Comparative Study of the Leaf Volatiles of *Arctostaphylos uva-ursi* (L.) Spreng. and *Vaccinium vitis-idaea* L. (Ericaceae)

Niko Radulović *, Polina Blagojević and Radosav Palić

Faculty of Science and Mathematics, University of Niš, 18000 Niš, Serbia;
E-Mails: blagojevicpolina@gmail.com (P.B.); radosavpalic@yahoo.com (R.P.)

* Author to whom correspondence should be addressed; E-Mail: vangelis0703@yahoo.com;
  Tel.: +381-62-80-49-210; Fax: +381-18-533-014.

Received: 28 June 2010; in revised form: 25 August 2010/ Accepted: 30 August 2010/
Published: 2 September 2010

**Abstract:** The first GC and GC/MS analyses of the essential oils hydrodistilled from dry leaves of *Arctostaphylos uva-ursi* and *Vaccinium vitis-idaea* enabled the identification of 338 components in total (90.4 and 91.7% of the total GC peak areas, respectively). Terpenoids, fatty acids, fatty acid- and carotenoid derived compounds were predominant in the two samples. Both oils were characterized by high relative percentages of α-terpineol and linalool (4.7-17.0%). Compositional data on the volatiles of the presently analyzed and some other Ericaceae taxa (literature data) were mutually compared by means of multivariate statistical analyses (agglomerative hierarchical cluster analysis and principal component analysis). This was done in order to determine, based on the essential oil profiles, possible mutual relationships of the taxa within the family, especially that of species from the genera *Arctostaphylos* and *Vaccinium*. Results of the chemical and statistical analyses pointed to a strong relation between the genera *Vaccinium* and *Arctostaphylos*.

**Keywords:** *Arctostaphylos uva-ursi* (L.) Spreng.; *Vaccinium vitis-idaea* L.; essential oil; α-terpineol; linalool; chemometrics
1. Introduction

It has been known for centuries that leaves of *Arctostaphylos uva-ursi* (L.) Spreng., Ericaceae (Bear's grape, bearberry) possess powerful astringent activity, mainly due to the presence of glycosides such as arbutin [1]. In 1601, Clusius reported its earlier use by Galen (ca. 130–200 C.E.) as a hemostatic. In modern Western medical practice, its use seems to begin with Spanish and Italian physicians (ca. 1730–1740 C.E.) for calculus complaints [2]. For more than 100 years now this plant species has been official in nearly all Pharmacopeias and is widely used for treating bladder and kidney disorders, inflammatory diseases of the urinary tract, urethritis, cystitis, for strengthening and imparting tone to the urinary passages, etc. [1,2]. During collection, bearberry is commonly confused with cowberry (*Vaccinium vitis-idaea* L.) and box (*Buxus sempervirens* L.). Poisonous *B. sempervirens* (similar morphological characteristics, but without the pharmacologically active arbutin) has occasionally been used to adulterate the drug [1,3]. *Vaccinium vitis-idaea* and other representatives of the genus *Vaccinium* (Ericaceae), on the other hand, could be regarded as suitable substitutions for *A. uva-ursi* (comparable content of arbutin and similar pharmacological action of leaves’ infusions) [1]. Some recent studies have shown that biologically active phenologlycosides, simple phenols, flavonoids, tannins, polysaccharides, etc. are also present in *V. vitis-idaea* and *A. uva-ursi* [4-8].

It has been previously shown that essential oils may, despite their small yield, contribute to the medicinal properties of the plant [9]. Moreover, volatile metabolites could be potentially used as a tool which could give a quick insight to the presence/absence (i.e. expression) of a certain biosynthetic “apparatus” in some plant taxa, and to some extent, to the (dis)similarity of the compared species on a molecular level [10]. To the best of our knowledge, there are no previous reports on the essential oil profile of *A. uva-ursi* and there is a limited data concerning the volatiles of *V. vitis-idaea* and only of the berries [11,12]. Thus, the aim of this work was to analyze in detail (using GC and GC/MS) and compare the chemical composition of the essential oils hydrodistilled from the dry leaves of *A. uva-ursi* and *V. vitis-idaea*, in order to determine if any further phytochemical similarities between the two species exist. Comparison of the compositional data of the oils from a number of Ericaceae taxa (present study and the literature data [13-23]) was achieved using multivariate statistical analyses (MVA: agglomerative hierarchical cluster analysis (AHC) and principal component analysis (PCA)).

2. Results and Discussion

GC and GC/MS analyses of the essential oils extracted from *Arctostaphylos uva-ursi* and *Vaccinium vitis-idaea* leaves enabled the identification of 338 different constituents (243 in *A. uva-ursi* and 187 in *V. vitis-idaea*, Table 1), representing 90.4 and 91.7% of the total GC peak areas, respectively. The major contributors to the *V. vitis-idaea* oil were α-terpineol (17.0%), pentacosane (6.4%), (E,E)-α-farnesene (4.9%), linalool (4.7%) and (Z)-hex-3-en-1-ol (4.4%). The same two constituents, α-terpineol (7.8%) and linalool (7.3%), were predominant in the oil of *A. uva-ursi*, additionally characterized by hexadecanoic acid (4.5%) and (E)-geranyl acetone (4.1%). Another common feature of the analyzed oils was the presence of terpenoids (46.8 and 49.5% in *A. uva-ursi* and *V. vitis-idaea* oils, respectively) and fatty acid derived compounds (34.1% - *V. vitis-idaea*, 10.7% - *A. uva-ursi* oil) in high relative amounts. Fatty acids and fatty acid esters (F, 11.8%), and carotenoid derived compounds
(CD, 14.1%) represented a significant portion of *A. uva-ursi* oil. The mentioned constituents belonging to F and CD classes were identified in the *V. vitis-idaea* oil as well, but were present in a considerably smaller relative amount.

Table 1. Chemical composition of the essential oils extracted from the leaves of *Arctostaphylos uva-ursi* and *Vaccinium vitis-idaea*.

