

## **Supplemental material**

### **Development of preparative and analytical methods of the hop bitter acid oxide fraction and chemical properties of its components**

#### **AUTHORSHIP**

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#### **Contents**

#### **Table S1**

**Table S1. Molecular Formula and Deduced Origin of the MHBA Components Indicated by HRMS Data**

peak No. <sup>a</sup>	retention time (min)	observed <i>m/z</i>	molecular formula <sup>b</sup>	deduced origin <sup>c</sup>	compound
1	2.98	271.1183	C <sub>13</sub> H <sub>20</sub> O <sub>6</sub>	posthumulone <sup>d</sup> (+O, +H <sub>2</sub> O, –methylpentenoyl group)	
	2.98	397.1860	C <sub>20</sub> H <sub>30</sub> O <sub>8</sub>	cohumulone (+2O, +H <sub>2</sub> O)	
2	3.61	379.1757	C <sub>20</sub> H <sub>28</sub> O <sub>7</sub>	cohumulone (+2O)	
	3.61	297.1340	C <sub>15</sub> H <sub>22</sub> O <sub>6</sub>	<i>n</i> - or adhumulone (+2O, –methylpentenoyl group)	
3	4.36	269.1026	C <sub>13</sub> H <sub>18</sub> O <sub>6</sub>	posthumulone <sup>d</sup> (+2O, –methylpentenoyl group)	
	4.36	381.1911	C <sub>20</sub> H <sub>30</sub> O <sub>7</sub>	cohumulone (+O, +H <sub>2</sub> O)	
4	4.80	321.1339	C <sub>17</sub> H <sub>22</sub> O <sub>6</sub>	cohumulone (+2O, –acetone)	
5	5.30	411.2014	C <sub>21</sub> H <sub>32</sub> O <sub>8</sub>	<i>n</i> - or adhumulone (+2O, +H <sub>2</sub> O)	
	5.30	393.1910	C <sub>21</sub> H <sub>30</sub> O <sub>7</sub>	<i>n</i> - or adhumulone (+2O)	
	5.30	335.1493	C <sub>18</sub> H <sub>24</sub> O <sub>6</sub>	<i>n</i> - or adhumulone (+2O, –acetone)	
	5.30	379.1754	C <sub>20</sub> H <sub>28</sub> O <sub>7</sub>	cohumulone (+2O)	
6	5.67	285.1340	C <sub>14</sub> H <sub>22</sub> O <sub>6</sub>	cohumulone (+O, +H <sub>2</sub> O, –methylpentenoyl group)	
7	5.85	395.1704	C <sub>20</sub> H <sub>28</sub> O <sub>8</sub>	cohumulone (+3O)	
8	6.29	397.1861	C <sub>20</sub> H <sub>30</sub> O <sub>8</sub>	cohumulone (+2O, +H <sub>2</sub> O)	
9	6.58	267.1234	C <sub>14</sub> H <sub>20</sub> O <sub>5</sub>	cohumulone (+O, –methylpentenoyl group)	<b>8a</b>
10	6.89	393.1912	C <sub>21</sub> H <sub>30</sub> O <sub>7</sub>	<i>n</i> - or adhumulone (+2O)	
11	7.19	363.1806	C <sub>20</sub> H <sub>28</sub> O <sub>6</sub>	cohumulone (+O)	
	7.19	381.1914	C <sub>20</sub> H <sub>30</sub> O <sub>7</sub>	cohumulone (+O, +H <sub>2</sub> O)	
	7.19	331.1184	C <sub>18</sub> H <sub>20</sub> O <sub>6</sub>	<i>n</i> - or adhumulone (+2O, –acetone, –4H)	
	7.19	411.2021	C <sub>21</sub> H <sub>32</sub> O <sub>8</sub>	<i>n</i> - or adhumulone (+2O, +H <sub>2</sub> O)	
12	7.40	379.1754	C <sub>20</sub> H <sub>28</sub> O <sub>7</sub>	cohumulone (+2O)	
13	7.56	319.1180	C <sub>17</sub> H <sub>20</sub> O <sub>6</sub>	cohumulone (+2O, –acetone, –2H)	
14	7.74	239.1288	C <sub>13</sub> H <sub>20</sub> O <sub>4</sub>	posthumulone <sup>d</sup> (–methylpentenoyl group, +2H)	
	7.74	395.1707	C <sub>20</sub> H <sub>28</sub> O <sub>8</sub>	cohumulone (+3O)	
	7.74	283.1185	C <sub>14</sub> H <sub>20</sub> O <sub>6</sub>	cohumulone (+2O, –methylpentenoyl group)	
15	8.28	393.1912	C <sub>21</sub> H <sub>30</sub> O <sub>7</sub>	<i>n</i> - or adhumulone (+2O)	
	8.28	379.1756	C <sub>20</sub> H <sub>28</sub> O <sub>7</sub>	cohumulone (+2O)	
	8.28	303.1232	C <sub>17</sub> H <sub>20</sub> O <sub>5</sub>	cohumulone (+O, –acetone, –2H)	
16	8.49	251.1285	C <sub>14</sub> H <sub>20</sub> O <sub>4</sub>	cohumulone (–methylpentenoyl group)	
	8.49	335.1494	C <sub>18</sub> H <sub>24</sub> O <sub>6</sub>	<i>n</i> - or adhumulone (+2O, –acetone)	
	8.49	321.1337	C <sub>17</sub> H <sub>22</sub> O <sub>6</sub>	cohumulone (+2O, –acetone)	
	8.49	307.1181	C <sub>16</sub> H <sub>20</sub> O <sub>6</sub>	posthumulone <sup>d</sup> (+2O, –acetone)	
	8.49	283.1182	C <sub>14</sub> H <sub>20</sub> O <sub>6</sub>	cohumulone (+2O, –methylpentenoyl group)	
17	8.71	321.1336	C <sub>17</sub> H <sub>22</sub> O <sub>6</sub>	cohumulone (+2O, –acetone)	

