Aromas from Quebec. V. Essential oils from the fruits and stems of *Heracleum maximum* Bartram and their unsaturated aliphatic acetates

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**ABSTRACT**

Both the fruits and stems of *Heracleum maximum* Bartram, a common Apiaceae found throughout northern North America, have been traditionally consumed as spice and food by American First Nations and settlers. As both parts of the plant bear a distinctive scent, they have been submitted to volatile constituent extraction and their essential oils were studied by GC–FID and GC–MS. The fruits’ oil was found to be mostly constituted of aliphatic esters, with octyl acetate (65.6%) as main constituent, while the stems yielded a generally terpenic oil, dominated by limonene (45.2%). These results were in line with data for other *Heracleum* species, and constitute the first study of the volatile constituents of *H. maximum*. The observation of several octadecenyl acetates as trace compounds in the stems’ oil allowed for the comprehensive identification of these uncommon and closely related isomers.

**Introduction**

*Heracleum maximum* Bartram (formerly *Heracleum lanatum* Michaux), a member of the Apiaceae, is a large herbaceous plant found across North America, and is commonly known as cow parsnip. Its sturdy, hollow stem reaches up to 3 meters, bearing a flattened inflorescence up to 20 cm wide. The fruits are winged and ridged schizocarps. The plant’s leaves bear three maple-shaped leaflets and their petioles are wrapped around the stalk (1–3). The species has had dietary uses: many native American populations consumed large quantities of the young and tender stalks as raw vegetables, hence another common name, Indian celery, used in soups and desserts (2, 4); the fruits have been also used as spices (1); parts of the stem have also served as a salt substitute (1, 4); and the Meskwaki people used the roots as food (1).

Previous studies have also found it to possess antibacterial and antifungal (5, 6), immunostimulant (2) and antidiabetic (7) properties. As many other Apiaceae, cow parsnip is known to produce a wide range of phototoxic furanocoumarins (2, 8–10), some of which are responsible for the antimycobacterial activity along with (3\text{R},8\text{S})-falcarindiol (11). The furanocoumarins are partly removed by peeling the stalks, a process largely applied by the natives to avoid undesirable toxicity (5).

The stem and fruits both possess a distinct scent (1, 2, 4), which likely contributed to their dietary uses. As the volatile compounds of *H. maximum* have not been studied before, specimens from Saguenay (Quebec, Canada) were picked in order to analyze the composition of the essential oil obtained from the stems and the fruits.

**Experimental**

**Plant material**

*Heracleum maximum* Bartram fruits were collected on 15 July 2014, and stems on 17 July 2014, from a dozen individuals in Saguenay (Quebec, Canada; 48°25′17″ N, 71°02′59″ W). Samples were stored at −15°C until extraction. A voucher specimen was deposited at the Louis-Marie Herbarium, Université Laval, Québec (code QFA0614542).

**Extraction**

Fruits from twelve individuals (123 g) were grossly ground and extracted using a Clevenger apparatus for 3 hours. Frozen stems from the same individuals (1.26 kg) were broken in pieces using a culinary robot and submitted to hydrodiffusion for 3 hours. Essential oil volumes were

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measured directly in the collecting burette. The oils were stored at 4°C until GC analysis.

**GC-FID and GC-MS analysis**

GC-FID analyses were carried out on an Agilent 6890N GC equipped with a split/splittless injector as well as two FID detectors. Columns: DB-5 30 m × 0.25 mm × 0.25 μm film thickness (Agilent Technologies, Santa Clara, CA, USA); SolgelWax (bonded polyethylene glycol) 30 m × 0.25 mm × 0.25 μm film thickness (SGE Analytical Science, Austin, TX, USA). Temperature program: 40°C for 2 minutes, 2°C/min up to 210°C, and 210°C for 13 minutes. Injection temperature: 220°C. Injection volume: 0.1 μL. Inlet pressure: 105.3 kPa. Carrier gas: He, flow rate: 1.4 mL/min. Injection mode: split (235:1). FID (260°C): H₂ flow: 40 mL/min; air flow: 450 mL/min; make up flow (N₂): 45 mL/min. Sampling rate: 0.04 min. Samples were also injected on an Agilent 7890A GC with a split/splittless injector coupled to an Agilent 5975C InertXL EI/CI mass spectrometer. Column: DB-5MS 30 m × 0.25 mm × 0.25 μm film thickness (Agilent Technologies, Santa Clara, CA, USA). Temperature program: same as in GC-FID. Injection temperature: 250°C. Injection volume: 1.0 μL. Inlet pressure: 48.7 kPa. Carrier gas: He, flow rate: 1.0 mL/min. Injection mode: split (50:1). MS interface temp.: 300°C; MS mode: EI; detector voltage: 1.34 kV; mass range: 40–550 u; scan speed: 1458.6 u/s. Data handling was carried out by means of ACD/Spectrus. Compounds were identified from their retention indexes as calculated from even-numbered C₈ to C₃₆ alkane standards and/or from MS databases (NIST08(30), Adams(40), MassFinder 3(41), and custom libraries built from pure compounds). Quantification comes from the FID detector response on the DB-5 column without any correction factor. An estimated experimental relative standard deviation on concentrations obtained by this method is ±1% for compounds representing at least 10% of the oil, ±3% for compounds between 1.0 and 10%, and ±6% for compounds between 0.1% and 1.0%.

