

### Supplementary Information

<b>Table S-1.</b> Mass measurement data of in-source CID spectra obtained at 90 V for kava powder and kavain. The corresponding spectra are shown in Fig. 6a.					
	<b>Formula</b>	<b>Measured</b>	<b>Calculated</b>	<b>Diff.<sup>†</sup></b>	<b>Rel. Int.<sup>‡</sup></b>
<b>Kava Powder</b>	$C_{14}H_{14}O_3 + H^+$	231.0996	231.0994	-0.2	13.1
	$C_{12}H_{11}$	155.0841	155.0861	2.0	15.1
	$C_{12}H_9$	153.0687	153.0704	1.7	13.4
	$C_{10}H_9$	129.0701	129.0704	0.3	9.7
	$C_9H_7$	115.0514	115.0548	3.0	24.7
<b>Kavain</b>	$C_{14}H_{14}O_3 + H^+$	231.1040	231.0994	-1.0	1.9
	$C_{12}H_{11}$	155.0868	155.0861	-0.7	46.1
	$C_{12}H_9$	153.0721	153.0704	-1.7	25.7
	$C_{10}H_9$	129.0701	129.0704	0.3	49.3
	$C_9H_7$	115.0560	115.0548	-1.2	100.0

<sup>†</sup>Differences are reported in millimass units (mmu). Measured masses fell within 5 mmu of the calculated masses.  
<sup>‡</sup>Relative intensities are reported in percent.

**Table S-2.** Mass measurement data of in-source CID spectra obtained at 90 V for kava powder and dihydrokavain. The corresponding spectra are shown in Fig. 6b.

	<b>Formula</b>	<b>Measured</b>	<b>Calculated</b>	<b>Diff. †</b>	<b>Rel. Int. ‡</b>
<b>Kava Powder</b>	C <sub>14</sub> H <sub>16</sub> O <sub>3</sub> + H <sup>+</sup>	233.1176	233.1177	1.0	5.5
	C <sub>13</sub> H <sub>15</sub> O	187.1076	187.1123	4.7	14.6
	C <sub>11</sub> H <sub>9</sub>	155.0841	155.0860	1.9	15.1
	C <sub>9</sub> H <sub>9</sub>	117.0680	117.0704	2.4	32.3
	C <sub>7</sub> H <sub>7</sub>	91.0556	91.0548	-0.8	32.1
<b>Dihydrokavain</b>	C <sub>14</sub> H <sub>16</sub> O <sub>3</sub> + H <sup>+</sup>	233.1187	233.1177	-1.0	9.4
	C <sub>13</sub> H <sub>15</sub> O	187.1092	187.1123	3.1	53.6
	C <sub>11</sub> H <sub>9</sub>	155.0868	155.0860	-0.8	54.4
	C <sub>9</sub> H <sub>9</sub>	117.0703	117.0704	0.1	100.0
	C <sub>7</sub> H <sub>7</sub>	91.0558	91.0548	-1.0	97.6
†Differences are reported in millimass units (mmu). Measured masses fell within 5 mmu of the calculated masses.					
‡Relative intensities are reported in percent.					

**Table S-3.** Mass measurement data of in-source CID spectra obtained at 90 V for kava powder and yangonin. The corresponding spectra are shown in Fig. 6c.

	<b>Formula</b>	<b>Measured</b>	<b>Calculated</b>	<b>Diff. †</b>	<b>Rel. Int. ‡</b>
<b>Kava Powder</b>	C <sub>15</sub> H <sub>14</sub> O <sub>4</sub> + H <sup>+</sup>	259.0942	259.0970	2.8	15.6
	C <sub>14</sub> H <sub>15</sub> O <sub>3</sub>	231.0996	231.1021	2.5	13.1
	C <sub>12</sub> H <sub>11</sub> O	171.0795	171.0809	1.4	6.9
	C <sub>10</sub> H <sub>9</sub> O <sub>2</sub>	161.0575	161.0603	2.8	40.3
<b>Yangonin</b>	C <sub>15</sub> H <sub>14</sub> O <sub>4</sub> + H <sup>+</sup>	259.0981	259.0970	-1.1	47.8
	C <sub>14</sub> H <sub>15</sub> O <sub>3</sub>	231.1009	231.1021	1.2	47.6
	C <sub>12</sub> H <sub>11</sub> O	171.0820	171.0809	-1.1	38.2
	C <sub>10</sub> H <sub>9</sub> O <sub>2</sub>	161.0605	161.0603	-0.2	100.0

†Differences are reported in millimass units (mmu). Measured masses fell within 5 mmu of the calculated masses.  
‡Relative intensities are reported in percent.

**Table S-4.** Mass measurement data of in-source CID spectra obtained at 90 V for kava powder and methysticin. The corresponding spectra are shown in Fig. 6d.