**Table S1. (continued)**

	8.71	379.1754	C <sub>20</sub> H <sub>28</sub> O <sub>7</sub>	cohumulone (+2O)	
	8.71	395.1702	C <sub>20</sub> H <sub>28</sub> O <sub>8</sub>	cohumulone (+3O)	
18	8.91	379.1757	C <sub>20</sub> H <sub>28</sub> O <sub>7</sub>	cohumulone (+2O)	
19	9.10	335.1495	C <sub>18</sub> H <sub>24</sub> O <sub>6</sub>	<i>n</i> - or adhumulone (+2O, –acetone)	
20	9.35	379.1758	C <sub>20</sub> H <sub>28</sub> O <sub>7</sub>	cohumulone (+2O)	
	9.35	409.1863	C <sub>21</sub> H <sub>30</sub> O <sub>8</sub>	<i>n</i> - or adhumulone (+3O)	
	9.35	349.1653	C <sub>19</sub> H <sub>26</sub> O <sub>6</sub>	posthumulone <sup>d</sup> (+O) or prehumulone <sup>e</sup> (+2O, –acetone)	
	9.35	307.1548	C <sub>17</sub> H <sub>24</sub> O <sub>5</sub>	cohumulone (+H <sub>2</sub> O, –acetone)	
21	9.69	379.1755	C <sub>20</sub> H <sub>28</sub> O <sub>7</sub>	cohumulone (+2O)	
	9.69	307.1181	C <sub>16</sub> H <sub>20</sub> O <sub>6</sub>	posthumulone <sup>d</sup> (+2O, –acetone)	
	9.69	407.1703	C <sub>21</sub> H <sub>28</sub> O <sub>8</sub>	<i>n</i> - or adhumulone (+3O, –2H)	
	9.69	409.1860	C <sub>21</sub> H <sub>30</sub> O <sub>8</sub>	<i>n</i> - or adhumulone (+3O)	
22	9.98	269.1390	C <sub>14</sub> H <sub>22</sub> O <sub>5</sub>	cohumulone (+H <sub>2</sub> O, –methylpentenoyl group)	
	9.98	379.1755	C <sub>20</sub> H <sub>28</sub> O <sub>7</sub>	cohumulone (+2O)	
	9.98	409.1859	C <sub>21</sub> H <sub>30</sub> O <sub>8</sub>	<i>n</i> - or adhumulone (+3O)	
23	10.45	379.1753	C <sub>20</sub> H <sub>28</sub> O <sub>7</sub>	cohumulone (+2O)	
	10.45	395.1703	C <sub>20</sub> H <sub>28</sub> O <sub>8</sub>	cohumulone (+3O)	
	10.45	303.1231	C <sub>17</sub> H <sub>20</sub> O <sub>5</sub>	cohumulone (+O, –acetone, –2H)	
	10.45	411.2014	C <sub>21</sub> H <sub>32</sub> O <sub>8</sub>	<i>n</i> - or adhumulone (+2O, +H <sub>2</sub> O)	
24	10.71	281.1391	C <sub>15</sub> H <sub>22</sub> O <sub>5</sub>	adhumulone (+O, –methylpentenoyl group)	<b>8c<sup>f</sup></b>
	10.71	379.1757	C <sub>20</sub> H <sub>28</sub> O <sub>7</sub>	cohumulone (+2O)	
	10.71	347.1495	C <sub>19</sub> H <sub>24</sub> O <sub>6</sub>	posthumulone <sup>d</sup> (+O, –2H)	
	10.71	409.1862	C <sub>21</sub> H <sub>30</sub> O <sub>8</sub>	<i>n</i> - or adhumulone (+3O)	
	10.71	393.1913	C <sub>21</sub> H <sub>30</sub> O <sub>7</sub>	<i>n</i> - or adhumulone (+2O)	
25	10.91	281.1388	C <sub>15</sub> H <sub>22</sub> O <sub>5</sub>	adhumulone (+O, –methylpentenoyl group)	<b>8c<sup>ff</sup></b>
	10.91	361.1648	C <sub>20</sub> H <sub>26</sub> O <sub>6</sub>	cohumulone (+O, –2H)	
	10.91	363.1803	C <sub>20</sub> H <sub>28</sub> O <sub>6</sub>	cohumulone (+O)	
	10.91	351.1440	C <sub>18</sub> H <sub>24</sub> O <sub>7</sub>	<i>n</i> - or adhumulone (+3O, –acetone)	
	10.91	411.2014	C <sub>21</sub> H <sub>32</sub> O <sub>8</sub>	<i>n</i> - or adhumulone (+2O, +H <sub>2</sub> O)	
	10.91	251.1283	C <sub>14</sub> H <sub>20</sub> O <sub>4</sub>	cohumulone (–methylpentenoyl group)	
	10.91	427.1963	C <sub>21</sub> H <sub>32</sub> O <sub>9</sub>	<i>n</i> - or adhumulone (+3O, +H <sub>2</sub> O)	
26	11.20	425.1810	C <sub>21</sub> H <sub>30</sub> O <sub>9</sub>	<i>n</i> - or adhumulone (+4O)	
27	11.46	281.1389	C <sub>15</sub> H <sub>22</sub> O <sub>5</sub>	<i>n</i> -humulone (+O, –methylpentenoyl group)	<b>8b</b>
	11.46	379.1755	C <sub>20</sub> H <sub>28</sub> O <sub>7</sub>	cohumulone (+2O)	
	11.46	393.1911	C <sub>21</sub> H <sub>30</sub> O <sub>7</sub>	<i>n</i> - or adhumulone (+2O)	
28	11.97	393.1911	C <sub>21</sub> H <sub>30</sub> O <sub>7</sub>	<i>n</i> - or adhumulone (+2O)	
	11.97	333.1337	C <sub>18</sub> H <sub>22</sub> O <sub>6</sub>	<i>n</i> - or adhumulone (+2O, –acetone, –2H)	
	11.97	281.1026	C <sub>14</sub> H <sub>18</sub> O <sub>6</sub>	cohumulone (+2O, –methylpentenoyl group, –2H)	
	11.97	409.1859	C <sub>21</sub> H <sub>30</sub> O <sub>8</sub>	<i>n</i> - or adhumulone (+3O)	
29	12.29	393.1913	C <sub>21</sub> H <sub>30</sub> O <sub>7</sub>	<i>n</i> - or adhumulone (+2O)	