**Chemicals**

Oleyl acetate was bought from TCI chemicals (Portland, OR 97203) 11-cis-vaccenyl acetate from Cayman Chemical (Ann Arbor, MI 48108), and (Z)-4-decenol and 9-decenol from Sigma-Aldrich (St-Louis, MO 63103). A drop of each of the two alcohols was also incubated in 500 μL acetone with 200 μL triethylamine and 100 μL acetic anhydride for 24 hours in order to perform acetylation prior to injection.

**Results and discussion**

**Fruits’ oil**

The fruits’ slightly yellow essential oil has an earthy and pungent spicy scent, and was obtained with a yield of 0.41%. Its composition is dominated by the presence of various saturated aliphatic esters (Figure 1). Octyl acetate accounts for almost 66% of the oil (Table 1). This major constituent is common to several members of the *Heracleum* genus. This is the case for *H. crenatifolium* (93%), *H. platytaenium* (85%) (12) and *H. paphlagonicum* (31.5%) (13) collected in Turkey, *H. siamicum* from Thailand (65.3%) (14), *H. spondyllum* ssp. *ternatum* (55–60%) from central Italy (15) and *H. moellendorfii* (63.8%) from China (16). Several other aliphatic esters are commonly found in *Heracleum* fruit oils, and *H. maximum* follows the same trend (Table 2).

A second group of observed compounds consists of unsaturated aliphatic esters, each accounting for 0.1–0.4% of the total FID signal, except for (Z)-3-octenyl acetate, accounting for 3.3%. The identification of (Z)-4-octenyl butyrate was obtained through its retention index values on both columns and its mass spectrum. These unsaturated aliphatic esters were observed in various *Heracleum* species. For example, nine (Z)-4-octenyl esters are present in the fruits of the oil of *H. paphlagonicum* (13) and four in that of *H. spondyllum* ssp. *ternatum* with percentages ranging from <0.1% to 0.6% except for (Z)-4-octenyl acetate (2–5.6%) (12) (Table 2). The percentages of the tentatively identified (Z)-5- and (Z)-6-decenyl acetates range between 0.1% and 0.3% in the *H. spondyllum* ssp. *ternatum* oil (12). As far as (Z)-5-dodecenyl acetate is concerned, this compound was observed in the fruit essential oil of *H. moellendorfii* cultivated in China (16). Finally, isopropyl senecioate (3-methyl-2-butenoate) was identified in *H. paphlagonicum* (13) and very recently in *H. spondyllum* L. ssp. *ternatum* (15).

Although hydrodiffusion of an essential oil is not the best way to appreciate the amounts of furanocoumarins, the presence of three of them (isobergapten, pimpinellin, and imperatorin) in trace amounts is not surprising. Pimpinellin and isobergapten were previously found in *H. lanatum* leaves (8) and *H. maximum* roots (11). Along with other furanocoumarins, they were too extracted with petroleum ether from *H. crenatiolium* (17). Angelicin and bergapten were also observed in the fruit oil of *H. paphlagonicum* (12).

One has to note the presence of very small percentages (<1%) of mono- and sesquiterpenes such as limonene (0.8%), germacrene D (0.3%) and amorpha-4,11-diene (0.3%), with only myrcene reaching a content of 1.6%. Terpinolene (10.8%) is one of the most important
compounds in the fruit oil of *H. antasiaticum* (18). The portrait of the fruit essential oil of *H. maximum* is completed by the presence of the polyyne (Z)-falcarinol (0.6%), as well as of several aliphatic alcohols and aldehydes. Octanol (6.2%) appears in the oils of several *Heracleum* species. Generally, its concentration remains below 4%, as it is the case in *H. sphondyllium* ssp. *ternatum* oil (12, 15).

**Stem’s oil**

The stems’ pale yellow essential oil has a fresh and zesty lemon scent, and was obtained with a yield of 0.02%. The composition of the oil extracted from stems is more conventional in that mono- and sesquiterpenes are the main constituents (Table 1, Figure 1). Limonene (45.3%) is by far the main compound followed by α-thujene, α-pinene and myrcene (each about 6%). The stem oil of *H. persicum*, collected in Iran before flowering, contains various monoterpenes such as terpinolene (20%), limonene and γ-terpinene (each about 11.5%), along with anethole (47%) (19). The anethole percentage increases to 60% after flowering. This compound has not been detected in *H. maximum*. The sesquiterpenic profile is interesting: along with germacrene D (1.2%), amorpha-4,11-diene (1.1%) and α-himachalene (tentative; 0.6%), isodaucene (0.5%) and traces of daucene are also detected. These uncommon compounds are characteristic of a number of Apiaceae: daucene is encountered, for example, in *Pimpinella affinis* stems (5.0%) (20) or in the aerial parts of *Ferula microcolea* (4.1%) (21), and, among others, in *Ferula glauca* roots (0.3–1.4%) (22), aerial parts of *Lomatium parryi* (0.6%) (23) and *Ferulago campestris* flowers and leaves (0.2–0.4%) (24).

