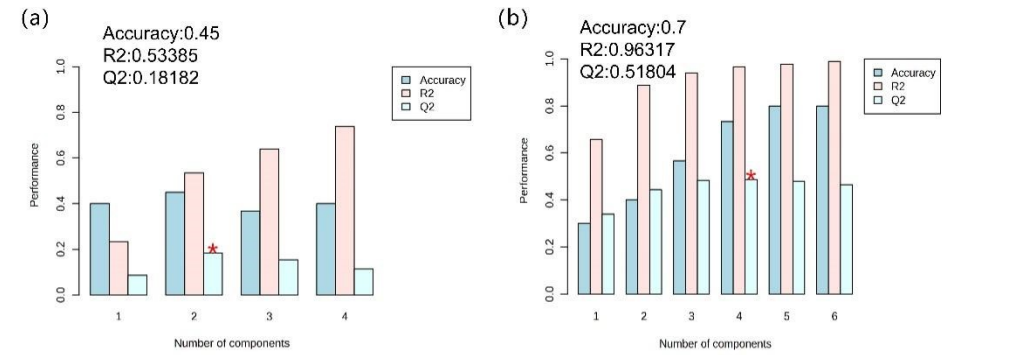
# List of Supplementary Materials


**Fig. S1** Mixi beverage process flow chart.




| Measure | 1 comps | 2 comps | 3 comps | 4 comps |
|---|---|---|---|---|
| Accuracy | 0.4 | 0.45 | 0.38333 | 0.38333 |
| R2 | 0.23244 | 0.53385 | 0.63705 | 0.73222 |
| Q2 | 0.088627 | 0.18182 | 0.14717 | 0.10614 |

| Measure | 1 comps | 2 comps | 3 comps | 4 comps | 5 comps | 6 comps |
|---|---|---|---|---|---|---|
| Accuracy | 0.33333 | 0.46667 | 0.63333 | 0.7 | 0.83333 | 0.83333 |
| R2 | 0.53158 | 0.85056 | 0.94806 | 0.96317 | 0.97386 | 0.98538 |
| Q2 | 0.28848 | 0.44903 | 0.50404 | 0.51804 | 0.50433 | 0.49639 |

**Fig. S2** Cross Validation score of PLS-DA Model for Mixi beverage. (a) Cross Validation score of PLS-DA Model for normal Mixi beverage in different batches; (b) Cross Validation score of PLS-DA Model for Mixi beverages treated under different (Treatment condition: normal; heating at 50 ℃ for 1 h; heating at 50 ℃ for 6 h; heating at 100 ℃ for 1 h; heating at 100 ℃ for 6 h; triple dilution).

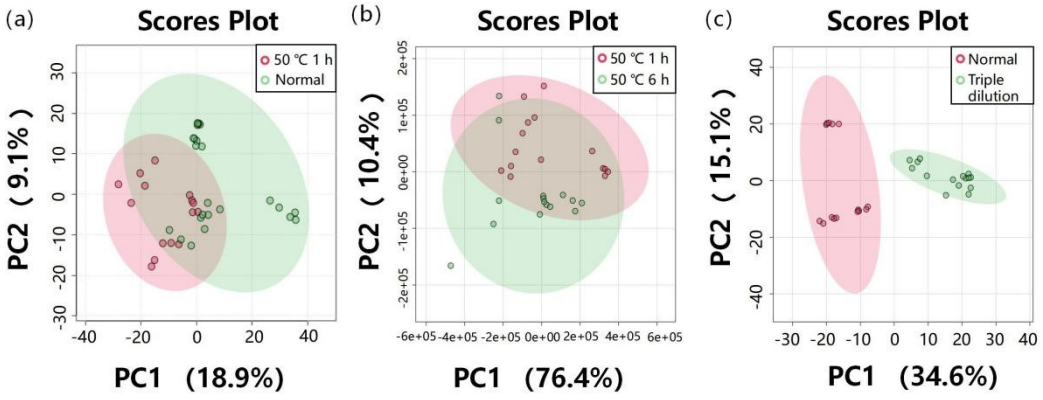



**Fig. S3** Principal component analysis of ND-EESI-MS data from MiXi beverage. (a) Heating at 50 ℃ for 1 h and normal; (b) Heating at 50 ℃ for 1 h and heating at 50 ℃ for 6 h; (c) Triple dilution and normal.

.

