

Table S1. Structural formula of polyphenols during the smoking process of Shanxi aged vinegar.

| Polyphenols | CAS Number | Compound Identification | Structure |
|-------------|------------|--|-----------|
| 1 | 121-33-5 | 4-Hydroxy-3-methoxy-benzaldehyde (Vanillin) | |
| 2 | 121-34-6 | 4-Hydroxy-3-methoxy-benzoic acid (Vanillic acid) | |
| 3 | 537-98-4 | (2E)-3-(4-Hydroxy-3-methoxyphenyl)-2-propenoic acid ((E)-Ferulic acid) | |
| 4 | 501-98-4 | (e)-3-(4-hydroxyphenyl)-2-propenoic acid ((E)-4-Hydroxycinnamic acid) | |
| 5 | 99-96-7 | 4-Hydroxybenzoic acid | |
| 6 | 93376-04-6 | (3R,4R)-Dihydro-3,4-bis[(3-hydroxy-4-methoxyphenyl) methyl]-2(3H)-furanone | |
| 7 | 55-10-7 | 4-Hydroxy-3-methoxymandelic acid | |
| 8 | 40979-91-7 | 1-(3-Hydroxy-4-methoxyphenyl)-1,2-ethanediol | |
| 9 | 99-10-5 | 3,5-Dihydroxybenzoic acid | |
| 10 | 3943-96-2 | (E)-3-(3-hydroxyphenyl) acrylic acid ethyl ester | |
| 11 | 1135-23-5 | 3-(4-Hydroxy-3-methoxyphenyl) propionic acid (Di-hydroferulic acid) | |
| 12 | 102-32-9 | 3,4-Dihydroxybenzenoacetic acid (Homoprotocatechuic acid) | |
| 13 | 154-23-4 | (2R,3S)-2-(3,4-Dihydroxyphenyl)-3,4-dihydro-2H-1-benzopyran-3,5,7-triol (Catechin) | |

Table S2. Variations of types and contents of amino acids and reducing sugars during the smoking process of Shanxi aged vinegar.

| Compounds | Smoking (mg/g Pei) | | | | |
|-----------|--------------------|--------------|--------------|--------------|--------------|
| | 1 day | 2 day | 3 day | 4 day | 5 day |
| Asp | 0.44 ± 0.06 | 0.41 ± 0.01 | 0.42 ± 0.02 | 0.54 ± 0.01 | 0.49 ± 0.02 |
| Thr | 0.39 ± 0.01 | 0.41 ± 0.05 | 0.36 ± 0.03 | 0.13 ± 0.03 | 0.12 ± 0.05 |
| Ser | 0.52 ± 0.01 | 0.32 ± 0.02 | 0.31 ± 0.03 | 0.28 ± 0.04 | 0.18 ± 0.05 |
| Glu | 0.97 ± 0.04 | 0.80 ± 0.03 | 0.58 ± 0.02 | 0 | 0 |
| Gly | 0.37 ± 0.01 | 0.31 ± 0.03 | 0.27 ± 0.02 | 0.36 ± 0.05 | 0.31 ± 0.03 |
| Ala | 1.73 ± 0.03 | 1.49 ± 0.04 | 1.19 ± 0.05 | 1.52 ± 0.02 | 1.42 ± 0.02 |
| Cys | 1.36 ± 0.12 | 0.94 ± 0.01 | 1.20 ± 0.04 | 1.19 ± 0.02 | 1.11 ± 0.02 |
| Val | 0.84 ± 0.01 | 0.68 ± 0.03 | 0.59 ± 0.04 | 0.64 ± 0.02 | 0.63 ± 0.03 |
| Ile | 0.51 ± 0.01 | 0.38 ± 0.03 | 0.35 ± 0.04 | 0.31 ± 0.01 | 0.32 ± 0.04 |
| Leu | 1.00 ± 0.03 | 0.78 ± 0.03 | 0.66 ± 0.05 | 0.46 ± 0.04 | 0.53 ± 0.05 |
| Phe | 0.49 ± 0.02 | 0.38 ± 0.01 | 0.28 ± 0.05 | 0.26 ± 0.03 | 0.26 ± 0.05 |
| His | 0.55 ± 0.04 | 0.56 ± 0.01 | 0.49 ± 0.04 | 0.49 ± 0.05 | 0.55 ± 0.03 |
| Lys | 0.32 ± 0.02 | 0.21 ± 0.05 | 0.19 ± 0.04 | 0.31 ± 0.04 | 0.11 ± 0.01 |
| Xylose | 15.43 ± 0.55 | 14.05 ± 0.46 | 13.01 ± 0.02 | 12.76 ± 0.23 | 12.95 ± 0.24 |
| Fructose | 7.79 ± 0.03 | 7.87 ± 0.02 | 7.68 ± 0.01 | 7.70 ± 0.04 | 7.69 ± 0.01 |
| Mannose | 10.18 ± 0.04 | 11.35 ± 0.42 | 11.77 ± 0.18 | 13.09 ± 0.18 | 11.49 ± 0.55 |
| Glucose | 1.08 ± 0.04 | 1.80 ± 0.02 | 0.70 ± 0.01 | 0.66 ± 0.01 | 0.63 ± 0.01 |
| Maltose | 26.63 ± 0.19 | 30.94 ± 0.20 | 23.50 ± 0.09 | 23.38 ± 0.01 | 23.37 ± 0.01 |