The presence of (Z)-falcarinol – [(Z)-heptadeca-1,9-diene-4,6-diyn-3-ol] – (3.3%) must be noted. This compound too was observed in other members of the Apiaceae family such as *Daucus carota* L. (25) and in low percentage in the aerial parts of the *H. transcaucasicum* oil (0.1%) (26) and in methanol extracts of the leaves and roots of *H. moellendorffii* (27). We have previously identified this compound in *Anthriscus sylvestris* root essential oil (28).

Three unknown compounds have been observed on both columns in the stems’ oil, with Unknown I also being a noticeable constituent among the volatile compounds from the fruits. From its MS spectra, Unknown I is not of terpenic nature. It more likely belongs to the aliphatic esters class. This assumption is further backed by the retention index difference between the polar and
| Compound                        | np1  | np2  | p3  | Fruits | Stems |
|--------------------------------|------|------|-----|--------|-------|
| Tiglic aldehyde               | 735  | 737  |     | t      |       |
| Prenol                        | 770  | 765  | 1298| 0.2    |       |
| Prenal                        | 779  | 778  |     | t      |       |
| Hexanal                       | 796  | 797  | 1053| t      |       |
| Isopropyl isobutyrate         | 796  | 790  | 935 | t      |       |
| Isopropyl butyrate            | 832  | 836  |     | t      |       |
| (E)-2-Hexenal                 | 838  | 846  | 1201| 0.1    |       |
| (E)-3-Hexenol                 | 843  | 844  | 1360| t      |       |
| (Z)-2-Hexenol                 | 853  | 854  | 1386| t      |       |
| Hexanol                       | 855  | 863  | 1333| 0.1    |       |
| 2-Methylbutyl acetate         | 866  | 875  |     | t      |       |
| Isopropyl 2-methylbutyrate    | 872  | 880  | 1031| t      | 0.1   |
| Isopropyl isovalerate         | 879  | 895  | 1049| t      | 0.2   |
| (Z)-4-Nonene                  | 881  | 885  | 885 | t      | t     |
| Nonane                        | 884  | 900  | 864 | t      | 0.1   |
| Isobutyl isobutyrate          | 899  | 908  | 1064| t      | 0.2   |
| Heptanal                      | 900  | 901  | 1161| t      |       |
| Tricyclene                    | 903  | 921  | 991 | t      |       |
| α-Thujene                     | 911  | 924  | 1011| 0.1    | 7.7   |
| α-Pinene                      | 917  | 932  | 1006 |0.3    | 6.0   |
| Camphene                      | 932  | 946  | 1035| 0.1    | 1.4   |
| (E)-2-Heptenal                | 943* | 947  |     | t      |       |
| Benzaldehyde                  | 943* | 952  | 1494| t**    |       |
| Isopropyl seneclioate         | 955  | 969  | 1215| t      | t     |
| Sabine                        | 962  | 969  | 1085| 0.2    | 9.5   |
| β-Pinene                      | 965  | 974  | 1069| t      | 2.5   |
| Octen-3-one                   | 974  | 972  |     | t      |       |
| Myrcene                       | 987  | 988  | 1138| 1.6    | 5.8   |
| Octanal                       | 990* | 998  | 1267| 0.9**  | 0.1   |
| Isobutyl 2-methylbutyrate     | 1001 | 1002 | 1149| 0.3    |       |
| Isobutyl isovalerate          | 1004 | 1005 | 1180| 0.2    |       |
| α-Terpine                     | 1011 | 1014 | 1155| 0.3    |       |
| Isoamyl isobutyrate           | 1014 | 1021 | 1172*|0.1    |       |
| Hexyl acetate                 | 1012 | 1007 | 1254| 0.4    |       |
| para-Cymene                   | 1019 | 1020 | 1248*| t      | 0.4   |
| Limonene                      | 1024*| 1024 | 1172*|0.8**  | 45.2**|
| +β-Phellandrene               | 1024*| 1025 | 1182| t**    | 0.7** |
| cis-β-Ocimene                 | 1035 | 1032 | 1220| t      | 0.2   |
| trans-β-Ocimene               | 1045 | 1044 | 1234| t      | 0.4   |
| Isopropyl hexanoate           | 1048 | 1049 |     | t      |       |
| (Z)-2-2-Octenal               | 1053*| 1056 | 1400*| t      |       |
| Isoamyl butyrate              | 1056 | 1052 |     | t      |       |
| γ-Terpine                     | 1053*| 1054 | 1222| t**    | 1.5   |
| (Z)-5-Octenol                 | 1060*| 1065 | 1577| 0.2**  |       |
| cis-Sabinene hydrate          | 1060*| 1065 | 1444*| t**    | 0.1   |
| 4-Nonanone                    | 1068 | 1305 | 1540| 6.2    | 0.2   |
| Octanol                       | 1070 | 1063 |     | t      |       |
| Isobutyl seneclioate          | 1076 | 1329 |     | t      |       |
| Terpinolene                   | 1082 | 1086 | 1263| 0.2    |       |
| 3-Nonanone                    | 1088 | 1089 | 1336| t      |       |
| Linalool                      | 1096*| 1095 | 1532| 0.1**  |       |
| Nonanal                       | 1101*| 1100 | 1373| 0.1    | +**   |
| 2-Methylbutyl 2-methylbutyrate| 1101*| 1101 | 1263| 0.2**  |       |
| Isoamyl isovalerate           | 1103 | 1103 | 1259| t      |       |
| 2-Methylbutyl isovalerate     | 1105 | 1103 | 1279| 0.1    |       |
| β-Thujone                     | 1109 | 1112 | 1407| t      |       |
| Heptyl acetate                | 1111 | 1112 | 1356| t      |       |
| cis-Limomene oxide            | 1130 | 1132 | 1413| t      |       |
| trans-Limomene oxide          | 1131 | 1137 | 1425| 0.1    |       |
| Unknown I                     | 1140 | 1332 | 0.4 | t      |       |
| Hexyl isobutyrate             | 1147 | 1147 | 1326| t      |       |
| Citronellal                   | 1148 | 1148 | 1457| t      |       |
| Borneol                       | 1162 | 1165 | 1668*| t      |       |
| Terpinen-4-ol                 | 1171 | 1174 | 1571*|t      | 0.4   |
| α-Terpineol                   | 1185 | 1186 | 1668*| t      |       |
| Hexyl butyrate                | 1190 | 1191 | 1400*|1.8    |       |
| Estragole                     | 1190 | 1195 | 1633*| 0.1   |       |
| (Z)-4-Decenyl                 | 1192 | 1193 | 1516| 0.1    | t     |
| (Z)-3-Octenyl acetate         | 1196 | 1194 | 1488*| 3.3    |       |
| (Z)-2-Octenyl acetate         | 1196 | 1197 |     | t      |       |
| (Z)-7-Decenyl                 | 1199 | 1199 | 1521| t      |       |

