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# VOLATILE AROMA CONSTITUENTS OF PARSLEY LEAVES

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**Key Word Index**—*Petroselinum crispum*; Umbelliferae; parsley; aroma volatiles.

**Abstract**—The aroma volatiles of a desert parsley were analysed using routine procedures, and 45 constituents were positively identified, including 11 not previously reported as parsley leaf volatiles. One component, 2-(*p*-tolyl)propan-2-ol, is a new aroma volatile and, together with *p*-mentha-1,3,8-triene, may be unique to parsley. Major constituents of the sample were 4-methoxy-6-(prop-2-enyl)benzo-1,3-dioxolan (myristicin), 4,7-dimethoxy-5-(prop-2-enyl)benzo-1,3-dioxolan (apiole), *β*-phellandrene, *p*-mentha-1,3,8-triene and 4-isopropenyl-1-methylbenzene. Aroma assessments during GC showed that apiole, in particular, had desirable parsley odour character.

## INTRODUCTION

Fresh leaves of parsley (*Petroselinum crispum* (Mill.) Nyman) are widely used whole as a garnish, but chopped, either fresh or dried, they add a strong characteristic flavour to many foods. However, there have been surprisingly few studies of the aroma volatiles responsible for parsley leaf flavour. Probably the first investigation was of a commercial leaf oil from Yugoslavia, and eight volatiles, including a previously unknown compound (*p*-mentha-1,3,8-triene), were identified by IR spectrometry [1, 2]. Some years later, Kasting *et al.* used more modern techniques (GC/MS) and identified an additional 42 volatiles, although a few of these were certainly artifacts or contaminants [3]. In 1975 Freeman *et al.* identified 14 constituents in the headspace vapours above minced parsley leaves, but only three of these were additional parsley volatiles [4]. In 1983 Vernon and Richard claimed a further 12 new parsley leaf volatiles [5], but in fact one had already been reported.

Parsley has been grown in Britain since the 16th century, but early cultivated forms had finely divided leaves which were not curled or crisped like those of the familiar modern cultivar (var. *crispum*). However, plain-leaved parsley (Italian parsley, var. *neapolitanum* Danert) is still grown on the Continent. In this investigation the aroma volatiles of a desert parsley (cultivated in an oasis area of the Libyan desert) were studied for the first time. The plant has much broader and less curled leaves than British parsley and grows taller.

## RESULTS AND DISCUSSION

Fresh parsley was purchased from local markets in Brack, Libya, and air dried. Valid aroma extracts were prepared using well-established procedures and were concentrated by high vacuum–low temperature distillation [6]. The resultant essences were found, on appropriate re-dilution, to possess a strong, characteristic parsley aroma.

Samples were analysed by GC and GC/MS, and results are given in Table 1. A number of GC columns was employed, including packed columns (PEG 20M) and fused silica capillary columns containing either bonded-phase BP1 (equivalent to OV 101) or BP20 (equivalent to PEG 20M). The retention data given in Table 1 were obtained using a 25 m fused silica column (BP20). Literature Kováts retention indices [7, 8] of most components (on PEG 20M) are also included in the Table, and confirm the general elution sequence (although it will be noticed that some compounds show slightly different relative elution behaviour on BP20 and PEG 20M, e.g. *α*-pinene and *α*-thujene, *γ*-terpinene and *trans*-*β*-ocimene). The qualitative data in Table 1 were obtained using both bonded-phase fused silica columns; some components were more readily identified by GC/MS using one particular phase. Where positive identities are given, the mass spectra obtained on GC/MS agreed with those in the literature.

The quantitative data in Table 1 show that in total about 7 mg of aroma components were obtained per gram of air-dried parsley (*ca* 0.7 % w/w). This represents an estimated level of *ca* 1.75 mg/g total volatiles for the fresh leaves, which is a very high concentration. Overall, 91 components were detected as parsley volatiles, of which 45 (comprising *ca* 96.9 % w/w of the sample) were positively identified, with a further 9 (*ca* 1.7 %) partially or tentatively characterized. The 37 (*ca* 1.4 %) unidentified components are not included in Table 1 and were present in such small amount that either no mass spectrum could be recorded or the spectrum was too poor for interpretation. Of the fully identified components, 11 are reported as parsley leaf volatiles for the first time, and these are indicated in Table 1 by +. The tentatively identified methylhexadiene and the dimethylbenzofuran would also be new for parsley leaf.

