NOVEL KEY AROMA COMPONENTS OF GALBANUM OIL

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Abstract

Considering the complexity and potency of the odour, galbanum oil was assumed to contain so far not identified compounds with high odour contribution. By gas chromatography-mass spectrometry-olfactometry analysis of galbanum oil, fruity-green-balsamic notes were detected at two different retention times. The mass spectra of the newly discovered notes were elucidated by conducting multidimensional gas chromatography-mass spectrometry-olfactometry (MD-GC-MS-O). By analysing the MS data, six chemical structures were proposed: (6E/Z,8E)-undeca-6,8,10-trien-2-one, (6E/Z,8E)-undeca-6,8,10-trien-3-one, and (6E/Z,8E)-undeca-6,8,10-trien-4-one. The compounds were then synthesised in an attempt to match the MS, retention indices, and odour qualities. The MD-GC-MS-O analyses of the candidate compounds led to the identification of the novel key aroma compounds, (6Z,8E)-undeca-6,8,10-trien-3-one and (6Z,8E)-undeca-6,8,10-trien-4-one, in galbanum oil. These compounds have fairly low thresholds in water of 0.010 ppb and 0.072 ppb, respectively.

Introduction

Galbanum oil is obtained by steam distillation of the resin of Ferula galbaniflua (Boissier et Buhse), a large Umbellifer plant that grows wild mainly in Iran, Turkey, Afghanistan, and neighbouring countries. The oil, a widely used ingredient in industry, has a powerful green odour with dry-woody, balsamic, and bark-like tonalities (1). In perfumery, the oil is used to confer green notes and augment fougeré, chypre, and oriental notes. In flavouring, it contributes to the savoury notes of curries and sauces.

Galbanum oil is mainly composed of hydrocarbon monoterpenes (2) such as β-pinene, α-pinene, and Δ₃-carene, but these components hardly contribute to the characteristic green notes. Instead, the tiny quantities of C11 hydrocarbons and methoxyypyrazines present in the oil contribute most to the aroma (3). But the complexity and potency of the green odour could not solely be explained by the compounds identified so far. Therefore, we assumed that there were clearly other hidden key odorants that contribute to the total aroma. In this study we used GC-MS-O to discover these components in a commercially available galbanum oil from Iran.

Experimental

Iranian galbanum oil was purchased from Nihon SiberHegner (Tokyo, Japan). (6E/Z,8E)-Undeca-6,8,10-trien-2-one (1) (6E:6Z = 47:53), (6E/Z,8E)-undeca-6,8,10-
trien-4-one (2) \((6E:6Z = 46:54)\) and \((6E/Z,8E)-undeca-6,8,10-trien-3-one (3) \((6E:6Z = 50:50)\) were synthesised in our laboratory (Figure 1).

**Figure 1. Syntheses of \((6E/Z,8E)-undeca-6,8,10-trien-2-one (1), (6E/Z,8E)-undeca-6,8,10-trien-4-one (2) and (6E/Z,8E)-undeca-6,8,10-trien-3-one (3)\)**

To concentrate the key aroma, commercial galbanum oil (950 g) was distilled to yield a distillate (103.2 g) which was confirmed to have the target odour of fruity-green-balsamic notes by GC-MS-O. Then silica gel chromatography was performed three times to yield a concentrated effluent (660 mg) having the target odour. Upon MD-GC-MS-O analysis of the concentrated effluent, the section of the chromatogram that was obtained via the first GC equipped with a polar column (TC-WAX) as containing the compound with the target odour was selectively injected to the second GC equipped with a nonpolar column (TC-1) and analysed by GC-MS-O.

The thresholds and odour qualities of synthesised \((6E/Z,8E)-undeca-6,8,10-trienones\) were evaluated in water solutions of a mixture of \((6E)\) and \((6Z)\)-isomers by a trained panel.

**Results**

To identify the odour-active compounds, we analysed galbanum oil by GC-MS-O and detected characteristic odours at five different retention times on a TC-WAX column. We were able to identify four odour-active compounds of five characteristic odours by matching them with MS, retention indices (RIs), and odour qualities, as follows: \((3E,5Z)-undeca-1,3,5-triene\) for the fruity and pineapple-like odour (RI= 1403), 2-isopropyl-3-methoxypyrazine for the earthy odour (RI= 1446), linalool for the fruity and floral odour (RI= 1550), and guaiacol for the medicinal odour (RI= 1863). For the fruity, green, and balsamic odour (RI= 1899), however, a low content of the odour-active compound and overlapping in the chromatogram with other compounds thwarted our attempt to obtain the MS. Therefore, we attempted to obtain the MS by concentrating the compound.

