Supplementary Material

1. Norway spruce balm samples

| Batch # | Date of harvest | Harvest location                | Commercial product | Batch # | Expiration date | Storage conditions |
|---------|-----------------|--------------------------------|-------------------|---------|-----------------|--------------------|
| NSB01 - NSB08 | 09.07.2016   | Promau Kitzhütte, Hollenstein, Lower Austria | NSB-CP1          | 552026 | 06/21           | stored at room temperature |
| NSB09 - NSB12 | 03.07.2016   | Gaflenz Heiligenstein, Upper Austria         | NSB-CP2          | 552014 | 01/19           | stored at room temperature |
| NSB13 | 2015            | Lungau, Salzburg                       | NSB-CP3          | 552014 | 01/19           | stored at 2 – 8°C |
| NSB14 | 15.05.2016      | Zillingtaler Wald, Burgenland            | NSB-CP4          | 160301 | 03/20           | stored at room temperature |
| NSB15 | 15.05.2016      |                                   | NSB-CP5          | 160301 | 03/20           | stored at 2 – 8°C |
| NSB16 | Spring 2016     | Pinsdorf, Upper Austria                |                   |        |                 |                    |
| NSB17 | 10.07.2015      | unknown                               |                   |        |                 |                    |
| NSB18 | 24.08.2016      | Lungau, Salzburg                       |                   |        |                 |                    |
| NSB19 | Harvest 2010-2016 | Austria                                |                   |        |                 |                    |
| NSB20 | Harvest 2010-2016 | Austria                                |                   |        |                 |                    |
| NSB21 | Harvest 2010-2016 | Austria                                |                   |        |                 |                    |
| NSB22 | 23.08.2017      | Lungau, Salzburg                       |                   |        |                 |                    |

Supplementary Table S1. Details for Norway Spruce Balm Samples NSB01-22 and Commercial Products Samples
2. Sample chromatogram

Supplementary Figure S1. PDA chromatogram of spruce balm sample NSB20 (at 215 nm) and UHPSFC-ESI-MS Extracted Ion Chromatograms (negative mode, 299 and 301 Da) of diterpene resin acids. Compound 1: Pimaric acid, 2: Sandaracopimaric acid (sample: sandarac resin), 3: Palustric acid, 4: Isopimaric acid, 5: Levopimaric acid, 6: Abietic acid, 8: Neoabietic acid
3. Validation

3.1. Sandarac resin

Supplementary Figure S2. GC-FID chromatogram of spruce balm sample NSB22 and sandarac resin. Compound 2: sandaracopimaric acid. GC-System Shimadzu GC-2010: stationary phase ZB-5 Zebron, 60 m, 0.25 mm, 0.25 µm; mobile phase: He (5.0), flow: 50 ml/min; temperature program: 5 min 100°C, 100-200°C rate 15°C/min, 200-250°C rate 2°C/min; injection volume: 1 µl, split ratio 1:100; detection: synthetic air (5.0), H₂ (5.0)

Supplementary Figure S3. Detailed section (RT 28.5-45 min) of GC-FID chromatogram of spruce balm sample NSB22 and sandarac resin. Compound 2: sandaracopimaric acid. GC-System Shimadzu GC-2010: stationary phase ZB-5 Zebron, 60 m, 0.25 mm, 0.25 µm; mobile phase: He (5.0), flow: 50
ml/min; temperature program: 5 min 100°C, 100-200°C rate 15°C/min, 200-250°C rate 2°C/min; injection volume: 1 µl, split ratio 1:100; detection: synthetic air (5.0), H₂ (5.0)

3.2. Linearity

![Linearity curve DHAA](image)

**Supplementary Figure S4.** Linearity curve of dehydroabiabetic acid

| c [mg/ml] | Run | RT [min] | Area       | Mean       |
|-----------|-----|----------|------------|------------|
| 7.335     | 1   | 13.725   | 475 897 268| 466 371 025|
|           | 2   | 13.738   | 419 734 916|            |
|           | 3   | 13.726   | 503 480 890|            |
| 2.445     | 1   | 13.766   | 255 190 971| 257 088 347|
|           | 2   | 13.760   | 257 112 675|            |
|           | 3   | 13.766   | 258 961 397|            |
| 0.7335    | 1   | 13.812   | 73 152 487 | 72 593 616 |
|           | 2   | 13.823   | 72 625 126 |            |
|           | 3   | 13.808   | 72 003 234 |            |
| 0.2445    | 1   | 13.870   | 19 252 645 | 20 360 947 |
|           | 2   | 13.884   | 20 679 791 |            |
|           | 3   | 13.874   | 21 150 404 |            |
| 0.07335   | 1   | 13.901   | 7 228 218  | 7 234 994  |
|           | 2   | 13.914   | 7 313 775  |            |
|           | 3   | 13.904   | 7 162 989  |            |
### Supplementary Table S2