Most of the identified parsley volatiles are terpenes. Twenty-two monoterpenes were detected comprising *ca* 51.8 % (w/w) of the sample; all were hydrocarbons, except for *α*-terpineol, 2-(*p*-tolyl)propan-2-ol and 2-(*p*-tolyl)propanal. Fourteen sesquiterpenes (*ca* 4.7 %) were also recognized, and again the majority (11) were hydro-

Table 1. Volatile components of parsley leaf

| Peak number* | Component | New | $R_t$ (min) | Kováts index (lit.)† | % rel. abund.‡ | μg/g‡ | Odour quality |
|---|---|---|---|---|---|---|---|
| 1 | Methyl alcohol plus dimethyl sulphide | | 2.0 | | 0.1 | 7.6 | Sulphurous, cabbage water, decaying vegetable |
| 2 | ? A methylhexadiene | + | 2.8 | | 0.3 | 20.0 | Slight caramel |
| 3 | An amine | | 3.2 | | 0.1 | 7.3 | Green, stale |
| 5 | α-Pinene | | 3.6 | 1039 | 5.1 | 353.0 | Mace, slight oil of wintergreen |
| 6 | α-Thujene | | 3.9 | 1036 | 0.1 | 6.5 | Fruity, buttery |
| 7 | Toluene | | 4.0 | 1055 | tr | tr | |
| 8 | Camphene | | 4.2 | 1079 | 0.2 | 12.9 | |
| 9 | Hexanal | + | 4.6 | 1084 | 0.1 | 7.9 | Green, cut grass |
| 10 | β-Pinene | | 5.0 | 1124 | 1.8 | 127.8 | Green, slightly fruity |
| 11 | Sabinene | | 5.4 | 1130 | 0.3 | 18.7 | — |
| 12 | Car-3-ene plus | | 5.6 | 1144 | 0.2 | 14.0 | — |
| | *m*- and/or *p*-xylene | | | *ca* 1144 | tr | tr | |
| 13 | Myrcene | | 6.2 | 1156 | 4.3 | 302.0 | Green, dried herbs |
| 14 | α-Phellandrene | | 6.4 | 1177 | 0.7 | 51.2 | Solvent, estery |
| 15 | Monoterpene hydrocarbon | | 6.6 | | tr | 2.7 | Fruity, estery |
| 16 | α-Terpinene | + | 6.9 | 1192 | tr | 1.6 | Nutmeg |
| 19 | Limonene | | 7.4 | 1206 | 3.6 | 252.0 | Lemongrass, fruity |
| 20 | β-Phellandrene | | 7.7 | 1216 | 12.4 | 867.2 | Fatty, oily |
| 21 | 2-Pentylfuran | + | 8.2 | 1229 | 0.1 | 3.6 | Putty, stale |
| 22 | *cis*-β-Ocimene | | 8.6 | 1228 | tr | 2.7 | |
| 23 | γ-Terpinene | | 9.0 | 1251 | 0.4 | 29.0 | Slightly sage, green |
| 24 | *trans*-β-Ocimene | | 9.2 | 1250 | 0.1 | 5.2 | — |
| 26 | *p*-Cymene | | 9.9 | 1272 | 1.4 | 97.8 | Fruity, citrus |
| 27 | α-Terpinolene | | 10.3 | 1287 | 2.1 | 148.1 | Mushrooms |
| 28 | *p*-Mentha-1,3,8-triene | | 14.8 | | 9.2 | 640.7 | Chewing gum, spearmint |