(Continued)
Table 1. (Continued).

| Compound                        | np1          | np2          | p3   | Fruits | Stems |
|---------------------------------|--------------|--------------|------|--------|-------|
| Decanal                         | 1202*        | 1201         | 1479 | 0.7**  | 0.1   |
| trans-Piperitol                 | 1206         | 1207         | 1717 | t      |       |
| Octyl acetate                   | 1210         | 1211         | 1460 | 65.6   | 0.8   |
| (Z)-4-Octenyl acetate           | 1215         | 1510         |      | 0.1    |       |
| Thymol methyl ether             | 1233         | 1232         | 1565 | 0.1    |       |
| Piperitone                       | 1247         | 1249         | 1682 | 0.1    |       |
| Geraniol                        | 1258         | 1249         | 1821 | 0.1    |       |
| (Z)-4-Decenol                   | 1258         | 1255         |      | t      |       |
| (E)-2-Decenal                   | 1266         | 1260         | 1664 | 0.1    |       |
| Decanol                          | 1273         | 1266         | 1744 | 0.1    |       |
| Bornyl acetate                  | 1282         | 1287         | 1546 | 0.1    | 1.4   |
| Heptyl butyrate<sup>1</sup>     | 1291         | 1289         | 1633 | t      |       |
| (Z)-Sabinyl acetate             | 1291         | 1289         | 1633 | t      |       |
| Nonyl acetate                   | 1312         | 1311         | 1561 | 0.1    |       |
| Myrtenyl acetate                | 1321         | 1324         | 1652 | 0.1    |       |
| (S)-Carvyl acetate              | 1335         | 1339         | 1706 | 0.1    |       |
| Benzyl butyrate                 | 1341         | 1343         |      | t      |       |
| α-Terpinyl acetate              | 1345         | 1346         | 1663 | 0.1    |       |
| Octyl isobutyrate               | 1349         | 1348         | 1529 | t      | t     |
| Citronellyl acetate             | 1352         | 1350         | 1642 | t      | 0.4   |
| cis-Carvyl acetate              | 1359         | 1365         | 1741 | t      |       |
| Neryl acetate                   | 1361         | 1359         | 1702 | t      |       |
| (Z)-2-Undecenal                 | 1366         | 1363         |      | t      |       |
| α-Copaene                       | 1370         | 1374         | 1464 | t      | 0.1   |
| (Z)-4-Octenyl butyrate          | 1374         | 1360         |      | 0.3    |       |
| Daucene                         | 1374         | 1380         | 1518 | t      |       |
| β-Bourbonene                    | 1378         | 1387         | 1486 | 0.2    |       |
| Geranyl acetate                 | 1379         | 1379         | 1736 | 0.1    | 0.5   |
| β-Cubebene                      | 1384*        | 1387         | 1510 | 0.1    | 0.1** |
| Benzyl 2-methylbutyrate         | 1384*        | 1392*        |      | t      |       |
| Decen-1-yl acetate (unknown isomer) | 1385       |              |      | 0.3    |       |
| (Z)-4-Decen-1-yl acetate        | 1386*        | 1389<sup>60</sup>  | 1680*| 0.3    | 0.1   |
| Hexyl hexanoate                 | 1386*        | 1382         | 1593 | 0.1**  |       |
| Octyl butyrate                  | 1386*        | 1391<sup>60</sup>  | 1601 | 7.9    | 0.1** |
| Phenylethyl isobutyrate         | 1388*        | 1393         | 1854 | 0.1**  |       |
| (Z)-5-Dodecenal                 | 1389         | 1389<sup>60</sup>  |      | t      |       |
| (Z)-5-Decen-1-yl acetate        | 1391         |              |      | 0.2    |       |
| (E)-4-Decen-1-yl acetate        | 1395         |              |      | 0.2    |       |
| Benzyll isovalerate             | 1395         | 1394<sup>60</sup>  |      | t      |       |