| RI | Class | Identification | Compound | *V. vitis-idaea, %* | *A. uva-ursi, %* |
|----|-------|----------------|----------|--------------------|-----------------|
| 725 | GL    | a, b           | (Z)-3-Penten-1-ol | tr                | tr              |
| 732 | GL    | a, b           | (E)-3-Penten-2-one | tr                | tr              |
| 744 | GL    | a, b           | (E)-2-Pentenal   | tr                | tr              |
| 762 | GL    | a, b, c        | 1-Pentanol      | tr                | tr              |
| 765 | GL    | a, b           | (Z)-2-Penten-1-ol | 0.8              | 0.2             |
| 772 | TH    | a, b           | 3-Methyl-2-buten-1-ol (syn. 4 prenol) | 0.1 |
| 772 | O     | a, b, c        | N,N-Dimethyl formamide | 0.4 |
| 781 | TH    | a, b           | 3-Methyl-2-butenal (syn. prenal) | tr              |                |
| 783 | GL    | a, b, c        | 2,4-Pentandione (syn. acetyl acetone) | tr              |                |
| 801 | GL    | a, b, c        | Hexanal         | tr                | 0.1             |
| 824 | MRP   | a, b           | Methylpyrazine  | tr                |                |
| 827 | O     | a, b, c        | Maleic anhydride | tr                |                |
| 832 | TH    | a, b, c        | 2-Methylbutanoic acid | tr              |                |
| 828 | GL/MRP| a, b, c        | Furfural        | 0.2              | 0.8             |
| 839 | GL    | a, b, c        | 4-Hydroxy-4-methyl-2-pentanone | tr              | tr              |
| 844 | GL    | a, b           | (E)-3-Hexen-1-ol | tr                | tr              |
| 854 | GL    | a, b           | (E)-2-Hexenal   | tr                | 0.7             |
| 854 | GL    | a, b           | (E)-2-Hexen-1-ol | 1.2              |                |
| 858 | GL    | a, b           | (Z)-3-Hexen-1-ol | 4.4              | tr              |
| 867 | GL    | a, b, c        | 1-Hexanol       | tr                | tr              |
| 863 | MRP   | a, b, c        | 3-Methylpyridine | 0.2              |                |
| 869 | MPR   | a, b           | α-Angelica lactone | tr                |                |
| 892 | AE    | a, b           | 1-Nonene        | tr                |                |
| 896 | O     | a, b           | 2-Methyl-2-cyclopentenone | tr              |                |
| 900 | TH    | a, b, c        | Isopropyl 3-methylbutanoate | 0.1 |
| 913 | GL    | a, b           | (E,E)-2,4-Hexadienal | tr              | tr              |
| 915 | MRP   | a, b, c        | 2-Acetylfluran  | tr                | 0.2             |
| 916 | MRP   | a, b           | Ethylpyrazine   | tr                |                |
| 920 | MRP   | a, b           | 2,3-Dimethylpyrazine | tr              |                |
| 935 | GL    | a, b           | 2-Methylpentanoic acid | tr              |                |
| 956 | GL    | a, b           | (E)-2-Heptenal  | tr                | 0.1             |
| 959 | MRP   | a, b           | 3-Ethylpyridine | 0.1              |                |
| 959 | GL    | a, b           | (Z)-3-Hepten-1-ol | tr              |                |
| 965 | MRP   | a, b, c        | Benzaldehyde    | 0.6              | 0.2             |
| 963 | MRP   | a, b           | 5-Methyl-2-furancarboxaldehyde | tr              |                |
| 967 | GL    | a, b, c        | 1-Heptanol      | tr                | tr              |
| 968 | MRP   | a, b           | 3-Ethenylpyridine | 0.4             |                |
| 971 | GL    | a, b, c        | Hexanoic acid   | 0.6              |                |
| 973 | GL    | a, b           | (E)-4-Octen-3-one | tr              |                |
| 978 | GL    | a, b           | 1-Octen-3-ol    | tr                | 0.1             |
| 978 | MRP   | a, b, c        | Phenol          | tr                |                |
| 986 | CR    | a, b           | 6-Methyl-5-hepten-2-one | 0.1             |                |
Table 1. Cont.

| Substance                                | Source | Concentration | Type |
|------------------------------------------|--------|---------------|------|
| Benzonitrile                             | GL     | a, b, c       | tr   |
| 2-Pentylfuran                            | MRP    | a, b          | tr   |
| 3-Octanol                                | MRP    | a, b          | tr   |
| (E,Z)-2,4-Heptadienal                    | GL     | a, b          | 0.3  |
| 2-Ethyl-6-methylpyrazine                 | MRP    | a, b          | tr   |
| 2-Ethyl-5-methylpyrazine                 | MRP    | a, b          | tr   |
| Trimethylpyrazine                         | MRP    | a, b          | tr   |
| (E,E)-2,4-Heptadienal                    | GL     | a, b          | 0.7  |
| 5-Ethyl-2-methylpyridine                 | MRP    | a, b          | tr   |
| Limonene                                 | TMA    | a, b, c       | tr   |
| 2-Ethylhexan-1-ol                        | G       | a, b          | 0.1  |
| p-Cymene                                 | TMA    | a, b, c       | tr   |
| (E)-3-Octen-2-one                        | GL     | a, b          | tr   |
| Benzyl alcohol                           | MRP    | a, b, c       | 0.7  |
| Phenylacetaldehyde                       | MRP    | a, b, c       | 1.0  |
| Salicylaldehyde                          | GL     | a, b, c       | tr   |
| 2-Methylphenol                           | O      | a, b, c       | 0.1  |
| 4-Methyldecanol                          | A      | a, b          | tr   |
| (Z)-2-Octen-2-one                        | GL     | a, b          | 0.1  |
| Pentyl isobutanoate                      | GL     | a, b, c       | tr   |
| (E)-2-Octen-3-ol                         | GL     | a, b, c       | 0.1  |
| 1-Octanol                                | GL     | a, b, c       | 0.9  |
| (E,E)-3,5-Octadien-2-one                 | GL     | a, b          | tr   |
| Acetophenone                             | O      | a, b, c       | tr   |
| 4-Methylbenzaldehyde                     | O      | a, b, c       | tr   |
| 4-Methylphenol                           | O      | a, b, c       | tr   |
| cis-Linalooloxide (furanoid)             | TMA    | a, b, c       | 0.5  |
| 3-Octanone                               | O      | a, b          | 0.7  |
| 3-Methylbenzaldehyde                     | TMA    | a, b, c       | tr   |
| α-Cumyl alcohol (syn. 2-phenyl-2-propanol)| TMA    | a, b, c       | tr   |
| trans-Linalooloxide (furanoid)           | TMA    | a, b, c       | 0.3  |
| p-Cymene                                 | TMM    | a, b          | 0.9  |
| 1-Octenol                                | GL     | a, b, c       | tr   |
| 1-Octen-4-ol                             | GL     | a, b          | tr   |
| Isobutyl tiglate                         | GL     | a, b          | 0.4  |
| Linalool                                 | TMA    | a, b, c       | 4.7  |
| Nonanal                                  | GL     | a, b, c       | 7.3  |
| Hotrienol                                | TM     | a, b          | tr   |
| 6-Methyl-3,5-heptadien-2-one             | CR     | a, b          | 1.8  |
| α-Thujone                                | TMT    | a, b, c       | tr   |
| 2,6-Dimethylcyclohexanol                 | O      | a, b          | 0.2  |
| 2-Phenyl-1-ethanol                       | MRP    | a, b, c       | 0.6  |
| Myrcenol                                 | TMA    | a, b          | tr   |
| β-Thujone                                | TMT    | a, b, c       | 0.1  |
| Dehydrosabinaketone                      | TMT    | a, b          | 0.1  |
| Isophorone                               | CR     | a, b, c       | tr   |
| α-Campholinal                            | TMP    | a, b          | tr   |
| (E)-3-Nonen-2-one                        | GL     | a, b          | tr   |
| Phenylacetonitrile                       | O      | a, b          | tr   |
| trans-Pinocarveol                        | TMP    | a, b, c       | tr   |
| Lilac aldehyde B                         | TMM    | a, b          | 0.2  |
| 4-Oxoisophorone                          | CR     | a, b          | tr   |
| Lilac aldehyde A                         | TMA    | a, b          | 0.8  |
| Camphor                                  | TMB    | a, b, c       | tr   |
| Lilac aldehyde A                         | TMA    | a, b          | 0.4  |
|   | Compound                          | Formula     | Concentration |
|---|-----------------------------------|-------------|---------------|
|1154| GL (E,Z)-2,6-Nonadienal           |             | 0.4           |
|1157| TMA Neroloxide                    |             | tr            |
|1158| TMM Menthone                      |             | 0.2           |
|1161| GL (E)-2-Nonenal                  |             | 0.3           |
|1165| TMA (Z)-β-Ocimeno                 |             | 0.1           |
|1167| O Benzyl acetate                  |             | tr            |
|1169| TMM Menthol                       |             | 0.3           |
|1169| TMA Lilac aldehyde C              |             | tr            |
|1170| F Octanoic acid                   |             | 0.7           |
|1171| TMM α-Phellandren-8-ol            |             | tr            |
|1172| TMM p-Mentha-1,5-dien-8-ol        |             | tr            |
|1173| TMA cis-Linalooloxide (pyranoid)  |             | tr            |
|1175| O Ethyl benzoate                  |             | tr            |
|1177| TMM Isomenthol                    |             | 1.9           |
|1179| TMA trans-Linalool oxide (pyranoid) |         | tr            |
|1181| O 2,4-Dimethylbenzaldehyde        |             | tr            |
|1182| TMM Terpinen-4-ol                 |             | 0.5           |
|1186| TMP Isoverbanol                   |             | tr            |
|1188| TMM neo-Isomenthol                |             | tr            |
|1189| TMM p-Cymen-8-ol                  |             | 0.2           |
|1190| O Naphthalene                     |             | tr            |
|1196| TMM α-Terpineole                  |             | 17.0          |
|1200| O Methyl salicylate               |             | 0.5           |
|1202| TMP Myrtenol                      |             | 0.1           |
|1203| TMM γ-Terpineol                   |             | tr            |
|1205| CR Safranal                       |             | tr            |
|1207| GL Decanal                        |             | 0.1           |
|1213| TMM trans-Piperitol               |             | tr            |
|1216| TMM Verbenone                     |             | 0.3           |
|1216| GL (E,E)-2,4-Nonadienal           |             | tr            |
|1221| TMM 1-p-Menthen-9-al isomer 1     |             | 0.4           |
|1223| TMM trans-Carveol                 |             | tr            |
|1223| TMM 1-p-Menthen-9-al isomer 2     |             | 0.5           |
|1226| CR β-Cyclocitral                  |             | 0.4           |
|1231| TMA (Z)-Ocimenone                 |             | tr            |
|1231| TMA Nerol                         |             | 0.2           |
|1237| TMM Thymol methyl ether           |             | 0.8           |
|1244| TMM Pulegone                      |             | 0.3           |
|1247| TMM Carvacrol methyl ether        |             | tr            |
|1249| TMM Carvone                       |             | 0.2           |
|1252| TMM Perilla ketone                |             | 0.1           |
|1256| TMA Geraniol                      |             | 1.5           |
|1259| TMM Piperitone                    |             | 0.2           |
|1263| GL (E)-2-Decenal                  |             | 0.5           |
|1263| GL Geraniol                       |             | 1.3           |
|1275| F Nonanoic acid                   |             | 0.4           |
|1277| TMM Perilla aldehyde              |             | 1.2           |
|1286| GL Vitispirane                    |             | 0.9           |
|1290| PP trans-Anethole                 |             | 0.6           |
|1290| TMB Isobornyl acetate             |             | tr            |
Table 1. Cont.