| 30 | *cis*-Hex-3-en-1-ol | | 16.2 | 1351 | 0.1 | 6.4 | Dandelions, green leaves |
| 31 | 4-Isopropenyl-1-methylbenzene | | 16.6 | | 7.2 | 500.6 | Meaty, musty, smoky |
| 34 | α-Cubebene | | 18.8 | *ca* 1485 | 0.2 | 12.9 | Green, floral, estery |
| 37 | Benzaldehyde | + | 19.4 | 1502 | tr | 2.4 | Green, caramel, roasted malt |
| 38 | α-Copaene | | 20.3 | 1520 | tr | tr | |
| 39 | Sesquiterpene hydrocarbon | | 20.8 | | 0.1 | 4.3 | |
| 43 | β-Elemene | | 23.0 | *ca* 1618 | 0.1 | 6.3 | Slightly nutty |
| 44 | β-Caryophyllene | | 23.4 | 1618 | 0.4 | 30.1 | Green sap |
| 47 | Phenylacetaldehyde | + | 25.1 | 1646 | 0.1 | 4.8 | Geranium, rose, floral, phenylacetaldehyde |
| 48 | γ-Elemene | | 25.6 | | 0.1 | 4.3 | Pine-like |
| 49 | α-Terpineol | | 26.0 | 1661 | 1.7 | 117.2 | Minty, spearmint |
| 51 | 4-Isopropylcyclohex-2-enone(cryptone) | | 26.2 | | 0.1 | 6.4 | Linseed oil, putty, musty, stale nuts |
| 52 | Sesquiterpene hydrocarbon | | 26.7 | | 0.4 | 30.9 | |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 55 | Sesquiterpene alcohol | | 27.4 | | 0.6 | 39.0 | Unpleasant green, dried herbs |
| 56 | A dimethylbenzofuran | + | 27.7 | | tr | tr | |
| 57 | γ-Cadinene | + | 28.0 | 1764 | 0.5 | 36.8 | Stale dried parsley |
| 61 | 2-(*p*-Tolyl)propanal plus<br>sesquiterpene hydrocarbon | | 29.2 | | 0.3<br>tr | 20.4<br>tr | Dried herbs, chemical solvent |
| 65 | *p*-Methylacetophenone plus<br>sesquiphellandrene | | 30.4 | 1750 | 1.9<br>tr | 133.3<br>1.9 | Jasmine, floral, almonds |
| 68 | β-Bisabolene | + | 30.8 | 1746 | 0.5 | 33.3 | Stale nuts, putty |
| 72 | α-Elemene | + | 32.6 | | 1.0 | 69.2 | Stored apples |
| 75 | 2-(*p*-Tolyl)propan-2-ol | + | 33.6 | | 0.7 | 47.3 | |
| 77 | Sesquiterpene alcohol | | 36.2 | | 0.2 | 11.8 | — |
| 79 | δ-Cadinol | + | 39.8 | 2150 | 0.6 | 40.6 | Baked apple, cloves |
| 83 | 5-(Prop-2-enyl)-1,2,3-trimethoxybenzene (elemicin) | + | 48.9 | | 0.3 | 18.5 | Musty, mouldy |
| 85 | 4-Methoxy-6-(prop-2-enyl)-benzo-1,3-dioxolan (myristicin) | | 50.6 | | 20.6 | 1435.0 | Nutmeg, cloves |
| 87 | 4,7-Dimethoxy-5-(prop-2-enyl)-benzo-1,3-dioxolan (apiole) | | 66.1 | | 18.3 | 1275.0 | Spicy, parsley |