| (Z)-6-Decen-1-yl acetate        | 1399         | 1404<sup>60</sup>  |      | t      |       |
| Methyl eugenol                  | 1400         | 1403         | 1977 | t      |       |
| 9-Decen-1-yl acetate            | 1405         | 1710         | 0.1  |       |       |
| Decyl acetate                   | 1409         | 1407         | 1664 | 0.2    |       |
| β-Caryophyllene                 | 1411*        | 1417         | 1557 | t      | 0.1** |
| 2,5-Dimethoxy-para-cymene       | 1411<sup>1</sup>  | 1424         | 1837 | t<sup>**</sup>  |       |
| Octyl 2-methylbutyrate          | 1429         | 1420<sup>60</sup>  | 1613 | t      |       |
| Octyl isovalerate               | 1442         | 1440<sup>60</sup>  | 1633 | t      |       |
| α-Humulene<sup>1</sup>          | 1446*        | 1452         | 1626 | t<sup>**</sup>  | 0.1** |
| α-Himachalene<sup>1</sup>       | 1451         | 1449         | 1616 | 0.2    | 0.6   |
| Amorph-4,11-diene                | 1455*        | 1449         | 1622 | 0.2**  | 1.1** |
| Amyl α-pyrone                   | 1455*        | 1514         | 2134 | 0.1**  |       |
| trans-β-Farnesene               | 1455*        | 1454         | 1649 | 0.1**  |       |
| γ-Murolene                      | 1472         | 1478         | 1626 | t      |       |
| Germancrene D                   | 1475         | 1484         | 1668<sup>1</sup>  | 0.3    | 1.2   |
| ar-Curcumene                    | 1479         | 1479         | 1741<sup>1</sup>  | t      | 0.1   |
| Phenylethyl isovalerate<sup>1</sup> | 1483        | 1487<sup>[27]</sup>  | 1949<sup>1</sup>  | 0.1    |       |
| α-Zingiberene                   | 1493*        | 1493         | 1694 | 0.2    | 0.3** |
| Isodiene                        | 1493*        | 1500         | 1686 | t      | 0.5** |
| epi-Cubebol                     | 1493*        | 1493         | 1841 | t      | t<sup>**</sup>  |
| β-Isobolene                     | 1501         | 1505         | 1699 | t      | 0.1   |
| cis-α-Isobolene                 | 1509         | 1506         | 1702<sup>1</sup>  | t      | 0.1   |
| Geranyl isobutyrate             | 1510*        | 1514         | 1792 | t<sup>**</sup>  |       |
| γ-Cadinene                      | 1510*        | 1513         | 1717 | t<sup>**</sup>  |       |
| Cubebol                         | 1513         | 1514         | 1905 | t      |       |
| β-Sesquiphellandrene            | 1520<sup>1</sup>  | 1521         | 1741<sup>1</sup>  | 0.1    | 0.4** |
| δ-Cadinene                      | 1520<sup>1</sup>  | 1522         | 1726 | t      | t<sup>**</sup>  |
| trans-γ-Isobolene               | 1528         | 1529         | 1726 | t      |       |
| Elemicin                        | 1554         | 1555         | 2186 | t      |       |
| Geranyl butyrate                | 1558         | 1562         | 1871 | t      |       |
| (Z)-4-Octenyl hexanoate         | 1569         | 1805<sup>1</sup>  |      | t      |       |
| Spathulanol                     | 1569         | 1577         | 2078 | t      |       |
| Octyl hexanoate                 | 1581         | 1565<sup>[28]</sup>  | 1796 | 2.2    | t     |

(Continued)
The derivatization of alkenes into methylsulfide adducts following the method of Buser et al. (29) confirmed these two assignations and led to the identification of three more compounds from their specific fragments (given in parentheses): (\(Z\))-5-decen-1-yl acetate (\(m/z = 115, 117, 292\)), (\(Z\))-6-decen-1-yl acetate (\(m/z = 103, 129, 292\)) and (\(E\))-4-decen-1-yl acetate, which has the same sulfide ions as its (\(Z\))-counterpart (\(m/z = 101, 131, 292\)). Only the first ester adduct (\(m/z = 101, 103, 292\)) could not be rationalized into a structure, possibly due to rearrangements.