Experimental data for the calculation of the linearity curve of dehydroabietic acid

| c [mg/ml] | Run | RT [min] | Area        | Mean       |
|-----------|-----|----------|-------------|------------|
| 7.5       | 1   | 13.917   | 499795141   | 498 286 885 |
|           | 2   | 13.916   | 498704548   |            |
|           | 3   | 13.914   | 496360967   |            |
| 2.5       | 1   | 13.929   | 252165844   | 251 661 129 |
|           | 2   | 13.931   | 251317481   |            |
|           | 3   | 13.931   | 251500063   |            |

### Supplementary Figure S5

Linearity curve of neoabietic acid

\[ y = 1E+08x - 70000 \]
\[ R^2 = 0.9966 \]
| Concentration | 1st run | 2nd run | 3rd run |
|---------------|---------|---------|---------|
| 0.75          | 61 879 886 | 61 778 821 | 61 505 179 |
| 0.25          | 20 945 889 | 21 217 309 | 20 947 667 |
| 0.075         | 6 827 319 | 6 764 087 | 6 812 575 |
| 0.025         | 2 145 625 | 2 162 849 | 2 100 747 |
| 0.0075        | 729 842  | 74 863 5 | 73 179 3 |
| 0.0025        | 368 469  | 368 446  | 357 978  |
| 0.00075       | 74 350   | 75 606   | 74 542   |

**Supplementary Table S3.** Experimental data for the calculation of the linearity curve of neoabietic acid

### 3.3. Specificity

| Reference substances | Extrak. Ion | Extract | Deviation |
|----------------------|------------|---------|-----------|
| Resin acid           | RT [min]   | Peak number | RT [min] | [min]    |
| Pimaric acid         | 12.072     | 301^-     | 12.160   | -0.088  |
| Sandaracopimaric acid* | 12.387     | 301^-     | 12.313   | 0.074   |
| Palustric acid       | 12.477     | 301^-     | 12.508   | -0.031  |
| Isopimaric acid      | 12.792     | 301^-     | 12.801   | -0.009  |
| Levopimaric acid     | 13.064     | 301^-     | 12.963   | 0.101   |
| Abietic acid         | 13.586     | 301^-     | 13.575   | 0.011   |
| Dehydroabietic acid  | 13.873     | 299^-     | 13.885   | -0.012  |
| Neoabietic acid      | 14.024     | 301^-     | 13.975   | 0.049   |

*Sandarac extract was tested

**Supplementary Table S4.** References of the resin acids were compared to the respective constituent of *Picea abies* balm extract NSB22. The deviation of the reference substance to the resin acid of the extract was calculated.
### 3.4. Accuracy

|                | DHAA Area | Recovery rate |
|----------------|-----------|---------------|
| **1**          |           |               |
| NSB22 2mg/ml   | 20 352 108|               |
| DHAA 0.183 mg/ml | 10 933 543|               |
| DHAA 0.244 mg/ml | 15 036 184|               |
| DHAA 0.305 mg/ml | 18 396 690|               |
| NSB22 2 mg/ml+DHAA 0.183 mg/ml | 32 220 874 | **97.1** |
| NSB22 2 mg/ml+DHAA 0.244 mg/ml | 38 094 500 | **92.9** |
| NSB22 2 mg/ml+DHAA 0.305 mg/ml | 43 683 516 | **88.7** |
| **2**          |           |               |
| NSB22 2mg/ml   | 19 722 408|               |
| DHAA 0.183 mg/ml | 10 802 031|               |
| DHAA 0.244 mg/ml | 15 237 185|               |
| DHAA 0.305 mg/ml | 17 770 642|               |
| NSB22 2 mg/ml+DHAA 0.183 mg/ml | 31 473 598 | **97.0** |
| NSB22 2 mg/ml+DHAA 0.244 mg/ml | 37 361 626 | **93.6** |
| NSB22 2 mg/ml+DHAA 0.305 mg/ml | 43 739 038 | **85.7** |
| **3**          |           |               |
| NSB22 2mg/ml   | 19 531 898|               |
| DHAA 0.183 mg/ml | 10 768 794|               |
| DHAA 0.244 mg/ml | 14 706 166|               |
| DHAA 0.305 mg/ml | 17 849 075|               |
| NSB22 2 mg/ml+DHAA 0.183 mg/ml | 31 312 698 | **96.8** |
| NSB22 2 mg/ml+DHAA 0.244 mg/ml | 36 838 298 | **92.9** |
| NSB22 2 mg/ml+DHAA 0.305 mg/ml | 43 734 973 | **85.5** |
| **Mean**       |           |               |
| NSB22 2mg/ml   | 19 868 805|               |
| DHAA 0.183 mg/ml | 10 834 789|               |
| DHAA 0.244 mg/ml | 14 993 178|               |
| DHAA 0.305 mg/ml | 18 005 469|               |
| NSB22 2 mg/ml+DHAA 0.183 mg/ml | 31 669 057 | **97.0** |
| NSB22 2 mg/ml+DHAA 0.244 mg/ml | 37 431 475 | **93.1** |
| NSB22 2 mg/ml+DHAA 0.305 mg/ml | 43 719 176 | **86.6** |