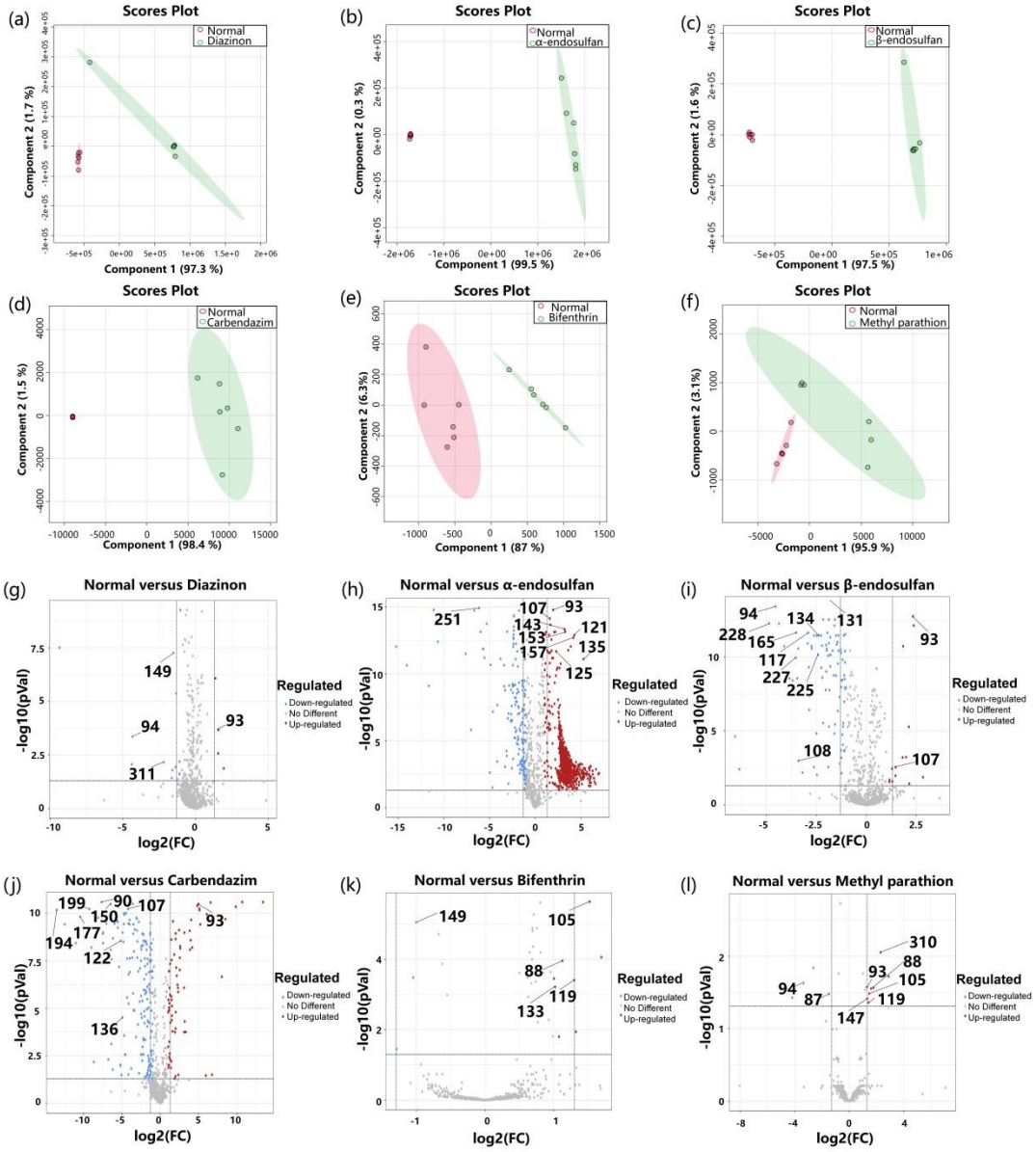



**Fig. S4** Partial least squares discrimination analysis and Volcano plot of ND-EESI-MS data from MiXi beverage before and after adding pesticide residues. (a) PLS-DA score plot of normal group and diazinon group; (b) PLS-DA score plot of normal group and α-endosulfan group; (c) PLS-DA score plot of normal group and β-endosulfan group; (d) PLS-DA score plot of normal group and carbendazim group; (e) PLS-DA score plot of normal group and bifenthrin group; (f) PLS-DA score plot of normal group and methyl parathion group; (g) Volcano plot of normal group and diazinon group; (h) Volcano plot of normal group and α-endosulfan group; (i) Volcano plot of normal group and β-endosulfan group; (j) Volcano plot of normal group and carbendazim group; (k) Volcano plot of normal group and bifenthrin group; (l) Volcano plot of normal group and methyl parathion group.