At least five octadecenyl acetates are observed in \(H. maximum\) stem essential oil. An attempt to produce the sulfide adducts proved fruitless given the small amount of oil available and the very small concentrations of these esters in the sample. Although several mass spectra are available from literature, their correct identification is not an easy task. For example, at least two dozens (including non-polar columns, which is consistent with an ester moiety. Unknowns II and II more reasonably belong to the oxygenated sesquiterpenes class. Unknown II’s molecular mass seems to be missing, as the large retention index difference indicates that it probably bears several oxygenated functions, while Unknown III is probably a sesquiterpenic alcohol, given its molecular mass and retention indexes.

**Disambiguation of unsaturated esters identification**

The MS of the six decen-1-yl acetates encountered in \(H. maximum\) fruits’ essential oil are so similar that any identification of their right structure is not obvious. The RI values available from literature and those measured in the present work also preclude a confident identification. Only (\(Z\))-4-decen-1-yl acetate and 9-decen-1-yl acetate could be formally identified by coinjection of pure compounds.

The derivatization of alkenes into methylsulfide adducts following the method of Buser et al. (29) confirmed these two assignations and lead to the identification of three more compounds from their specific fragments (given in parentheses): (\(Z\))-5-decen-1-yl acetate (\(m/z = 115, 117, 292\)), (\(Z\))-6-decen-1-yl acetate (\(m/z = 103, 129, 292\)) and (\(E\))-4-decen-1-yl acetate, which has the same sulfide ions as its (\(Z\))-counterpart (\(m/z = 101, 131, 292\)). Only the first ester adduct (\(m/z = 101, 103, 292\)) could not be rationalized into a structure, possibly due to rearrangements.

At least five octadecenyl acetates are observed in \(H. maximum\) stem essential oil. An attempt to produce the sulfide adducts proved fruitless given the small amount of oil available and the very small concentrations of these esters in the sample. Although several mass spectra are available from literature, their correct identification is not an easy task. For example, at least two dozens (including

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**Table 1. (Continued).**

| Compound | Retention Indexes | % on DB-S |
|----------|------------------|-----------|
| np\(^1\) | np\(^2\) | p\(^3\) | Fruits | Stems |
| 1587 | 1805* | t | |
| 1592 | 1597\[^{[2]}\] | 1925 | 0.1 | |
| 1608 | 1611 | 1900 | t | t |
| 1615 | 1619 | 2348 | t | t |
| 1617 | 1622 | t | t |
| 1620 | 1627 | t | t |
| 1635 | 1640 | 2139 | t | t |
| 1639 | 1645 | t | t |
| 1648 | 1652 | 2180 | t | t |
| 1654* | 2576 | 0.5 | |
| 1679 | 1685 | 2300* | t | 0.1 |
| 1685 | 2242 | 0.3 | |
| 1727 | 1733 | t | t |
| 1752 | 1755\[^{[3]}\] | 2064 | t | t |
| 1756 | 2699 | t | t |
| 1776 | 1779\[^{[2]}\] | 1993 | t | t |
| 1779 | 1998 | t | t |
| 1812 | 1811\[^{[4]}\] | t | t |
| 1843 | 2114 | t | t |
| 1879 | 1874 | 2356 | t | 0.1 |
| 1900 | 1900 | 1899 | t | t |
| 1962 | 1959 | 2864 | 0.2 | t |
| 1993 | 1995\[^{[3]}\] | 2920\[^{[1]}\] | t | t |
| 2007 | 2022\[^{[3]}\] | t | t |
| 2007 | 2003 | t | t |
| 2030 | 2035 | 2974 | 0.6 | 3.3 |
| 2035 | 2033 | t | t |
| 2059 | 2062\[^{[3]}\] | 2585 | t | 0.1 |
| 2081 | 2077 | 2561 | 0.1 | t |
| 2106 | t | t | t |
| 2139 | t | t | t |
| 2179 | t | t | t |
| 2185 | 2185\[^{[4]}\] | 2509 | 0.1 | t |
| 2190 | 2513 | t | t |
| 2196 | 2515 | t | t |
| 2202 | 2523 | t | t |
| 2206 | 2209 | 2486 | t | t |
| 2289 | 2300 | 2486 | t | t |
| 2316 | t | t | t |
| Total identified | 97.8 | 98.4 |

Notes: *Compound coelutes with others on this column. **Percentage from SgelWax column, given for compounds coeluting on DB-5. t: Trace (<0.05%).

