

(+)-3-Carene as a key compound in syntheses of 6,6-dimethylbicyclo[3.1.0]hexane derivatives with olfactory properties¹

STANISŁAW LOCHYŃSKI, *Institute of Organic Chemistry, Biochemistry and Biotechnology, Technical University of Wrocław, Wyb. Wyspiańskiego 27, 50-370 Wrocław, Poland.*

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Synopsis

The synthesis of new 6,6-dimethylbicyclo[3.1.0]hexane derivatives with various substituents at the C-3 position are described. Alcohols, esters, ketones, and nitriles possess interesting olfactory properties. Odor characteristics and the odor–structure relationship are presented.

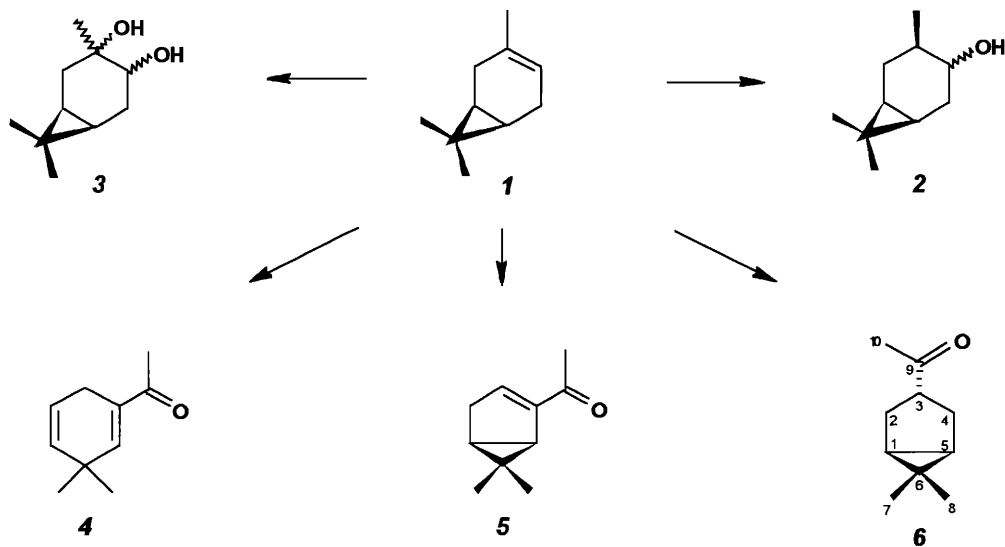
INTRODUCTION

(+)-3-Carene (1), a major constituent of Polish turpentine, is a natural, inexpensive, easily available raw material. During several years of study of the stereochemistry and chemical transformations of the carene system, some simple preparative methods for the syntheses of various compounds with olfactory properties were elaborated. Previously (2–5), we described syntheses of compounds 2 and 3 (Scheme 1), in which the carene system was preserved and further compounds formed from the intermolecular rearrangement of the *gem*-dimethylbicyclo[4.1.0]heptane system into the *gem*-dimethylcyclohexadienone (4) and derivatives. Other functionalization of carene gave the *gem*-dimethylbicyclo[3.1.0]hexane system, substituted at C-2 and C-3 positions, namely derivatives of ketones 5 and 6. In this paper, I present a series of new compounds containing the 6,6-dimethylbicyclo[3.1.0]hexane system, with various substituents at the C-3 position obtained using compound 6 as a key substance.

RESULTS AND DISCUSSION

The starting material, *trans*-3-acetyl-6,6-dimethylbicyclo[3.1.0]hexane (6), was obtained from (+)-3-carene via (–)-3,4-dibromocarene as described earlier (6). The structure of ketone 6 allowed us to carry out various synthetic operations the aim of which was to modify the side chain substituted at C-3. Two reactions are most useful: (a) the Grignard and Wittig reactions with the further one carried out in a classical manner or (b) a Wadsworth-Emmons modification (7). The full synthetic scheme is outlined below.

¹ This paper was presented as a preliminary communication in 1993. See ref. (1).



