

# Odor Analysis of (E)- and (Z)-3,7-Dimethyl-4-octen-1-ols and Their Derivatives

By Czeslaw Wawrzenczyk, Institute of Fundamental Chemistry, Agricultural University, Wrocław;  
Robert Obara, Institute of Chemistry, Pedagogical University, Kielce;  
and Jozef Gora, Institute of General and Food Chemistry, Technical University, Lodz, Poland

We studied the relationship between the shape of the molecule and the odor properties of the isoprenoid compounds, focusing our attention on how these odor properties were influenced by the configuration of the double bond.

This article describes a study of a group of (E)-compounds and a separate group of (Z)-compounds obtained from (E)- and (Z)-isomers of 3,7-dimethyl-4-octen-1-ol.

## Materials and Methods

3,7-Dimethyl-4-octen-1-ol, however isomeric to known monoterpene alcohols citronellol and menthocytronellol, has never been identified in natural materials. Earlier, this alcohol was obtained as a mixture of (E)- and (Z)-isomers<sup>1</sup> or in mixture with menthocytronellol.<sup>2</sup> Both pure isomers of 3,7-dimethyl-4-octen-1-ol were synthesized by us<sup>3,4</sup> according to Scheme 1.

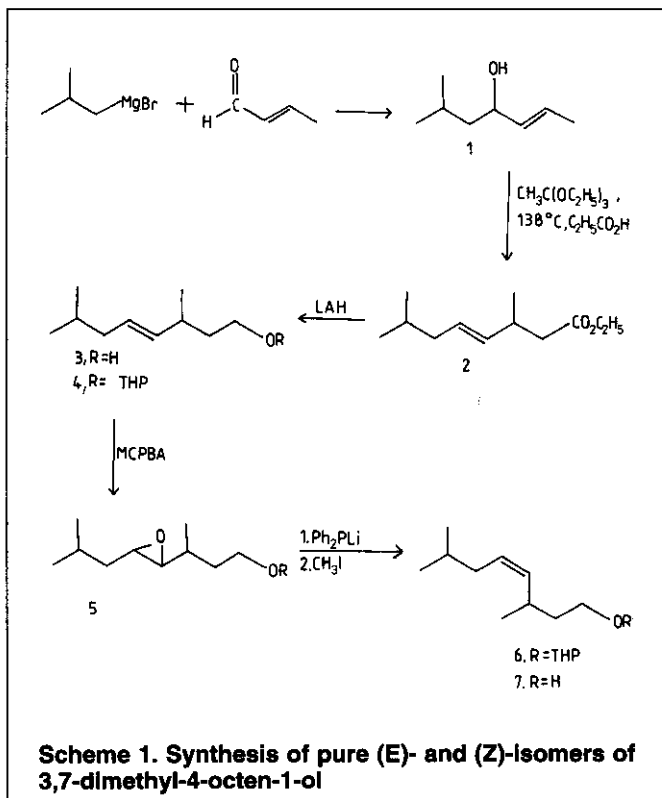
The Grignard reaction of crotonaldehyde with isobutylmagnesium bromide afforded allylic alcohol [1] which was subjected to the Claisen rearrangement by the orthoacetate modification.<sup>5</sup> According to the <sup>1</sup>H-NMR ( $J_{H-5,H-6} = 16$  Hz) and IR ( $\bar{\nu} = 970$  cm<sup>-1</sup>) data, the double bond in the resulting  $\gamma,\delta$ -unsaturated ester [2] (yield 89%) has the (E)-configuration. The ester [2] was reduced with lithium aluminium hydride to alcohol [3] (yield 94%).

The (Z)-isomer [7] (above 97% purity, gc) of 3,7-dimethyl-4-octen-1-ol was obtained via isomerization of alcohol [3]. For this purpose, alcohol [3] was transformed in tetrahydropyran ether [4] which was epoxidized with m-chloroperbenzoic acid (MCPBA) to epoxy ether [5]. Deoxygenation of the epoxy ether [5] was carried out according to a procedure described by Vedejs and Fuchs,<sup>6</sup> leading to a compound with the (Z) double bond (ether [6]). Deprotection of ether [6] with pyridine p-toluenesulfonate (PPTS) afforded alcohol [7] (45% yield based on alcohol [3]). The (Z)-configuration of the double bond in alcohol [7] was confirmed by <sup>1</sup>H-NMR ( $J_{H-5,H-6} = 11.5$  Hz) as well as by IR ( $\bar{\nu} = 710$  cm<sup>-1</sup>).

Having at our disposal the two isomeric alcohols [3] and [7], we could now synthesize two groups of corresponding derivatives as depicted in Scheme 2.