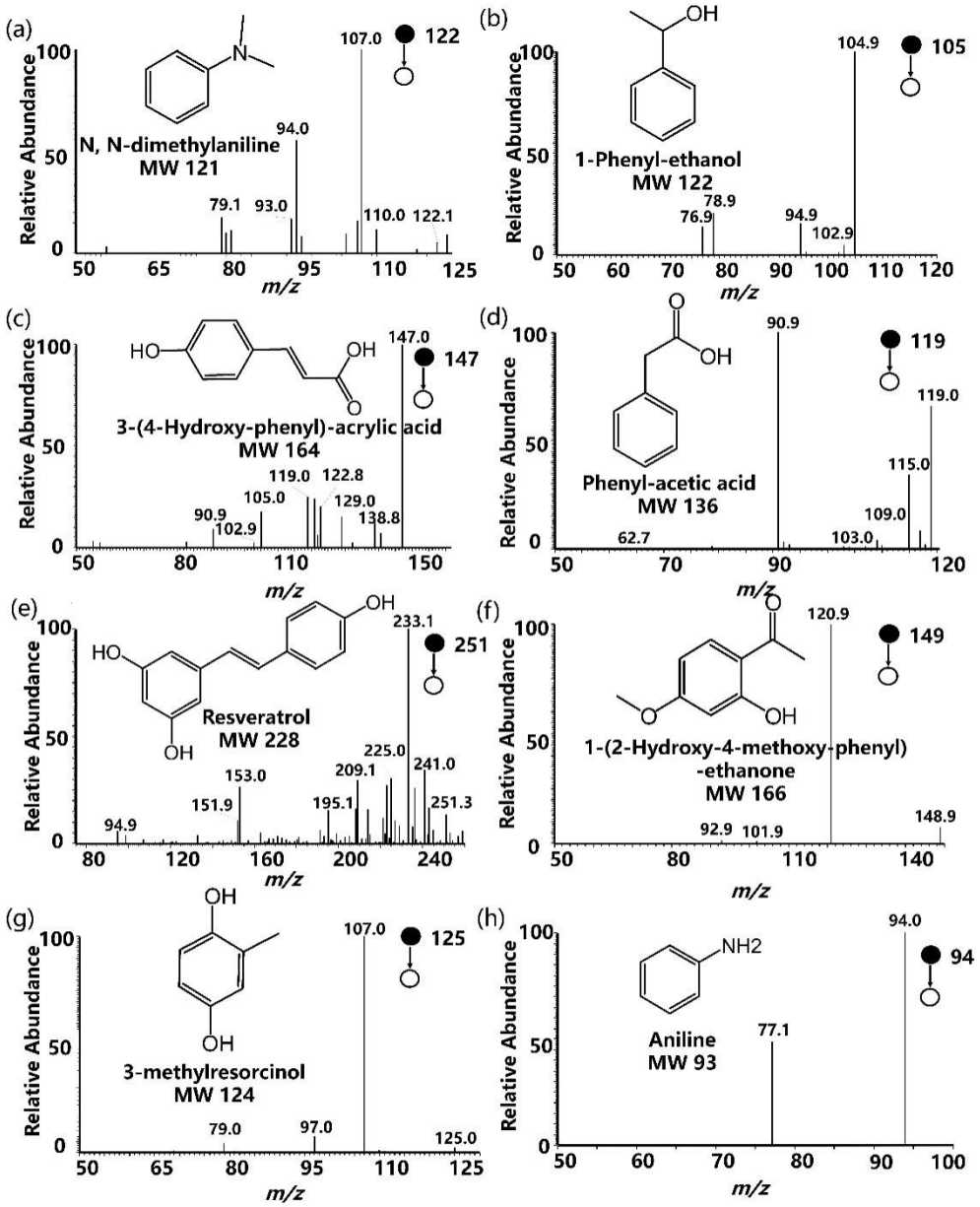



**Fig. S5** Differential ion ND-EESI-MS spectra of MiXi beverage before and after adding pesticide residues. (a) N, N-dimethylaniline; (b) 1-Phenyl-ethanol; (c) 3-(4-Hydroxy-phenyl)-acrylic acid; (d) Phenyl-acetic acid; (e) Resveratrol; (f) 1-(2-Hydroxy-4-methoxy-phenyl)-ethenone; (g) 3-methylresorcinol; (h) Aniline.

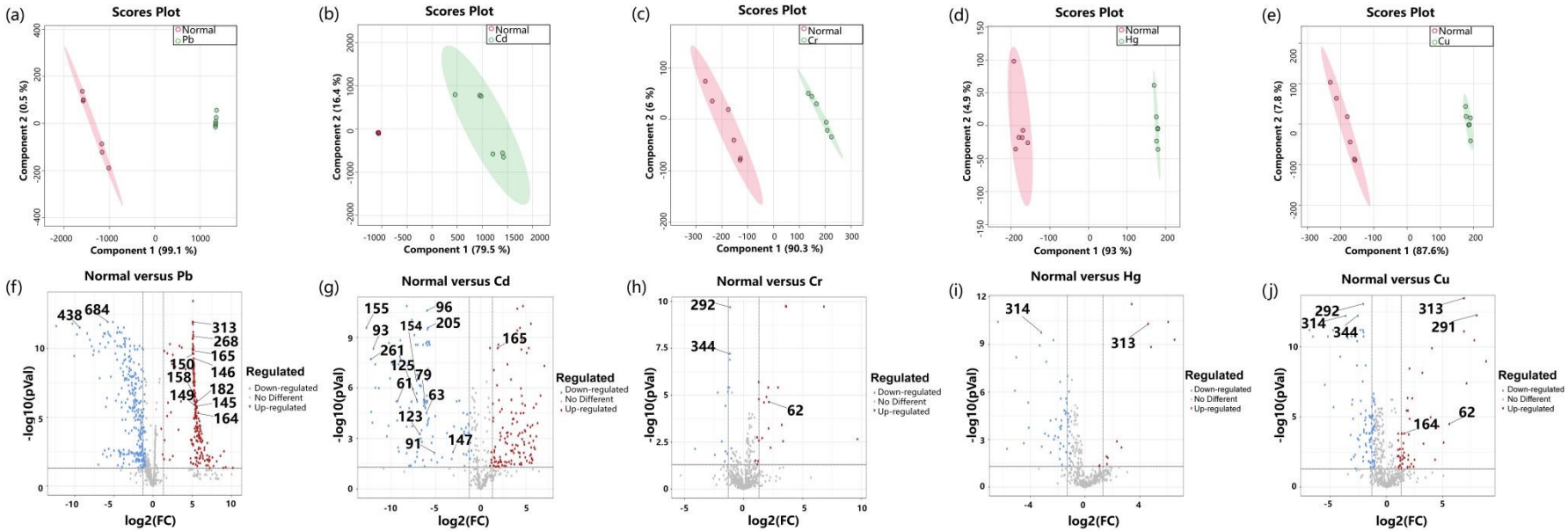



**Fig. S6** Partial least squares discrimination analysis and Volcano plot of ND-EESI-MS data from MiXi beverage before and after adding heavy metals. (a) PLS-DA score plot of normal group and $Pb^{2+}$ group; (b) PLS-DA score plot of normal group and $Cd^{2+}$ group; (c) PLS-DA score plot of normal group and $Cr^{3+}$ group; (d) PLS-DA score plot of normal group and $Hg^{2+}$ group; (e) PLS-DA score plot of normal group and $Cu^{2+}$ group; (f) Volcano plot of normal group and $Pb^{2+}$ group; (g) Volcano plot of normal group and $Cd^{2+}$ group; (h) Volcano plot of normal group and $Cr^{3+}$ group; (i) Volcano plot of normal group and $Hg^{2+}$ group; (j) Volcano plot of normal group and $Cu^{2+}$ group.