| 1294 | TMM  | a, b, c | Thymol  | 2.0 |
| 1294 | AE   | a, b    | 1-Tridecene | tr  |
| 1296 | GL   | a, b    | (E,Z)-2,4-Decadienal | tr  | tr  |
| 1297 | TMM  | a, b, c | Menthyl acetate | tr  |
| 1299 | O    | a, b    | 2-Methylnaphthalene | tr  |
| 1300 | O    | a, b, c | Indole | tr  |
| 1300 | A    | a, b, c | Tridecane | tr  |
| 1304 | TMM  | a, b, c | Carvacrol | 0.9 |
| 1304 | TMM  | a, b    | Perilla alcohol | tr  |
| 1309 | GL   | a, b    | Undecanal | 0.1 |
| 1313 | CR   | a, b    | Riesling acetal | 1.4 |
| 1317 | O    | a, b    | 1-Methylnaphthalene | tr  |
| 1318 | PP   | a, b    | 4-Vinylguaiaconol | tr  | tr  |
| 1319 | GL   | a, b    | (E,E)-2,4-Decadienal | 0.8 | 1.7 |
| 1323 | O    | a, b    | 2,4,6-Trimethylbenzaldehyde | tr  | 0.1 |
| 1326 | GL   | a, b    | (Z)-3-Hexenyl tiglate | tr  |
| 1336 | A    | a, b    | Branched alkane | tr  |
| 1341 | CR   | a, b    | (E,E)-2,5-Epoxy-6,8-megastigmadiene | tr  |
| 1344 | A    | a, b    | Branched alkane | tr  |
| 1353 | TMM  | a, b    | α-Terpineol acetate | 0.7 |
| 1359 | O    | a, b    | 1,1,6-Trimethyl-1,2-dihydonaphthalene | 0.2 | 0.6 |
| 1361 | PP   | a, b, c | Eugenol | 0.7 | tr  |
| 1363 | TMA  | a, b    | Hydroxy citronellol (syn. 3,7-dimethyl-1,7-octanediol) | tr  |
| 1366 | GL   | a, b    | (E)-2-Undecenal | tr  | 0.2 |
| 1367 | F    | a, b    | γ-Nonalactone | tr  |
| 1371 | CR   | a, b    | (E,Z)-4,6,8-Megastigmatriene | tr  |
| 1370 | F    | a, b, c | Decanoic acid | tr  | 0.8 |
| 1377 | A    | a, b    | 3-Methyltridecane | tr  |
| 1383 | CR   | a, b    | α-Ionol | 0.3 |
| 1383 | GL   | a, b    | (Z)-3-Hexenyl hexanoate | 0.8 |
| 1384 | O    | a, b, c | Biphenyl | tr  |
| 1388 | GL   | a, b    | (Z)-3-Hexenyl (Z)-3-hexenoate | 0.3 |
| 1390 | CR   | a, b    | (E)-β-Damasconone | 0.3 |
| 1391 | GL   | a, b    | (E)-2-Hexenyl caproate | tr  |
| 1396 | AE   | a, b    | 1-Dodecene | tr  |
| 1398 | CR   | a, b    | (Z)-Jasmonone | tr  |
| 1400 | A    | a, b, c | Tetradecane | tr  | tr  |
| 1404 | CR   | a, b    | (2E)-3-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2-propenal | tr  | 0.4 |
| 1407 | CR   | a, b    | Hexahydrospseudoionone | tr  |
| 1409 | O    | a, b    | (syn. tetrahydrogeranyl acetone) | tr  | 0.1 |
| 1411 | AL   | a, b    | Dodecanal | tr  | tr  |
| 1416 | O    | a, b    | 1-Ethenylnaphthalene | tr  |
| 1420 | CR   | a, b    | (E)-β-Damascone | tr  |
| 1423 | TS   | a, b    | β-Cedrene | 0.2 |
| 1424 | O    | a, b    | 1,3-Dimethylnaphthalene | tr  |
| 1427 | TSCR | a, b, c | β-Caryophyllene | 2.9 | 0.9 |
|   |   |   |   |   |
|---|---|---|---|---|
| 1433 | CR | a, b, c | (E)-α-Ionone | 0.1 |
| 1440 | TS | a, b | Calarene (syn. β-Gurjunene) | tr |
| 1444 | O | a, b | 2,3-Dimethylnaphthalene | tr |
| 1454 | O | a, b | Acenaphthylene | tr |
| 1456 | CR | a, b | (E)-Geranyl acetone | tr |
| 1457 | A | a, b | 4-Methylpentadecane | tr |
| 1460 | TSF | a, b | (E)-β-Farnesene | tr |
| 1462 | TSH | a, b, c | α-Humulene | 1.1 1.2 |
| 1463 | A | a, b | 2-Methyltetradecane | tr |
| 1465 | F | a, b | Undecanoic acid | 0.2 |
| 1466 | ALC | a, b | 1-Dodecanol | tr |
| 1468 | TSCD | a, b | γ-Muurolene | 0.6 |
| 1472 | TSED | a, b, c | (E)-β-Ionone | 1.1 1.3 |
| 1474 | TSED | a, b | β-Selinene | tr |
| 1477 | TS | a, b | α-Zingiberene | 0.6 |
| 1478 | FAD | a, b | 2-Tridecanone | tr |
| 1480 | TSED | a, b | δ-Selinene | tr |
| 1481 | A | a, b, c | Pentadecane | tr |
| 1482 | TSED | a, b | α-Selinene | 0.8 |
| 1483 | O | a, b | Benzyl tiglate | tr |
| 1486 | TSCD | a, b | α-Muurolene | 0.2 |
| 1488 | TSAG | a, b | 4-epi-cis-Dihydroagarofuran | tr |
| 1490 | TSF | a, b | (E,E)-α-Farnesene | 4.9 |
| 1491 | AL | a, b | Tridecanal | tr |
| 1492 | TS | a, b | β-Bisabolene | 0.3 |
| 1493 | TSCD | a, b | γ-Cadinene | tr |
| 1494 | TSED | a, b | δ-Cadinene | 0.9 |
| 1496 | TSED | a, b | 7-epi-α-Selinene | tr |
| 1497 | PP | a, b, c | Myristicin | 0.6 |
| 1499 | TSCD | a, b | trans-Cadina-1,4-diene | tr |
| 1501 | CR | a, b | Lilial | tr |
| 1502 | CR | a, b | (E,Z)-Pseudoionone | 0.3 |
| 1503 | CR | a, b | Dihydroactinidiolide | 0.1 |
| 1504 | A | a, b | Branched alkane | tr |
| 1505 | TSCD | a, b | α-Cadinene | tr |
| 1506 | TSCD | a, b | α-Calacorene | 0.2 |
| 1507 | TSAG | a, b | α-Agarofuran | 1.8 |
| 1508 | F | a, b, c | Dodecanoic acid | 0.6 1.8 |
| 1509 | O | a, b | 2,3,5-Trimethylnaphthalene | 0.2 |
| 1510 | O | a, b | 3-Methylpentadecane | tr |
| 1511 | GL | a, b | (Z)-3-Hexenyl benzoate | tr |
| 1512 | GL | a, b | (Z)-Dihydropimarane | 0.8 |
| 1513 | TSF | a, b | (Z)-Dihydroapofarnesol | 0.8 |
| 1514 | TS | a, b | Spathulenol | tr |
| 1515 | O | a, b | 9H-Fluorene | 0.6 |
| 1516 | CR | a, b | (E,E)-Pseudoionone | 0.4 |
| 1517 | TSCR | a, b, c | Caryophyllene oxide | 0.8 |
| 1518 | AE | a, b | 1-Hexadecene | tr |
| 1519 | O | a, b | 3,3'-Dimethylbiphenyl | tr |
| 1520 | A | a, b, c | Hexadecane | 0.7 |
| 1521 | TS | a, b | Viridiflorol | 0.1 |
| 1522 | TS | a, b | 4(14)-Salvialen-1-one | tr |
| 1523 | TSH | a, b | Humulene epoxide I | 0.1 |
Table 1. Cont.