**Table S1. (continued)**

30	12.54	333.1338	C <sub>18</sub> H <sub>22</sub> O <sub>6</sub>	<i>n</i> - or adhumulone (+2O, –acetone, –2H)	
	12.54	379.1755	C <sub>20</sub> H <sub>28</sub> O <sub>7</sub>	cohumulone (+2O)	
	12.54	363.1806	C <sub>20</sub> H <sub>28</sub> O <sub>6</sub>	cohumulone (+O)	
	12.54	393.1912	C <sub>21</sub> H <sub>30</sub> O <sub>7</sub>	<i>n</i> - or adhumulone (+2O)	
	12.54	409.1861	C <sub>21</sub> H <sub>30</sub> O <sub>8</sub>	<i>n</i> - or adhumulone (+3O)	
31	12.73	363.1806	C <sub>20</sub> H <sub>28</sub> O <sub>6</sub>	cohumulone (+O)	<b>9a</b>
32	12.97	393.1912	C <sub>21</sub> H <sub>30</sub> O <sub>7</sub>	<i>n</i> - or adhumulone (+2O)	
33	13.15	379.1751	C <sub>20</sub> H <sub>28</sub> O <sub>7</sub>	cohumulone (+2O)	<b>7a</b>
	13.15	335.1490	C <sub>18</sub> H <sub>24</sub> O <sub>6</sub>	<i>n</i> - or adhumulone (+2O, –acetone)	
	13.15	409.1854	C <sub>21</sub> H <sub>30</sub> O <sub>8</sub>	<i>n</i> - or adhumulone (+3O)	
34	13.46	305.1388	C <sub>17</sub> H <sub>22</sub> O <sub>5</sub>	cohumulone (+O, –acetone)	<b>11a</b>
	13.46	393.1911	C <sub>21</sub> H <sub>30</sub> O <sub>7</sub>	<i>n</i> - or adhumulone (+2O)	
	13.46	317.1388	C <sub>18</sub> H <sub>22</sub> O <sub>5</sub>	<i>n</i> - or adhumulone (+O, –acetone, –2H)	
35	13.62	361.1649	C <sub>20</sub> H <sub>26</sub> O <sub>6</sub>	cohumulone (+O, –2H)	
	13.62	393.1911	C <sub>21</sub> H <sub>30</sub> O <sub>7</sub>	<i>n</i> - or adhumulone (+2O)	
36	13.90	335.1494	C <sub>18</sub> H <sub>24</sub> O <sub>6</sub>	<i>n</i> - or adhumulone (+2O, –acetone)	
	13.90	237.1129	C <sub>13</sub> H <sub>18</sub> O <sub>4</sub>	posthumulone <sup>d</sup> (–methylpentenoyl group)	
	13.90	393.1911	C <sub>21</sub> H <sub>30</sub> O <sub>7</sub>	<i>n</i> - or adhumulone (+2O)	
	13.90	377.1599	C <sub>20</sub> H <sub>26</sub> O <sub>7</sub>	cohumulone (+2O, –2H)	
	13.90	379.1755	C <sub>20</sub> H <sub>28</sub> O <sub>7</sub>	cohumulone (+2O)	
	13.90	411.1653	C <sub>20</sub> H <sub>28</sub> O <sub>9</sub>	cohumulone (+4O)	
37	14.26	393.1906	C <sub>21</sub> H <sub>30</sub> O <sub>7</sub>	<i>n</i> - or adhumulone (+2O)	
	14.26	409.1853	C <sub>21</sub> H <sub>30</sub> O <sub>8</sub>	<i>n</i> - or adhumulone (+3O)	
38	14.78	393.1911	C <sub>21</sub> H <sub>30</sub> O <sub>7</sub>	<i>n</i> - or adhumulone (+2O)	
	14.78	377.1597	C <sub>20</sub> H <sub>26</sub> O <sub>7</sub>	cohumulone (+2O, –2H)	
39	15.07	363.1806	C <sub>20</sub> H <sub>28</sub> O <sub>6</sub>	cohumulone (+O)	<b>10a</b>
40	15.28	393.1909	C <sub>21</sub> H <sub>30</sub> O <sub>7</sub>	<i>n</i> - or adhumulone (+2O)	
	15.28	335.1856	C <sub>19</sub> H <sub>28</sub> O <sub>5</sub>	cohulupone (+H <sub>2</sub> O)	
	15.28	283.1545	C <sub>15</sub> H <sub>24</sub> O <sub>5</sub>	<i>n</i> - or adhumulone (+H <sub>2</sub> O, –methylpentenoyl group)	
41	15.72	375.1805	C <sub>21</sub> H <sub>28</sub> O <sub>6</sub>	<i>n</i> - or adhumulone (+O, –2H)	
	15.72	361.1649	C <sub>20</sub> H <sub>26</sub> O <sub>6</sub>	cohumulone (+O, –2H)	
	15.72	377.1958	C <sub>21</sub> H <sub>30</sub> O <sub>6</sub>	<i>n</i> - or adhumulone (+O)	
	15.72	363.1805	C <sub>20</sub> H <sub>28</sub> O <sub>6</sub>	cohumulone (+O)	
	15.72	263.1284	C <sub>15</sub> H <sub>20</sub> O <sub>4</sub>	<i>n</i> - or adhumulone (–methylpentenoyl group, –2H)	
	15.72	317.1388	C <sub>18</sub> H <sub>22</sub> O <sub>5</sub>	<i>n</i> - or adhumulone (+O, –acetone, –2H)	
	15.72	393.1910	C <sub>21</sub> H <sub>30</sub> O <sub>7</sub>	<i>n</i> - or adhumulone (+2O)	
	15.72	409.1860	C <sub>21</sub> H <sub>30</sub> O <sub>8</sub>	<i>n</i> - or adhumulone (+3O)	
42	16.16	393.1910	C <sub>21</sub> H <sub>30</sub> O <sub>7</sub>	adhumulone (+2O)	<b>7c<sup>f</sup></b>
	16.16	379.1754	C <sub>20</sub> H <sub>28</sub> O <sub>7</sub>	cohumulone (+2O)	<b>6a</b>
	16.16	351.1806	C <sub>19</sub> H <sub>28</sub> O <sub>6</sub>	posthumulone <sup>d</sup> (+H <sub>2</sub> O)	

