Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 1995, **5(3)**, 115–118
Mendeleev Communications

Substitution Pattern at the Double Bond as a Factor in the Green Odour of the C_5-C_{10} Alkenols

Andrei A. Vasil'ev,*[a] Georgii V. Cherkaev[b] and Marina A. Nikitina[b]

[a] *N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 117913 Moscow, Russian Federation. Fax: +7 095 135 5328; e-mail: L110@suearn2.bitnet*
[b] *Research and Production Centre "Synthetic and Natural Fragrances", 117393 Moscow, Russian Federation.*

The type of odour of 47 C_5-C_{10} alkenols has been compared with the standard fragrance of leaf alcohol [3(*Z*)-hexen-1-ol] using a four-point scale; the structure–odour relationship shows the similarity of their odour to that of the standard to depend on the substitution pattern at the double bond and the number of carbon atoms in their molecules.

The green scent as a perfume character has not been defined thoroughly inasmuch as it is not associated with any particular substance. Among all the known chemicals bearing this odour the structural analogues may be confined to certain restricted groups, so the difference in their olfactive properties in some cases appears to be very significant.[1–3]

In the work presented during the search for a potential substitute for the leaf alcohol [3(*Z*)-hexen-1-ol] **1**, a very important perfume component with a fresh green odour, we have synthesized and tested about fifty olefinic alcohols **2**–**48** (Table 1; for their synthesis see our previous papers[4–6]). These alkenols can be distinguished from **1** by the carbon chain

Table 1 The similarity (A–D)[a] of the alkenols C_5-C_{10} to the standard odour of leaf alcohol.

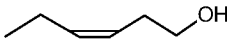
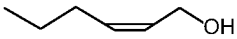
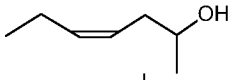
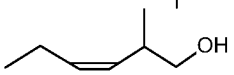
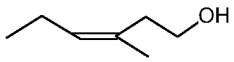
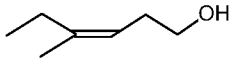
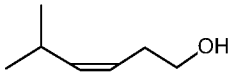
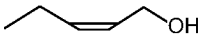
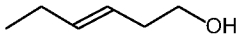
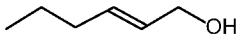
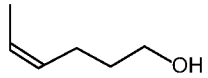
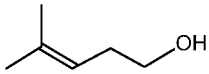
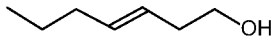
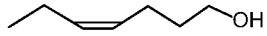
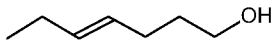
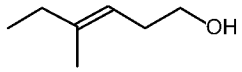
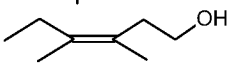
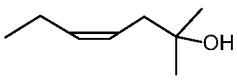
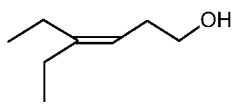
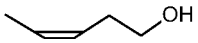
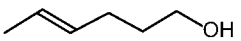
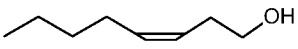
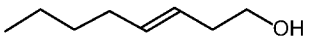
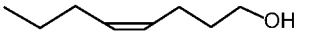
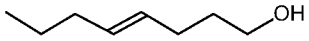
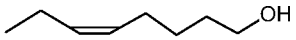
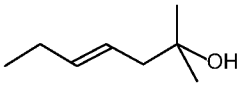
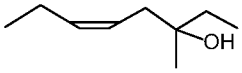
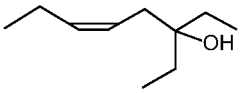
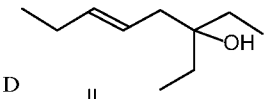
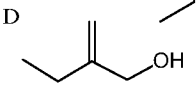
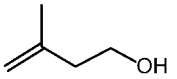
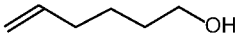
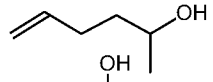
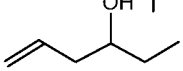
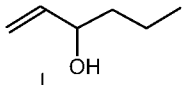
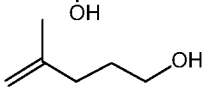
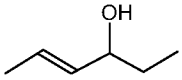
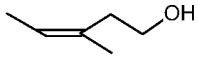
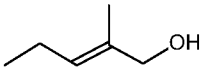
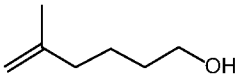
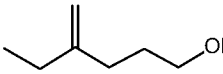
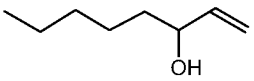
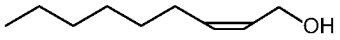
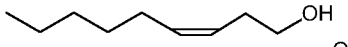
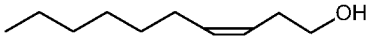
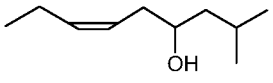
Compound	Structural formula	Odour characteristic	Number of structural variations[b] compared with **1**	Number of carbon atoms in the molecule
1		Fresh green	Standard	C_6
Group A				
2		Green	1	C_6
3		Green with a weak fatty nuance	1	C_7
4		Green but less delicious than **1**	1	
5		Green	1	
6		Green with a weak minty nuance	1	
7		Green with a weak floral nuance	1	
8		Green	1	
Group B				
9		Green with a strong chemical note	1	C_5
10		Green with a floral nuance	1	C_6
11		Green with a fatty nuance	2	
12		Harsh green with a strong fatty note	1	
13		Green with a chemical nuance	2	
14		Green with citrus and chemical nuances	2	C_7
15		Green with fatty and iris nuances	1	
16		Green with chemical and iris notes	2	
17		Green with floral and chemical notes	2	
18		Green with a turpentine nuance	2	C_8
19		Pungent green, floral	2	
20		Green with chemical and camphor nuances	2	
Group C				
21		Vegetable with a green note	1	C_5
22		Fatty unpleasant with a green nuance	2	C_6
23		Pungent green with fatty and iris notes	2	C_8