**Supplementary Table S5.** The spruce balm sample NSB22 was spiked with three different concentrations of dehydroabietic acid (DHAA) and analyzed in triplicates. The recovery rate of dehydroabietic acid in the spiked samples was calculated.
|                | NeoAA Area | Recovery rate |
|----------------|------------|---------------|
| NSB22 2 mg/ml  | 43 792     |               |
| NeoAA_0.0013 mg/ml | 66 768     |               |
| NeoAA_0.00174 mg/ml | 93 922     |               |
| NeoAA_0.0022 mg/ml | 124 029    |               |
| NSB22 2 mg/ml+NeoAA_0.0013 mg/ml | 113 330    | 102.5         |
| NSB22 2 mg/ml+NeoAA_0.00174 mg/ml | 161 836    | 117.5         |
| NSB22 2 mg/ml+NeoAA_0.0022 mg/ml | 193 022    | 115.0         |
| NSB22 2 mg/ml  | 41 530     |               |
| NeoAA_0.0013 mg/ml | 67 831     |               |
| NeoAA_0.00174 mg/ml | 111 900    |               |
| NeoAA_0.0022 mg/ml | 148 402    |               |
| NSB22 2 mg/ml+NeoAA_0.0013 mg/ml | 121 101    | 110.7         |
| NSB22 2 mg/ml+NeoAA_0.00174 mg/ml | 157 672    | 102.8         |
| NSB22 2 mg/ml+NeoAA_0.0022 mg/ml | 202 629    | 106.7         |
| NSB22 2 mg/ml  | 48 613     |               |
| NeoAA_0.0013 mg/ml | 72 781     |               |
| NeoAA_0.00174 mg/ml | 102 771    |               |
| NeoAA_0.0022 mg/ml | 140 906    |               |
| NSB22 2 mg/ml+NeoAA_0.0013 mg/ml | 120 861    | 99.6          |
| NSB22 2 mg/ml+NeoAA_0.00174 mg/ml | 147 631    | 97.5          |
| NSB22 2 mg/ml+NeoAA_0.0022 mg/ml | 194 101    | 102.4         |
| NSB22 2 mg/ml  | 44 645     |               |
| NeoAA_0.0013 mg/ml | 69 127     |               |
| NeoAA_0.00174 mg/ml | 102 864    |               |
| NeoAA_0.0022 mg/ml | 137 779    |               |
| NSB22 2 mg/ml+NeoAA_0.0013 mg/ml | 118 431    | 104.1         |
| NSB22 2 mg/ml+NeoAA_0.00174 mg/ml | 155 713    | 105.6         |
| NSB22 2 mg/ml+NeoAA_0.0022 mg/ml | 196 584    | 107.8         |

**Supplementary Table S6.** The spruce balm sample NSB22 was spiked with three different concentrations of neoabietic acid (NeoAA) and analyzed in triplicates. The recovery rate of neoabietic acid in the spiked samples was calculated.
3.5. Precision – Repeatability