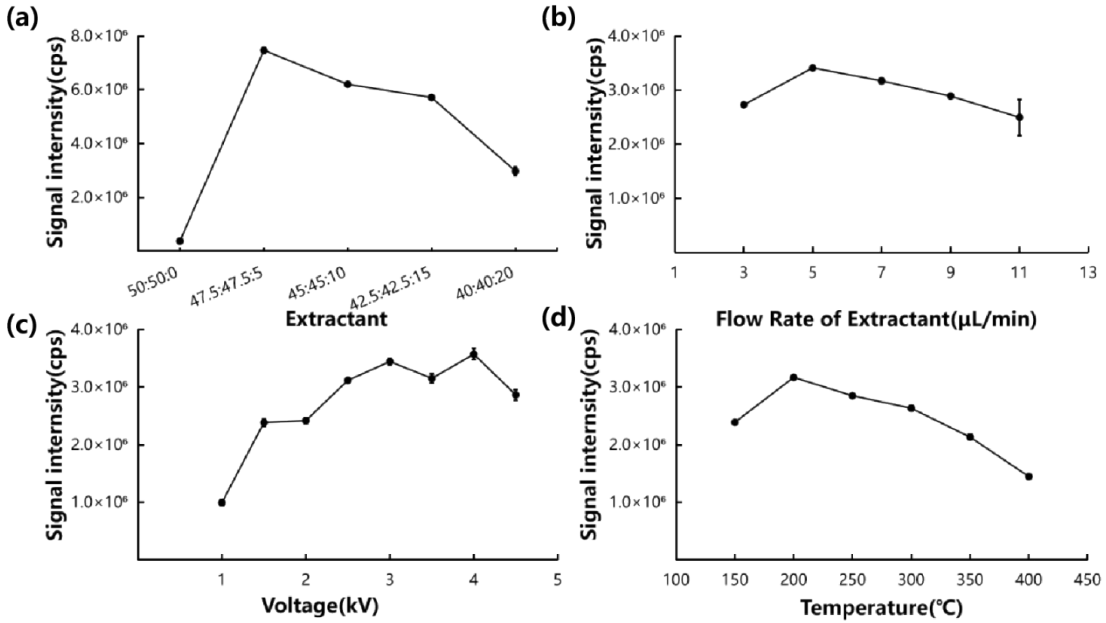



**Fig. S7** The parameters that affect detection of Mixi beverage. The extractant (a), the flow rate of extractant (b), the voltage (c), the temperature (d).

**Table S1** Compounds identified in MiXi beverage

| No. | Compound | Formular | Molecular mass | Charge form | *m/z* | Major MS/MS fragments |
|---|---|---|---|---|---|---|
| 1 | Adenine | $C_5H_5N_5$ | 135.1 | $[M+H]^+$ | 136.1 | 119.1, 94.2, 92.5 |
| 2 | Oleic acid | $C_{18}H_{34}O_2$ | 282.5 | $[M+H]^+$ | 283.3 | 265.4, 253.1, 223.4 |

| | | | | | | |
|---|---|---|---|---|---|---|
| 3 | Nuciferine | $C_{19}H_{21}NO_2$ | 295.4 | $[M+H]^+$ | 296.4 | 104.1, 164.4, 208.1, 237.2, 265.1, 278.4, 287.0 |
| 4 | Acetic acid | $C_2H_4O_2$ | 60.1 | $[M+K]^+$ | 99.0 | 81.1, 71.2, 57.4 |
| 5 | Tridecanoic acid | $C_{13}H_{26}O_2$ | 214.3 | $[M+Na]^+$ | 235.2 | 180.5, 176.1, 93.2 |
| 6 | Polyporenic acid C | $C_{31}H_{46}O_4$ | 482.0 | $[M+Na]^+$ | 505.0 | 465.3, 446.9, 309.0 |
| 7 | Arginine | $C_6H_{14}N_4O_2$ | 174.2 | $[M+H]^+$ | 175.1 | 158.1, 130.1, 70.1, 60.0 |
| 8 | Asparagic acid | $C_4H_7NO_4$ | 133.1 | $[M+H]^+$ | 134.1 | 88.1, 74.0 |
| 9 | Glutamic acid | $C_5H_9NO_4$ | 147.1 | $[M+H]^+$ | 148.1 | 130.0, 84.0, 56.0 |
| 10 | Valine | $C_5H_{11}NO_2$ | 117.2 | $[M+H]^+$ | 118.1 | 58.1, 56.1 |
| 11 | Gynesine | $C_7H_7NO_2$ | 136.1 | $[M+H]^+$ | 138.1 | 120.2, 92.1, 78.0 |
| 12 | Proline | $C_5H_9NO_2$ | 115.1 | $[M+H]^+$ | 116.1 | 70.1 |
| 13 | Chlorogenic acid | $C_{16}H_{18}O_9$ | 354.3 | $[M+H]^+$ | 355.1 | 337.1, 181.1, 163.4, 145.0 |
| 14 | Riboflavin | $C_{17}H_{20}N_4O_6$ | 376.4 | $[M+H]^+$ | 377.2 | 243.0, 200.4, 172.1 |
| 15 | (-)-Epicatechin gallate | $C_{22}H_{18}O_{10}$ | 442.4 | $[M+H]^+$ | 443.1 | 291.1, 273.2, 139.1, 123.2 |
| 16 | Nonanoic acid | $C_9H_{18}O_2$ | 158.2 | $[M+H]^+$ | 159.1 | 117.1, 141.4, 135.1 |
| 17 | Palmitoleic acid | $C_{16}H_{30}O_2$ | 254.4 | $[M+H]^+$ | 255.2 | 213.4, 195.1, 237.3, 231.2, 227.2 |