*Order of elution from a BP20 GC column.

†Lit. [7, 8].

‡Quantitative data are derived from triplicate analyses and agreed ±1%.

tr, Trace.

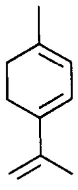
carbons, the remainder being alcohols. The most abundant terpenes were *β*-phellandrene (*ca* 12.4%) and *p*-mentha-1,3,8-triene (*ca* 9.2%). The identification of *ca* 3.6% of limonene and trace amounts of *cis*-*β*-ocimene is worthy of comment. These compounds were reported as constituents of Yugoslav commercial leaf oil [1, 2], but they were not detected in either of the subsequent more detailed studies of Swedish [3] and British [4] parsleys, although limonene was identified in French parsley [5]. Kasting *et al.* pointed out that parsley seed oil contains both of these compounds and suggested that there might have been contamination of the Yugoslav leaf oil with seed material [3]. Such contamination was not possible in our work, and so limonene and *cis*-*β*-ocimene are indeed genuine constituents of parsley leaf.

As well as *p*-mentha-1,3,8-triene (**1**), a closely related compound, 4-isopropenyl-1-methylbenzene (**2**), has also been previously reported as a major volatile of parsley leaf [1–5], and in our analysis it was found to be present to the extent of *ca* 7.2% (Table 1). However, whilst the menthatriene is unique to parsley, the isopropenylmethylbenzene has been relatively widely reported as a volatile, e.g. of citrus fruits, currants, anis, mace and coffee [9]. One of the new terpenoid parsley constituents is 2-(*p*-tolyl)propan-2-ol (**3**) which is closely related to **1** and **2**. It can be considered to be a hydration product of the isopropenylmethylbenzene, but in addition it is structurally related to *α*-terpineol (**4**) as a tetradehydro derivative. *α*-Terpineol is also a parsley leaf volatile (Table 1), and indeed it was the only other monoterpene alcohol detected. However, also identified was the aldehyde 2-(*p*-tolyl)propanal (**5**), previously reported for parsley [5], which can also be considered a member of this structurally-related series. Presumably all five compounds are linked biosynthetically (together they comprised *ca* 19.1% of the total volatiles in our sample). As well as being a new volatile for parsley leaf, 2-(*p*-tolyl)propan-2-ol has not before been reported as an aroma volatile of any other system. Thus, together with the menthatriene, it would appear on present evidence to be unique to parsley.

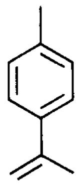
Two of the best known aroma constituents of parsley are myristicin and apiole, and in our analysis they account for *ca* 20.6 and 18.3%, respectively, of the total volatiles. However, they do have wider occurrence and, for example, both have been found in celery, and myristicin has also been reported in carrot, anis, nutmeg, mace, pepper, etc. [9]. Systematic names for these compounds are given in Table 1 (peaks 85 and 87), showing their structural relationship (**6** and **7**). Another new parsley constituent identified in this work is elemicin or 5-(prop-2-enyl)-1,2,3-trimethoxybenzene (peak 83, Table 1), but again this has wider occurrence and has, for example, been reported in elemi oil, banana, anis, origanum and mace [9]. From its structure (**8**) it can be seen that it is related to myristicin and apiole, and again there may well be biosynthetic links between these three compounds. Although elemicin has not previously been identified as a parsley leaf volatile, Garnero *et al.* reported 5-(prop-2-enyl)-1,2,3,4-tetramethoxybenzene to be a constituent of parsley leaf oil [1]. Subsequent studies [3–5] have not confirmed that identification, and nor could the compound be detected in this work. Taking into account that Garnero *et al.* were only able to use IR spectrometry as their analytical technique [1], it may be that they misinterpreted the trimethoxybenzene as the tetramethoxy analogue. Alternatively, perhaps the latter compound was a contaminant from seed oil subsequently suspected to be present [3].

Myristicin is also well known as the chief hallucinogenic principle of nutmeg. In addition, it is interesting to note that elemicin, which has also been found in nutmeg [10], has much structural similarity with the classic hallucinogen of the peyote cactus, mescalin (or 5-(2-aminoethyl)-1,2,3-trimethoxybenzene). Although myristicin and elemicin are present in parsley leaf in total at *ca* 363 μg/g fresh weight, this is about one fiftieth of their combined concentration in nutmeg [10], and we have not seen it suggested that parsley has any hallucinogenic properties.

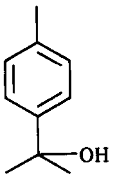
With regard to the important characteristic aroma components of parsley, Garnero *et al.* described *p*-