|     |     |     |             |     |
|-----|-----|-----|-------------|-----|
| 1611| TS  | a, b| Cedrol      | 0.2 |
| 1614| AL  | a, b| Tetradecanal| tr  |
| 1615| AL  | a, b| (E)-7-Tetradecenal | tr  |
| 1619| TSH | a, b| Humulene epoxide II | tr  |
| 1629| F   | a, b,c| Isopropyl laurate | tr  |
| 1629| TSED| a, b| 10-epi-γ-Eudesmol | 3.0 |
| 1634| O   | a, b,c| Benzophenone | tr  |
| 1638| O   | a, b| 4-Methyldibenzofuran | tr  |
| 1640| TSED| a, b| γ-Eudesmol | tr  |
| 1646| TSCR| a, b| Caryophylla-3(15),7(14)-dien-6-ol | tr  |
| 1649| TSCD| a, b| γ-Cadinol | 0.3 |
| 1650| TSCD| a, b| Cubenol | tr  |
| 1654| TSCD| a, b| α-Muurolol | 0.2 |
| 1659| TSED| a, b| α-Eudesmol | tr  |
| 1662| TSER| a, b| Valerianol | 1.7 |
| 1665| A   | a, b| 2-Methylhexadecane | tr  |
| 1666| TSCD| a, b| α-Cadinol | 0.2 |
| 1667| TSED| a, b| 7-epi-α-Eudesmol | tr  |
| 1675| ALC | a, b| 1-Tetradecanol | 0.9 |
| 1676| TSF | a, b| Hexahydrofarnesol | 0.1 |
| 1683| O   | a, b| Hexyl salicylate | tr  |
| 1694| AE  | a, b| 1-Heptadecene | tr  |
| 1695| TSCD| a, b| Amorpha-4,9-dien-2-ol | 0.1 |
| 1698| TS  | a, b| Acorenone | 0.2 |
| 1700| A   | a, b,c| Heptadecane | 0.3 |
| 1705| TSGER| a, b,c| Germacrone | 1.1 |
| 1716| AL  | a, b| Pentadecanal | 0.3 |
| 1719| TSF | a, b| (E,E)-Farnesal | tr  |
| 1725| O   | a, b| 2,6-Diisopropynaphthalene | 0.2 |
| 1727| F   | a, b,c| Methyl tetradecanoate | tr  |
| 1755| A   | a, b| 5-Methylheptadecane | tr  |
| 1764| A   | a, b| 2-Methylheptadecane | tr  |
| 1765| F   | a, b,c| Tetradecanoic acid | 1.2 |
| 1772| O   | a, b,c| Benzyl benzoate | tr  |
| 1784| O   | a, b,c| Phenanthrene | 0.1 |
| 1794| AE  | a, b| 1-Octadecene | tr  |
| 1795| F   | a, b,c| Ethyl tetradecanoate | tr  |
| 1800| A   | a, b,c| Octadecane | 0.1 |
| 1818| AL  | a, b| Hexadecanal | tr  |
| 1828| F   | a, b,c| Isopropyl myristate | tr  |
| 1839| F   | a, b| 15-Pentadecanolide (syn. exaltolide) | tr  |
| 1844| TSF | a, b| (E,E)-2,6-Farnesyl acetate | tr  |
| 1848| CR  | a, b| Hexahydrofarnesyl acetone | 1.7 |
| 1862| F   | a, b| Pentadecanoic acid | tr  |
| 1876| O   | a, b,c| Benzyl salicylate | tr  |
| 1883| ALC | a, b,c| 1-Hexadecanol | tr  |
| 1894| AE  | a, b| 1-Nonadecene | tr  |
| 1900| A   | a, b,c| Nonadecane | tr  |
| 1921| CR  | a, b| (E,E)-5,9-Farnesyl acetone | 0.7 |
| 1928| F   | a, b,c| Methyl hexadecanoate | tr  |
| 1930| O   | a, b| 2-Methylanthracene | tr  |
| 1941| F   | a, b| (Z)-9-Hexadecenoic acid (syn. palmitoleic acid) | 0.2 |
| 1950| TD  | a, b| Isophytol | tr  |
| Year | Source | Constituent | Description | Molecules 2010, 15 | Molecules 2010, 15 |
|------|--------|-------------|-------------|------------------|------------------|
| 1968 | F      | Hexadecanoic acid | tr | 4.5 |
| 1975 | TD     | Sandaracopimara-8(14),15-diene | tr | tr |
| 1982 | ALC    | 1-Heptadecanol | tr | tr |
| 1994 | AE     | 1-Eicosene | tr | tr |
| 1996 | F      | Ethyl hexadecanoate | tr | 0.2 |
| 2000 | A      | Eicosane | tr | 0.1 |
| 2003 | TD     | Manoyl oxide | 1.4 | 0.1 |
| 2025 | TD     | 13-epi-Manool oxide | 2.0 | tr |
| 2034 | CR     | (E,E)-Geranyl linalool | tr | tr |
| 2070 | TD     | ar-Abietatriene | tr | tr |
| 2094 | AE     | 1-Heneicosene | tr | tr |
| 2100 | A      | Heneicosan | 0.3 | 0.1 |
| 2116 | TD     | (E)-Phytol | tr | 3.3 |
| 2116 | AL     | Nonadecanal | tr | tr |
| 2136 | AE     | Linoleic acid | 0.3 | 0.3 |
| 2138 | A      | Branched alkane | tr | tr |
| 2143 | F      | Linolenic acid | 1.2 | 1.2 |
| 2155 | F      | (E,E)-9,12-Octadecadienoic acid (syn. linoleic acid) | 0.8 | 0.8 |
| 2172 | AE     | 1-Nonadecanol | tr | tr |
| 2180 | A      | Branched alkane | tr | tr |
| 2194 | AE     | 1-Docosene | 0.8 | tr |
| 2200 | A      | Docosane | 0.5 | tr |
| 2219 | AL     | Eicosan | tr | tr |
| 2294 | AE     | 1-Tricosene | 0.3 | 0.3 |
| 2300 | A      | Tricosan | 2.1 | 0.2 |
| 2395 | AE     | 1-Tetracosene | 1.4 | 1.4 |
| 2352 | F      | δ-Octadecalactone | tr | 0.1 |
| 2394 | AE     | 1-Tetracosene | tr | tr |
| 2400 | A      | Tetracosan | 1.2 | 1.2 |
| 2495 | AE     | 1-Pentacosen | tr | tr |
| 2500 | A      | Pentacosan | 6.4 | 6.4 |
| 2596 | AE     | 1-Hexacosen | 1.1 | 1.1 |
| 2600 | A      | Hexacosan | 0.6 | 0.6 |
| 2700 | A      | Heptacosan | 2.9 | 2.9 |
| 2297 | AE     | 1-Octacosan | 1.6 | 1.6 |
| 2900 | A      | Nonacosan | 2.0 | 2.0 |
| 2998 | AE     | 1-Triacontan | tr | tr |
| 3100 | A      | Hentriacontane | tr | tr |