Table 1 (continued)

24		Fatty floral with a pungent green nuance	3	
25		Fatty with green and iris nuances	2	
26		Floral with fatty and green nuances	3	
27		Green with spicy and fatty nuances	2	
28		Floral with green and woody-turpentine nuances	3	
29		Green with floral and turpentine nuances	3	C_9
30		Green with floral and turpentine nuances	4	C_{10}
31		Green with fruity and turpentine nuances	5	
Group D				
32		Chemical	4	C_5
33		Harsh chemical with a camphor note	3	
34		Fatty unpleasant	2	C_6
35		Harsh fatty unpleasant	3	
36		Chemical	4	
37		Harsh chemical	5	
38		Harsh fatty unpleasant	3	
39		Chemical	4	
40		Turpentine	2	
41		Turpentine	4	
42		Floral with a fresh note	3	C_7
43		Camphor with a minty nuance	3	
44		Mushroom	7	C_8
45		Fatty with green and iris nuances	4	C_9
46		Violet leaves with iris and fatty notes	3	
47		Aldehydic with a fruity nuance	4	C_{10}
48		Mushroom with a green nuance	4	

[a] A, close to the standard; B, rather close to the standard but with other notable scents; C, slightly reminiscent of the standard; D, other types of odour. [b] A single structural variation implies insertion of one carbon unit or its removal, or transfer of the double bond into the adjacent position, or a reversal of its configuration.

length, the position and configuration of the double bond and the presence of substituents in different places in the molecules. It should be noted that similar investigations were performed earlier but only within the narrow limit of unbranched alkenols,[7–9] so there has been little evidence with which to realize the origin of the green odour.

During organoleptic tests on the alkenols **2**–**48** we have defined not only the "verbal" characteristics of their odour, but also evaluated their similarity to the standard (which was considered to be the smell of the leaf alcohol **1** itself). As a result the alkenols **2**–**48** were divided into four groups: A, close to the standard; B, rather close but with other notable scents; C, slightly reminiscent of the standard; and D, other types of fragrance (see Table 1).