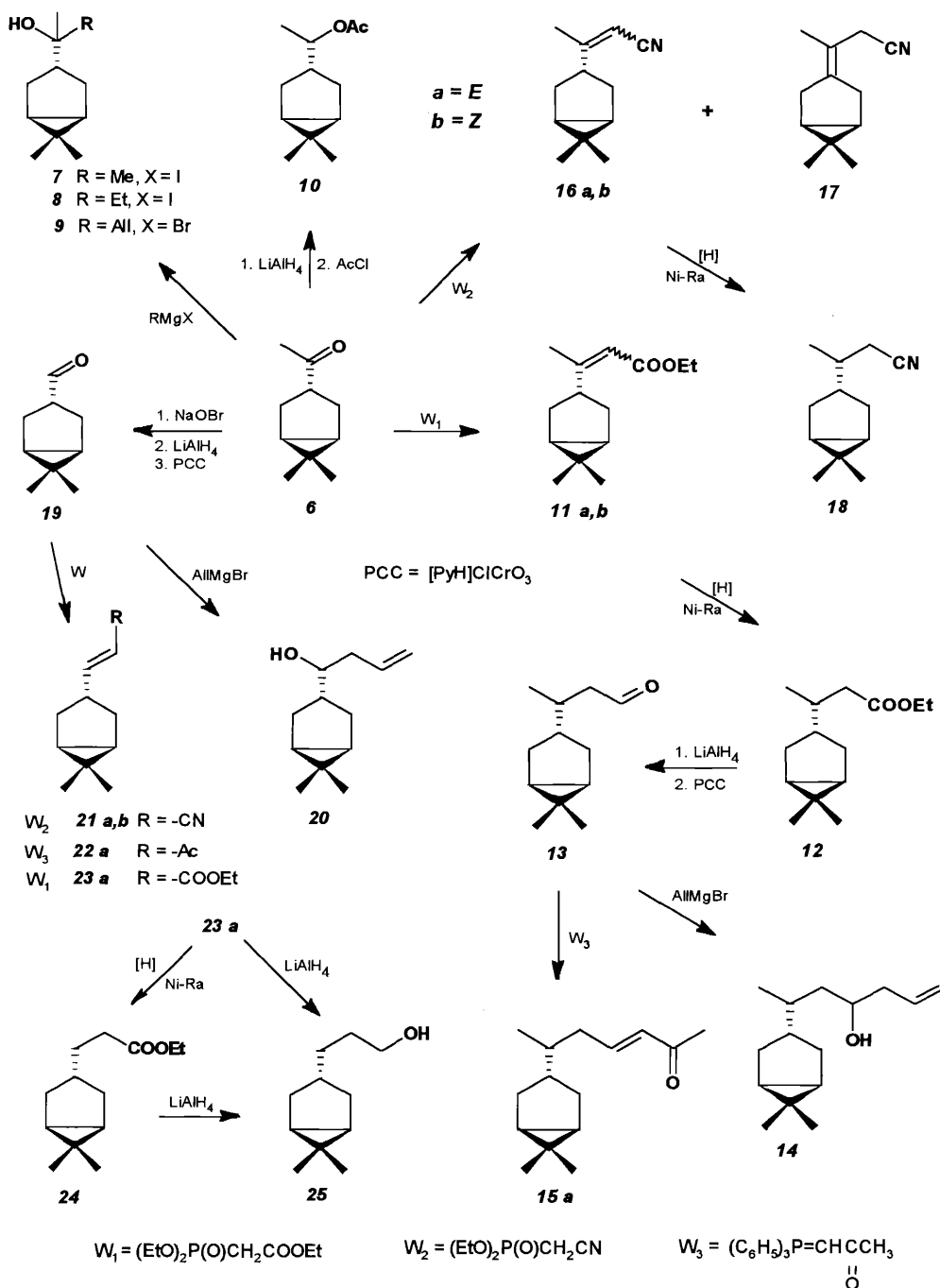
Scheme 1

In the first step, ketone **6** was converted by means of the Grignard reaction into the appropriate tertiary alcohols **7**, **8**, or **9**. Reduction of **6** with LiAlH_4 was followed by esterification with acetyl chloride afforded acetate, **10**.