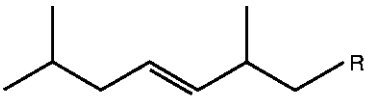
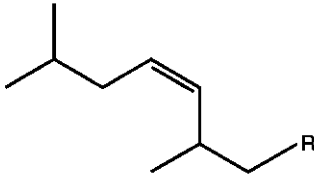
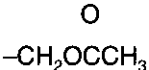
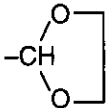
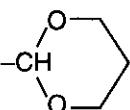
Acetylation (acetyl chloride or acetic acid anhydride, respectively) of [3] and [7] delivers the isomeric (E)- and (Z)-acetates [8a] and [8b] in high yields (85-92%).<sup>7,8</sup>

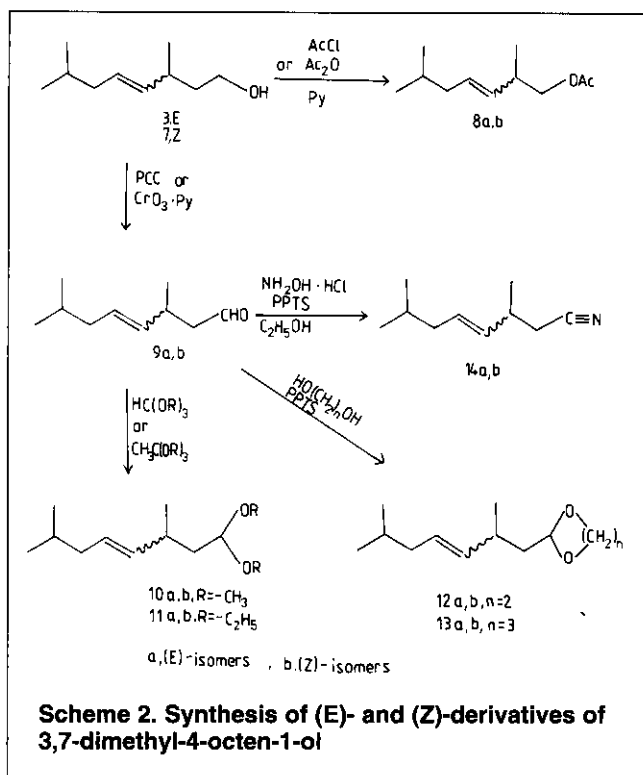
Aldehyde [9a] was synthesized by oxidation of alcohol [3] with pyridine chlorochromate.<sup>9</sup> Application of the same reagent as well as of pyridine dichromate for oxidation of alcohol [7] didn't afford aldehyde [9b] in satisfactory yield; cyclic carbonyl products formed<sup>10</sup> even though sodium acetate was used in the reaction medium. Finally, aldehyde



ODOR ANALYSIS

**Table I. Odor descriptions of the synthesized (E)- and (Z)-isomers**

	(E)- isomers	(Z)- isomers
R		
-CH <sub>2</sub> OH	<b>3</b> C <sub>10</sub> H <sub>20</sub> O intensive, agreeable, citronellal-like with marked rose note	<b>7</b> C <sub>10</sub> H <sub>20</sub> O medium-intensive, agreeable mushroom with vegetable note
	<b>8a</b> C <sub>12</sub> H <sub>22</sub> O <sub>2</sub> intensive, agreeable, fruity with wild strawberry note	<b>8b</b> C <sub>12</sub> H <sub>22</sub> O <sub>2</sub> medium-intensive, fruity-floral, sweet
-CHO	<b>9a</b> C <sub>10</sub> H <sub>18</sub> O intensive, fresh verdure with coriander oil note, unlike citronellal odor	<b>9b</b> C <sub>10</sub> H <sub>18</sub> O intensive, fresh, floral with marked cuminic note, unlike citronellal odor
-CH(OCH <sub>3</sub> ) <sub>2</sub>	<b>10a</b> C <sub>12</sub> H <sub>24</sub> O <sub>2</sub> intensive, agreeable, fresh, floral with fruity note, resembling dried apricot and mango	<b>10b</b> C <sub>12</sub> H <sub>24</sub> O <sub>2</sub> medium-intensive, similar to odor of (E)-isomer but less fresh and less marked dried apricot note
-CH(OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	<b>11a</b> C <sub>14</sub> H <sub>28</sub> O <sub>2</sub> intensive, floral with yeasts note	<b>11b</b> C <sub>14</sub> H <sub>22</sub> O <sub>2</sub> medium-intensive, agreeable floral with tea-rose and peony note
	<b>12a</b> C <sub>12</sub> H <sub>22</sub> O <sub>2</sub> medium-intensive, agreeable, floral with fruit note, odor similar to <b>13a</b> but without ambergis note	<b>12b</b> C <sub>12</sub> H <sub>22</sub> O <sub>2</sub> medium-intensive, agreeable floral with marked humus-woody note
	<b>13a</b> C <sub>13</sub> H <sub>24</sub> O <sub>2</sub> medium-intensive, more intensive than the (Z)-isomer, agreeable, fresh, floral with ambergis note	<b>13b</b> C <sub>13</sub> H <sub>24</sub> O <sub>2</sub> medium-intensive, fruity-floral with slightly fresh note
-CN	<b>14a</b> C <sub>10</sub> H <sub>17</sub> N intensive, fresh, citrus-floral, with marked citrus note	<b>14b</b> C <sub>10</sub> H <sub>17</sub> N intensive, agreeable, penetrating, citrus-cuminic like neral with marked note of coriander oil and carrot leaves



[9b] was obtained when the chromium trioxide-pyridine complex<sup>11,17</sup> was used for oxidation of alcohol [7].