| Concentration (mg/ml) | Run 1 | Run 2 | Run 3 | Mean | SD | RSD |
|-----------------------|-------|-------|-------|------|----|-----|
|                       | RT    | Area  | RT    | Area | RT | Area |
| 0.625                 |       |       |       |      |    |     |
| 1                     | 11.947| 100 734| 12.000| 99 370| 12.032| 96 899| 99 001| 1 587| 1.6 |
| 2                     | 12.122| 358 872| 12.180| 373 379| 12.166| 384 815| 372 355| 10 616| 2.9 |
| 3                     | 12.199| 119 338| 12.261| 105 639| 12.256| 123 405| 116 127| 7 600| 6.5 |
| 4                     | 12.637| 552 477| 12.676| 549 646| 12.690| 564 260| 555 461| 6 328| 1.1 |
| 5                     | 12.719| 204 037| 12.786| 195 530| 12.789| 198 150| 199 239| 3 557| 1.8 |
| 6                     | 13.487| 41 983 | 13.475| 38 784| 13.522| 44 494| 41 754| 2 337| 5.6 |
| 7                     | 13.733| 4 729 646| 13.776| 4 777 050| 13.768| 4 809 858| 4 772 185| 32 927| 0.7 |
| 8                     | 13.799| 34 033 | 13.856| 30 066| 13.836| 34 935| 33 011| 2 115| 6.4 |

| Concentration (mg/ml) | Run 1 | Run 2 | Run 3 | Mean | SD | RSD |
|-----------------------|-------|-------|-------|------|----|-----|
|                       | RT    | Area  | RT    | Area | RT | Area |
| 1.250                 |       |       |       |      |    |     |
| 1                     | 11.743| 215 858| 11.932| 195 089| 11.950| 211 049| 207 332| 8 877| 4.3 |
| 2                     | 11.894| 760 452| 12.125| 804 084| 12.132| 741 675| 768 737| 26 143| 3.4 |
| 3                     | 11.962| 277 328| 12.199| 227 231| 12.196| 271 967| 258 842| 22 459| 8.7 |
| 4                     | 12.420| 1 202 828| 12.622| 1 122 395| 12.646| 1 191 860| 1 172 361| 35 614| 3.0 |
| 5                     | 12.507| 378 278| 12.726| 430 982| 12.743| 429 799| 413 020| 24 571| 5.9 |
| 6                     | 13.213| 65 718 | 13.462| 63 592| 13.416| 71 167| 66 826| 3 190| 4.8 |
| 7                     | 13.517| 9 894 656| 13.749| 9 827 699| 13.751| 10 048 112| 9 923 489| 92 264| 0.9 |
| 8                     | 13.603| 65 470 | 13.810| 62 235| 13.820| 75 362| 67 689| 5 584| 8.2 |

| Concentration (mg/ml) | Run 1 | Run 2 | Run 3 | Mean | SD | RSD |
|-----------------------|-------|-------|-------|------|----|-----|
|                       | RT    | Area  | RT    | Area | RT | Area |
| 1.875                 |       |       |       |      |    |     |
| 1                     | 11.926| 313 752| 11.927| 339 717| 11.921| 316 352| 323 274| 11 676| 3.6 |
| 2                     | 12.099| 1 120 618| 12.100| 1 112 769| 12.108| 1 128 706| 1 120 698| 6 506| 0.6 |
| 3                     | 12.156| 473 630| 12.159| 429 758| 12.169| 397 591| 433 660| 31 165| 7.2 |
| 4                     | 12.652| 1 933 482| 12.616| 1 777 968| 12.626| 1 824 312| 1 845 254| 65 192| 3.5 |
| 5                     | 12.719| 517 400| 12.706| 574 492| 12.716| 554 283| 548 725| 23 637| 4.3 |
| 6                     | 13.391| 108 108| 13.420| 101 959| 13.417| 124 673| 111 580| 9 592| 8.6 |
| 7                     | 13.722| 15 403 | 13.708| 15 179 091| 13.716| 14 747 474| 15 110 139| 272 365| 1.8 |
| 8                     | 13.793| 99 771 | 13.783| 102 051| 13.779| 108 963| 103 595| 3 908| 3.8 |

**Supplementary Table S7.** Three different concentrations of sample NSB22 were analyzed in triplicates to assess the repeatability. The relative standard deviation was calculated for each resin acid at each concentration (pimaric acid (1), sandaracopimaric acid (2), palustric acid (3), isopimaric acid (4), levopimaric acid (5), abietic acid (6), dehydroabietic acid (7), and neoabietic acid (8)).
3.5. Precision - Intermediate Precision