The reaction of **6** with W_1 (diethyl ethoxycarbonyl methylphosphonate) gave a mixture of (*E*) and (*Z*) isomers (4:1 ratio) of α,β -unsaturated esters (**11a,b**). The hydrogenation of this mixture afforded ester **12** (**8**), which after reduction with lithium aluminium hydride and oxidation with pyridinium chlorochromate (PCC) (**9**) afforded the aldehyde **13**. This unstable crude aldehyde is readily oxidizable in air. Its reaction with allylmagnesium bromide gave secondary alcohol **14**. By the application of the stereoselective Wittig-Horner reaction with W_3 (acetylidenetriphenylphosphate), aldehyde **13** was converted into (*E*) isomer of α,β -unsaturated ketone **15a**.

The reaction of **6** with W_2 (diethyl cyanomethylphosphonate) gave a mixture of α,β -unsaturated nitrile **16a,b** and β,γ -unsaturated nitrile **17**. The ratio of both forms (α,β and β,γ) depended on the solvent that was used in the reaction. If a mixture of DMF and 1,4-dioxane (2:1) was used, α,β -unsaturated nitriles **16a,b** in the ratio of 3:1 were obtained. The mixture of (*E*) and (*Z*) isomers provided saturated nitrile (**18**) by means of hydrogenation in the presence of Raney-nickel. Using a pure dimethylformamide (DMF) as a solvent, the migration of a double bond to the position β,γ (in 90% yield) was observed (Scheme 2).

Finally, ketone **6** was converted into aldehyde **19** by the three-step procedure: degradation by the haloform reaction with sodium hypobromite, followed by reduction with LiAlH_4 , and finally oxidation with PCC. Aldehyde **19** (readily oxidizable in air) was an intermediate for elongation of the side chain at the C-3 position, using all the above-described reactions. Thus the Grignard reaction with allylmagnesium bromide afforded secondary alcohol **20**, while the reaction with W_2 in DMF gave a mixture of (*E*) and (*Z*) isomers of α,β -unsaturated nitriles **21a,b** in the ratio of 1:1. Aldehyde **19** in the reaction



Scheme 2

with W_3 (acetylidenetriphenylphosphate) gave the pure isomer (*E*) of α,β -unsaturated ketone $22a$, and the Wadsworth-Emmons procedure with W_1 transformed 19 into the pure isomer (*E*) of α,β -unsaturated ester $23a$, which after hydrogenation in the presence of Raney-nickel was converted into the saturated ester 24 (10). Reduction of 24 with

LiAlH_4 afforded alcohol 25 (11). It is worth noting that the direct reduction of ester 23a with LiAlH_4 gave the same result.

Summing up, synthesis of eighteen new compounds containing the *gem*-dimethylbicyclo[3.1.0]hexane system substituted at C-3 and differing with the position of the double bond and with the kind of functional group (alcohol, ester, nitrile, ketone) allowed us to study the odor characteristics of this group of compounds in some detail. Generally, derivatives of bicyclo[3.1.0]hexane exhibit stronger odor properties than corresponding derivatives of cyclohexane (4). As seen from Table I, the obtained compounds may be classified into several groups, based on their odor properties.

The first group is composed of alcohols 7, 8, 9, 14, 20, and 25, which exhibit medium-intensive floral odors with various notes, depending on their chemical structure. For example, tertiary alcohols possess a lilac-woody note (7,8) and a fungal note (9),

Table I
Physicochemical Constants and Odor Characteristics of 3-Substituted-6,6-Dimethylbicyclo[3.1.0]Hexane Derivatives