**Table S1. (continued)**

	16.16	411.2015	C <sub>21</sub> H <sub>32</sub> O <sub>8</sub>	<i>n</i> - or adhumulone (+2O, +H <sub>2</sub> O)	
43	16.70	361.1648	C <sub>20</sub> H <sub>26</sub> O <sub>6</sub>	cohumulone (+O, -2H)	
	16.70	249.1127	C <sub>14</sub> H <sub>18</sub> O <sub>4</sub>	cohumulone (-methylpentenoyl group, -2H)	
	16.70	393.1909	C <sub>21</sub> H <sub>30</sub> O <sub>7</sub>	<i>n</i> - or adhumulone (+2O)	
	16.70	391.1753	C <sub>21</sub> H <sub>28</sub> O <sub>7</sub>	<i>n</i> - or adhumulone (+2O, -2H)	
	16.70	375.1804	C <sub>21</sub> H <sub>28</sub> O <sub>6</sub>	<i>n</i> - or adhumulone (+O, -2H)	
	16.70	379.1753	C <sub>20</sub> H <sub>28</sub> O <sub>7</sub>	cohumulone (+2O)	
	16.70	409.1858	C <sub>21</sub> H <sub>30</sub> O <sub>8</sub>	<i>n</i> - or adhumulone (+3O)	
44	17.12	377.1961	C <sub>21</sub> H <sub>30</sub> O <sub>6</sub>	adhumulone (+O)	<b>9c</b>
	17.12	393.1910	C <sub>21</sub> H <sub>30</sub> O <sub>7</sub>	adhumulone (+2O)	<b>7c<sup>ff</sup></b>
	17.12	279.1232	C <sub>15</sub> H <sub>20</sub> O <sub>5</sub>	<i>n</i> - or adhumulone (+O, -methylpentenoyl group, -2H)	
45	17.35	361.1650	C <sub>20</sub> H <sub>26</sub> O <sub>6</sub>	cohumulone (+O, -2H)	
	17.35	379.1754	C <sub>20</sub> H <sub>28</sub> O <sub>7</sub>	cohumulone (+2O)	
46	17.57	377.1962	C <sub>21</sub> H <sub>30</sub> O <sub>6</sub>	<i>n</i> -humulone (+O)	<b>9b</b>
47	17.96	393.1906	C <sub>21</sub> H <sub>30</sub> O <sub>7</sub>	<i>n</i> -humulone (+2O)	<b>7b</b>
48	18.20	361.1650	C <sub>20</sub> H <sub>26</sub> O <sub>6</sub>	cohumulone (+O, -2H)	
49	18.51	375.1805	C <sub>21</sub> H <sub>28</sub> O <sub>6</sub>	<i>n</i> - or adhumulone (+O, -2H)	
	18.51	333.1337	C <sub>18</sub> H <sub>22</sub> O <sub>6</sub>	<i>n</i> - or adhumulone (+2O, -acetone, -2H)	
	18.51	251.1285	C <sub>14</sub> H <sub>20</sub> O <sub>4</sub>	cohumulone (-methylpentenoyl group)	
	18.51	319.1545	C <sub>18</sub> H <sub>24</sub> O <sub>5</sub>	adhumulone (+O, -acetone)	<b>11c</b>
50	18.75	393.1914	C <sub>21</sub> H <sub>30</sub> O <sub>7</sub>	<i>n</i> - or adhumulone (+2O)	
	18.75	391.1758	C <sub>21</sub> H <sub>28</sub> O <sub>7</sub>	<i>n</i> - or adhumulone (+2O, -2H)	
	18.75	377.1964	C <sub>21</sub> H <sub>30</sub> O <sub>6</sub>	<i>n</i> - or adhumulone (+O)	
	18.75	425.1812	C <sub>21</sub> H <sub>30</sub> O <sub>9</sub>	<i>n</i> - or adhumulone (+4O)	
	18.75	349.2016	C <sub>20</sub> H <sub>30</sub> O <sub>5</sub>	<i>n</i> - or adhumulone (+H <sub>2</sub> O)	
	18.75	363.1809	C <sub>20</sub> H <sub>28</sub> O <sub>6</sub>	cohumulone (+O)	
51	18.91	319.1546	C <sub>18</sub> H <sub>24</sub> O <sub>5</sub>	<i>n</i> -humulone (+O, -acetone)	<b>11b</b>
52	19.21	263.1286	C <sub>15</sub> H <sub>20</sub> O <sub>4</sub>	<i>n</i> - or adhumulone (-methylpentenoyl group, -2H)	
	19.21	363.1809	C <sub>20</sub> H <sub>28</sub> O <sub>6</sub>	cohumulone (+O)	
	19.21	393.1914	C <sub>21</sub> H <sub>30</sub> O <sub>7</sub>	adhumulone (+2O)	<b>6c<sup>f</sup></b>
	19.21	303.1234	C <sub>17</sub> H <sub>20</sub> O <sub>5</sub>	cohumulone (+O, -acetone, -2H)	
	19.21	319.1547	C <sub>18</sub> H <sub>24</sub> O <sub>5</sub>	<i>n</i> - or adhumulone (+O, -acetone)	
53	19.55	363.1805	C <sub>20</sub> H <sub>28</sub> O <sub>6</sub>	cohumulone (+O)	
	19.55	377.1960	C <sub>21</sub> H <sub>30</sub> O <sub>6</sub>	adhumulone (+O)	<b>10c</b>
	19.55	251.1283	C <sub>14</sub> H <sub>20</sub> O <sub>4</sub>	cohumulone (-methylpentenoyl group)	
	19.55	393.1907	C <sub>21</sub> H <sub>30</sub> O <sub>7</sub>	<i>n</i> - or adhumulone (+2O)	
54	19.94	377.1960	C <sub>21</sub> H <sub>30</sub> O <sub>6</sub>	<i>n</i> -humulone (+O)	<b>10b</b>
	19.94	349.2012	C <sub>20</sub> H <sub>30</sub> O <sub>5</sub>	<i>n</i> - or adhumulone (+H <sub>2</sub> O)	
	19.94	393.1907	C <sub>21</sub> H <sub>30</sub> O <sub>7</sub>	adhumulone (+2O)	<b>6c<sup>ff</sup></b>
55	20.33	393.1909	C <sub>21</sub> H <sub>30</sub> O <sub>7</sub>	<i>n</i> -humulone (+2O)	<b>6b</b>