| | | | | | | |
|---|---|---|---|---|---|---|
| 18 | Linolenic acid | $C_{18}H_{30}O_2$ | 254.4 | $[M+Na]^+$ | 277.4 | 273.1, 265.2, 255.1, 245.1 |
| 19 | Hexanoic acid | $C_6H_{12}O_2$ | 116.2 | $[M+H]^+$ | 117.1 | 99.2, 71.3, 57.2 |
| 20 | Heptanoic acid | $C_7H_{14}O_2$ | 130.2 | $[M+H]^+$ | 131.1 | 113.1, 101.2, 85.2, 71.4 |
| 21 | Lauric acid | $C_{12}H_{24}O_2$ | 200.3 | $[M+H]^+$ | 201.2 | 183.0. 171.1, 85.0 |
| 22 | Palmitic acid | $C_{16}H_{32}O_2$ | 256.4 | $[M+H]^+$ | 257.3 | 239.4, 215.1, 197.2 |
| 23 | Pentadecenoic acid | $C_{15}H_{21}O_2$ | 233.3 | $[M+Na]^+$ | 263.2 | 257.0, 221.1, 203.2 |
| 24 | Linoleic acid | $C_{18}H_{32}O_2$ | 280.5 | $[M+H]^+$ | 281.3 | 263.2, 239.4, 221.3 |
| 25 | Stearic acid | $C_{18}H_{36}O_2$ | 284.5 | $[M+H]^+$ | 285.3 | 243.2, 241.4, 225.1, 213.2 |
| 26 | Behenic acid | $C_{22}H_{44}O_2$ | 340.6 | $[M+H]^+$ | 341.3 | 323.2, 305.4, 281.2 |
| 27 | Liensinine | $C_{37}H_{42}N_2O_6$ | 610.7 | $[M+H]^+$ | 611.0 | 192.4, 205.7, 475.0, 489.2, 503.4, 565.9, 579.1, 593.0 |
| 28 | Neferine | $C_{38}H_{44}N_2O_6$ | 624.8 | $[M+H]^+$ | 625.0 | 205.5, 297.1, 403.2, 463.1, 489.4, 579.8, 593.4, 607.2 |
| 29 | Lotusine | $C_{19}H_{24}NO_3$ | 363.3 | $[M+H]^+$ | 314.0 | 107.1, 174.7, 236.8, 251.2, 269.0, 271.0, 283.4, 298.2 |
| 30 | Tuduranine | $C_{18}H_{19}NO_3$ | 297.1 | $[M+H]^+$ | 298.1 | 283.1, 268.1, 239.1, 206.1 |
| 31 | Adenosine | $C_{10}H_{13}N_5O_4$ | 267.1 | $[M+H]^+$ | 268.1 | 236.1, 220.1, 192.1, 176.2 |

| | | | | | | |
|---|---|---|---|---|---|---|
| 32 | Higenamine | $C_{16}H_{17}NO_3$ | 271.1 | $[M+H]^+$ | 272.1 | 240.1, 178.1, 149.1, 119.0 |
| 33 | Coclaurine | $C_{17}H_{19}NO_3$ | 285.1 | $[M+H]^+$ | 286.1 | 272.1, 255.1, 191.2, 161.0 |
| 34 | N-Methylcoclaurine | $C_{18}H_{21}NO_3$ | 299.2 | $[M+H]^+$ | 300.2 | 271.1, 269.1, 251.1, 225.1 |
| 35 | Agnuside | $C_{22}H_{26}O_{11}$ | 466.2 | $[M+H]^+$ | 467.2 | 427.1, 271.0, 247.0, 220.0 |
| 36 | Pronuciferine | $C_{19}H_{21}NO_3$ | 311.2 | $[M+H]^+$ | 312.2 | 283.1, 269.1, 241.1, 174.1 |
| 37 | 2,4,7-Trimethoxyphenanthrene | $C_{17}H_{16}O_3$ | 268.1 | $[M+H]^+$ | 269.1 | 254.1, 241.1, 237.2, 222.4 |
| 38 | Dauriciline | $C_{36}H_{40}N_2O_6$ | 596.3 | $[M+H]^+$ | 597.3 | 566.2, 554.5, 416.2, 298.1 |
| 39 | Sinomenine | $C_{19}H_{23}NO_4$ | 329.2 | $[M+H]^+$ | 330.2 | 272.1, 267.1, 163.1, 123.0 |
| 40 | Leonticine | $C_{20}H_{25}NO_3$ | 327.2 | $[M+H]^+$ | 328.2 | 300.1, 283.1, 252.1, 174.4 |
| 41 | Isovitexin | $C_{21}H_{20}O_{10}$ | 432.1 | $[M+H]^+$ | 433.1 | 399.1, 355.1, 295.2, 271.0 |
| 42 | Berbamine | $C_{37}H_{40}N_2O_6$ | 608.9 | $[M+H]^+$ | 609.3 | 566.2, 473.2, 404.1, 312.1 |
| 43 | Goshuyuamide-I | $C_{19}H_{19}N_3O$ | 305.2 | $[M+H]^+$ | 306.2 | 291.1, 275.1, 164.1 |
| 44 | Benzopyran derivative III | $C_{32}H_{28}O_{10}$ | 572.2 | $[M+Na]^+$ | 595.2 | 530.2, 465.1, 365.1, 287.0 |
| 45 | Benzopyran derivative I | $C_{32}H_{28}O_9$ | 556.2 | $[M+Na]^+$ | 579.2 | 447.1, 405.0, 393.1, 257.4 |
| 46 | Tetrandrine | $C_{38}H_{42}N_2O_6$ | 622.3 | $[M+H]^+$ | 623.3 | 580.3, 548.2, 487.2, 472.2 |

| | | | | | | |
|---|---|---|---|---|---|---|
| 47 | Quercetin-3-me thylether | $C_{16}H_{12}O_7$ | 316.1 | $[M+H]^+$ | 317.1 | 302.0, 285.0, 127.1 |
| 48 | Erigosler A | $C_{27}H_{26}O_{13}$ | 558.1 | $[M+H]^+$ | 559.1 | 541.13, 439.09, 317.06, 127.04 |
| 49 | Dehydrocorydaline | $C_{22}H_{23}NO_4$ | 365.2 | $[M+H]^+$ | 366.2 | 228.1, 151.1, 162.0, 137.0 |
| 50 | Glycerol monopalmitale | $C_{19}H_{38}O_4$ | 330.3 | $[M+Na]^+$ | 353.3 | 313.2, 257.2, 239.2 |
| 51 | Glyceryl monostearate | $C_{21}H_{42}O_4$ | 358.3 | $[M+H]^+$ | 359.3 | 341.3, 267.2, 71.0, 57.0 |
| 52 | 5α,8α-Peroxydehydrotumulosic acid | $C_{31}H_{46}O_6$ | 514.7 | $[M+H]^+$ | 515.3 | 497.3, 433.3, 425.3, 415.3, 385.2, 377.2, 335.2, 247.2 |
| 53 | Tumulosic acid | $C_{31}H_{50}O_4$ | 486.7 | $[M+H]^+$ | 487.4 | 469.4, 451.4, 343.3, 313.2, 295.2 |
| 54 | 29-Hydroxypolyporenic acid C | $C_{31}H_{46}O_5$ | 498.7 | $[M+H]^+$ | 499.3 | 481.3, 463.3, 421.3, 325.2, 307.2 |
| 55 | 25-Hydroxypachimic acid | $C_{33}H_{52}O_6$ | 544.8 | $[M+H]^+$ | 545.4 | 527.4, 451.3, 433.1, 295.1 |
| 56 | Dehydrotumulosic acid | $C_{31}H_{48}O_4$ | 484.7 | $[M+H]^+$ | 485.4 | 467.3, 449.3, 311.2, 293.2 |
| 57 | Dehydropachymic acid | $C_{33}H_{50}O_5$ | 526.8 | $[M+H]^+$ | 527.4 | 509.4, 449.3, 353.2 |
| 58 | Pachymic acid | $C_{33}H_{52}O_5$ | 528.8 | $[M+H]^+$ | 529.4 | 511.4, 451.4, 295.2 |
| 59 | Dehydrotrametenolic acid | $C_{30}H_{46}O_3$ | 454.7 | $[M+H]^+$ | 455.4 | 437.3, 311.2 |
| 60 | Trametenolic acid | $C_{30}H_{48}O_3$ | 456.7 | $[M+H]^+$ | 457.4 | 439.4, 313.2 |
| 61 | D-Glucose | $C_6H_{12}O_6$ | 180.2 | $[M+H]^+$ | 180.9 | 138.9, 98.9 |