Compound	Yield ¹ (%)	b.p. (°C/mm Hg)	n_D^{20}	Odor characteristics
7	80.0	67/3	1.4798	Medium-intensive floral, with lilac and turpentine note
8	93.0	69/3	1.4828	Medium-intensive floral, with weaker lilac and turpentine note than 7
9	78.0	86/1	1.4878	Medium-intensive floral, with agreeable fungal note
10	71.0	89/4	1.4577	Medium-intensive, agreeable, fresh, floral, with lilac, lavender, and woody note
11a,b	68.6	112–116/4	1.4763	Medium-intensive fruity, with bilberry note
12	63.4	90/2	1.4655	Medium-intensive, agreeable, fruity, with apple note, similar to 11a,b
13	—	—	—	Sharp, penetrating, fruity-flora, with citrus note
14	17.0	105/1	1.4865	Medium-intensive, agreeable, floral, with marked moldy note
15a	18.1	131/4	1.4938	Medium-intensive, agreeable, fresh, fruity
16a,b	50.5	99–101/4	1.5027	Intensive, penetrating, fresh, with lemon-cumin note
17	42.8	101–104/4	1.4935	Medium-intensive, penetrating, less fresh, with less lemon-cumin note than 16a,b
18	46.5	94/4	1.4812	Intensive, penetrating, fresh, with weaker lemon-cuminic note than 16a,b
20	22.0	94/4	1.4867	Medium-intensive, penetrating, floral, with fruity-moldy note
21a,b	49.7	99–101/4	1.4878	Intensive, penetrating, cuminic, with aniseed note
22a	28.0	111/4	1.4958	Medium-intensive, agreeable, fresh, floral, β -ionone-like, with woody note
23a	26.2	117/6	1.4779	Medium intensive, agreeable, fresh, fruity, with mango and wild-strawberry note
24	24.6	89/2	1.4660	Medium-intensive, agreeable, fresh, fruity with weaker wild-strawberry note than 12
25	22.1	89/4	1.4745	Medium-intensive, agreeable, floral, with leaf-green note

¹ Yields calculated on 6.

secondary alcohols a moldy note (14) and a fruity-moldy note (20), and primary alcohol a leaf-green note (25). Based on its odorous properties, acetate 10 might be also included in this group. It exhibits very interesting and quite unusual sensory properties in comparison with other acetates.

Esters 11a,b, 12, 23a, and 24 form the second group of compounds. All of them exhibit medium-intensive fruity odors with various notes, and their characteristics also strongly depend on their chemical structure. It is worth noting that structurally related unsaturated compound 23a and saturated ester 24 show a significant strawberry note in olfactory studies. The odors of a similar pair of compounds, 11a,b and 12, differ in this respect, having bilberry and apple notes, respectively. Because of an interesting fruity flavor with a lemon note, aldehyde 13 might also be considered as a member of this group. Third, small group of compounds, namely ketones 15a and 22a, exhibits a floral-fruity flavor.

Finally, nitriles 16a,b, 17, 18, and 21a,b might be considered as a separate group of flavorants because of their sharp penetrating odor with characteristic fruity-cuminic notes. Hydrogenation of the double bonds in described compounds causes a significant decrease in the intensity of olfactory properties.

EXPERIMENTAL

The course of all reactions, composition of products, and their purities were checked by means of thin-layer chromatography (TLC) and gas chromatography (GC). TLC was carried out on silica gel G (Merck). Chromatograms were developed with a mixture of hexane, ethyl ether, or acetone applied in various ratios and detected with 20% ethanolic H_2SO_4 containing *ca.* 0.1% of p-anisaldehyde, followed by heating to 120°C. Column chromatography was performed on silica gel (Kieselgel 60, 230–400-mesh, Merck). Analytical GC was performed on a GCHF-18.3.4 and 18.3.6 (Chromatron) apparatus using the following: 15% Carbowax 1000 on Chromosorb P; 2% DEGS on Chromosorb G; 20% PEGA on Chromosorb G or 10% XE-60 on Chromosorb G; column length 1 or 3 m; temperature 140–180°C. Melting points (uncorrected) were determined on a Boetius apparatus. IR spectra were taken for liquid films or KBr pellets on a Perkin-Elmer 621 spectrophotometer. 1H NMR spectra were recorded for 10% CCl_4 or $CDCl_3$ solution on a 100-MHz Tesla BS 478 apparatus with HMDS as external standard.²

OLFACTORY EVALUATION

Odor properties of the synthesized compounds were determined by Prof. Józef Góra strictly following the described procedure (12).

INITIAL MATERIALS

(+)-3-Carene (Institute of Chemical Industry, Warsaw), b.p. 79°C/28 mmHg, $n_D^{20} =$

² All analyses (IR, NMR, GC, elemental analyses) were performed in the Laboratory of Instrumental Analysis, Institute of Organic Chemistry, Biochemistry and Biotechnology, Technical University of Wrocław.