\(^{[1]}\) Non-polar column: DB-5. Rf from R.P. Adams’ book (40), unless otherwise indicated. \(^{[2]}\) Polar column: SgelWax. Mass spectra of unknown compounds, Ei, 1.34 kV, 300°C, m/z (rel. int.): Unknown I: 141 (26), 97 (33), 87 (100), 84 (90), 68 (16), 56 (17), 55 (32), 43 (27), 41 (29); Unknown II: 202 (70), 187 (8), 161 (15), 147 (100), 146 (24), 145 (29), 133 (15), 131 (22), 117 (21), 115 (19), 91 (25), 77 (14); Unknown III: 222 (3), 204 (15), 189 (7), 161 (14), 148 (9), 137 (100), 121 (30), 119 (79), 109 (43), 95 (34), 93 (42), 84 (70), 83 (34), 69 (56), 67 (27), 55 (46), 41 (63).
Table 2. Content (%) of some major esters among various *Heracleum* species fruits' essential oils.

| Compounds            | *H. maximum* | *H. crenatfolium* | *H. platytaenium* | *H. sphondylum* ssp. *temnatum* | *H. moellecorffii* | *H. antasisticum* | *H. paphlanicum* | *H. pyrenacum* ssp. *polinianum* | *H. orphnidis* | *H. persicum* | *H. rechingeri* | *H. gorphanicum* | *H. anisactis* | *H. pastinifolium* | *H. rawwianum* | *H. sibiricum* | *H. candleanum* |
|----------------------|--------------|-------------------|-------------------|---------------------------------|-------------------|-------------------|-----------------|---------------------------------|----------------|---------------|----------------|----------------|----------------|----------------|---------------|---------------|----------------|
| Hexyl acetate        | 0.4          | t                 | 0.1               | 1.3                             | -                 | t                 | -               | t                 | 0.4             | t             | 0.5             | 1.9             | -              | t               | 0.5           | -             | -              |
| Hexyl butyrate       | 1.8          | -                 | 0.4               | 17.0                            | -                 | 0.2               | -               | 2.2               | 21.5            | 22.5-35.4      | t               | t               | 17.7           | 38.4          | 33.3          | 5.3            |
| Hexyl hexanoate      | 0.1          | -                 | 0.1               | 5.2                             | -                 | -                 | 0-3.0           | -                 | 3.7             | 3.3           | 6.2             | 0.3             | 0.2           | 0.5            | -             | -             |
| Octyl acetate        | 65.6         | 93.7; 88.4        | 87.6              | 31.5                            | 65.3              | 31.6; 54.9-60.2   | 63.8            | 17.4              | 19.0-27.0       | 50.5           | 84.5            | 20.5             | 13.8          | 18.4          | 48.7           | 59.5          |
| Octyl butyrate       | 7.9          | t; 0.2            | 0.4               | 3.2                             | -                 | 37.7; 10.1-13.4   | 12.2            | -                 | 2.1-2.6         | 0.6            | 4.1             | 3.1             | 2.0           | 16.8          | 9.7            | 4.4           |
| Octyl hexanoate      | 2.2          | t; 0.7            | 3.0               | 10.2                            | -                 | 0.9; 3.0-4.8      | 0.8             | -                 | 3.5             | 9.7           | 1.6             | 0.1             | 0.5           | 2.5            | 0.5           | 0.2          |
| Octyl octanoate      | t            | -; 0.4            | 0.7               | 0.1                             | -                 | t                 | -               | -                 | 1.1             | 0.3           | 0.8             | -               | t             | -              | -             | -             |
| Decyl acetate        | 0.2          | 0.7; 0.5          | 0.3               | 0.2                             | -                 | 0.5; 0.5-0.8      | 0.6             | -                 | 1.2             | 1.0           | -               | -               | -             | -              | -             | -             |
| Decyl butyrate       | t            | -                 | -                 | -                               | -                 | 0.3               | -               | -                 | 1.2             | -             | -               | -               | -             | -              | -             | -             |
| Decyl hexanoate      | t            | -                 | -                 | -                               | -                 | -                 | -               | -                 | -               | -             | -               | -               | -             | -              | -             | -             |
| (Z)-4-Octenyl acetate| 0.1          | 0.1; 1.0          | 2.1               | 5.6                             | -                 | 3.3               | -               | -                 | -               | -             | -               | -               | -             | -              | -             | -             |
| (Z)-4-Octenyl butyrate| 0.3        | -                 | t                 | 0.6                             | -                 | 2.6               | -               | -                 | -               | -             | -               | -               | -             | -              | -             | -             |

Reference: This work (12); (17) (12) (13) (14) (12); (15) (16) (18) (19) (50) (50) (56) (56) (56) (56) (56) (56) (56) (56) (56) (56) (57) (58)
To our knowledge, the RI values on the DB-5 column for the $n$-C$_{18}$ monoene acetates have not been published altogether, contrarily to their C$_{12}$, C$_{14}$ and C$_{16}$ counterparts (32) (Table 3). The RI values measured for each of the five observed compounds (Figure 2) shed some light. For example, the saturated $n$-C$_{14}$ and $n$-C$_{16}$ acetates elute from the DB-5 column before the two last monoene compounds listed in Table 3. On this basis, one can eliminate the presence of the $n$-C$_{15}$ and $n$-C$_{16}$ and probably the $n$-C$_{17}$ isomers. Moreover, the RI values seem to increase as the double bond position $x$ increases beyond 7. Thus, we suggest that the observed $n$-octadecenyl acetates were those indicated in the last (Z) and (E) isomers) of analogues are included in the NIST database (30). Unfortunately, these MS are very similar, and subtle differences introduced by the analytical methods used make it difficult to ascertain the double bond position of the compounds, $x$, on the basis of their sole MS spectra. From the intensity of the peak $m/z = 68$, one can eliminate the presence of 2-, 3-, 15- and 16-octadecenyl acetates. The best fits with the NIST database for the most intense peak (RI(DB-5) = 2184) are: $x = 13$, 935; $x = 12$, 926; $x = 9$, 924 and $x = 11$, 920. The observed MS for this peak is almost identical to that of the synthetic cis-vaccenyl acetate [(Z)-11-octadecenyl acetate] reported in literature (31).

