

**Table S1:** The limits of detection (LOD) and quantification (LOQ) for internal standard (Fluoranthene-D10)

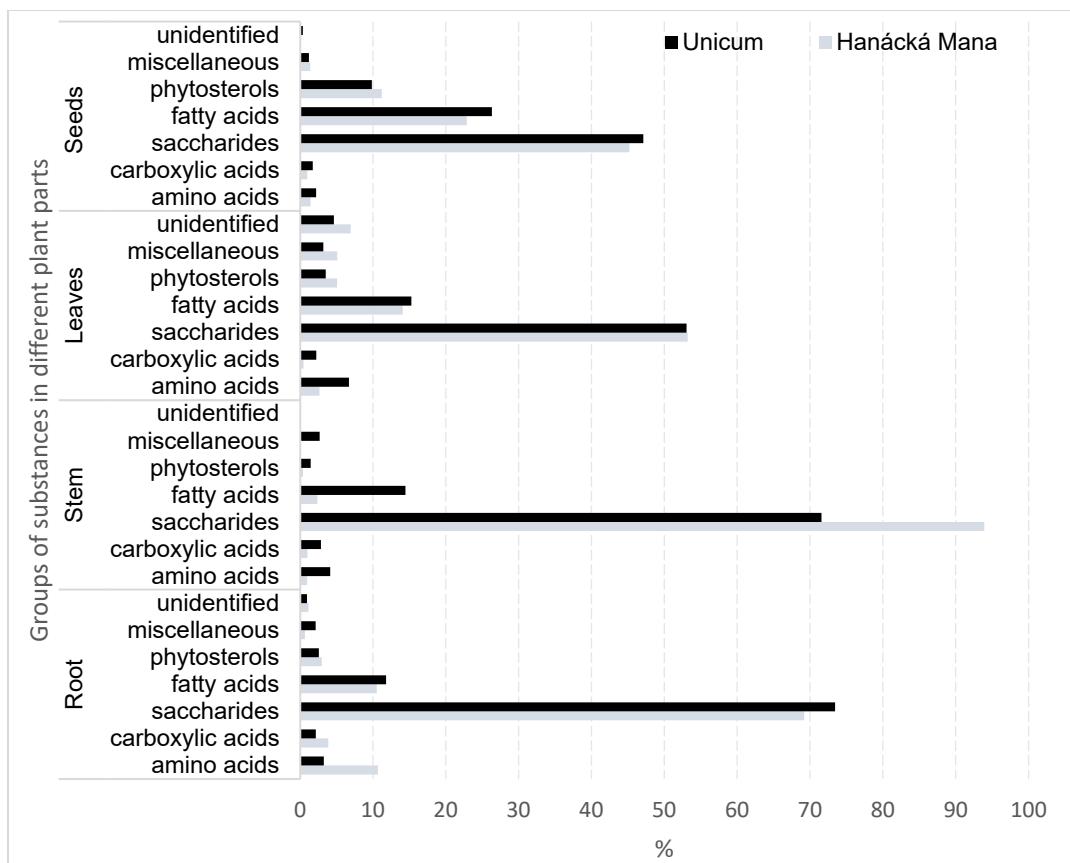
Variety	Hanácká Mana				Unicum			
Plant part	roots	stems	leaves	seeds	roots	stems	leaves	seeds
S/N	401	297	211	653	306	339	241	405
Area	20753371	25539484	30916506	28529223	22825276	30340553	28782286	22789320
LOD [ng/ml]	8.90	12.02	16.92	5.47	11.67	10.53	14.81	8.81
LOQ [ng/ml]	29.68	40.07	56.40	18.22	38.89	35.10	49.38	29.38

c(IS) = 1.19 ug/ml of extract

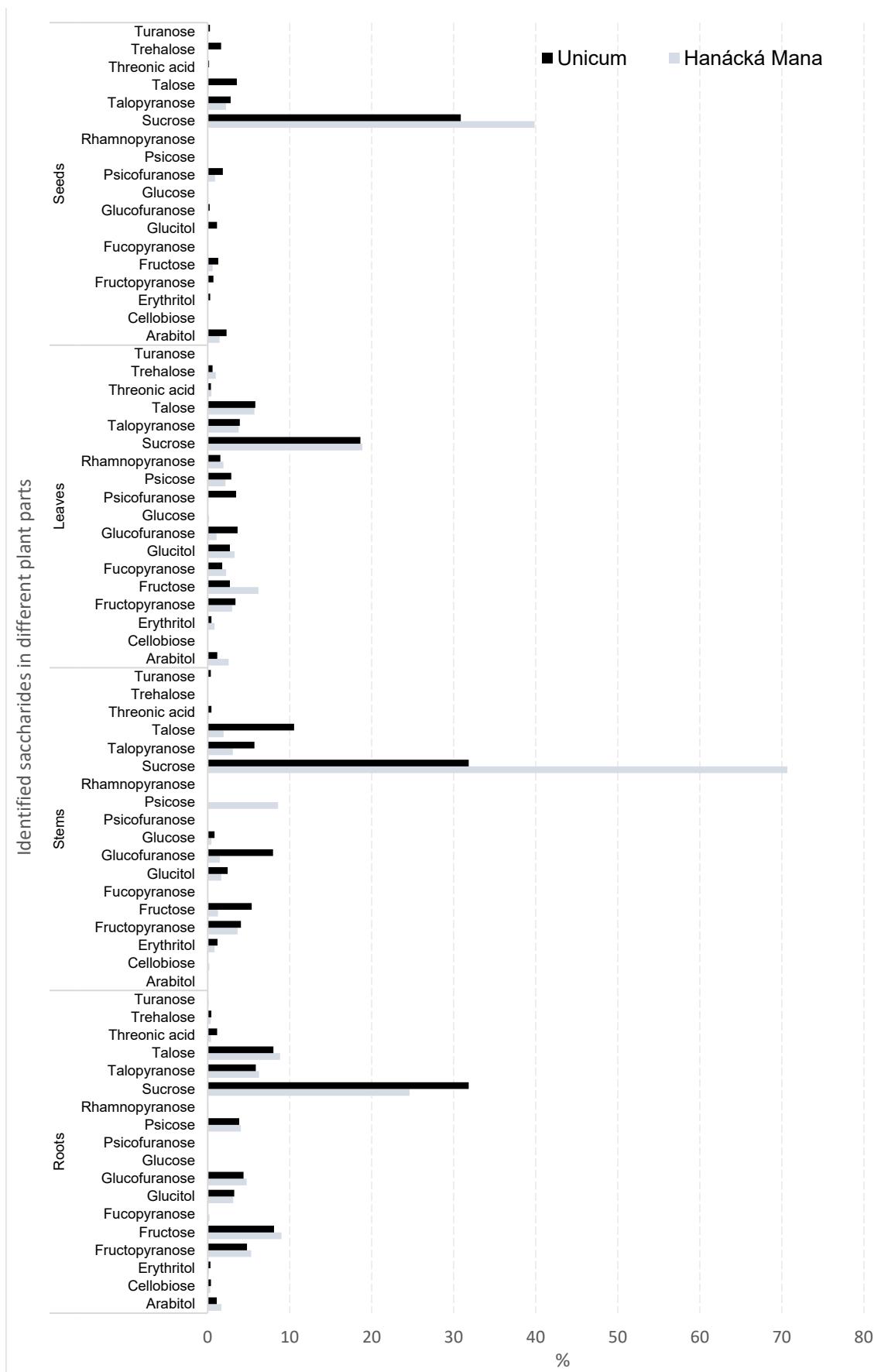
**Table S2:** Components identified in proso millet

RT (min)	Compound	Molecular Formlua	MW	MF
4.15	Alanin-2TMS	C <sub>9</sub> H <sub>23</sub> NO <sub>2</sub> Si <sub>2</sub>	233.46	919
4.64	Valin-2TMS	C <sub>11</sub> H <sub>27</sub> NO <sub>2</sub> Si <sub>2</sub>	261.51	916
4.82	Glycerol-3TMS	C <sub>12</sub> H <sub>32</sub> O <sub>3</sub> Si <sub>3</sub>	308.64	897
4.84	Phosphoric acid-3TMS	C <sub>15</sub> H <sub>41</sub> O <sub>6</sub> PSi <sub>4</sub>	460.80	909
4.94	Isoleucin-2TMS	C <sub>12</sub> H <sub>29</sub> NO <sub>2</sub> Si <sub>2</sub>	275.54	871