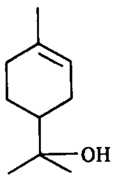
**1**



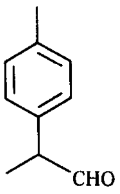
**2**



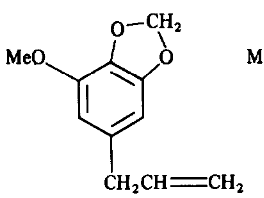
**3**



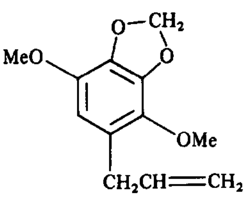
**4**



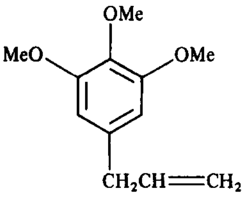
**5**



**6**



**7**



**8**

mentha-1,3,8-triene as having the odour of parsley leaves [1]. However, Kasting *et al.* showed that this compound was only one of several that gave a parsley-like aroma including, in particular, β-phellandrene and the GC peak that comprised a mixture of terpinolene and 4-isopropenyl-1-methylbenzene [3]. Freeman *et al.* agreed with these findings, but separated terpinolene and the isopropenylmethylbenzene to show that it was the latter that possessed the parsley-like character [4]. It would thus appear that there is a reasonable consensus that β-phellandrene, *p*-mentha-1,3,8-triene and 4-isopropenyl-1-methylbenzene are important contributors to parsley leaf flavour, although recently Vernon and Richard have claimed that β-phellandrene, *p*-mentha-1,3,8-triene and myristicin are not characteristic of parsley flavour [5]. The individual aroma descriptions recorded in this project (Table 1) agree reasonably well in detail with those previously reported (and particularly those of Kasting *et al.* [3]), but only one constituent was specifically described as having desirable parsley character, and that was apiole. Surprisingly, the previous workers [3–5] did not report any aroma quality for apiole, but there seems little doubt that it should be added to the above list of characteristic aroma constituents of parsley leaf.

## EXPERIMENTAL

Fresh parsley was obtained from local markets in Brack, Libya and air dried to *ca* 25% of fresh weight.

*Sample preparation.* A stirred slurry of 87.7 g of chopped dried parsley in 1750 ml $H_2O$ was extracted for 3 hr using a modified [11] Likens and Nickerson apparatus [12] and 2-methylbutane (60 ml) as solvent. Extracts were subsequently concd as previously described [11].

*GC.* FID-GC: 25 m × 0.2 mm i.d. fused silica capillary column coated with BP20 (or BP1) bonded phase; hydrogen, 1.2 ml/min; temp. programme, 70° for 5 min then 3°/min to 180°; detector and injection point heaters, 275° and 250°, respectively; injection volume, typically 0.1 μl at 25:1 split. A 5.5 m × 4 mm i.d. glass column packed with 10% PEG 20 M was also used.

*GC-MS.* A Kratos MS25 instrument was used, linked on-line to a Kratos DS50 data processing system. Capillary GC conditions as above were used, with He as carrier gas. The single stage all glass jet separator was at 250°. Significant operating parameters of the MS were: ionization voltage, 70 eV; ionization current, 100 μA; source temp., 225°; accelerating voltage, 1.33 kV; resolution, 1500; scan speed, 1 sec/decade (repetitive throughout run).

*Quantitative assessment.* Samples were prepared in such a manner that a known aliquot of the parsley sample was analysed. Quantitative data were then derived both from the TIC monitor trace during GC-MS, and from the GC-FID trace during routine GC. EtOAc (0.050 M) was used as quantitative GC standard and corrections were made for the carbon-number of the identified constituents. An average correction factor was applied to unidentified GC peaks.

*Odour assessment.* Aromas of the separated components of the sample were assessed at an odour port following GC. An outlet splitter at 10:1 diverted the major fraction of the eluate through a heated line to the outside of the GC oven for aroma assessment by three subjects.

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## REFERENCES

1. Garnero, J., Benezet, L., Peyron, L. and Chrétien-Bessière, Y. (1967) *Bull. Soc. Chim. Fr.* **12**, 4679.
2. Garnero, J. and Chrétien-Bessière, Y. (1968) *France Parfums* **60**, 332.
3. Kasting, R., Andersson, J. and von Sydow, E. (1972) *Phytochemistry* **11**, 2277.
4. Freeman, G. G., Whenham, R. J., Self, R. and Eagles, J. (1975) *J. Sci. Food Agric.* **26**, 465.
5. Vernon, F. and Richard, H. M. J. (1983) *Lebensm.-Wiss. u.-Technol.* **16**, 32.
6. MacLeod, A. J. and de Troconis, N. G. (1982) *J. Agric. Food Chem.* **30**, 515.
7. Andersen, N. H. and Falcone, M. S. (1969) *J. Chromatogr.* **44**, 52.
8. Jennings, W. G. and Shibamoto, T. (1980) *Qualitative Analysis of Flavour and Fragrance Volatiles by Glass Capillary Gas Chromatography*. Academic Press, New York.
9. Van Straten, S., Maarse, H., de Beauveser, J. C. and Visscher, C. A. (1983) *Volatile Compounds in Foods*, 5th edn. Division for Nutrition and Food Research TNO, Zeist.
10. Schenk, H. P. and Lamparsky, D. (1981) *J. Chromatogr.* **204**, 391.
11. MacLeod, A. J. and Cave, S. J. (1975) *J. Sci. Food. Agric.* **26**, 351.
12. Likens, S. T. and Nickerson, G. B. (1964) *Proc. Am. Soc. Brew. Chem.* 5.