Table S-1 Molecular, retention time, accurate mass, mass errors of fipronil, metabolites and enantiomers

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Compound | Molecularformula | Retention time(min) | Deprotonated ion | Mass error(ppm) |
| Theoretical | Experimental |
| F | C12H4Cl2F6N4OS | 6.08 | 434.9309 | 434.9301 | -1.8 |
| F-des | C12H4Cl2F6N4 | 6.14 | 386.9639 | 386.9630 | -2.3 |
| F-sulfide | C12H4Cl2F6N4S | 6.26 | 418.9359 | 418.9355 | -1.0 |
| F-sulfone | C12H4Cl2F6N4O2S | 6.24 | 450.9258 | 450.9250 | -1.8 |
| (*R*)- F | C12H4Cl2F6N4OS | 14.36 | 434.9309 | 434.9312 | -0.7 |
| (*S*)- F | C12H4Cl2F6N4OS | 15.13 | 434.9309 | 434.9314 | -1.1 |

Table S-2. Linearity, coefficient of determination, recoveries and LOQs of fipronil, metabolites and enantiomers in tea shoots and green tea

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Compound | Linearity range(μg kg-1) | R2 | Spiking levels(μg kg-1) | Recovery, % (RSD, %, n=5) | LOQs(μg kg-1) |
| Tea shoots | Green tea | Tea shoots | Green tea |
| Rac-F | 2-400 | 0.9991 | 0.9981 | 2 | 94(6.7) | 103(6.1) | 2 |
| 10 | 98(3.9) | 96(1.8) |
| 100 | 92(2.1) | 105(2.6) |
| F-des | 2-400 | 0.9982 | 0.9988 | 2 | 95(7.6) | 97(4.9) | 2 |
| 50 | 89(2.0) | 95(1.9) |
| 100 | 103(2.6) | 91(2.8) |
| F-sulfide | 2-400 | 0.9985 | 0.9973 | 2 | 94(8.5) | 96(6.3) | 2 |
| 50 | 105(4.7) | 92(5.0) |
| 100 | 95(3.1) | 107(2.7) |
| F-sulfone | 2-400 | 0.9990 | 0.9987 | 2 | 93(8.2) | 98(6.1) | 2 |
| 50 | 95(4.0) | 98(3.5) |
| 100 | 103(3,7) | 92(4.5) |
| (*R*)- Fipronil | 10-500 | 0.9958 | 0.9965 | 10 | 102(10.6) | 95(8.9) | 10 |
| 50 | 96(5.6) | 91(4.9) |
| 100 | 97(5.5) | 99(6.3) |
| (*S*)- Fipronil | 10-500 | 0.9962 | 0.9980 | 10 | 102(9.7) | 94(9.1) | 10 |
| 50 | 106(5.3) | 93(5.6) |
| 100 | 97(5.2) | 90(6.0) |

Table S-3. Residue levels (μg kg-1) of fipronil (F) and its metabolites in tea shoots and mature leaves (n=3)

|  |  |  |
| --- | --- | --- |
|  | Compound | Collection time (day) |
| 0 | 1 | 3 | 5 | 7 | 10 | 14 | 21 | 28 | 35 |
| Mature leaf | F | 1.22×104±1.39×103 | 1.45×103±111 | 609±81 | 425±41 | 334±41 | 159±17 | 63.4±7.6 | 48.5±5.5 | 10.6±2.5 | 2.5±0.8 |
| F-des | 302±29 | 60.5±7.8 | 77.0±6.8 | 52.9±6.1 | 23.6±2.8 | 22.7±3.0 | 7.7±1.1 | 6.9±0.6 | 7.9±0.7 | <LOD |
| F-sulfide | 149±15 | 19.8±2.4 | 14.1±2.0 | 6.61±1.03 | 3.3±0.7 | 2.6±0.5 | <LOD | <LOD | <LOD | <LOD |
| F-sulfone | 10.6±0.2 | 8.8±0.2 | 19.6±1.8 | 12.5±1.5 | 7.9±0.8 | 4.7±0.8 | 4.3±0.7 | 4.8±0.7 | 4.4±0.5 | <LOD |
| Total | 1.27×104±1.44×103 | 154×103±112 | 720±92 | 497±49 | 369±45 | 189±21 | 75.4±9.4 | 60.2±6.7 | 22.9±3.5 | 2.5±0.8 |
| Tea shoots | F | 7.27×103±883 | 1.67×103±199 | 820±97 | 565±70 | 144±22 | 74.2±9.2 | 12.4±1.5 | 4.2±0.6 | <LOD | <LOD |
| F-des | 102±14 | 51.2±7.0 | 39.4±5.9 | 7.53±1.1 | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD |
| F-sulfide | 98.0±16.4 | 22.7±3.8 | 9.8±1.3 | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD |
| F-sulfone | 7.2±0.6 | 22.3±4.1 | 12.8±1.7 | 2.6±0.4 | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD |
| Total | 7.48×103±891 | 1.76×103±201 | 882±96 | 575±71 | 144±22 | 74.2±9.2 | 12.4±1.5 | 4.2±0.6 | <LOD | <LOD |



B

A

(S)-

(R)-

(S)-

(R)-



Figure S-1. Chromatograms of (*R*)-Fipronil and (*S*)-fipronil obtained from HPLC coupled with an OD-H chiral column (250 mm × 4.6 mm i.d., Daicel Chemical Industries, Japan) (A) and UPLC Q-Exactive Orbitrap MS coupled with an AD-RH chiral column (4.6 mm × 150 mm, particle size 5 μm) (Daicel Chiral Technologies (China) Co., Ltd, Shanghai) (B)