| 1,875 mg/ml | 1 - Day 1 | 1 - Day 2 | 1 - Day 3 | Mean | SD | RSD |
|-------------|----------|----------|----------|------|----|-----|
| | RT | Area | RT | Area | RT | Area | | |
| 1 | 12.233 | 351 699 | 12.221 | 339 092 | 12.169 | 307 323 | 332 705 | 18 671 | 5.6 |
| 2 | 12.399 | 1 550 033 | 12.390 | 1 462 874 | 12.329 | 1 197 898 | 1 403 602 | 149 743 | 10.7 |
| 3 | 12.530 | 255 956 | 12.586 | 252 296 | 12.479 | 221 569 | 243 274 | 15 420 | 6.3 |
| 4 | 12.876 | 3 151 372 | 12.881 | 2 994 062 | 12.803 | 2 469 172 | 2 871 535 | 291 672 | 10.2 |
| 5 | 13.080 | 147 524 | 13.076 | 269 641 | 12.956 | 255 158 | 224 108 | 54 475 | 24.3 |
| 6 | 13.648 | 206 573 | 13.669 | 215 831 | 13.573 | 151 821 | 191 408 | 28 246 | 14.8 |
| 7 | 13.961 | 16 786 | 16 786 | 248 | 13.956 | 15 400 355 | 13.881 | 12 284 812 | 15 157 138 | 1 439 764 | 9.5 |
| 8 | 14.026 | 96 778 | 14.026 | 91 851 | 13.947 | 71 104 | 86 578 | 11 125 | 12.8 |

| 1,875 mg/ml | 2 - Day 1 | 2 - Day 2 | 2 - Day 3 | Mean | SD | RSD |
|-------------|----------|----------|----------|------|----|-----|
| | RT | Area | RT | Area | RT | Area | | |
| 1 | 12.275 | 360 760 | 12.213 | 354 763 | 12.161 | 262 696 | 326 073 | 44 881 | 13.8 |
| 2 | 12.439 | 1 477 809 | 12.378 | 1 407 038 | 12.337 | 1 184 938 | 1 356 595 | 124 771 | 9.2 |
| 3 | 12.574 | 254 729 | 12.516 | 258 742 | 12.463 | 250 286 | 254 586 | 3 454 | 1.4 |
| 4 | 12.936 | 3 186 087 | 12.883 | 2 923 543 | 12.845 | 2 457 941 | 2 855 857 | 301 093 | 10.5 |
| 5 | 13.120 | 170 620 | 13.056 | 247 813 | 13.026 | 225 742 | 214 725 | 32 462 | 15.1 |
| 6 | 13.738 | 203 439 | 13.647 | 174 961 | 13.598 | 169 427 | 182 609 | 14 901 | 8.2 |
| 7 | 14.018 | 16 141 | 13.963 | 15 426 084 | 13.929 | 12 893 322 | 14 820 263 | 1 393 495 | 9.4 |
| 8 | 14.093 | 94 815 | 14.020 | 94 711 | 13.979 | 78 992 | 89 506 | 7 435 | 8.3 |

| 1,875 mg/ml | 3 - Day 1 | 3 - Day 2 | 3 - Day 3 | Mean | SD | RSD |
|-------------|----------|----------|----------|------|----|-----|
| | RT | Area | RT | Area | RT | Area | | |
| 1 | 12.261 | 338 056 | 12.211 | 308 585 | 12.183 | 289 265 | 311 969 | 20 062 | 6.4 |
| 2 | 12.429 | 1 265 966 | 12.370 | 1 397 354 | 12.367 | 1 107 744 | 1 257 021 | 118 402 | 9.4 |
| 3 | 12.569 | 247 782 | 12.501 | 269 735 | 12.487 | 216 667 | 244 728 | 21 772 | 8.9 |
| 4 | 12.943 | 2 735 245 | 12.873 | 2 895 296 | 12.863 | 2 277 077 | 2 635 873 | 261 986 | 9.9 |
| 5 | 13.143 | 143 091 | 13.042 | 243 962 | 13.027 | 245 517 | 210 857 | 47 922 | 22.7 |
| 6 | 13.715 | 190 935 | 13.651 | 206 293 | 13.630 | 169 931 | 189 053 | 14 904 | 7.9 |
| 7 | 14.092 | 14 212 | 14 212 | 017 | 13.954 | 15 477 498 | 13.936 | 11 927 762 | 13 872 426 | 1 468 933 | 10.6 |
| 8 | 14.092 | 75 108 | 14.023 | 89 201 | 13.990 | 75 734 | 80 014 | 6 501 | 8.1 |