	<b>Formula</b>	<b>Measured</b>	<b>Calculated</b>	<b>Diff.<sup>†</sup></b>	<b>Rel. Int.<sup>‡</sup></b>
<b>Kava Powder</b>	C <sub>15</sub> H <sub>14</sub> O <sub>5</sub> + H <sup>+</sup>	275.0898	275.0919	2.1	0.4
	C <sub>10</sub> H <sub>7</sub> O <sub>2</sub>	159.0464	159.0446	0.2	12.8
	C <sub>11</sub> H <sub>9</sub>	141.0672	141.0704	3.2	8.0
	C <sub>8</sub> H <sub>7</sub>	103.0511	103.0548	3.7	20.8
<b>Methysticin</b>	C <sub>15</sub> H <sub>14</sub> O <sub>5</sub> + H <sup>+</sup>	275.0967	275.0919	-4.8	1.1
	C <sub>10</sub> H <sub>7</sub> O <sub>2</sub>	159.0445	159.0446	0.1	100.0
	C <sub>11</sub> H <sub>9</sub>	141.0691	141.0704	1.3	25.8
	C <sub>8</sub> H <sub>7</sub>	103.0529	103.0548	1.9	69.5

<sup>†</sup>Differences are reported in millimass units (mmu). Measured masses fell within 5 mmu of the calculated masses.  
<sup>‡</sup>Relative intensities are reported in percent.

**Table S-5.** Mass measurement data of in-source CID spectra obtained at 90 V for kava powder and dihydromethysticin. The corresponding spectra are shown in Fig. 6e.

	<b>Formula</b>	<b>Measured</b>	<b>Calculated</b>	<b>Diff.<sup>†</sup></b>	<b>Rel. Int.<sup>‡</sup></b>
<b>Kava Powder</b>	C <sub>15</sub> H <sub>16</sub> O <sub>5</sub> + H <sup>+</sup>	277.1068	277.1076	0.8	0.4
	C <sub>10</sub> H <sub>9</sub> O <sub>2</sub>	161.0575	161.0603	2.8	40.3
	C <sub>8</sub> H <sub>7</sub> O <sub>2</sub>	135.0442	135.0446	0.4	17.2
	C <sub>9</sub> H <sub>7</sub> O	131.0470	131.0497	2.7	31.1
	C <sub>8</sub> H <sub>7</sub>	103.0511	103.0507	-0.4	20.8
<b>Dihydromethysticin</b>	C <sub>15</sub> H <sub>16</sub> O <sub>5</sub> + H <sup>+</sup>	277.1074	277.1076	0.2	2.0
	C <sub>10</sub> H <sub>9</sub> O <sub>2</sub>	161.0575	161.0603	2.8	54.2
	C <sub>8</sub> H <sub>7</sub> O <sub>2</sub>	135.0452	135.0446	-0.6	100.0
	C <sub>9</sub> H <sub>7</sub> O	131.0500	131.0497	-0.3	57.4
	C <sub>8</sub> H <sub>7</sub>	103.0526	103.0507	-1.9	44.2
<sup>†</sup> Differences are reported in millimass units (mmu). Measured masses fell within 5 mmu of the calculated masses. <sup>‡</sup> Relative intensities are reported in percent.					

**Table S-6.** Mass measurement data of in-source CID spectra obtained at 90 V for kava powder and flavokavain B. The corresponding spectra are shown in Fig. 6f.

	<b>Formula</b>	<b>Measured</b>	<b>Calculated</b>	<b>Diff.<sup>†</sup></b>	<b>Rel. Int.<sup>‡</sup></b>
<b>Kava Powder</b>	C <sub>17</sub> H <sub>17</sub> O <sub>4</sub> + H <sup>+</sup>	285.1111	285.1127	1.6	7.3
	C <sub>17</sub> H <sub>15</sub> O <sub>4</sub>	283.0983	283.0970	-1.3	0.7
	C <sub>16</sub> H <sub>12</sub> O <sub>4</sub>	268.0785	268.0736	-4.9	0.4
	C <sub>9</sub> H <sub>9</sub> O <sub>4</sub>	181.0506	181.0500	-0.6	100.0
	C <sub>9</sub> H <sub>7</sub> O	131.0470	131.0498	2.8	31.1
	C <sub>8</sub> H <sub>7</sub>	103.0511	103.0507	-0.4	20.8
<b>Flavokavain B</b>	C <sub>17</sub> H <sub>17</sub> O <sub>4</sub> + H <sup>+</sup>	285.1119	285.1127	0.8	16.0
	C <sub>17</sub> H <sub>15</sub> O <sub>4</sub>	283.0960	283.0970	1.0	35.8
	C <sub>16</sub> H <sub>12</sub> O <sub>4</sub>	268.0747	268.0736	-0.9	20.6
	C <sub>9</sub> H <sub>9</sub> O <sub>4</sub>	181.0484	181.0500	1.6	100.0
	C <sub>9</sub> H <sub>7</sub> O	131.0479	131.0498	0.9	43.2
	C <sub>8</sub> H <sub>7</sub>	103.0535	103.0507	-2.8	24.4
<sup>†</sup> Differences are reported in millimass units (mmu). Measured masses fell within 5 mmu of the calculated masses. <sup>‡</sup> Relative intensities are reported in percent.					