| Total | 91.7 | 90.4 |
| Number of constituents | 187 | 243 |
| Terpenoids (T) | 49.5 | 46.8 |
| Hemiterpenoids (TH) | tr | 0.2 |
| Monoterpenoids (TM) | 27.4 | 35.6 |
| Oxygenated | 27.4 | 35.6 |
| Hydrocarbons | tr | tr |
| Acyclic (TMA) | 7.6 | 14.7 |
| p-Menthane (TMM) | 19.8 | 17.4 |
| Bornane (TMB) | 0.0 | 2.2 |
| Thujane (TMT) | 0.0 | 0.9 |
| Pinane (TMP) | tr | 0.4 |
| Sesquiterpenoids (TS) | 18.7 | 7.4 |
| Oxygenated | 9.2 | 2.1 |
| Hydrocarbons | 9.5 | 5.3 |
In respect to the skeleton-types of the identified constituents, the monoterpenoid fractions of both *V. vitis-idaea* and *A. uva-ursi* oils could be considered as rather simple. Interestingly, not taking into account some trace constituents, the monoterpenoid fractions of both oils were completely comprised of oxygenated derivatives. In *V. vitis-idaea* oil only acyclic (7.6%), *p*-menthane (19.8%) and pinane-type (tr) monoterpenoids were detected. Acyclic (14.7%) and monoterpenoids with a *p*-menthane (17.4%) skeleton dominated the monoterpenoid fraction of *A. uva-ursi* oil as well, and only small relative amounts of pinane (0.4%), bornane (2.2%) and thujane-type (0.9%) compounds were detected. α-Terpnyl cation, produced by the biosynthetic cyclization of linalyl diphosphate, the intermediate from which *p*-menthane type monoterpenoids are derived, is known to be the precursor of other classes of cyclic monoterpenoids including bornanes, pinanes and thujanes [24]. Biosynthesis of linalool is closely related to linalyl diphosphate, and α-terpineol could be considered as a direct biosynthetic product of α-terpnyl cation, formed by quenching the mentioned cation with water [24]. Both linalool and α-terpineol were by far the most abundant compounds in the monoterpenoid fractions of *A. uva-ursi* and *V. vitis-idaea* oils. Having the above mentioned in mind, one could speculate that both taxa have a relatively primitive monoterpenoid biosynthetic “apparatus”, capable of producing predominantly metabolites from the “beginning” of the mentioned metabolic pathway. It seems that a similar consideration stands for some other taxa from the genus *Vaccinium* as well. In different *Vaccinium* species (*V. corrymbosum*, *V. oxycoccus*, *V. macrocarpon*, *V. arctostaphylos*) α-terpineol...
and/or linalool were recognized as major, or one of the major volatile metabolites [14,25-29]. Nevertheless, this should be taken with a grain of salt, since only the volatile metabolites have been investigated. In the studied species monoterpenes could be potentially present as glycosides, and thus non-volatile under hydrodistillation and/or GC conditions. α-Terpineol and some other terpenoid compounds were previously also recognized as *V. macrocarpon* cuticle wax constituents [30]. According to Croteau et al., the presence of these compounds in the cuticle wax could suggest that these substances might have a certain role in the plants’ defense mechanisms [30].

Although the relative amount of volatile sesquiterpenoids was considerably lower than that of monoterpenoids in both *A. uva-ursi* and *V. vitis-idaea* oils, sesquiterpenoid fractions were, concerning skeleton-types of identified constituents, much more heterogenic (Table 1). A number of different skeleton-types of volatile sesquiterpenoids were dominant in the oils of the two taxa: farnesanes (5.7%), caryophyllanes (3.7%) eudesmanes (3.0%) in *V. vitis-idaea* oil and cadinanes (2.7%), eudesmanes (1.4%) and humulanes (1.3%) in *A. uva-ursi* oil.

It might be assumed that certain volatiles listed in Table 1, identified in both *A. uva-ursi* and *V. vitis-idaea* oils, could be considered artifacts of the isolation procedure, and not direct products of plant metabolism. For example, a number of compounds from the Table 1 are most probably products of Maillard-type reactions including the thermal fragmentation of amino acids and sugars, alone or in conjunction, during hydrodistillation [31]. “Green leaf” volatiles, on the other hand, are most probably produced by enzymatic degradation of unsaturated fatty acids, as in desiccation, *i.e.* as a stress-induced response of plants, produced during collection and preparation of plant samples [32]. Alongside “green leaf” and other fatty acid derived compounds (FAD), fatty acid and fatty acid esters (F) and carotenoid derived compounds (CD) represented more than one third of both analyzed oils. Volatile profiles of some other representatives of the genus *Vaccinium* were also dominated by FAD, F and/or CD compounds [13,33,34]. All these species could be considered as essential oil-poor species (oil yield less than 0.1%). All mentioned above seems to further corroborate the hypothesis proposed by us in a previous publication [10]. We have noticed that the correlation between the essential oil yield and composition (classes of compounds) exists [10]. Most frequently, essential oil-rich species (oil yield much higher than 0.1%) produce considerable amount of monoterpenoids or phenylpropanoids, while in the oils of essential oil-poor species, FAD, F and CD compounds are the dominant volatile metabolites [10].