The similarity to the standard of the odour of the compounds under examination was found to decrease gradually along with an increase in the structural variations in the initial molecule **1**. The substances belonging to the groups A, B and C exhibit this decrease, which is mainly due to homologization (lengthening, shortening or branching of the carbon chain); changing the position or configuration of the double bond exerts a smaller effect (see, *e.g.*, the odour of the isomeric octenols **23**–**27**). A further increase in the structural variations leads to a weakening of the green note and finally its extinction (alcohols **32**–**48**, group D).

Screening of the compounds from group D shows that besides the higher leaf alcohol homologues **45**–**48** there is a noticable number of C_5-C_8 alkenols **32**–**44**. The majority are distinguished by the terminal double bond; alcohols **39** and **40** possess β-methyl substituents and only alcohol **41** contains a β-ethyl group (that the latter alcohol belongs to group D may be attributed to the significant number of structural variations compared with the standard **1**).

Thus, relying on the statistics obtained we may conclude that one of the necessary conditions for the olefinic alcohol odour being close to the leaf alcohol fragrance is a combination of two factors: the presence of an alkyl substituent (usually not lower than C_2) at the β-position of the double bond in relation to the hydroxy alkyl group, and the number of carbon atoms in the molecule being C_5–C_{10} (better still, C_6–C_8). The methyl-substituted analogues have no green odour (alcohols **39** and **40**) or cannot be employed in perfumery because of unpleasant undertones (alcohols **12**, **13**, **21** and **22**).

An important perfumery point is that the odour of the (*Z*)-isomers is more pronounced compared with the respective (*E*)-isomers (*cf.* refs. 6,7).

Replacement of the double bonds by triple bonds or cyclopropanes, retaining their substituted environment, does not lead to a disappearance of the green notes, as has been intimated earlier.[3,6] In contrast, the corresponding saturated alkanols belong exclusively to group D. Interestingly, most of the known green-odoured fragrances of other chemotypes (*cf.* refs. 1,3) should be related by our scale to the groups C and D; this conforms with the absence of the thorough determination of the "green odour".

Here the tendency discovered to maintain the initial odour of leaf alcohol after some structural variations is worthy of note. A similar phenomenon does not occur among the musk or amber fragrances, which would often lose their characteristic smell upon insignificant changes in the standard structures (see, *e.g.*, ref. 10).

The results obtained might be useful in studying the olfactory mechanism as well as in technology and perfumery, though leaf alcohol still remains unsurpassable in its fragrance.

References

1 A. F. Morris, *Perfumer and Flavorist,* 1981, **6**, 1.
2 H. Boelens, *Cosmet. Perfum.*, 1974, **89**, 70.
3 S. Arctander, *Perfume and Flavor Chemicals,* Montclair, New York, 1969, vols. 1 and 2.
4 A. A. Vasil'ev, G. V. Cherkaev and M. A. Nikitina, *Zh. Org. Khim.*, 1992, **28**, 271 (*Russ. J. Org. Chem.*, 1992, **28**, 220).
5 A. A. Vasil'ev, G. V. Cherkaev and M. A. Nikitina, *Zh. Org. Khim.*, 1993, **29**, 889 (*Russ. J. Org. Chem.*, 1993, **29**, 735).
6 A. A. Vasil'ev, G. V. Cherkaev and M. A. Nikitina, *Zh. Org. Khim.*, 1994, **30**, 816 (in Russian).
7 P. Z. Bedoukian, *J. Agric. Food Chem.*, 1971, **19**, 1111.
8 A. Hatanaka, T. Kajiwara, H. Horino and K. Inokuchi, *Z. Naturforsch., Teil C: Biosci.,* 1992, **47**, 183.
9 G. S. Clark, *Perfumer and Flavorist,* 1990, **15**, 47.
10 G. Ohloff, *Riechstoffe und Geruchssin,* Springer-Verlag, Berlin, Heidelberg, 1990 (in German).

Received: Moscow, 19th December 1994
Cambridge, 31st January 1995; Com. 4/07814D