**Table S-7.** Mass measurement data of in-source CID spectra obtained at 90 V for kava powder and flavokavain A. The corresponding spectra are shown in Fig. 6g.

	<b>Formula</b>	<b>Measured</b>	<b>Calculated</b>	<b>Diff.<sup>†</sup></b>	<b>Rel. Int.<sup>‡</sup></b>
<b>Kava Powder</b>	C <sub>18</sub> H <sub>19</sub> O <sub>5</sub> + H <sup>+</sup>	315.1232	315.1232	0.0	5.9
	C <sub>18</sub> H <sub>17</sub> O <sub>5</sub>	313.1072	313.1076	0.4	2.1
	C <sub>17</sub> H <sub>14</sub> O <sub>5</sub>	298.0876	298.0841	-3.5	0.5
	C <sub>9</sub> H <sub>9</sub> O <sub>4</sub>	181.0506	181.0500	-0.6	100.0
	C <sub>10</sub> H <sub>9</sub> O <sub>2</sub>	161.0575	161.0603	2.8	40.3
<b>Flavokavain A</b>	C <sub>18</sub> H <sub>19</sub> O <sub>5</sub> + H <sup>+</sup>	315.1214	315.1232	1.8	35.2
	C <sub>18</sub> H <sub>17</sub> O <sub>5</sub>	313.1120	313.1076	-4.4	41.2
	C <sub>17</sub> H <sub>14</sub> O <sub>5</sub>	298.0844	298.0841	-0.3	12.2
	C <sub>9</sub> H <sub>9</sub> O <sub>4</sub>	181.0507	181.0500	-0.7	100.0
	C <sub>10</sub> H <sub>9</sub> O <sub>2</sub>	161.0605	161.0603	-0.2	68.8

<sup>†</sup>Differences are reported in millimass units (mmu). Measured masses fell within 5 mmu of the calculated masses.  
<sup>‡</sup>Relative intensities are reported in percent.

**Table S-8.** Mass measurement data of in-source CID spectra obtained at 90 V for betel oil and isoeugenol. The corresponding spectra are shown in Fig. 7a.

	<b>Formula</b>	<b>Measured</b>	<b>Calculated</b>	<b>Diff.<sup>†</sup></b>	<b>Rel. Int.<sup>‡</sup></b>
<b>Betel Oil</b>	C <sub>10</sub> H <sub>12</sub> O <sub>2</sub> + H <sup>+</sup>	165.0907	165.0916	0.9	5.8
	C <sub>10</sub> H <sub>12</sub> O <sub>2</sub>	164.0846	164.0837	-0.9	6.1
	C <sub>8</sub> H <sub>9</sub> O <sub>2</sub>	137.0600	137.0603	0.3	4.1
	C <sub>8</sub> H <sub>9</sub>	105.0696	105.0704	0.8	37.3
	C <sub>7</sub> H <sub>7</sub>	91.0540	91.0548	0.8	76.5
	C <sub>6</sub> H <sub>5</sub>	77.0369	77.0391	2.2	100.0
<b>Isoeugenol</b>	C <sub>10</sub> H <sub>12</sub> O <sub>2</sub> + H <sup>+</sup>	165.0882	165.0916	3.4	20.5
	C <sub>10</sub> H <sub>12</sub> O <sub>2</sub>	164.0824	164.0837	1.3	33.2
	C <sub>8</sub> H <sub>9</sub> O <sub>2</sub>	137.0604	137.0603	-0.1	76.0
	C <sub>8</sub> H <sub>9</sub>	105.0695	105.0704	0.9	100.0
	C <sub>7</sub> H <sub>7</sub>	91.0561	91.0548	-1.3	24.6
	C <sub>6</sub> H <sub>5</sub>	77.0383	77.0391	0.8	45.9

<sup>†</sup>Differences are reported in millimass units (mmu). Measured masses fell within 5 mmu of the calculated masses.  
<sup>‡</sup>Relative intensities are reported in percent.



**Table S-9.** Mass measurement data of in-source CID spectra obtained at 90 V for betel oil and  $\beta$ -caryophyllene. The corresponding spectra are shown in Fig. 7b.