| | | | | | | |
|---|---|---|---|---|---|---|
| 62 | Methyl 2-undecynoate | $C_{12}H_{20}O_2$ | 196.3 | $[M+H]^+$ | 197.0 | 178.9, 166.9, 164.9,147.0 |
| 63 | Epicatechin gallate | $C_{22}H_{18}O_{10}$ | 442.4 | $[M-H]^-$ | 441.1 | 289.1, 169.0, 125.0 |
| 64 | Histidine | $C_6H_9N_3O_2$ | 155.2 | $[M-H]^-$ | 154.1 | 137.0, 136.1, 93.1, 65.0 |
| 65 | Malic acid | $C_4H_6O_5$ | 134.1 | $[M-H]^-$ | 133.0 | 115.0, 87.0, 71.0 |
| 66 | Citric acid | $C_6H_8O_7$ | 192.1 | $[M-H]^-$ | 191.0 | 129.1, 111.0, 83.0 |
| 67 | Uridine | $C_9H_{12}N_2O_6$ | 244.2 | $[M-H]^-$ | 243.1 | 200.1, 140.0, 122. 0 |
| 68 | Gallic acid | $C_7H_6O_5$ | 170.1 | $[M-H]^-$ | 169.0 | 125.0, 107.0, 79.0 |
| 69 | Tryptophan | $C_{11}H_{12}N_2O_2$ | 204.2 | $[M-H]^-$ | 203.1 | 185.0, 159.1, 142.1, 116.1 |
| 70 | p-Hydroxybenzoic acid | $C_7H_6O_3$ | 138.1 | $[M-H]^-$ | 137.0 | 93.0, 75.0, 65.0 |
| 71 | 4-Hydroxyphenylacetic acid | $C_8H_8O_3$ | 152.2 | $[M-H]^-$ | 151.0 | 107.1, 77.0 |
| 72 | Caffeic acid | $C_9H_8O_4$ | 180.2 | $[M-H]^-$ | 179.0 | 134.0, 117.0, 89.0 |
| 73 | Syringaresinol | $C_{22}H_{26}O_8$ | 418.4 | $[M-H]^-$ | 417.2 | 402.1, 181.0, 166.0, 151.0 |

| | | | | | | |
|---|---|---|---|---|---|---|
| 74 | Euryalin B | $C_{30}H_{36}O_9$ | 540.6 | $[M-H]^-$ | 539.2 | 341.1, 319.1, 326.1 |
| 75 | Buddlenol E | $C_{31}H_{36}O_{11}$ | 584.6 | $[M-H]^-$ | 583.2 | 387.1, 195.0, 165.0 |
| 76 | Orientin | $C_{21}H_{20}O_{11}$ | 448.4 | $[M-H]^-$ | 447.0 | 357.2, 327.1, 297.2 |
| 77 | Isovitexin | $C_{21}H_{20}O_{10}$ | 432.4 | $[M-H]^-$ | 431.0 | 340.7, 311.2, 281.1 |
| 78 | Hyperoside | $C_{21}H_{20}O_{12}$ | 464.4 | $[M-H]^-$ | 463.0 | 301.4, 300.1, 271.3 |
| 79 | Melim | $C_{27}H_{30}O_{16}$ | 610.5 | $[M-H]^-$ | 609.0 | 301.2, 300.4, 271.2 |

**Table S2** Regression equations, LODs and LOQs of four pesticide analytes

| No. | Analyte | Linear range (μg $L^{-1}$) | Regression equation y =a*x* + b | $R^2$ | LOD (μg $L^{-1}$) | LOQ (μg $L^{-1}$) | ME |
|---|---|---|---|---|---|---|---|
| 1 | Diazinon | 5.00-200.00 | $y = 19.826x + 290.56$ | 0.9982 | 0.05 | 0.15 | 0.88 |
| 2 | β-Endosulfan | 5.00-200.00 | $y = 60.577x + 11.591$ | 0.9940 | 0.04 | 0.12 | 0.95 |
| 3 | Carbendazim | 5.00-200.00 | $y = 4.1758x + 21.816$ | 0.9979 | 0.43 | 1.30 | 0.94 |
| 4 | Methyl parathion | 5.00-200.00 | $y = 20.049x - 18.186$ | 0.9933 | 0.06 | 0.18 | 0.91 |

[a] *x* represents the concentration of the solution containing analyte and *y* denotes the signal intensity of quantitative ion.