**Table S1. (continued)**

56	20.72	361.1651	C <sub>20</sub> H <sub>26</sub> O <sub>6</sub>	cohumulone (+O, -2H)
	20.72	377.1963	C <sub>21</sub> H <sub>30</sub> O <sub>6</sub>	<i>n</i> - or adhumulone (+O)
	20.72	393.1913	C <sub>21</sub> H <sub>30</sub> O <sub>7</sub>	<i>n</i> - or adhumulone (+2O)
57	21.26	349.2012	C <sub>20</sub> H <sub>30</sub> O <sub>5</sub>	<i>n</i> - or adhulupone (+H <sub>2</sub> O)
	21.26	365.1960	C <sub>20</sub> H <sub>30</sub> O <sub>6</sub>	cohumulone (+H <sub>2</sub> O)
	21.26	375.1805	C <sub>21</sub> H <sub>28</sub> O <sub>6</sub>	<i>n</i> - or adhumulone (+O, -2H)
	21.26	393.1910	C <sub>21</sub> H <sub>30</sub> O <sub>7</sub>	<i>n</i> - or adhumulone (+2O)
	21.26	379.1754	C <sub>20</sub> H <sub>28</sub> O <sub>7</sub>	cohumulone (+2O)
	21.26	407.1702	C <sub>21</sub> H <sub>28</sub> O <sub>8</sub>	<i>n</i> - or adhumulone (+3O, -2H)
58	21.66	375.1808	C <sub>21</sub> H <sub>28</sub> O <sub>6</sub>	<i>n</i> - or adhumulone (+O, -2H)
	21.66	363.1809	C <sub>20</sub> H <sub>28</sub> O <sub>6</sub>	cohumulone (+O)
	21.66	393.1914	C <sub>21</sub> H <sub>30</sub> O <sub>7</sub>	<i>n</i> - or adhumulone (+2O)
59	22.09	375.1807	C <sub>21</sub> H <sub>28</sub> O <sub>6</sub>	<i>n</i> - or adhumulone (+O, -2H)
	22.09	393.1913	C <sub>21</sub> H <sub>30</sub> O <sub>7</sub>	<i>n</i> - or adhumulone (+2O)
	22.09	395.2068	C <sub>21</sub> H <sub>32</sub> O <sub>7</sub>	<i>n</i> - or adhumulone (+O, +H <sub>2</sub> O)
	22.09	361.1652	C <sub>20</sub> H <sub>26</sub> O <sub>6</sub>	cohumulone (+O, -2H)
60	22.35	333.1703	C <sub>19</sub> H <sub>26</sub> O <sub>5</sub>	posthumulone <sup>d</sup> (isomerization)
	22.35	263.1286	C <sub>15</sub> H <sub>20</sub> O <sub>4</sub>	<i>n</i> - or adhumulone (-methylpentenoyl group, -2H)
61	22.54	375.1808	C <sub>21</sub> H <sub>28</sub> O <sub>6</sub>	<i>n</i> - or adhumulone (+O, -2H)
	22.54	349.2015	C <sub>20</sub> H <sub>30</sub> O <sub>5</sub>	<i>n</i> - or adhulupone (+H <sub>2</sub> O)
	22.54	409.2227	C <sub>22</sub> H <sub>34</sub> O <sub>7</sub>	prehumulone <sup>e</sup> (+O, +H <sub>2</sub> O)
	22.54	393.1913	C <sub>21</sub> H <sub>30</sub> O <sub>7</sub>	<i>n</i> - or adhumulone (+2O)
62	22.85	361.1649	C <sub>20</sub> H <sub>26</sub> O <sub>6</sub>	cohumulone (+O, -2H)
	22.85	363.1804	C <sub>20</sub> H <sub>28</sub> O <sub>6</sub>	cohumulone (+O)
63	23.08	375.1806	C <sub>21</sub> H <sub>28</sub> O <sub>6</sub>	<i>n</i> - or adhumulone (+O, -2H)
64	23.34	377.1961	C <sub>21</sub> H <sub>30</sub> O <sub>6</sub>	<i>n</i> - or adhumulone (+O)
	23.34	331.1908	C <sub>20</sub> H <sub>28</sub> O <sub>4</sub>	<i>n</i> - or adhulupone (isomerization)
	23.34	343.1543	C <sub>20</sub> H <sub>24</sub> O <sub>5</sub>	cohumulone (-4H)
	23.34	363.1805	C <sub>20</sub> H <sub>28</sub> O <sub>6</sub>	cohumulone (+O)
	23.34	393.1910	C <sub>21</sub> H <sub>30</sub> O <sub>7</sub>	<i>n</i> - or adhumulone (+2O)
	23.34	439.2329	C <sub>23</sub> H <sub>36</sub> O <sub>8</sub>	possible minor congener of α-acids <sup>g</sup> (+2O, +H <sub>2</sub> O)
65	23.62	361.1653	C <sub>20</sub> H <sub>26</sub> O <sub>6</sub>	cohumulone (+O, -2H)
	23.62	333.1703	C <sub>19</sub> H <sub>26</sub> O <sub>5</sub>	posthumulone <sup>d</sup> (isomerization)
	23.62	391.1759	C <sub>21</sub> H <sub>28</sub> O <sub>7</sub>	<i>n</i> - or adhumulone (+2O, -2H)
66	23.86	377.1962	C <sub>21</sub> H <sub>30</sub> O <sub>6</sub>	<i>n</i> - or adhumulone (+O)
67	24.09	411.2014	C <sub>21</sub> H <sub>32</sub> O <sub>8</sub>	<i>n</i> - or adhumulone (+2O, +H <sub>2</sub> O)
	24.09	363.1808	C <sub>20</sub> H <sub>28</sub> O <sub>6</sub>	cohumulone (+O)
	24.09	331.1910	C <sub>20</sub> H <sub>28</sub> O <sub>4</sub>	<i>n</i> - or adhulupone (isomerization)
	24.09	317.1391	C <sub>18</sub> H <sub>22</sub> O <sub>5</sub>	<i>n</i> - or adhumulone (+O, -acetone, -2H)
	24.09	393.1914	C <sub>21</sub> H <sub>30</sub> O <sub>7</sub>	<i>n</i> - or adhumulone (+2O)