4.99	Proline-2TMS	C <sub>11</sub> H <sub>25</sub> NO <sub>2</sub> Si <sub>2</sub>	259.50	772
5.01	Succinic acid-2TMS	C <sub>10</sub> H <sub>22</sub> O <sub>4</sub> Si <sub>2</sub>	266.00	873
5.15	Fumaric acid-2TMS	C <sub>10</sub> H <sub>20</sub> O <sub>4</sub> Si <sub>2</sub>	260.44	894
5.18	Serin-3TMS	C <sub>12</sub> H <sub>31</sub> NO <sub>3</sub> Si <sub>3</sub>	321.64	920
5.3	Threonin-3TMS	C <sub>13</sub> H <sub>33</sub> NO <sub>3</sub> Si <sub>3</sub>	335.66	890
5.73	Malic acid-3TMS	C <sub>13</sub> H <sub>30</sub> O <sub>5</sub> Si <sub>3</sub>	350.63	931
5.82	mezo-Erythritol-4TMS	C <sub>16</sub> H <sub>42</sub> O <sub>4</sub> Si <sub>4</sub>	410.85	919
5.98	Pyroglutamic acid-2TMS	C <sub>11</sub> H <sub>23</sub> NO <sub>3</sub> Si <sub>2</sub>	273.48	896
6.07	Threonic acid-4TMS	C <sub>16</sub> H <sub>40</sub> O <sub>5</sub> Si <sub>4</sub>	424.83	862
6.47	Rhamnopyranose-4TMS	C <sub>18</sub> H <sub>44</sub> O <sub>5</sub> Si <sub>4</sub>	452.88	910
6.57	Phenylalanine-2TMS	C <sub>15</sub> H <sub>27</sub> NO <sub>2</sub> Si <sub>2</sub>	309.55	884
6.68	Lauric acid-TMS (Dodecanoic)	C <sub>15</sub> H <sub>32</sub> O <sub>2</sub> Si	272.50	880