**Table S3** Analysis results of pesticide analytes in Mixi beverage by ND-EESI-MS and LC-MS

| **Method** | **ND-EESI-MS** | | | **LC-MS** | | |
|---|---|---|---|---|---|---|
| Pesticide | Accuracy (%) | Repeatability (%) | Analysis time of a single sample | Accuracy (%) | Repeatability (%) | Analysis time of a single sample |
| Diazinon | 92.3<br>93.5 | 2.70<br>3.45 | 1 min | 94.7<br>99.7 | 4.09<br>1.64 | 10h |

| | | | | | |
|---|---|---|---|---|---|
| | 91.8 | 2.78 | 99.6 | 2.74 | |
| | 96.9 | 0.67 | 94.9 | 2.09 | |
| β-Endosulfan | 98.6 | 1.96 | 99.4 | 4.84 | |
| | 95.1 | 0.89 | 96.0 | 6.43 | |
| | 91.4 | 1.51 | 97.1 | 1.90 | |
| Carbendazim | 102.6 | 2.67 | 96.6 | 4.56 | |
| | 96.7 | 1.34 | 94.4 | 4.01 | |
| | 93.8 | 0.55 | 94.7 | 2.32 | |
| Methyl parathion | 107.8 | 1.88 | 97.9 | 3.01 | |
| | 99.7 | 2.41 | 97.8 | 1.84 | |

**Table S4** Regression equations, LODs and LOQs of five heavy metals

| No. | Analyte | Linear range (μg $L^{-1}$) | Regression equation $y = ax + b$ | $R^2$ | LOD (μg $L^{-1}$) | LOQ (μg $L^{-1}$) | ME | GB 5749-2022 (ng/L) |
|---|---|---|---|---|---|---|---|---|
| 1 | $(CH_3COO)_2Pb·3H_2O$ | 0.50-20.00 | $y = 0.4237x + 3.8629$ | 0.9942 | 1.32 | 4.01 | 0.93 | $1\times10^4$ |
| 2 | $CdCl_2$ | 0.50-20.00 | $y = 14.362x + 37.648$ | 0.9914 | 0.06 | 0.19 | 0.94 | $5\times10^3$ |
| 3 | $Cr(NO_3)_3$ | 0.50-20.00 | $y = 0.9221x + 22.389$ | 0.9963 | 0.61 | 1.84 | 0.92 | $4\times10^3$ |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 4 | $Hg(NO_3)_2$ | 0.50-20.00 | $y$ =1.3182$x$ + 0.914 | 0.9558 | 0.92 | 2.79 | 0.80 | $1\times10^3$ |
| 5 | $Cu(NO_3)_2$ | 0.50-200.00 | $y$ = 0.6876$x$ + 9.915 | 0.9982 | 1.44 | 4.36 | 0.99 | $1\times10^6$ |

[a] $x$ represents the concentration of the solution containing analyte and $y$ denotes the signal intensity of quantitative ion.

**Table S5** Analysis results of heavy metals in Mixi beverage by ND-EESI-MS and ICP-MS

| **Method** | **ND-EESI-MS** | | | **ICP-MS** | | |
|---|---|---|---|---|---|---|
| Heavy metals | Accuracy (%) | Repeatability (%) | Analysis time of a single sample | Accuracy (%) | Repeatability (%) | Analysis time of a single sample |
| Pb | 104.0 | 1.23 | 1 min | 106.8 | 5.59 | 13h |
| | 95.6 | 2.57 | | 101.9 | 2.98 | |
| | 96.2 | 0.89 | | 104.0 | 0.85 | |
| Cd | 98.0 | 2.12 | | 105.9 | 2.78 | |
| | 100.8 | 1.45 | | 99.2 | 2.46 | |
| | 101.7 | 2.03 | | 99.9 | 1.72 | |
| Cr | 92.0 | 3.66 | | 123.1 | 22.58 | |
| | 92.8 | 1.98 | | 100.2 | 0.99 | |
| | 91.4 | 0.55 | | 99.1 | 1.62 | |
| Hg | 91.0 | 2.71 | | 68.0 | 38.49 | |
| | 98.4 | 3.34 | | 84.8 | 17.47 | |
| | 97.8 | 2.09 | | 103.3 | 12.98 | |
| Cu | 107.1 | 2.82 | | 98.4 | 17.55 | |
| | 95.9 | 1.17 | | 103.1 | 6.68 | |

| | | | | | | |
|---|---|---|---|---|---|---|
| | | 101.8 | 1.30 | | 99.7 | 4.20 |

**Table S6** Mixi beverage sample information

| No. | Product name | Specification/mL | Batch | Color | Preparation method |
|---|---|---|---|---|---|
| 1 | Miyoumimi botanical beverage | 400 | 20220507 | Ivory-white | 50 ℃ heated 1 h |
| 2 | Miyoumimi botanical beverage | 400 | 20220507 | Ivory-white | 50 ℃ heated 6 h |
| 3 | Miyoumimi botanical beverage | 400 | 20220507 | Ivory-white | 100 ℃ heated 1 h |
| 4 | Miyoumimi botanical beverage | 400 | 20220507 | Ivory-white | 100 ℃ heated 6 h |
| 5 | Miyoumimi botanical beverage | 400 | 20220507 | Ivory-white | Mercantile samples are diluted three times with ultra-pure water |

**Table S7** Analytical results of pesticide residue spiked samples

| Sample | Sample background value (μg $L^{-1}$) | Added value (μg $L^{-1}$) | Measured value (μg $L^{-1}$) | Recovery rate (%) | RSD (%) |
|---|---|---|---|---|---|
| Diazinon | 12.98 | 10 | 22.21 | 92.3 | 2.70 |
| | | 50 | 59.73 | 93.5 | 3.45 |
| | | 100 | 104.79 | 91.8 | 2.78 |
| β-Endosulfan | 7.34 | 10 | 17.03 | 96.9 | 0.67 |
| | | 50 | 56.64 | 98.6 | 1.96 |
| | | 100 | 102.40 | 95.1 | 0.89 |
| Carbendazim | 10.74 | 10 | 19.88 | 91.4 | 1.51 |
| | | 50 | 62.04 | 102.6 | 2.67 |
| | | 100 | 107.44 | 96.7 | 1.34 |
| Methyl parathion | 5.12 | 10 | 14.50 | 93.8 | 0.55 |
| | | 50 | 59.03 | 107.8 | 1.88 |
| | | 100 | 104.84 | 99.7 | 2.41 |