Table 3. Retention indexes values of (Z)-monoene acetates on non-polar columns.

| Double bond position, $x$ | n-C$_{12}$ | n-C$_{14}$ | n-C$_{16}$ | n-C$_{18}$ |
|---------------------------|----------|----------|----------|-----------|
| saturated                 | 1609     | 1811     | 2013     | 2209      |
| 3                         | 1591     | 1791     | 1994     | 2190      |
| 4                         | 1589     | 1787     | 1987     | 2190      |
| 5                         | 1592     | 1790     | 1989     | 2193      |
| 6                         | 1593     | 1789     | 1987     | 2193      |
| 7                         | 1598     | 1792     | 1988     | 2200      |
| 8                         | 1605     | 1796     | 1990     | 2206      |
| 9                         | 1611     | 1801     | 1993     | 2184,5    |
| 10                        | 1630     | 1807     | 1998     | 2186      |
| 11                        | 1812     | 2004     | 2191     | 2192      |
| 12                        | 1831     | 2011     | 2192     | 2193      |
| 13                        |          | 2016     | 2200     | 2200      |
| 14                        |          | 2033     |          | 2202      |
| 15                        |          |          | 2212     | 2212      |
| 16                        |          |          |          | 2250**    |
| 17                        |          |          |          | HP-SMS [39] |

Notes: *Tentative identification (see discussion). **Obtained by interpolation, ±20 units.

To our knowledge, the RI values on the DB-5 column for the $n$-C$_{18}$ monoene acetates have not been published altogether, contrarily to their C$_{12}$, C$_{14}$ and C$_{16}$ counterparts (32) (Table 3). The RI values measured for each of the five observed compounds (Figure 2) shed some light. For example, the saturated $n$-C$_{14}$ and $n$-C$_{16}$ acetates elute from the DB-5 column before the two last monoene compounds listed in Table 3. On this basis, one can eliminate the presence of the $n$-C$_{15}$ and $n$-C$_{16}$ and probably the $n$-C$_{17}$ isomers. Moreover, the RI values seem to increase as the double bond position $x$ increases beyond 7. Thus, we suggest that the observed $n$-octadecenyl acetates were those indicated in the last

Figure 2. Close-up of the stems’ essential oil chromatogram obtained with FID on a DB-5 column around the $n$-octadecenyl acetates timeframe. Identified compounds are (Z)-falcarinol (A), oleyl alcohol (B), octadecanol (C), (E)-falcarinol? (D), (Z)-10-octadecenyl acetate (E), oleyl acetate (F), (Z)-vaccenyl acetate (G), (Z)-12-octadecenyl acetate (H), (Z)-13-octadecenyl acetate (I), octadecyl acetate (J) and tricosane (K).
column of Table 3. The reported RI(DB-5) value for (Z)-vaccenyl acetate is 2192 (31). The definitive identification was obtained by the injection of the pure compound. The identity of oleyl acetate [(Z)-9-octadecenyl acetate] was confirmed in the same way.

Another study gives the relative retention time of the octadecenyl acetates to eicosane on a HP-1 column in isotherm conditions (33). There is a clear effect of the double bond position. As soon as the x value is higher than 8, higher x values result in longer retention times. Simultaneously, the vapor pressure of the compound becomes lower. Of course, this discussion takes into account the (Z) isomers and obliterates the (E) isomers. These cis compounds have similar MS and RI values (32).

These natural n-octadecenyl acetates are not very common. Several of them are observed in animals as pheromones or venoms. In the Plant kingdom, they generally are individually observed. Among the tentatively identified acetates, only the (E)-10 and the 11-isomers are reported in one member of the Brassicaceae (34) and the Asteraceae (35) family, respectively. On the other hand, the (Z)-3, (Z)-6-, (Z)-9 and seventeen isomers are observed in Apiaceae (36), Rubiaceae (37), Caesalpiniaefae (38) and Araliaceae families (39) families.

In conclusion, examination of the chromatograms obtained for the essential oils of the fruits and stems of *Heracleum maximum* leads to the identification of 114 and 126 compounds, respectively. The fruits’ essential oil is rich in aliphatic esters, mainly octyl acetate, in line with previously reported data for other Apiaceae species. As soon as the x value is higher than 8, higher x values result in longer retention times. Simultaneously, the vapor pressure of the compound becomes lower. Of course, this discussion takes into account the (Z) isomers and obliterates the (E) isomers. These cis compounds have similar MS and RI values (32).

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Disclosure statement

No potential conflict of interest was reported by the authors.

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