6.93	Fucose/Fucopyranose-4TMS	C <sub>18</sub> H <sub>44</sub> O <sub>5</sub> Si <sub>4</sub>	452.88	885
7.05	Arabitol-5TMS	C <sub>20</sub> H <sub>52</sub> O <sub>5</sub> Si <sub>5</sub>	513.05	924
7.09	Pentahydroxycyclohexanone-5TMS	C <sub>21</sub> H <sub>50</sub> O <sub>6</sub> Si <sub>5</sub>	539.04	707
7.32	Phosphoric acid, 2,3-bis(trimethylsiloxy)propyl bis(trimethylsilyl) ester	C <sub>15</sub> H <sub>41</sub> O <sub>6</sub> PSi <sub>4</sub>	460.80	820
7.47	Glutamine-3TMS	C <sub>14</sub> H <sub>34</sub> N <sub>2</sub> O <sub>3</sub> Si <sub>3</sub>	362.69	868
7.69	Fructofuranose-5TMS	C <sub>21</sub> H <sub>52</sub> O <sub>6</sub> Si <sub>5</sub>	541.06	923
7.74	Psicofuranose-5TMS	C <sub>21</sub> H <sub>52</sub> O <sub>6</sub> Si <sub>5</sub>	541.06	900
7.87	Fructopyranose-5TMS	C <sub>21</sub> H <sub>52</sub> O <sub>6</sub> Si <sub>5</sub>	541.06	890
7.98	Glucofuranose-5TMS	C <sub>6</sub> H <sub>12</sub> O <sub>6</sub> Si <sub>5</sub>	320.58	< 700
8.15	Tetradecanoic acid-TMS	C <sub>17</sub> H <sub>36</sub> O <sub>2</sub> Si	300.60	832

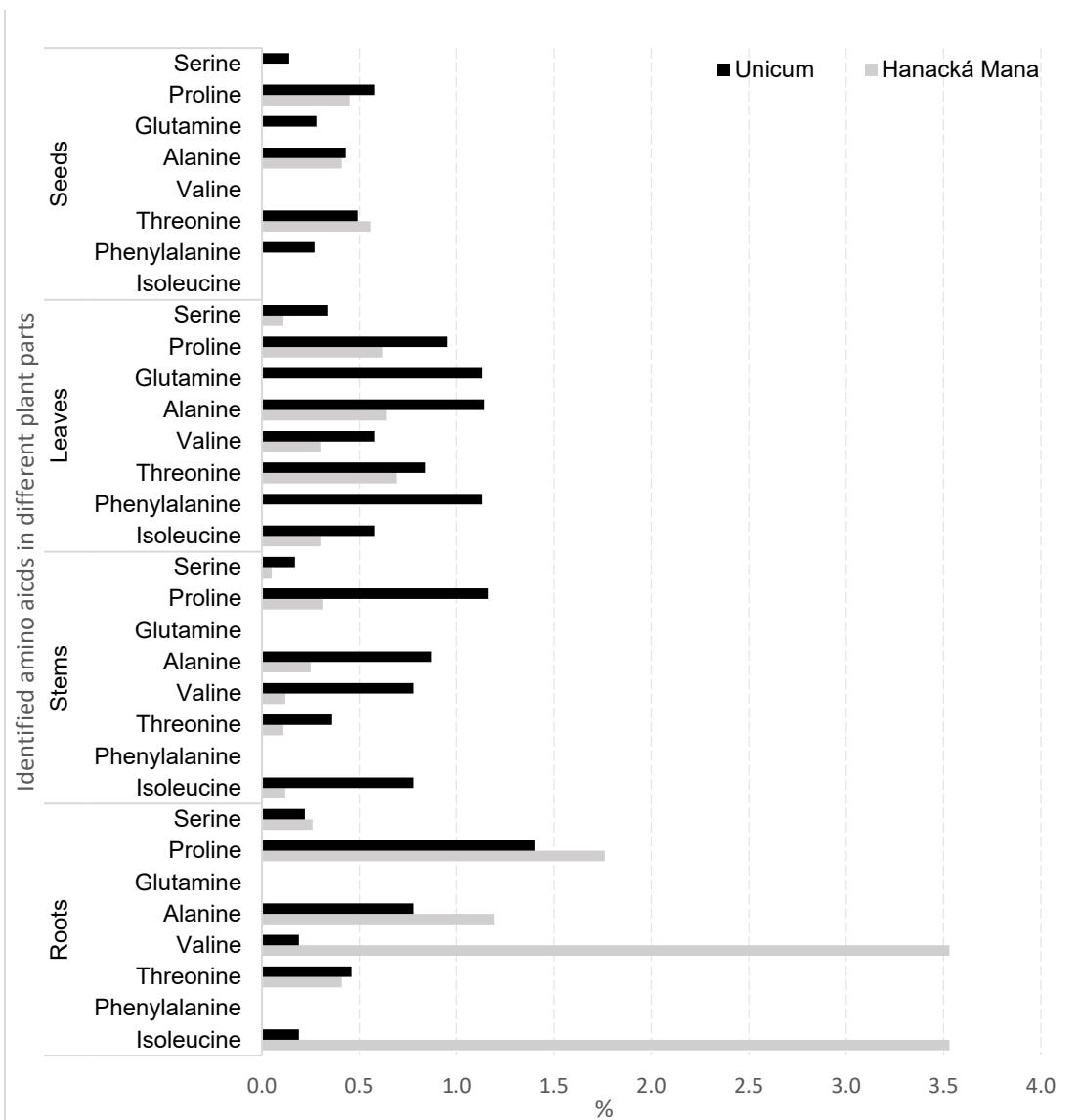