After thorough studies, we found that the target compound was fairly low in both volatility and polarity. By a combined method of distillation and repeated silica gel chromatography, we removed low-boiling compounds, hydrocarbon terpenes, oxygenated terpenes and polar compounds from commercial oil in sequence and finally obtained a concentrated effluent having the target odour, which was then analysed by MD-GC-MS-O. As a result, although we had presumed that the aroma would originate from only one compound, we were surprised to detect the target
fruity-green-balsamic odour at two different retention times (RI= 1316 and 1328) on the TC-1 column. We thus obtained the pure MS of two compounds, hereinafter referred to as “unknown A” and “unknown B”.

Two features of the unknowns suggested that the compounds were structural isomers: (i) their similar fruity-green-balsamic odour, and (ii) the correspondence of the molecular weight (MW) of 164. The fragment ions at m/z 43 and 71 of unknown A were characteristic of an acetyl group or a butyroyl group, whereas the fragment ion at m/z 57 of unknown B was characteristic of a propionyl group. These data suggested that an oxygen atom was present in the molecules. The MW of the unknowns (164) minus that of an oxygen atom (16) plus that of two hydrogen atoms (2) is 150, exactly the same MW of (3E,5Z)-undeca-1,3,5-triene, one of the characteristic odour components of galbanum oil. Thus, we assumed that the chemical structures of the unknowns were oxygenated isomers of (3E,5E/Z)-undeca-1,3,5-triene, namely, (6E/Z,8E)-undeca-6,8,10-trien-2-one (1) or (6E/Z,8E)-undeca-6,8,10-trien-4-one (2) for unknown A and (6E/Z,8E)-undeca-6,8,10-trien-3-one (3) for unknown B.

The syntheses of the candidate compounds, (6E/Z,8E)-undeca-6,8,10-trien-2-one (1), (6E/Z,8E)-undeca-6,8,10-trien-4-one (2) and (6E/Z,8E)-undeca-6,8,10-trien-3-one (3), were accomplished by application of a Wittig reaction with the same phosphonium salt 6 (4) as the key step (Figure 1).

![Figure 2. Mass spectra (MS-EI) of (I) (6E/Z,8E)-undeca-6,8,10-trien-2-one (1), (II) (6E/Z,8E)-undeca-6,8,10-trien-4-one (2) and (III) (6E/Z,8E)-undeca-6,8,10-trien-3-one (3).](image)

**Table 1.** Retention indices of unknowns and (6E/Z,8E)-undeca-6,8,10-trienones on TC-WAX and TC-1 columns.

<table>
<thead>
<tr>
<th>No.</th>
<th>Compound</th>
<th>RI on TC-WAX</th>
<th>RI on TC-1</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Unknown A</td>
<td>1899</td>
<td>1316</td>
</tr>
<tr>
<td></td>
<td>Unknown B</td>
<td>1899</td>
<td>1328</td>
</tr>
<tr>
<td>1a</td>
<td>(6Z,8E)-Undeca-6,8,10-trien-2-one</td>
<td>1913</td>
<td>1320</td>
</tr>
<tr>
<td>1b</td>
<td>(6E,8E)-Undeca-6,8,10-trien-2-one</td>
<td>1947</td>
<td>1338</td>
</tr>
<tr>
<td>2a</td>
<td>(6Z,8E)-Undeca-6,8,10-trien-4-one</td>
<td>1899</td>
<td>1316</td>
</tr>
<tr>
<td>2b</td>
<td>(6E,8E)-Undeca-6,8,10-trien-4-one</td>
<td>1899</td>
<td>1328</td>
</tr>
<tr>
<td>3a</td>
<td>(6Z,8E)-Undeca-6,8,10-trien-3-one</td>
<td>1899</td>
<td>1328</td>
</tr>
<tr>
<td>3b</td>
<td>(6E,8E)-Undeca-6,8,10-trien-3-one</td>
<td>1924</td>
<td>1339</td>
</tr>
</tbody>
</table>

For confirmation, the synthesised compounds were analysed according to the same method used to analyse unknowns in galbanum oil. Although the odour of the ketone 1 was similar to that of unknown A, the MS and RI of the ketone 1 did not match those of unknown A. However, finally, we identified unknown A as (6Z,8E)-undeca-6,8,10-trien-4-one (2a), a novel compound in galbanum oil, by matching the