Supplementary Table S8. Spruce balm sample NSB22 was analyzed at a concentration of 1,875 mg/ml in triplicates over three days to assess the intermediate precision (pimaric acid (1), sandaracopimaric acid (2), palustric acid (3), isopimaric acid (4), levopimaric acid (5), abietic acid (6), dehydroabietic acid (7), and neoabietic acid (8)). Table S10 summarizes the mean values, SD and RSD of all intermediate precision – experiments
### Supplementary Table S9
The results of the intermediate precision experiments are summarized. The mean value, SD and RSD are calculated for each resin acid (pimaric acid (1), sandaracopimaric acid (2), palustric acid (3), isopimaric acid (4), levopimaric acid (5), abietic acid (6), dehydroabietic acid (7), and neoabietic acid (8)).

| All experiments | Mean  | SD    | RSD  |
|-----------------|-------|-------|------|
| 1               | 323 582 | 31 568 | 9.8  |
| 2               | 1 339 073 | 145 159 | 10.8 |
| 3               | 247 529 | 16 325 | 6.6  |
| 4               | 2 787 755 | 305 009 | 10.9 |
| 5               | 216 563 | 46 226 | 21.3 |
| 6               | 187 690 | 20 685 | 11.0 |
| 7               | 14 616 609 | 1 534 054 | 10.5 |
| 8               | 85 366  | 9 461  | 11.1 |

### 3.6. Detection limit (LOD) and Quantitation limit (LOQ)

| # | RT [min] | Height | # | RT [min] | Height | # | RT [min] | Height |
|---|----------|--------|---|----------|--------|---|----------|--------|
| 1 | 1.007    | 1965   | 6 | 6.045    | 1149   | 11| 11.050   | 1404   |
| 2 | 2.010    | 1196   | 7 | 7.003    | 1479   | 12| 12.005   | 1061   |
| 3 | 2.996    | 2100   | 8 | 7.971    | 1063   | 13| 13.072   | 2042   |
| 4 | 4.006    | 1479   | 10.067 | 1238   | 15| 15.927   | 1641   |
| 5 | 5.042    | 1106   | 10| 9.011    | 1576   | 14| 15.126   | 1296   |

Mean: 1453

### Supplementary Table S10
Noise value at 10 different time points of a solvent blank for the calculation of the signal/noise ratio of dehydroabietic acid

| c [mg/ml] | height | S/N factor | Mean |
|-----------|--------|------------|------|
| LOD       | 0.00075 | 6.0        | 5.7  |
|           | 8661   | 8376       | 7807 |
| LOQ       | 0.0025 | 18403      | 19554 | 20432 |
|           | 12.7   | 13.5       | 14.1  |

### Supplementary Table S11
Limit of detection (LOD) and limit of quantitation (LOQ) of dehydroabietic acid
| #  | RT [min] | Height | #  | RT [min] | Height | #  | RT [min] | Height |
|----|----------|--------|----|----------|--------|----|----------|--------|
| 1  | 1.036    | 1073   | 6  | 6.011    | 1726   | 11 | 10.979   | 1124   |
| 2  | 1.976    | 1109   | 7  | 7.010    | 1577   | 12 | 11.979   | 1276   |
| 3  | 2.893    | 1127   | 8  | 7.943    | 865    | 13 | 13.000   | 1572   |
| 4  | 3.979    | 1317   | 9  | 9.009    | 1440   | 14 | 15.004   | 1085   |
| 5  | 5.068    | 1707   | 10 | 10.031   | 1154   | 15 | 15.996   | 1280   |

**Mean:** 1295

**Supplementary Table S12.** Noise value at 10 different time points of a solvent blank for the calculation of the signal/noise ratio of neoabietic acid.

|                | c [mg/ml] | height | S/N factor | Mean |
|----------------|-----------|--------|------------|------|
| **LOD**        | 0.001     | 6269   | 4.8        | **5.0** |
|                |           | 5553   | 4.3        |       |
|                |           | 7690   | 5.9        |       |
| **LOQ**        | 0.002     | 11294  | 8.7        | **9.3** |
|                |           | 12484  | 9.6        |       |
|                |           | 12475  | 9.6        |       |

**Supplementary Table S13.** Limit of detection (LOD) and limit of quantitation (LOQ) of neoabietic acid.
## 4. Quantitation