8.44	Psicose-5TMS	C <sub>21</sub> H <sub>52</sub> O <sub>6</sub> Si <sub>5</sub>	541.06	875
8.49	Talose-5TMS	C <sub>21</sub> H <sub>52</sub> O <sub>6</sub> Si <sub>5</sub>	541.10	904
8.87	Sorbitol-6TMS	C <sub>24</sub> H <sub>62</sub> O <sub>6</sub> Si <sub>6</sub>	615.26	907
8.94	Glucose-5TMS	C <sub>21</sub> H <sub>52</sub> O <sub>6</sub> Si <sub>5</sub>	541.06	
9.04	Cinnamic acid-2TMS	C <sub>15</sub> H <sub>24</sub> O <sub>3</sub> Si <sub>2</sub>	308.52	864
9.28	Talose/Talopyranose-5TMS	C <sub>21</sub> H <sub>52</sub> O <sub>6</sub> Si <sub>5</sub>	541.06	913
10.15	Palmitic acid-TMS	C <sub>19</sub> H <sub>40</sub> O <sub>2</sub> Si	328.61	893
11.71	Tetramethyl-2-hexadecene-1-ol-TMS	C <sub>23</sub> H <sub>48</sub> OSi	368.71	928
12.20	Linoleic acid-TMS	C <sub>21</sub> H <sub>38</sub> O <sub>2</sub> Si	350.61	889
12.27	Octadecenoic acid	C <sub>18</sub> H <sub>34</sub> O <sub>2</sub>	282.50	796
12.61	Stearic acid-TMS	C <sub>21</sub> H <sub>44</sub> O <sub>2</sub> Si	356.66	923
14.00	Retinal	C <sub>20</sub> H <sub>28</sub> O	284.44	729
15.30	Eicosanoic acid-TMS	C <sub>23</sub> H <sub>48</sub> O <sub>2</sub> Si	384.71	852