1.4758, $\alpha_D^{20} = +14.0^\circ$, was transformed, via crystalline (-)-3,4-dibromocarane, to the *trans*-3-acetyl-6,6-dimethylbicyclo[3.1.0]hexane (6) according to the known procedure (6).

GENERAL PROCEDURE FOR THE WADSWORTH-EMMONS REACTION

Appropriate phosphonate W_1 or W_2 (0.09 mole) was added dropwise to a suspension of NaH (0.09 mole) in anhydrous DMF (50 ml), and the mixture was stirred vigorously until the evolution of hydrogen ceased. To the solution of sodium salt of phosphonate was added dropwise ketone or aldehyde (0.03 mole) in DMF (40 ml), and it was heated at 60–65°C approximately 2–3 h. When TLC control showed absence of starting ketone or aldehyde, the mixture was diluted with water (300 ml), extracted with diethyl ether, and dried over $MgSO_4$. The residue after removal of the solvent was purified by column chromatography and distilled *in vacuo*.

GENERAL PROCEDURE FOR THE WITTIG REACTION WITH STABILIZED YLIDS

The solution of aldehyde (0.03 mole) and acetylidenophosphorane W_3 (0.06 mole) in anhydrous methylene chloride (200 ml) was refluxed to the moment when TLC control showed absence of substrate. Then methylene chloride was evaporated and hexane (100 ml) was added to the residue. Precipitated triphenylphosphine oxide was filtered off and washed several times with hexane. After evaporation of the solvent, the crude product was chromatographed on a column and distilled *in vacuo*.

GENERAL PROCEDURE FOR THE GRIGNARD REACTION

Aldehyde or ketone (0.03) in anhydrous diethyl ether (20 ml) was added dropwise to the Grignard reagent formed from appropriate alkyl halide (0.03 mole) and magnesium (0.03 mole) in anhydrous diethyl ether (60 ml). The mixture was stirred for 2–4 h. Then NH_4Cl solution was added, and the product was extracted with diethyl ether. The ethereal solution was washed with saturated NaCl solution and dried ($MgSO_4$). The crude product was purified by column chromatography (if necessary) and distilled *in vacuo*.

GENERAL PROCEDURE FOR OXIDATION WITH PCC

Alcohol (0.03 mole) was added in one portion to a slurry of pyridinium chlorochromate (0.07 mole) and anhydrous sodium acetate (0.012 mole) in anhydrous methylene chloride (100 ml). The mixture was stirred at room temperature for 3 h. Then the methylene chloride was evaporated and the residue was extracted with petroleum ether. The ethereal solution was filtered through "Florasil" and evaporated. The crude aldehyde was chromatographed on a column immediately before use (readily oxidizable in air).

GENERAL PROCEDURE FOR REDUCTION WITH $LiAlH_4$

Carbonyl compound (ester, ketone; 0.030 mole) in diethyl ether (35 ml) was added dropwise to the suspension of lithium aluminium hydride (0.050 mole) in diethyl ether