	<b>Formula</b>	<b>Measured</b>	<b>Calculated</b>	<b>Diff.<sup>†</sup></b>	<b>Rel. Int.<sup>‡</sup></b>
<b>Betel Oil</b>	$C_{15}H_{24} + H^+$	205.1963	205.1956	-0.7	0.8
	$C_{11}H_{17}$	149.1323	149.1330	0.7	1.4
	$C_9H_{11}$	119.0852	119.0861	0.9	13.5
	$C_7H_{11}$	95.0838	95.0861	2.3	14.0
	$C_6H_9$	81.0675	81.0704	2.9	32.7
<b><math>\beta</math>-Caryophyllene</b>	$C_{15}H_{24} + H^+$	205.1943	205.1956	1.3	5.2
	$C_{11}H_{17}$	149.1338	149.1330	-0.8	37.9
	$C_9H_{11}$	119.0863	119.0861	0.2	38.2
	$C_7H_{11}$	95.0862	95.0861	-0.1	99.3
	$C_6H_9$	81.0672	81.0704	3.2	100.0

<sup>†</sup>Differences are reported in millimass units (mmu). Measured masses fell within 5 mmu of the calculated masses.

<sup>‡</sup>Relative intensities are reported in percent.

**Table S-10.** Mass measurement data of in-source CID spectra obtained at 90 V for betel oil and  $\alpha$ -terpinene. The corresponding spectra are shown in Fig. 7c.

	<b>Formula</b>	<b>Measured</b>	<b>Calculated</b>	<b>Diff.<sup>†</sup></b>	<b>Rel. Int.<sup>‡</sup></b>
<b>Betel Oil</b>	$C_{10}H_{14} + H^+$	137.1322	137.1330	0.8	4.1
	$C_8H_9$	105.0696	105.0704	-3.5	37.3
	$C_7H_7$	91.0540	91.0548	0.8	76.5
	$C_6H_9$	81.0675	81.0704	2.9	32.7
	$C_6H_5$	77.0369	77.0391	2.2	100.0
	$C_5H_7$	67.0526	67.0548	2.2	24.7
<b><math>\alpha</math>-Terpinene</b>	$C_{10}H_{14} + H^+$	137.1297	137.1330	3.3	7.9
	$C_8H_9$	105.0694	105.0704	1.0	26.7
	$C_7H_7$	91.0563	91.0548	-1.5	59.3
	$C_6H_9$	81.0688	81.0704	1.6	100.0
	$C_6H_5$	77.0385	77.0391	0.6	65.3
	$C_5H_7$	67.0543	67.0548	0.5	64.6

<sup>†</sup>Differences are reported in millimass units (mmu). Measured masses fell within 5 mmu of the calculated masses.  
<sup>‡</sup>Relative intensities are reported in percent.

**Table S-11.** Mass measurement data of in-source CID spectra obtained at 90 V for betel oil and eugenyl acetate. The corresponding spectra are shown in Fig. 7d.

	<b>Formula</b>	<b>Measured</b>	<b>Calculated</b>	<b>Diff.<sup>†</sup></b>	<b>Rel. Int.<sup>‡</sup></b>
<b>Betel Oil</b>	C <sub>12</sub> H <sub>14</sub> O <sub>3</sub> + H <sup>+</sup>	207.1031	207.1021	-1.0	1.3
	C <sub>8</sub> H <sub>9</sub> O <sub>2</sub>	137.0600	137.0603	0.3	4.1
	C <sub>8</sub> H <sub>9</sub>	105.0696	105.0704	0.8	37.3
	C <sub>8</sub> H <sub>7</sub>	103.0531	103.0548	1.7	29.5
	C <sub>7</sub> H <sub>7</sub>	91.0540	91.0548	0.8	76.5
	C <sub>6</sub> H <sub>5</sub>	77.0369	77.0391	2.2	100.0
	<b>Eugenyl Acetate</b>	C <sub>12</sub> H <sub>14</sub> O <sub>3</sub> + H <sup>+</sup>	207.1016	207.1021	0.5
C <sub>8</sub> H <sub>9</sub> O <sub>2</sub>		137.0588	137.0603	1.5	54.9
C <sub>8</sub> H <sub>9</sub>		105.0694	105.0704	1.0	46.8
C <sub>8</sub> H <sub>7</sub>		103.0526	103.0548	2.2	100.0
C <sub>7</sub> H <sub>7</sub>		91.0563	91.0548	-1.5	42.5
C <sub>6</sub> H <sub>5</sub>		77.0385	77.0391	0.6	35.9

<sup>†</sup>Differences are reported in millimass units (mmu). Measured masses fell within 5 mmu of the calculated masses.  
<sup>‡</sup>Relative intensities are reported in percent.