16.43	Sucrose-8TMS	C <sub>36</sub> H <sub>86</sub> O <sub>11</sub> Si <sub>8</sub>	919.75	882
17.37	Sucrose-8TMS	C <sub>36</sub> H <sub>86</sub> O <sub>11</sub> Si <sub>8</sub>	919.75	856
18.08	Sucrose-8TMS	C <sub>36</sub> H <sub>86</sub> O <sub>11</sub> Si <sub>8</sub>	919.75	930
19.13	Turanose-8TMS	C <sub>36</sub> H <sub>86</sub> O <sub>11</sub> Si <sub>8</sub>	919.75	801
19.24	Cellobiose-8TMS	C <sub>36</sub> H <sub>86</sub> O <sub>11</sub> Si <sub>8</sub>	919.75	< 700
19.52	Trehalose-8TMS	C <sub>36</sub> H <sub>86</sub> O <sub>11</sub> Si <sub>8</sub>	919.75	913
19.62	Linoleic acid, 1,3-bis-(O-TMS)-2-propyl ester	C <sub>27</sub> H <sub>54</sub> O <sub>4</sub> Si <sub>2</sub>	498.9	719
19.66	Aucubin-6TMS	C <sub>33</sub> H <sub>70</sub> O <sub>9</sub> Si <sub>6</sub>	779.41	758
20.51	Squalene	C <sub>30</sub> H <sub>50</sub>	410.72	795
20.77	Tetracosanoic acid-TMS	C <sub>27</sub> H <sub>56</sub> O <sub>2</sub> Si	440.80	828
22.57	1-Glyceryl mono-eicosanoate-2TMS	C <sub>29</sub> H <sub>62</sub> O <sub>4</sub> Si <sub>2</sub>	530.97	682
22.84	Tocopherol-TMS	C <sub>32</sub> H <sub>58</sub> O <sub>2</sub> Si	502.90	893