As previously mentioned, there are no reports concerning the volatile metabolites of *A. uva-ursi*, and there are only two references on *V. vitis-idaea* volatiles, however different parts of the plant (berries instead of leaves), using a different methodology (minced berries were treated with a pectinolytic enzyme and after that volatiles of the obtained juice and pressed residue were separately studied), have been analyzed [11,12]. Volatile profile of *V. vitis-idaea* barriers differs significantly from the corresponding profile of the leaves. For example, the most dominant volatile of the pressed residue of minced berries was benzyl alcohol (40.2%), found only as the minor contributor of the leaves’ oil. α-Terpineol and linalool (dominant volatiles of *V. vitis-idaea* leaves) on the other hand, represented in total only 1.0% of berry extract. This plant organ specification, concerning production/accumulation of volatiles, is not unusual. For example, differences in the chemical composition of *Artemisia absinthium* root and aerial parts oils pointed out to the possibility that different metabolic pathways could be operational in different organs of the same plant species [35].
Still, some similarities between *V. vitis-idaea* berry and leaf essential oil profiles could be observed. For instance, fatty acid related compounds, one of the dominant groups of constituents in the leaf oil, represented a significant portion of the berry extract (ca. 20%) [11,12].

Both species analyzed herein belong to the plant family Ericaceae. The latter comprises some 100-125 genera and more than 3,000 species [36] that are, generally speaking, poorly studied in respect to volatile metabolites. Table 2 lists the Ericaceae taxa whose essential oils were previously chemically analyzed using a methodology comparable to that applied in this work [13-23]. Compositional data on the essential oils of the species listed in Table 2 (28 samples in total) were mutually compared by means of multivariate statistical analyses (MVA: AHC and PCA).

**Table 2.** List of essential oil samples used in statistical analyses.

| Taxon (plant part) | Main oil constituent | Ref. | Des. |
|--------------------|----------------------|------|------|
| *Arctostaphylos uva-ursi* (L.) Spreng. (leaves) | α-Terpineol (7.8%) | Present study | Obs1 |
| *Vaccinium vitis-idaea* (leaves) | α-Terpineol (17.0%) | Present study | Obs2 |
| *V. arctostaphylos* L. (shoots) | Hexadecanoic acid (27.0%) | Present study | Obs3 |
| *V. arctostaphylos* (aerial parts) | α-Terpineol (15.0%) | Present study | Obs4 |
| *Rhododendron macronatum* G. don (flowers) | Linolenic acid (39.7%) | [15] | Obs5 |
| *R. simii* Planch. (flowers) | Linolenic acid (36.4%) | [15] | Obs6 |
| *R. simii* (leaves) | Phytole [15] (15.2%) | [15] | Obs7 |
| *R. naemkwanense* Merr. (leaves) | 9,12-Octadecadienoic acid (45.3%) | [15] | Obs8 |
| *R. anthopogon* D. Don (aerial parts) | α-Pinene (37.4%) | [16] | Obs9 |
| *R. aureum* Georgi. (leaves) | Calarene (34.4%) | [17] | Obs10 |
| *R. aureum* (leaves) | Calarene (66.4%) | [17] | Obs11 |
| *R. aureum* (leaves) | Calarene (26.2%) | [17] | Obs12 |
| *R. aureum* (leaves) | Calarene (41.3%) | [17] | Obs13 |
| *R. aureum* (leaves) | β-Bourbonene (27.4%) | [17] | Obs14 |
| *R. aureum* (leaves) | Calarene (48.8%) | [18] | Obs15 |
| *R. aureum* (leaves) | Calarene (36.2%) | [18] | Obs16 |
| *R. aureum* (leaves) | Calarene (16.2%) | [18] | Obs17 |
| *R. dauricum* L. (leaves) | trans-Caryophyllene (19.1%) | [18] | Obs18 |
| *R. dauricum* (leaves) | γ-Cadinene (17.4%) | [18] | Obs19 |
| *R. dauricum* (leaves) | trans-Caryophyllene (17.0%) | [18] | Obs20 |
| *R. tomentosum* (Stokes) H. Harmaja (leaves) (former name *Ledum palustre* L.) | Palustrol (22.8%) | [19] | Obs21 |
| *Ledum palustre* var. angustum N. Busch | Ascaridole (26.8%) | [20] | Obs22 |
| *Erica manipuliflora* Salisb. (aerial parts) | Heptacosane (19.9%) | [21] | Obs23 |
| *E. manipuliflora* (aerial parts) | 1-Octen-3-ol (16.2%) | [21] | Obs24 |
| *Gaultheria fragrantissima* Wall. (leaves) | Methyl salicylate (99.2%) | [22] | Obs25 |
| *G. fragrantissima* (steams) | Methyl salicylate (99.5%) | [22] | Obs26 |
| *G. fragrantissima* (flowering twigs) | Methyl salicylate (99.4%) | [22] | Obs27 |
| *Arbutus unedo* L. (leaves) | (E)-2-Decenal (12.0%) | [23] | Obs28 |

1 Ref.-reference; 2 Des.-designation; 3 Correct isomer not specified in the original reference; 4 Name of component (incomplete and unclear) given as in the original reference.
Figure 1. (a) Dendrogram (AHC analysis) representing chemical composition dissimilarity relationships of 28 essential oil samples (observations) obtained by Euclidian distance dissimilarity (dissimilarity within the interval [0, 27000], using aggregation criterion-Ward's method). Four groups of samples (C1-C4) were found. (b) Principal component analysis ordination of 28 oil samples (observations). Axes (F1 and F2 factors-the first and second principal component) refer to the ordination scores obtained from the samples. Axis F1 accounts for ca. 13% and axis F2 accounts for a further 11% of the total variance.

This was done in order to determine, based on the essential oil profiles, possible mutual alliance of the taxa within the family, especially that of species from the genera *Arctostaphylos* and *Vaccinium*. Principal component analysis (PCA) and agglomerative hierarchical clustering (AHC) were both performed using the Excel program plug-in XLSTAT version 2008.6.07. Both methods were applied utilizing the mean values of the relative abundances of the constituents of compared essential oils as variables (only constituents with percentage higher than 1% in at least one sample were taken into account). AHC was determined using Pearson dissimilarity where the aggregation criterion were simple linkage, unweighted pair-group average and complete linkage and Euclidean distance where the aggregation criterion were weighted pair-group average, unweighted pair-group average and Ward’s method. PCA of the Pearson (n) type was performed. Results of the MVA analyses are given in
Figures 1 and 2. In the dendrogram of the AHC analysis (Figure 1), four different classes of samples (C1-C4) can be observed. Class C1 (Obs25-Obs27) groups essential oils (almost pure methyl salicylate) obtained from different parts of Gaultheria fragrantissima (wintergreen) [22]. Class C2 consists exclusively of Rhododendron aureum oils (Obs10-Obs17), all characterized with a high level of the sesquiterpene calarene [17,18]. Oils obtained from flowers of R. mucronatum and R. simii (Obs5 and Obs 6; high level of linolenic acid) form a separate class C3 [15]. All other samples [13-23], including those that correspond to A. uva-ursi (Obs1), V. vitis-idaea (Obs2) and V. arctostaphylos (Obs3 and Obs4) are recognized as statistically not different and grouped in C4. It must be stressed that samples Obs1-Obs4 are basically characterized by very low Euclidian distance. In the same time, different species from the genus Rhododendron are separated in statistically different groups (C2, C3 and C4) [15,20]. Results of AHC suggest that taxa from the genera Vaccinium and Arctostaphylos are closely related. This is observable from the PCA biplot as well (Figure 2), where A. uva-ursi (Obs1) and V. arctostaphylos (Obs4) oils are mutually characterized with similar values of F1 and F2 factors. Moreover, samples corresponding to Vaccinium, Arctostaphylos and Arbutus taxa (Obs1, Obs2, Obs4 and Obs28) are, based on PCA results, clearly separated from other considered oils (Figure 2). One could find results of both AHC and PCA a bit surprising, having in mind that classical taxonomy places genera Vaccinium and Arctostaphylos in different subfamilies of Ericaceae (Vaccinioideae and Arbutoideae) [37]. Results of molecular studies within the Ericaceae clearly separated taxa belonging to the mentioned genera [37,38]. Nevertheless, mutual alliance of Arbutus and Arctostaphylos (Arbutoideae; Obs1, Obs22) is recognized by both molecular [37,38] and chemotaxonomical studies (present work).