**Table S1. (continued)**

68	24.31	363.1806	C <sub>20</sub> H <sub>28</sub> O <sub>6</sub>	cohumulone (+O)
	24.31	377.1962	C <sub>21</sub> H <sub>30</sub> O <sub>6</sub>	<i>n</i> - or adhumulone (+O)
69	24.72	363.1804	C <sub>20</sub> H <sub>28</sub> O <sub>6</sub>	cohumulone (+O)
	24.72	361.1649	C <sub>20</sub> H <sub>26</sub> O <sub>6</sub>	cohumulone (+O, -2H)
	24.72	393.1910	C <sub>21</sub> H <sub>30</sub> O <sub>7</sub>	<i>n</i> - or adhumulone (+2O)
70	25.00	375.1805	C <sub>21</sub> H <sub>28</sub> O <sub>6</sub>	<i>n</i> - or adhumulone (+O, -2H)
	25.00	379.1754	C <sub>20</sub> H <sub>28</sub> O <sub>7</sub>	cohumulone (+2O)
	25.00	265.1077	C <sub>14</sub> H <sub>18</sub> O <sub>5</sub>	cohumulone (+O, -methylpentenoyl group, -2H)
	25.00	345.1700	C <sub>20</sub> H <sub>26</sub> O <sub>5</sub>	cohumulone (-2H)
	25.00	359.1857	C <sub>21</sub> H <sub>28</sub> O <sub>5</sub>	<i>n</i> - or adhumulone (-2H)
71	25.24	361.1651	C <sub>20</sub> H <sub>26</sub> O <sub>6</sub>	cohumulone (+O, -2H)
	25.24	411.2018	C <sub>21</sub> H <sub>32</sub> O <sub>8</sub>	<i>n</i> - or adhumulone (+2O, +H <sub>2</sub> O)
	25.24	393.1914	C <sub>21</sub> H <sub>30</sub> O <sub>7</sub>	<i>n</i> - or adhumulone (+2O)
	25.24	377.1964	C <sub>21</sub> H <sub>30</sub> O <sub>6</sub>	<i>n</i> - or adhumulone (+O)
72	25.47	333.2064	C <sub>20</sub> H <sub>30</sub> O <sub>4</sub>	<i>n</i> - or adhulupone (+2H)
	25.47	349.1649	C <sub>19</sub> H <sub>26</sub> O <sub>6</sub>	posthumulone <sup>d</sup> (+O)
	25.47	379.1754	C <sub>20</sub> H <sub>28</sub> O <sub>7</sub>	cohumulone (+2O)
	25.47	447.2380	C <sub>23</sub> H <sub>36</sub> O <sub>7</sub>	colupulone (+3O)
73	25.65	393.1913	C <sub>21</sub> H <sub>30</sub> O <sub>7</sub>	<i>n</i> - or adhumulone (+2O)
74	25.94	375.1806	C <sub>21</sub> H <sub>28</sub> O <sub>6</sub>	<i>n</i> - or adhumulone (+O, -2H)
	25.94	377.1599	C <sub>20</sub> H <sub>26</sub> O <sub>7</sub>	cohumulone (+2O, -2H)
	25.94	361.1651	C <sub>20</sub> H <sub>26</sub> O <sub>6</sub>	cohumulone (+O, -2H)
75	26.20	379.1754	C <sub>20</sub> H <sub>28</sub> O <sub>7</sub>	cohumulone (+2O)
	26.20	421.2223	C <sub>23</sub> H <sub>34</sub> O <sub>7</sub>	possible minor congener of α-acids <sup>g</sup> (+2O)
76	26.83	331.1908	C <sub>20</sub> H <sub>28</sub> O <sub>4</sub>	<i>n</i> - or adhulupone (isomerization)
	26.83	349.2013	C <sub>20</sub> H <sub>30</sub> O <sub>5</sub>	<i>n</i> - or adhulupone (+H <sub>2</sub> O)
	26.83	409.1860	C <sub>21</sub> H <sub>30</sub> O <sub>8</sub>	<i>n</i> - or adhumulone (+3O)
	26.83	423.2382	C <sub>23</sub> H <sub>36</sub> O <sub>7</sub>	possible minor congener of α-acids <sup>g</sup> (+O, +H <sub>2</sub> O)
	26.83	375.1805	C <sub>21</sub> H <sub>28</sub> O <sub>6</sub>	<i>n</i> - or adhumulone (+O, -2H)
77	27.06	347.1857	C <sub>20</sub> H <sub>28</sub> O <sub>5</sub>	cohumulone (isomerization)
	27.06	375.1807	C <sub>21</sub> H <sub>28</sub> O <sub>6</sub>	<i>n</i> - or adhumulone (+O, -2H)
	27.06	391.1756	C <sub>21</sub> H <sub>28</sub> O <sub>7</sub>	<i>n</i> - or adhumulone (+2O, -2H)
	27.06	409.1861	C <sub>21</sub> H <sub>30</sub> O <sub>8</sub>	<i>n</i> - or adhumulone (+3O)
78	27.24	351.1808	C <sub>19</sub> H <sub>28</sub> O <sub>6</sub>	posthumulone <sup>d</sup> (+H <sub>2</sub> O)
	27.24	345.1704	C <sub>20</sub> H <sub>26</sub> O <sub>5</sub>	cohumulone (-2H)
	27.24	375.1809	C <sub>21</sub> H <sub>28</sub> O <sub>6</sub>	<i>n</i> - or adhumulone (+O, -2H)
	27.24	391.1759	C <sub>21</sub> H <sub>28</sub> O <sub>7</sub>	<i>n</i> - or adhumulone (+2O, -2H)
79	27.42	289.1439	C <sub>17</sub> H <sub>22</sub> O <sub>4</sub>	cohumulone (-acetone)
	27.42	333.1700	C <sub>19</sub> H <sub>26</sub> O <sub>5</sub>	posthumulone <sup>d</sup> (isomerization)
	27.42	423.2378	C <sub>23</sub> H <sub>36</sub> O <sub>7</sub>	possible minor congener of α-acids <sup>g</sup> (+O, +H <sub>2</sub> O)