23.40	Hexacosanoic acid-TMS	C <sub>29</sub> H <sub>60</sub> O <sub>2</sub> Si	468.90	823
24.96	Tocopherol-TMS	C <sub>32</sub> H <sub>58</sub> O <sub>2</sub> Si	502.89	912
25.06	Cholesterol-TMS	C <sub>30</sub> H <sub>54</sub> OSi	458.84	897
26.94	Campesterol-TMS	C <sub>31</sub> H <sub>56</sub> OSi	472.86	870
27.31	Miliacin	C <sub>31</sub> H <sub>52</sub> O	440.70	811
27.47	Stigmasterol-TMS	C <sub>32</sub> H <sub>56</sub> OSi	484.87	918
28.79	$\beta$ -Sitosterol-TMS	C <sub>32</sub> H <sub>58</sub> OSi	486.89	901
29.07	Triacontoxy-TMS	C <sub>33</sub> H <sub>70</sub> OSi	510.99	746
29.32	Amyrin_TMS	C <sub>33</sub> H <sub>58</sub> OSi	498.90	860
29.53	Germanicol-TMS	C <sub>33</sub> H <sub>58</sub> OSi	498.90	762
31.50	probably Triacontanoic acid-TMS	C <sub>33</sub> H <sub>68</sub> O <sub>2</sub> Si	524.98	< 700
35.12	Dotriacontyloxy-TMS	C <sub>35</sub> H <sub>74</sub> OSi	539.04	746



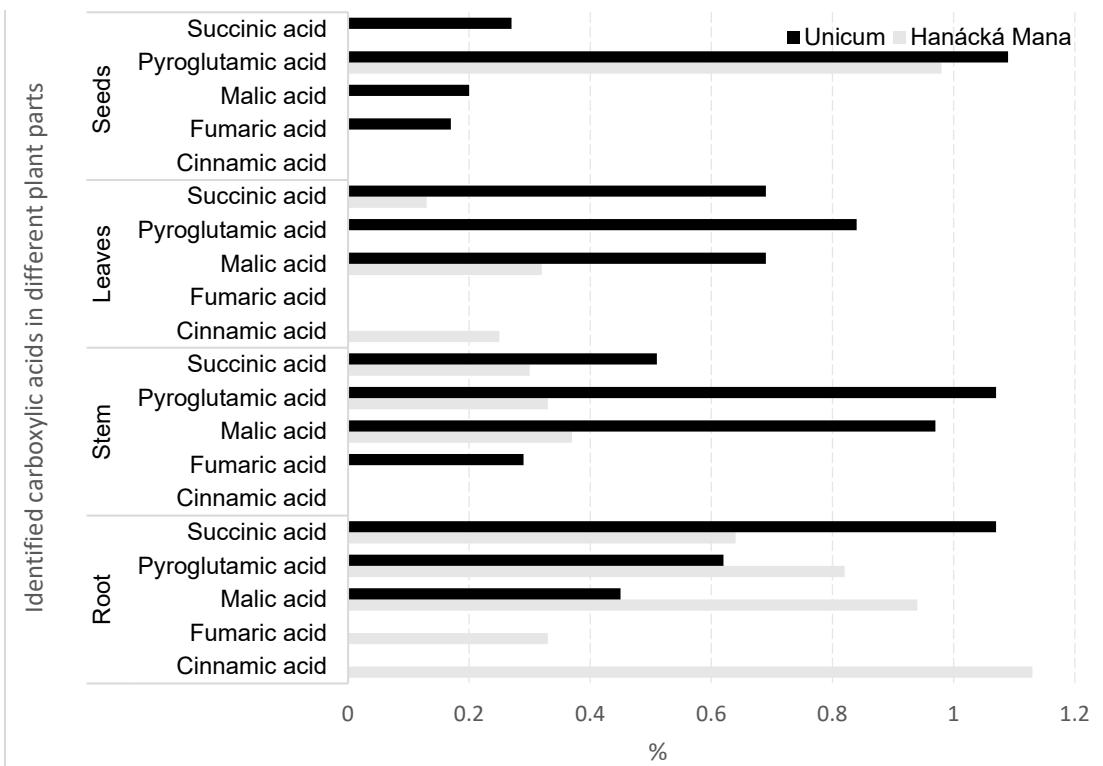
**Figure S1.** Comparison of the relative representation of the sums of the peak areas of the identified main groups of substances to the total area of all peaks (%) in Hanácká Mana and Unicum varieties of proso millet.