3. Experimental

3.1. Plant material

Leaves of V. vitis-idaea were collected from the slopes of Stara Planina Mountain (near the mountain top Babin Zub), S. Serbia, at the beginning of July, 2007. Voucher specimens were deposited in the Herbarium of the Faculty of Science and Mathematics, University of Niš, under acquisition number 20074. Leaves of A. uva-ursi were obtained from a local pharmacy (in 2006). Botanical identification was performed by N.R.

3.2. Isolation of the essential oils

Air-dried, to constant weight, leaves of A. uva-ursi and V. vitis-idaea (three batches of about 500 g of each sample) was subjected to hydrodistillation with ca. 2 L of distilled water for 2.5 h using the original Clevenger-type apparatus [39]. The semi-solid yellowish essential oils (30 ± 1 mg per batch) of both species were obtained with a yield of 0.06% (w/w, typical value). Due to the small sample size of 30 mg of the isolated essential oils, which were not completely liquid, the volume of the oils was not measured. The obtained oils were separated by extraction with diethyl ether (Merck, Darmstadt Germany) and dried over anhydrous sodium sulfate (Aldrich, St. Louis, MO, USA). The solvent was evaporated under a gentle stream of nitrogen at room temperature, in order to exclude any loss of the essential oil, and immediately analyzed. When the oil yields were determined, after the bulk of ether
was removed under a stream of N₂, the residue was exposed to vacuum at room temperature for a short period to eliminate the solvent completely. The pure oil was then measured on an analytical balance and multiple gravimetric measurements were taken during 24 h to ensure that all of the solvent had evaporated.

3.3. Gas chromatography and gas chromatography-mass spectrometry

The GC/MS analysis was repeated three times for each sample using a Hewlett-Packard 6890N gas chromatograph. The gas chromatograph was equipped with a fused silica capillary column HP-5MS (5% phenylmethylsiloxane, 30 m × 0.25 mm, film thickness 0.25 μm, Agilent Technologies, Palo Alto, CA, USA) and coupled with a 5975B mass selective detector from the same company. The injector and interface were operated at 250 °C and 300 °C, respectively. The oven temperature was raised from 70 °C to 290 °C at a heating rate of 5 °C/min and then isothermally held for 10 min. As a carrier gas helium at 1.0 mL/min was used. The samples, 1 μL of the oil solutions in diethyl ether (1:100), was injected in a pulsed split mode (the flow was 1.5 mL/min for the first 0.5 min and then set to 1.0 mL/min throughout the remainder of the analysis; split ratio 40:1). mass selective detector was operated at the ionization energy of 70 eV, in the 35–500 amu range with a scanning speed of 0.34 s. GC (FID) analysis was carried out under the same experimental conditions using the same column as described for the GC/MS. The percentage composition was computed from the GC peak areas without the use of correction factors. Qualitative analysis of the essential oil constituents was based on several factors. Firstly, the comparison of the essential oils linear retention indices relative to retention times of C₇-C₃₁ n-alkanes on the HP-5MS column [40] with those reported in the literature [41]. Secondly, by comparison of their mass spectra with those of authentic standards, as well as those from Wiley 6, NIST02, MassFinder 2.3. Also, a homemade MS library with the spectra corresponding to pure substances and components of known essential oils was used, and finally, wherever possible, by coinjection with an authentic sample (Table 1). Relative standard deviation (RSD) of repeated measurements (independent sample preparations and GC-MS) was for all substances below 1%. The only exceptions which had higher RSD were minor components such as α-agarofuran, (E)-β-ionone, pulegone, safranal and dodecanoic acid where RSD was 2, 6, 7, 9 and 12%, respectively.

4. Conclusions

Comparison of the compositional data of the essential oils extracted from A. uva-ursi, V. vitis-idaea and 12 other Ericaceae taxa (six different genera; available literature data) pointed out to a high level of similarity of Vaccinium and Arctostaphylos species. Based on the identity and relative abundance of the dominant volatile metabolites produced by the compared Ericaceae taxa, it seems that the level of mutual correspondence between A. uva-ursi and V. vitis-idaea species is more significant than that of any of the two taxa and the rest of the compared species. This is partially due to the fact that α-terpineol and linalool were among the dominant contributors to the volatile profiles of both A. uva-ursi and V. vitis-idaea. Furthermore, the most abundant classes of compounds in both oils were basically the same (monoterpenoids, fatty acid derived compounds and carotenoid derived compounds). All stated above additionally corroborates the same pharmacological applications of two herbs. It must be
stressed once again that essential oils may, despite the small yield, contribute to the medicinal properties of the plant [9].

Acknowledgements

The authors are very grateful to the Ministry of Science and Technological Development of Serbia (Project 142054 B), for the financial support of this work.

References and Notes

1. Tucakov, J. *Lečenje Biljem, Fitoterapija*; Rad: Belgrade, Serbia, 1979; pp. 479-481.
2. Grieve, M. *A Modern Herbal*; Dover Publications, Inc.: New York, NY, USA, 1979.
3. Bruneton, J. *Pharmacognosy, Phytochemistry, Medicinal Plants*; Lavoisier Publishing: Paris, France, 1995.
4. Rimando, A.; Kalt, W.; Magee, J.; Dewey, J.; Ballington, J. Resveratrol, pterostilbene, and piceatannol in *Vaccinium* berries. *J. Agric. Food Chem.* 2004, 52, 4713-4719.
5. Pegg, R.B.; Rybarczyk, A.; Amarowicz, R. Chromatographic separation of tannin fractions from a bearberry-leaf (*Arctostaphylos uva-ursi* L. Sprengel) extract by SE-HPLC - a short report. *Polish J. Food Nutr. Sci.* 2008, 58, 485-490.
6. Lehtonen, H.-M.; Lehtinen, O.; Suomela, J.-P.; Viitanen, M.; Kallio, H. Flavonol glycosides of sea buckthorn (*Hippophae rhamnoides* ssp. *sinensis*) and lingonberry (*Vaccinium vitis-idaea*) are bioavailable in humans and monoglucuronidated for excretion. *J. Agric. Food Chem.* 2010, 58, 620-627.
7. Ek, S.; Kartimo, H.; Mattila, S.; Tolonen, A. Characterization of phenolic compounds from lingonberry (*Vaccinium vitis-idaea*). *J. Agric. Food Chem.* 2006, 54, 9834-9842.
8. Ho, K.Y.; Tsai, C.C.; Huang, J.S.; Chen, C.P.; Lin, T.C; Lin, C.C. Antimicrobial activity of tannin components from *Vaccinium vitis-idaea* L. *J. Pharm. Pharmacol.* 2001, 53, 187-191.
9. Radulović, N.; Stojanović, G.; Palić, R. Composition and antimicrobial activity of *Equisetum arvense* L. essential oil. *Phytother. Res.* 2006, 20, 85-88.
10. Radulović, N.; Bлагожевић, П.; Palić, R. Fatty acid derived compounds – the dominant volatile class of essential oil poor *Sonchus arvensis* subsp. *uliginosus* (Bieb.) Nyman. *Nat. Prod. Commun.* 2009, 4, 405-410.
11. Anjou, K.; Von Sydow, E. The aroma of cranberries. I. *Vaccinium vitis-idaea* L. *Acta Chem. Scand.* 1967, 21, 945-952.
12. Anjou, K.; Von Sydow, E. The aroma of cranberries. III. The juice of *Vaccinium vitis-idaea* L. *Acta Chem. Scand.* 1967, 23, 109-114.
13. Sedaghatsoor, S.; Kashi, A.K.; Talaei, A.R.; Khalighi, A. Essential oils of qare-qat (*Vaccinium arctostaphylos*) shoots and chemical composition of berries. *Int. J. Agric. Biol.* 2006, 8, 45-46.
14. Nickavar, B.; Salehi-Sormagi, M.H.; Amin, G.; Daneshtalab, M. Steam volatiles of *Vaccinium arctostaphylos*. *Pharm. Biol.* 2002, 40, 448-449.
15. Zhao, C.; Li, X.; Liang, Y.; Fang, H.; Huang, L.; Guo, F. Comparative analyses of chemical components of essential oils from different samples of *Rhododendron* with the help of chemometrics. *Chemometr. Intell. Lab. Syst.* 2006, 82, 218-228.
16. Innocenti, G.; Dall’Acqua, S.; Scialino, G.; Banfi, E.; Sosa, S.; Gurung, K.; Barbera, M.; Carrara, M. Chemical composition and biological properties of *Rhododendron anthopogon* essential oil. *Molecules* **2010**, *15*, 2326-2338.