| Ret.-time ([min]) | 1       | 2       | 3       | 4       | 5       | 6       | 7       | 8       | Total   |
|-------------------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| NSB01             | 0.3 ± 0.005 | 1.3 ± 0.038 | 3.8 ± 0.026 | 3.4 ± 0.046 | 4.6 ± 0.089 | 2.4 ± 0.072 | 7.1 ± 0.051 | 2.3 ± 0.049 | 25.1 ± 0.181 |
| NSB02             | 0.3 ± 0.006 | 1.4 ± 0.011 | 3.1 ± 0.042 | 2.5 ± 0.023 | 4.9 ± 0.02 | 2.0 ± 0.015 | 7.7 ± 0.054 | 1.8 ± 0.045 | 23.7 ± 0.122 |
| NSB03             | 0.3 ± 0.011 | 1.5 ± 0.012 | 0.2 ± 0.016 | 2.2 ± 0.004 | 0.02 ± 0.021 | 0.5 ± 0.008 | 10.5 ± 0.062 | 0.0 ± 0.004 | 15.3 ± 0.076 |
| NSB04             | 0.3 ± 0.012 | 1.1 ± 0.010 | 2.7 ± 0.019 | 3.2 ± 0.031 | 3.5 ± 0.003 | 1.8 ± 0.024 | 10.2 ± 0.133 | 1.0 ± 0.034 | 23.8 ± 0.187 |
| NSB05             | 0.4 ± 0.018 | 1.6 ± 0.038 | 4.5 ± 0.118 | 3.7 ± 0.043 | 7.8 ± 0.060 | 2.6 ± 0.032 | 5.7 ± 0.046 | 3.1 ± 0.037 | 29.3 ± 0.270 |
| NSB06             | 0.4 ± 0.006 | 1.6 ± 0.03 | 4.7 ± 0.007 | 3.7 ± 0.044 | 10.8 ± 0.108 | 2.0 ± 0.158 | 3.8 ± 0.023 | 3.9 ± 0.135 | 31.0 ± 0.415 |
| NSB07             | 0.2 ± 0.007 | 1.5 ± 0.028 | 3.2 ± 0.056 | 2.7 ± 0.042 | 6.9 ± 0.021 | 2.8 ± 0.004 | 5.3 ± 0.062 | 3.6 ± 0.025 | 26.3 ± 0.062 |
| NSB08             | 0.3 ± 0.020 | 1.9 ± 0.031 | 3.2 ± 0.041 | 3.3 ± 0.020 | 6.9 ± 0.032 | 2.0 ± 0.020 | 9.1 ± 0.044 | 2.5 ± 0.019 | 29.1 ± 0.077 |
| NSB09             | 0.4 ± 0.008 | 1.3 ± 0.031 | 0.5 ± 0.030 | 2.0 ± 0.020 | 0.4 ± 0.018 | 0.4 ± 0.009 | 10.3 ± 0.085 | 0.1 ± 0.008 | 15.4 ± 0.125 |
| NSB10             | 0.6 ± 0.016 | 2.0 ± 0.032 | 4.1 ± 0.032 | 3.5 ± 0.013 | 10.4 ± 0.047 | 2.4 ± 0.040 | 5.6 ± 0.002 | 3.7 ± 0.053 | 32.2 ± 0.059 |
| NSB11             | 0.5 ± 0.003 | 2.0 ± 0.047 | 4.0 ± 0.006 | 2.5 ± 0.053 | 9.2 ± 0.076 | 1.6 ± 0.194 | 5.2 ± 0.019 | 2.4 ± 0.188 | 27.4 ± 0.556 |
| NSB12             | 0.4 ± 0.011 | 1.5 ± 0.022 | 5.5 ± 0.013 | 2.0 ± 0.049 | 30.8 ± 0.138 | 1.9 ± 0.059 | 1.7 ± 0.017 | 3.1 ± 0.085 | 46.9 ± 0.275 |
| NSB13             | 0.1 ± 0.034 | 0.6 ± 0.132 | 0.2 ± 0.077 | 1.4 ± 0.315 | 0.1 ± 0.017 | 0.3 ± 0.093 | 5.6 ± 1.217 | 0.0 ± 0.002 | 58.4 ± 1.879 |
| NSB14             | 0.2 ± 0.004 | 0.8 ± 0.014 | 1.1 ± 0.004 | 3.8 ± 0.027 | 0.5 ± 0.043 | 1.4 ± 0.007 | 6.8 ± 0.052 | 0.4 ± 0.006 | 15.0 ± 0.094 |
| NSB15             | 0.2 ± 0.016 | 1.3 ± 0.028 | 0.3 ± 0.018 | 1.7 ± 0.027 | 0.1 ± 0.022 | 0.2 ± 0.009 | 9.0 ± 0.075 | 0.0 ± 0.004 | 12.8 ± 0.078 |
| NSB16             | 0.2 ± 0.022 | 1.2 ± 0.018 | 2.2 ± 0.025 | 2.1 ± 0.045 | 5.8 ± 0.068 | 1.6 ± 0.133 | 5.3 ± 0.034 | 1.6 ± 0.118 | 20.0 ± 0.360 |