**Table S1. (continued)**

80	27.71	375.1807	C <sub>21</sub> H <sub>28</sub> O <sub>6</sub>	<i>n</i> - or adhumulone (+O, -2H)	
	27.71	363.1808	C <sub>20</sub> H <sub>28</sub> O <sub>6</sub>	cohumulone (+O)	
	27.71	331.1546	C <sub>19</sub> H <sub>24</sub> O <sub>5</sub>	posthumulone <sup>d</sup> (-2H)	
	27.71	335.1859	C <sub>19</sub> H <sub>28</sub> O <sub>5</sub>	cohulupone (+H <sub>2</sub> O)	
	27.71	393.1913	C <sub>21</sub> H <sub>30</sub> O <sub>7</sub>	<i>n</i> - or adhumulone (+2O)	
	27.71	423.2381	C <sub>23</sub> H <sub>36</sub> O <sub>7</sub>	possible minor congener of α-acids <sup>g</sup> (+O, +H <sub>2</sub> O)	
	27.71	345.1703	C <sub>20</sub> H <sub>26</sub> O <sub>5</sub>	cohumulone (-2H)	
81	27.97	377.1960	C <sub>21</sub> H <sub>30</sub> O <sub>6</sub>	<i>n</i> - or adhumulone (+O)	
	27.97	421.2223	C <sub>23</sub> H <sub>34</sub> O <sub>7</sub>	possible minor congener of α-acids <sup>g</sup> (+2O)	
82	28.20	375.1805	C <sub>21</sub> H <sub>28</sub> O <sub>6</sub>	<i>n</i> - or adhumulone (+O, -2H)	
	28.20	357.1699	C <sub>21</sub> H <sub>26</sub> O <sub>5</sub>	<i>n</i> - or adhumulone (-4H)	
	28.20	345.1700	C <sub>20</sub> H <sub>26</sub> O <sub>5</sub>	cohumulone (-2H)	
83	28.46	421.2225	C <sub>23</sub> H <sub>34</sub> O <sub>7</sub>	possible minor congener of α-acids <sup>g</sup> (+2O)	
	28.46	377.1964	C <sub>21</sub> H <sub>30</sub> O <sub>6</sub>	<i>n</i> - or adhumulone (+O)	
	28.46	365.1965	C <sub>20</sub> H <sub>30</sub> O <sub>6</sub>	cohumulone (+H <sub>2</sub> O)	
	28.46	393.1914	C <sub>21</sub> H <sub>30</sub> O <sub>7</sub>	<i>n</i> - or adhumulone (+2O)	
84	28.90	345.1703	C <sub>20</sub> H <sub>26</sub> O <sub>5</sub>	cohumulone (-2H)	
	28.90	363.1809	C <sub>20</sub> H <sub>28</sub> O <sub>6</sub>	cohumulone (+O)	
	28.90	375.1808	C <sub>21</sub> H <sub>28</sub> O <sub>6</sub>	<i>n</i> - or adhumulone (+O, -2H)	
	28.90	419.2070	C <sub>23</sub> H <sub>32</sub> O <sub>7</sub>	possible minor congener of α-acids <sup>g</sup> (+2O, -2H)	
85	29.18	351.1807	C <sub>19</sub> H <sub>28</sub> O <sub>6</sub>	cohulupone (+O, +H <sub>2</sub> O)	
86	29.53	377.1963	C <sub>21</sub> H <sub>30</sub> O <sub>6</sub>	<i>n</i> - or adhumulone (+O)	
	29.53	363.1808	C <sub>20</sub> H <sub>28</sub> O <sub>6</sub>	cohumulone (+O)	
87	29.91	375.1805	C <sub>21</sub> H <sub>28</sub> O <sub>6</sub>	<i>n</i> - or adhumulone (+O, -2H)	
88	30.44	333.1701	C <sub>19</sub> H <sub>26</sub> O <sub>5</sub>	posthumulone <sup>d</sup> (isomerization)	
	30.44	363.1806	C <sub>20</sub> H <sub>28</sub> O <sub>6</sub>	cohumulone (+O)	
	30.44	279.1233	C <sub>15</sub> H <sub>20</sub> O <sub>5</sub>	<i>n</i> - or adhumulone (+O, -methylpentenoyl group, -2H)	
	30.44	377.1962	C <sub>21</sub> H <sub>30</sub> O <sub>6</sub>	<i>n</i> - or adhumulone (+O)	
	30.44	431.2432	C <sub>25</sub> H <sub>36</sub> O <sub>6</sub>	colupulone (+2O)	
89	30.93	303.1599	C <sub>18</sub> H <sub>24</sub> O <sub>4</sub>	<i>n</i> - or adhumulone (-acetone)	
	30.93	375.1808	C <sub>21</sub> H <sub>28</sub> O <sub>6</sub>	<i>n</i> - or adhumulone (+O, -2H)	
	30.93	391.1758	C <sub>21</sub> H <sub>28</sub> O <sub>7</sub>	<i>n</i> - or adhumulone (+2O, -2H)	
	30.93	363.1809	C <sub>20</sub> H <sub>28</sub> O <sub>6</sub>	cohumulone (+O)	
90	31.19	393.1912	C <sub>21</sub> H <sub>30</sub> O <sub>7</sub>	<i>n</i> - or adhumulone (+2O)	
91	31.40	363.1807	C <sub>20</sub> H <sub>28</sub> O <sub>6</sub>	cohumulone (+O)	<b>5a</b>
92	31.91	365.1963	C <sub>20</sub> H <sub>30</sub> O <sub>6</sub>	cohumulone (+H <sub>2</sub> O)	
	31.91	359.1858	C <sub>21</sub> H <sub>28</sub> O <sub>5</sub>	<i>n</i> - or adhumulone (-2H)	
93	32.22	365.1959	C <sub>20</sub> H <sub>30</sub> O <sub>6</sub>	cohumulone (+H <sub>2</sub> O)	
	32.22	359.1855	C <sub>21</sub> H <sub>28</sub> O <sub>5</sub>	<i>n</i> - or adhumulone (-2H)	
	32.22	377.1960	C <sub>21</sub> H <sub>30</sub> O <sub>6</sub>	<i>n</i> - or adhumulone (+O)	