Table II
Spectral Data and Elemental Analysis of Products

Compound	¹ H-NMR (CCl ₄ , δ)	IR (cm ⁻¹)	Elem. Anal. %C, %H, %N
7	1.24 (s, 6H, (CH ₃) ₂ C<); 1.38 (s, 6H, -C(CH ₃) ₂ OH); 2.34 (s, 1H, -OH)	3380 (vs,vb), 3000 (s), 2965 and 2930 (vs), 2865 (m), 1465 and 1460 (m), 1365 (s), 1125 (s)	C ₁₁ H ₂₀ O (168.28) Calcd: 78.51, 11.98 Found: 78.38, 12.02
8	1.25 (s, 6H, (CH ₃) ₂ C<); 1.32 (s, 3H, CH ₃ -C-OH); 5.20 (q, 2H, J=7Hz, -CH ₂ CH ₃)	3415 (vs,vb), 3000 (s), 2970 and 2940 (vs), 2865 (s), 1455 (s), 1370 (s), 1120 (s)	C ₁₂ H ₂₂ O (182.31) Calcd: 79.06, 12.16 Found: 78.89, 12.19
9	1.30 (s, 6H, (CH ₃) ₂ C<); 1.38 (s, 3H, CH ₃ -C-OH); 1.81 (s, 1H, -OH); 2.41 (d, 2H, J=7Hz, -CH ₂ -CH=CH ₂); 3.55-3.95 (m, 1H, -CH(OH)-); 5.21-5.43 (m, 2H, H ₂ C=CH-); 5.84-6.28 (m, 1H, H ₂ C=CH-)	3440 (vs,vb), 3085 (m), 3020 (m), 2985 (w), 2930 (vs), 2865 (s), 1640 (m), 1115 (s) 990 (m), 905 (s)	C ₁₃ H ₂₂ O (194.30) Calcd: 80.35, 11.41 Found: 80.26, 11.34
10	1.24 (s, 6H, (CH ₃) ₂ C<); 1.41 (d, 3H, J=6Hz, CH ₃ CH-); 2.24 (s, 3H, CH ₃ CO-); 4.88 (qt, 1H, J=6Hz, -HCOAc)	3005 (m), 2975 (m), 2975 (s), 2940 (s), 1725 (s), 1455 (s) 1365 (m), 1235 (s)	C ₁₁ H ₂₀ O ₂ (184.28) Calcd: 73.43, 10.27 Found: 73.27, 10.41
11a,b	a: 1.27 and 1.28 (2s, 6H, (CH ₃) ₂ C<); 1.54 (t, 3H, J=7Hz, CH ₃ CH ₂ O-); 2.40 (s, 3H, =CCH ₃), 2.93 (qt, 1H, J=8Hz, H at C-3); 4.37 (q, 2H, J=7Hz, CH ₃ CH ₂ -); 5.85 (s, 1H, =CH-) b: 1.26 and 1.36 (2s, 6H, (CH ₃) ₂ C<); 1.54 (t, 3H, J=7Hz, CH ₃ CH ₂ -); 2.13 (s, 3H, =CCH ₃); 4.37 (q, 2H, J=7Hz, CH ₃ CH ₂ -); 4.62 (qt, 1H, J=8Hz, H at C-3); 5.75 (s, 1H, =CH-)	a: and b: 3010 (m), 2980 (m), 2940 (s), 2865 (m), 1705 (vs), 1640 (s)	C ₁₄ H ₂₂ O ₂ (222.23) Calcd: 75.63, 9.97 Found: 75.41, 10.07
12	1.23 (s, 6H, (CH ₃) ₂ C<); 1.40 (d, 3H, J=6Hz, -CHCH ₃); 1.54 (t, 3H, J=7Hz, CH ₃ CH ₂ -); 4.36 (q, 2H, J=7Hz, CH ₃ CH ₂ -)	3005 (m), 2955 (s), 2920 (vs), 2865 (s), 1735 (vs), 1155 (s)	C ₁₄ H ₂₄ O ₂ (224.34) Calcd: 77.95, 10.78 Found: 77.59, 10.82

Table II (continued)