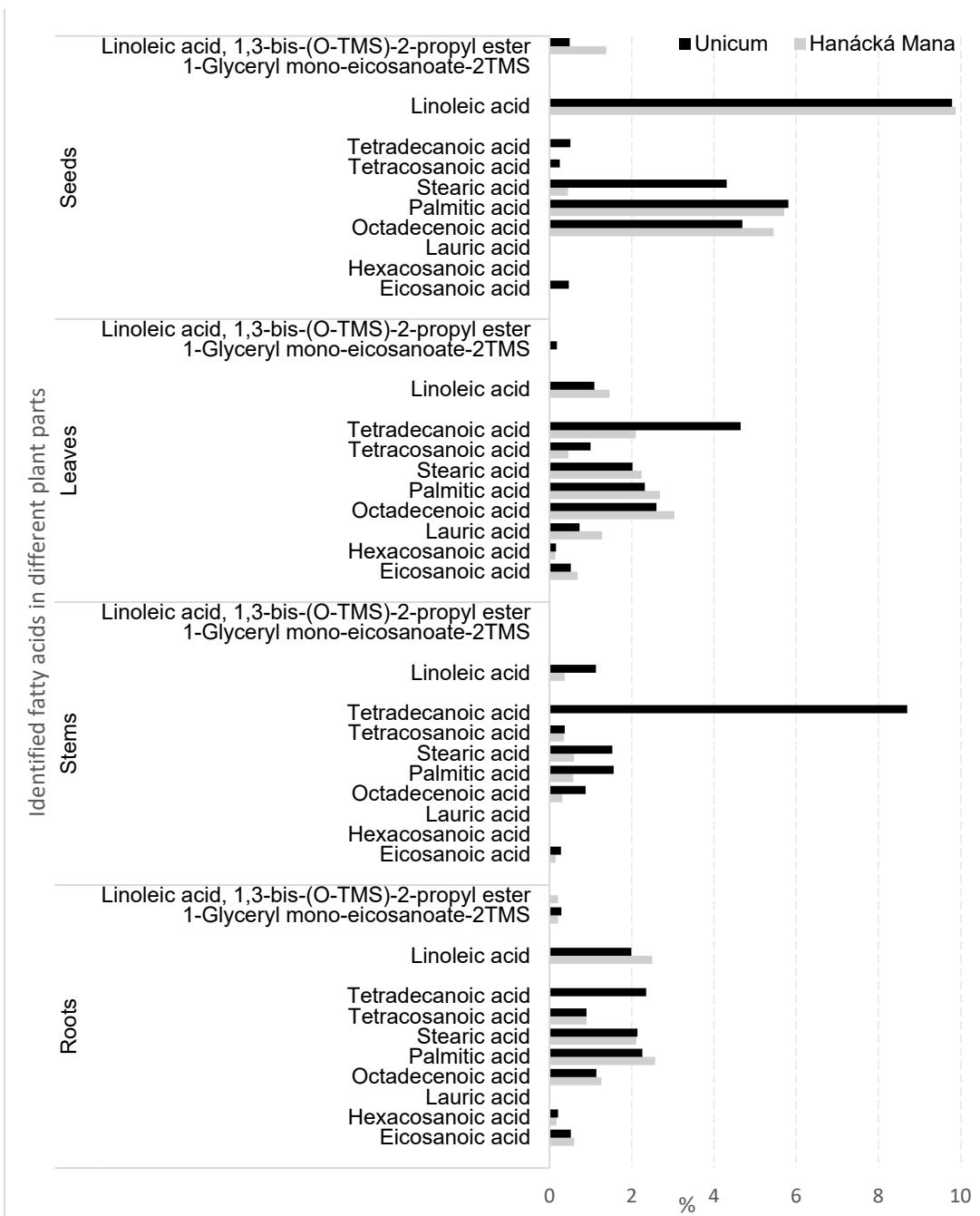
**Figure S2.** Comparison of the relative representation of the areas of individual peaks of the identified saccharides to the total area of all peaks (%) in Hanácká Mana and Unicum varieties of proso millet.



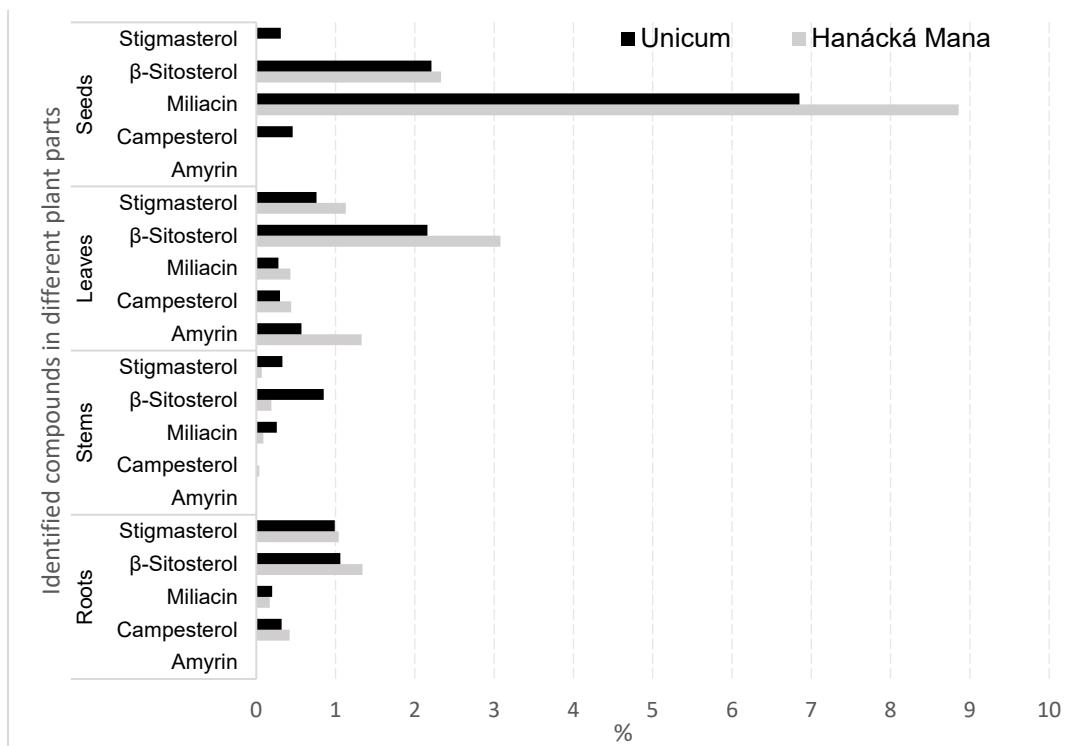
**Figure S3.** Comparison of the relative representation of the areas of individual peaks of identified amino acids to the total area of all peaks (%) in varieties Hanacká Mana and Unicum of proso millet.



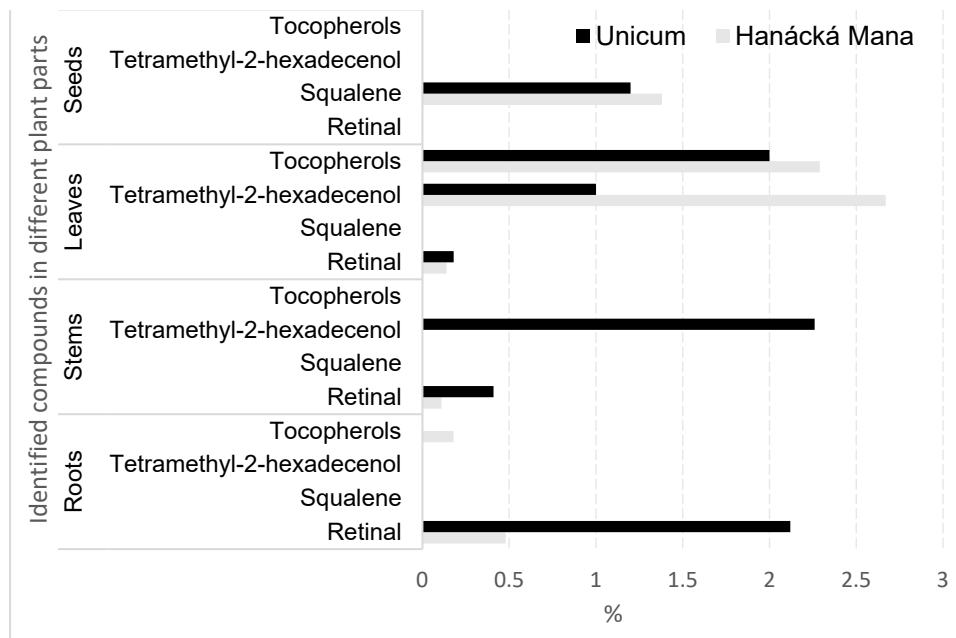
**Figure S4.** Comparison of the relative representation of the areas of individual peaks of identified carboxylic acids to the total area of all peaks (%) in varieties Hanácká Mana and Unicum of proso millet.



**Figure S5.** Comparison of the relative representation of the areas of individual peaks of identified fatty acids to the total area of all peaks (%) in varieties Hanácká Mana and Unicum of proso millet.



**Figure S6.** Comparison of the relative representation of the areas of individual peaks of identified phytosterols, amyrin and miliacin to the total area of all peaks (%) in varieties Hanácká Mana and Unicum of proso millet.



**Figure S7.** Comparison of the relative representation of the areas of individual peaks of identified miscellaneous compounds to the total area of all peaks (%) in varieties Hanácká Mana and Unicum of proso millet.