Aldehydes [9a] and [9b] were the starting materials in the synthesis of corresponding acyclic acetals [10a,b] and [11a,b] and also in corresponding cyclic acetals [12a,b] and [13a,b]. For the acyclic acetals, triethyl or trimethyl orthoformate was used, or, for the first time as far as we know, triethyl or trimethyl orthoacetate.<sup>13,14</sup> Dioxolanes [12a,b] and dioxanes [13a,b] were synthesized by reaction of aldehydes [9a] or [9b] with ethylene glycol or 1,3-propanediol, respectively, and *p*-toluenesulfonic acid or pyridine *p*-toluenesulfonate as acidic catalyst.<sup>15,16</sup>

Isomeric nitriles [14a] and [14b] were obtained in satisfactory yields (57-65%) from aldehydes [9a] and [9b] by dehydration of their oximes.<sup>17,18</sup>

The purity of compounds obtained was checked by gas and thin-layer chromatography. All compounds, for which the odor was evaluated, were above 97% (gc). Their odor characteristics are given in Table I.

## Results and Discussion

Due to their pleasant, original odors and natural origin, the monoterpene alcohols geraniol, nerol and citronellol as well as their derivatives are used in many fragrance compositions.<sup>19</sup> This group of well-known compounds has also been studied for structure-odor relationships as a consequence of configurational differences in their molecular structure. The double bond with (*E*)-configuration makes the molecule rather linear whereas a (*Z*)-configuration makes it more ball shaped.

A few years ago, we presented studies<sup>20</sup> describing the

influence of the placement of the double bond in the isoprenoid chain on the odor properties of some isomeric compounds. Having now at our disposal two further groups of isomeric (E)- and (Z)-compounds, we could draw some additional conclusions with respect to the configuration of the double bond and its influence on the odor.

The comparative olfactory analysis of isomeric pairs of compounds shows essential differences in the character as well as in the intensity of the odors. The most distinct difference in kind was observed for the (E)- and (Z)-isomers of the title alcohol. The (E)-isomer [3] is characterized by a pronounced floral odor whereas the (Z)-isomer [7] has a more mushroom-like odor with a vegetable note.

In general, with the exception of alcohol [7], compounds with (Z)-configuration of the double bond are characterized by pleasant floral or floral-fruity odor notes whereas (E)-isomers exhibit odors with more distinctly marked fruity notes.

Furthermore, it can be noticed that the odors of (E)-isomers, in most of the tested pairs, are more intensive than those of the corresponding (Z)-isomers.

#### References

Address correspondence to Jozef Gora, Institute of General and Food Chemistry, Technical University of Lodz, ul. Stefanowskiego 4/10, 90-924 Lodz, Poland.

1. WE Parham and HE Holmquist, *J Am Chem Soc* **76** 1173 (1954)
2. French Patent 1479677 (1967)
3. C Wawrzenczyk, Z Przepiorka and A Zabza, *Pol J Chem* **55** 819 (1981)
4. C Wawrzenczyk, *Structural Analogues of Insect Juvenile Hormones*, Wroclaw: Wroclaw Technical University Press (1985)
5. WS Johnson, L Werthemann, WR Bartlett, TJ Brocksom, TT Li, DJ Faulkner and MR Peterson, *J Am Chem Soc* **92** 741 (1970)
6. E Vedejs and PL Fuchs, *J Am Chem Soc* **95** 825 (1973)
7. Polish Pat Appl 93588, C Wawrzenczyk and R Obara (1992)
8. Polish Pat Appl 293589, R Obara and C Wawrzenczyk (1992)
9. EJ Corey and JW Suggs, *Tetrahedron Lett* 2647 (1975)
10. EJ Corey and G Schmidt, *Tetrahedron Lett* 399 (1979)
11. R Ratcliff and R Rodehorst, *J Org Chem* **35** 4000 (1970)
12. Polish Pat Appl 293587, R Obara and C Wawrzenczyk (1992)
13. Polish Pat Appl 293655, C Wawrzenczyk, R Obara and J Gora (1992)
14. Polish Pat Appl 293656, R Obara, C Wawrzenczyk and J Gora (1992)
15. Polish Pat Appl 293653, R Obara, C Wawrzenczyk and J Gora (1992)
16. Polish Pat Appl 293654, C Wawrzenczyk, R Obara and J Gora (1992)
17. Polish Pat 115359, C Wawrzenczyk, Z Przepiorka, A Zabza and J Gora (1982)
18. Polish Pat Appl 293657, C Wawrzenczyk, R Obara and J Gora (1992)
19. H Boelens, in *Fragrance Chemistry*, ET Theimer, ed, Academic Press (1982) p 123
20. C Wawrzenczyk, A Zabza and J Gora, *Perf & Flav* **8** 39 (1983)