17. Olennikov, D.N.; Dudareva, L.V.; Osipenko, S.N.; Penzina, T.A. Chemical composition of *Rhododendron aureum* (gold rosebay) essential oil from Pribaikal’e (Russian Federation). *J. Serb. Chem. Soc.* **2010**, *75*, 209-215.

18. Olennikov, D.N.; Dudareva, L.V.; Osipenko, S.N.; Penzina, T.A. Chemical composition of essential oils from leaves of *Rhododendron dauricum* and *R. aureum*. *Chem. Nat. Compd.* **2009**, *45*, 450-452.

19. Jaenson, T.G.T.; Pålsson, K.; Borg-Karlson, A.-K. Evaluation of extracts and oils of tick-repellent plants from Sweden. *Med. Vet. Entomol.* **2005**, *19*, 345-352.

20. Ueyama, Y.; Hashimoto, S.; Nii, H.; Furukawa, K. Constituents of the essential oil from *Ledum palustre* var. angustum N. Busch. *Nippon Nogei Kagaku Kaishi* **1989**, *63*, 849-851.

21. Tzitsa, R.; Tzakou, O.; Loukis, A. Volatile constituents of *Erica manipuliflora* from Greece. *J. Essent. Oil Res.* **2000**, *12*, 67-68.

22. Rana, V.S.; Verdeguer, M.; Blazguez, M.A. Methyl salicylate: a major constituent of the leaves, flowering twigs and steams of *Gaultheria fragrantissima* Wall. oils. *Indian Perfumer* **2009**, *53*, 47-48.

23. Kivcak, B.; Mert, T.; Demirci, B.; Baser, K.H.C. Composition of the essential oil of *Arbutus unedo*. *Chem. Nat. Compd.* **2001**, *37*, 445-446.

24. Dewick, P.M. The biosynthesis of C5-C25 terpenoid compounds. *Nat. Prod. Rep.* **1999**, *16*, 97-130.

25. Liburd, O.E. Identification of host volatile compounds for monitoring blueberry maggot fly. *Small Fruits Rev.* **2004**, *3*, 307-312.

26. Hirvi, T.; Honkanen, E.; Pyysalo, T. The aroma of cranberries. *Z. Lebensm. Unters. Forsch.* **1981**, *172*, 365-367.

27. Anjou, K.; Von Sydow, E. The aroma of cranberries. II. *Vaccinium macrocarpon* Ait. *Acta Chem. Scand.* **1967**, *21*, 2076-2082.

28. Di Cesare, L.F.; Nani, R.; Proietti, M.; Giombelli, R. Volatile composition of the fruit and juice of blueberry cultivars grown in Italy. *Ind. Aliment.* **1999**, *38*, 277-282.

29. Horvat, R.J.; Schlotzhauer, W.S.; Chortyk, O.T.; Nottingham, S.F.; Payne, J.A. Comparison of volatile compounds from rabbiteye blueberry (*Vaccinium ashei*) and deerberry (*V. stamineum*) during maturation. *J. Essent. Oil Res.* **1996**, *8*, 645-648.

30. Croteau, R.; Fagerson, I.S. Volatile substances derived from the cuticle wax of cranberry. *Phytochemistry* **1971**, *10*, 3247-3249.

31. Hatanaka, A. The fresh green odor emitted by plants. *Food Rev. Int.* **1996**, *12*, 303-350.

32. Oh, Y.-C.; Hartman, T.G.; Ho, C.-T. Volatile compounds generated from the Maillard reaction of Pro-Gly, Gly-Pro, and a mixture of glycine and proline with glucose. *J. Agric. Food Chem.* **1992**, *40*, 1878-1880.

33. Forney, C.F. Horticultural and other factors affecting aroma volatile composition of small fruit. *Horttechnology* **2001**, *11*, 529-538.
34. Von Sydow, E.; Andersson, J.; Anjou, K.; Karlsson, G.; Land, D.; Griffiths, N. Aroma of bilberries (*Vaccinium myrtillus*). II. Evaluation of the press juice by sensory methods and by gas chromatography and mass spectrometry. *Lebensmittel-Wissenschaft Technol.* 1970, 3, 11-17.

35. Blagojević, P.; Radulović, N.; Palić, R.; Stojanović, G. Chemical composition of the essential oils of Serbian wild-growing *Artemisia absinthium* and *Artemisia vulgaris*. *J. Agric. Food Chem.* 2006, 54, 4780-4789.

36. Webb, D.A. Ericaceae. In *Flora Europaea*; Tutin, T.G., Heywood, V.H., Burges, N.A., Moore, D.M., Valentine, D.H., Walters, S.M., Webb, D.A., Eds.; Cambridge University Press: Cambridge, UK, 1972; Volume 3.

37. Cullings, K. Molecular phylogeny of Monotropoideae (Ericaceae) with a note on the placement of the Pyroloideae. *J. Evol. Biol.* 1994, 5, 501-516.

38. Hileman, L.C.; Vasey, M.C.; Parker, V.T. Phylogeny and biogeography of the Arbutoideae (Ericaceae): implications for the Madrean-Tethyan hypothesis. *Syst. Bot.* 2001, 26, 131-143.

39. Clevenger, J.P. Content of essential oil in plants. *Amer. Perfumer Essent. Oil Rev.* 1928, 23, 467-503.

40. Van den Dool, H.; Kratz, P.D. A generalization of the retention index system including linear temperature programmed gas-liquid partition chromatography. *J. Chromatogr.* 1963, 11, 463-471.

41. Adams, R.P. *Identification of Essential Oil Components by Gas Chromatography/Mass Spectrometry*, 4th ed.; Allured Publishing Corporation: Carol Stream, IL, USA, 2007.

*Sample Availability:* Samples of the *A. uva-ursi* and *V. vitis-idaea* essential oils are available from the authors.

© 2010 by the authors; licensee MDPI, Basel, Switzerland. This article is an Open Access article distributed under the terms and conditions of the Creative Commons Attribution license (http://creativecommons.org/licenses/by/3.0/).