| NSB17             | 0.4 ± 0.016 | 1.3 ± 0.024 | 2.2 ± 0.034 | 2.3 ± 0.030 | 3.9 ± 0.121 | 1.1 ± 0.067 | 6.7 ± 0.034 | 1.2 ± 0.025 | 19.1 ± 0.324 |
| NSB18             | 0.4 ± 0.013 | 1.6 ± 0.016 | 2.8 ± 0.035 | 2.8 ± 0.017 | 0.6 ± 0.004 | 3.3 ± 0.011 | 8.0 ± 0.019 | 0.8 ± 0.04 | 20.2 ± 0.348 |
| NSB19             | 0.7 ± 0.008 | 1.6 ± 0.013 | 0.2 ± 0.016 | 1.7 ± 0.062 | 0.1 ± 0.021 | 0.2 ± 0.006 | 9.3 ± 0.032 | 0.0 ± 0.002 | 13.8 ± 0.133 |
| NSB20             | 0.6 ± 0.01 | 1.9 ± 0.041 | 1.9 ± 0.016 | 3.3 ± 0.046 | 2.0 ± 0.071 | 1.4 ± 0.038 | 8.8 ± 0.032 | 0.9 ± 0.016 | 20.9 ± 0.203 |
| NSB21             | 0.5 ± 0.005 | 2.3 ± 0.025 | 2.6 ± 0.064 | 3.6 ± 0.025 | 3.2 ± 0.001 | 2.3 ± 0.022 | 7.8 ± 0.012 | 1.8 ± 0.017 | 24.0 ± 0.070 |
| NSB22             | 0.2 ± 0.009 | 0.8 ± 0.01 | 0.3 ± 0.01 | 1.9 ± 0.01 | 0.1 ± 0.033 | 0.2 ± 0.007 | 9.2 ± 0.112 | 0.0 ± 0.001 | 12.7 ± 0.132 |
| Mean              | 0.4 ± 0.150 | 1.5 ± 0.398 | 2.5 ± 1.612 | 2.7 ± 0.743 | 5.2 ± 6.601 | 1.6 ± 0.908 | 7.2 ± 2.215 | 1.6 ± 1.316 | 22.7 ± 8.404 |
|     | 1     | 2     | 3     | 4     | 5     | 6     | 7     | 8     | Total |
|-----|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Ret.-time ([min]) | 12.150±0.03 | 12.316±0.02 | 12.518±0.03 | 12.812±0.05 | 13.065±0.05 | 13.629±0.04 | 13.931±0.04 | 14.058±0.05 |       |
| NSB-CP1 | n.d.  | n.d.  | 0.02 (±0.001) | 0.07 (±0.001) | 0.11 (±0.002) | 0.15 (±0.005) | 0.28 (±0.008) | 0.05 (±0.007) | 0.64 (±0.014) |
| NSB-CP 2 | n.d.  | n.d.  | 0.02 (±0.001) | 0.08 (±0.002) | 0.11 (±0.004) | 0.17 (±0.003) | 0.26 (±0.005) | 0.06 (±0.002) | 0.70 (±0.006) |
| NSB-CP 3 | n.d.  | n.d.  | 0.03 (±0.001) | 0.08 (±0.001) | 0.12 (±0.004) | 0.17 (±0.004) | 0.26 (±0.004) | 0.07 (±0.002) | 0.73 (±0.009) |
| NSB-CP4 | 0.05 (±0.004) | 0.24 (±0.009) | 0.79 (±0.016) | 0.48 (±0.007) | 1.9 (±0.012) | 0.53 (±0.009) | 0.57 (±0.005) | 0.71 (±0.021) | 5.27 (±0.052) |
| NSB-CP5 | 0.06 (±0.003) | 0.26 (±0.011) | 0.81 (±0.008) | 0.50 (±0.014) | 2.46 (±0.026) | 0.48 (±0.013) | 0.5 (±0.005) | 0.82 (±0.026) | 5.88 (±0.049) |

**Supplementary Table S14.** Retention times (min ±SD), contents and total contents (%) ±SD of the eight diterpene acids (pimaric acid (1), sandaracopimaric acid (2), palustric acid (3), isopimaric acid (4), levopimaric acid (5), abietic acid (6), dehydroabietic acid (7), and neoabietic acid (8)) in Norway Spruce Balm (samples NSB01-22) and commercial products (NSB-CP1-5). Contents of compounds 1-6 were calculated as neoabietic acid (8).