**Table S8** Analytical results of heavy metal spiked samples

| Sample | Sample background value (μg $L^{-1}$) | Added value (μg $L^{-1}$) | Measured value (μg $L^{-1}$) | Recovery rate (%) | RSD (%) |
|---|---|---|---|---|---|
| $(CH_3COO)_2Pb·3H_2O$ | 4.49 | 1 | 5.53 | 104.0 | 1.23 |
| | | 5 | 9.27 | 95.6 | 2.57 |

| | | | | | |
|---|---|---|---|---|---|
| | | 10 | 14.11 | 96.2 | 0.89 |
| | | 1 | 1.85 | 98.0 | 2.12 |
| $CdCl_2$ | 0.87 | 5 | 5.91 | 100.8 | 1.45 |
| | | 10 | 11.04 | 101.7 | 2.03 |
| | | 1 | 4.88 | 92.0 | 3.66 |
| $Cr(NO_3)_3$ | 3.96 | 5 | 8.60 | 92.8 | 1.98 |
| | | 10 | 13.10 | 91.4 | 0.39 |
| | | 1 | 1.42 | 101.0 | 2.71 |
| $Hg(NO_3)_2$ | 0.51 | 5 | 5.43 | 98.4 | 3.34 |
| | | 10 | 10.29 | 97.8 | 2.09 |
| | | 10 | 70.97 | 107.1 | 2.82 |
| $Cu(NO_3)_2$ | 60.26 | 50 | 108.21 | 95.9 | 1.17 |
| | | 100 | 162.05 | 101.8 | 1.30 |

**Table S9** Mobile phase program for gradient elution

| **T/min** | **Volume fraction (%)** | |
|---|---|---|
| | **Mobile phase A** | **Mobile phase B** |
| 0 | 90 | 10 |
| 1 | 90 | 10 |
| 4 | 40 | 60 |
| 8 | 10 | 90 |
| 9 | 10 | 90 |
| 9.1 | 90 | 10 |

| | | |
|---|---|---|
| 12 | 90 | 10 |

**Table S10** Multiple reaction monitoring parameters for the determination of four pesticide residues

| Analyte | Acquisition mode | Retention time (min) | Declustering voltage (V) | Collision energy (V) | Precursor ion (*m/z*) | Quantitative ion (*m/z*) |
|---|---|---|---|---|---|---|
| Diazinon | $[M+H]^+$ | 3.65 | 85 | 25.8 | 192.1 | 160.1* |
| | | | 95 | 42 | | 132.1 |
| β-Endosulfan | $[M+H]^+$ | 6.22 | 100 | 24 | 264.0 | 232.1* |
| | | | 103 | 28 | | 125.1 |
| Carbendazim | $[M+H]^+$ | 7.28 | 100 | 28 | 305.1 | 169.1* |
| | | | 100 | 28 | | 153.1 |

| | | | | | | |
|---|---|---|---|---|---|---|
| Methyl parathion | $[M+H]^+$ | 8.06 | -74 | -22 | 406.8 | 306.8* |
| | | | -70 | -15 | | 268.7 |

* represents quantitative ions.

**Table S11** Reference conditions for sample digestion system

| Digestion Method | Step | Temperature (℃) | Ramp time (min) | Hold time (min) |
|---|---|---|---|---|
| Microwave digestion | 1 | 120 | 5 | 5 |
| | 2 | 150 | 5 | 10 |
| | 3 | 190 | 5 | 20 |

**Table S12** Concentration of four pesticide residue standard solutions

| No. | Pesticide residue | Concentration of standard curve (μg $L^{-1}$) |
|---|---|---|
| 1 | Diazinon | 5, 10, 20, 50, 100, 200 |
| 2 | β-Endosulfan | 5, 10, 20, 50, 100, 200 |
| 3 | Carbendazim | 5, 10, 20, 50, 100, 200 |
| 4 | Methyl parathion | 5, 10, 20, 50, 100, 200 |

**Table S13** Concentration of five heavy metals standard solutions

| No. | Heavy metal | Concentration of standard curve (μg $L^{-1}$) |
|---|---|---|
| 1 | $(CH_3COO)_2Pb·3H_2O$ | 0.5, 1, 2, 5, 10, 20 |
| 2 | $CdCl_2$ | 0.5, 1, 2, 5, 10, 20 |
| 3 | $Cr(NO_3)_3$ | 0.5, 1, 2, 5, 10, 20 |
| 4 | $Hg(NO_3)_2$ | 0.5, 1, 2, 5, 10, 20 |
| 5 | $Cu(NO_3)_2$ | 5, 10, 20, 50, 100, 200 |

**Table S14** Mixi beverage spiked with concentrations of four pesticide residue solutions

| No. | Pesticide residue | Spiked concentration (μg $L^{-1}$) |
|---|---|---|
| 1 | Diazinon | 10, 50, 100 |
| 2 | β-Endosulfan | 10, 50, 100 |
| 3 | Carbendazim | 10, 50, 100 |
| 4 | Methyl parathion | 10, 50, 100 |

**Table S15** Mixi beverage spiked with concentrations of five heavy metals solutions

| No. | Heavy metal | Spiked concentration (μg $L^{-1}$) |
|---|---|---|
| 1 | $(CH_3COO)_2Pb·3H_2O$ | 1, 5, 10 |

| | | |
|---|---|---|
| 2 | $CdCl_2$ | 1, 5, 10 |
| 3 | $Cr(NO_3)_3$ | 1, 5, 10 |
| 4 | $Hg(NO_3)_2$ | 1, 5, 10 |
| 5 | $Cu(NO_3)_2$ | 10, 50, 100 |