**Table S1. (continued)**

94	32.91	349.2014	C <sub>20</sub> H <sub>30</sub> O <sub>5</sub>	<i>n</i> - or adhulupone (+H <sub>2</sub> O)	
	32.91	377.1962	C <sub>21</sub> H <sub>30</sub> O <sub>6</sub>	<i>n</i> - or adhumulone (+O)	
	32.91	437.2174	C <sub>23</sub> H <sub>34</sub> O <sub>8</sub>	possible minor congener of $\alpha$ -acids <sup>g</sup> (+3O)	
	32.91	395.2066	C <sub>21</sub> H <sub>32</sub> O <sub>7</sub>	<i>n</i> - or adhumulone (+O, +H <sub>2</sub> O)	
	32.91	409.1859	C <sub>21</sub> H <sub>30</sub> O <sub>8</sub>	<i>n</i> - or adhumulone (+3O)	
95	33.58	365.1961	C <sub>20</sub> H <sub>30</sub> O <sub>6</sub>	<i>n</i> - or adhulupone (+O, +H <sub>2</sub> O)	
	33.58	347.1856	C <sub>20</sub> H <sub>28</sub> O <sub>5</sub>	cohumulone (isomerization)	<b>3a</b>
	33.58	377.1960	C <sub>21</sub> H <sub>30</sub> O <sub>6</sub>	<i>n</i> - or adhumulone (+O)	
96	33.87	359.1856	C <sub>21</sub> H <sub>28</sub> O <sub>5</sub>	<i>n</i> - or adhumulone (−2H)	
	33.87	333.1701	C <sub>19</sub> H <sub>26</sub> O <sub>5</sub>	posthumulone <sup>d</sup> (isomerization)	
97	34.13	377.1962	C <sub>21</sub> H <sub>30</sub> O <sub>6</sub>	adhumulone (+O)	<b>5c<sup>f</sup></b>
	34.13	347.1856	C <sub>20</sub> H <sub>28</sub> O <sub>5</sub>	cohumulone (isomerization)	<b>4a</b>
	34.13	387.1803	C <sub>22</sub> H <sub>28</sub> O <sub>6</sub>	prehumulone <sup>e</sup> (+O, −4H)	
98	34.77	317.1752	C <sub>19</sub> H <sub>26</sub> O <sub>4</sub>	cohulupone	<b>12a</b>
99	35.16	377.1962	C <sub>21</sub> H <sub>30</sub> O <sub>6</sub>	adhumulone (+O)	<b>5c<sup>ff</sup></b>
100	35.60	377.1964	C <sub>21</sub> H <sub>30</sub> O <sub>6</sub>	<i>n</i> -humulone (+O)	<b>5b</b>
101	35.91	365.1962	C <sub>20</sub> H <sub>30</sub> O <sub>6</sub>	cohumulone (+H <sub>2</sub> O)	
102	36.63	347.1857	C <sub>20</sub> H <sub>28</sub> O <sub>5</sub>	cohumulone (isomerization)	
103	37.84	277.1441	C <sub>16</sub> H <sub>22</sub> O <sub>4</sub>	prehumulone <sup>e</sup> (−methylpentenoyl group, −2H)	
	37.84	361.2014	C <sub>21</sub> H <sub>30</sub> O <sub>5</sub>	<i>n</i> - and adhumulone (isomerization)	<b>3b, 3c</b>
104	38.25	361.2016	C <sub>21</sub> H <sub>30</sub> O <sub>5</sub>	<i>n</i> - and adhumulone (isomerization)	<b>4b, 4c</b>
105	39.04	331.1910	C <sub>20</sub> H <sub>28</sub> O <sub>4</sub>	<i>n</i> - and adhulupone	<b>12b, 12c</b>
	39.04	363.1808	C <sub>20</sub> H <sub>28</sub> O <sub>6</sub>	cohumulone (+O)	
106	39.92	379.2119	C <sub>21</sub> H <sub>32</sub> O <sub>6</sub>	<i>n</i> - or adhumulone (+H <sub>2</sub> O)	
107	40.26	377.1964	C <sub>21</sub> H <sub>30</sub> O <sub>6</sub>	<i>n</i> - or adhumulone (+O)	

<sup>a</sup>Shown in Fig. 3B.<sup>b</sup>Indicated by observed accurate *m/z*.<sup>c</sup>Possible reactions to yield the molecule are given in parentheses.<sup>d</sup>A minor congener of  $\alpha$ -acids, which possesses a propanoyl side chain.<sup>e</sup>A minor congener of  $\alpha$ -acids, which possesses an isohexanoyl side chain.

<sup>f</sup>Each of the following compounds exists as two diastereomers: adhumulinone [adhumulinone A (**5c**) and adhumulinone B (**5c'**)]; 4'-hydroxyalloadhumulinone [4'-hydroxyalloadhumulinone A (**6c**) and 4'-hydroxyalloadhumulinone B (**6c'**)]; 4'-hydroxyallo-*cis*-adhumulinone [4'-hydroxyallo-*cis*-adhumulinone A (**7c**) and 4'-hydroxyallo-*cis*-adhumulinone B (**7c'**)]; and *cis*-oxyadhumulinic acid [*cis*-oxyadhumulinic acid A (**8c**) and *cis*-oxyadhumulinic acid B (**8c'**)].

<sup>g</sup>A possible minor congener of  $\alpha$ -acids, which possesses an isoheptanoyl side chain.