Compound	¹ H-NMR (CCl ₄ , δ)	IR (cm ⁻¹)	Elem. Anal. %C, %H, %N
14	1.22 (s, 6H, (CH ₃) ₂ C<); 2.15 (s, 1H, -OH); 3.75-4.02 (m, 1H, -CHOH-), 5.22-5.46 (m, 2H, -CH=CH ₂), 5.86-6.30 (m, 1H, -CH ₂ -CH-CH ₂)	3355 (vs,vb), 3080 (w), 3005 (m), 2925 (vs), 2865 (s), 1640 (w), 1445 (m), 1365 (w).	C ₁₅ H ₂₆ O (222.37) Calcd: 81.02, 11.79 Found: 81.10, 11.71
15a	1.22 (s, 6H, (CH ₃) ₂ C<); 2.43 (s, 3H, CH ₃ CO-); 6.24 (d, 1H, J=16Hz, -CH=CH-CO-); 6.93 (dt, 1H, -C(H _c) ₂ CH _b =CH _a -, J _{ab} =16Hz, J _{bc} =8Hz)	3005 (s), 2925 and 2865 (vs), 1690 and 1665 (vs), 1620 (s), 1445 and 1425 (s), 1370 and 1355 (s)	C ₁₅ H ₂₄ O (220.35) Calcd: 81.76, 10.98 Found: 81.51; 11.10
16a,b	1.27 and 1.37 (2s, 6H, (CH ₃) ₂ C<); 2.32 (s, 3H, =CCH ₃); 2.91 (qt, 1H, J=8Hz, H at C-3, isomer E); 3.50-3.70 (m, 1H, H at C-3, isomer Z); 5.18 (s, 1H, =CH-, isomer Z); 5.33 (s, 1H, =CH-, isomer E)	3010 (m), 2940 (s), 1865 (m), 2220 (m), 1635 (s), 1450 and 1375 (m)	C ₁₂ H ₁₇ N (175.27) Calcd: 82.23, 9.78, 7.99. Found: 82.40, 9.80, 8.10
17	1.30 (s, 6H, (CH ₃) ₂ C<); 1.41 (d, 3H, J=6Hz, -CHCH ₃)	3020 (vs), 2950 (vs), 2870 (vs), 2220 (m), 1460 (s), 1375 (s)	
18	1.12 and 1.28 (2s, 6H, (CH ₃) ₂ C<); 2.03 (s, 3H, =CCH ₃); 3.20 (s, 2H, -CH ₂ CN)	3030 (s), 2995 (vs), 2265 (m), 1440 (s), 1420 (s), 1375 (s)	
20	1.22 (s, 6H, (CH ₃) ₂ C<); 1.99 (s, 1H, -OH); 3.47-3.70 (m, 1H, -CH(OH)-); 5.21-5.43 (m, 2H, H ₂ C=CH); 5.84-6.28 (m, 1H, H ₂ C=CH-)	3365 (vs,vb), 3075 (m), 3005 (s), 2980 (w), 2935 (vs), 2860 (s), 1640 (m), 1005 (s), 990 (m), 905 (s)	C ₁₂ H ₂₀ O (180.29) Calcd: 79.94, 11.18 Found: 79.52, 11.28
21a,b	1.26 and 1.35 (2s, 6H, (CH ₃) ₂ C<); 2.60-3.08 (m, 1H, H at C-3, isomer E); 3.13-3.60 (m, 1H, H at C-3, isomer Z); 5.35 (s, 1H, -CH=CHCN, isomer Z); 5.41 (s, 1H, -CH=CHCN, isomer E); 6.58 (dd, 1H, -CH _c CH _b =CH _a -, J _{ab} =10Hz, J _{bc} =9Hz, isomer Z); 6.79 (dd, 1H, CH _c CH _b =CH _a -, J _{ab} =16Hz, J _{bc} =9Hz, isomer E).	3020 (m), 2940 (s), 2865 (m), 2215 (s), 1620 (m), 1450 and 1375 (m), 975 (s); 715 (m)	C ₁₁ H ₁₅ N (161.25) Calcd: 81.94, 9.38, 8.69. Found: 82.03, 9.30, 8.77

Table II (continued)

Compound	¹ H-NMR (CCl ₄ , δ)	IR (cm ⁻¹)	Elem. Anal. %C, %H, %N
22a	1.26 and 1.29 (2s, 6H, (CH ₃) ₂ C<); 2.13 (d, 4H, J=7Hz, -CH ₂ CHCH ₂ -); 2.42 (s, 3H, CH ₃ CO-); 2.63-3.08 (m, 1H, H at C-3); 6.01 (d, 1H, J=16Hz, -CH=CH-CO-); 6.83 (dd, 1H, -CH _c CH _b =CH _a -, J _{ab} =16Hz, J _{bc} =8Hz)	3015 (s), 2935 and 2865 (vs), 1675 (vs), 1625 (s), 1445 and 1425 (s), 1370 and 1355 (s), 980 (s)	C ₁₂ H ₁₈ O (178.27) Calcd: 80.85, 10.18 Found 80.68, 10.23
23a	1.27, 1.30 (2s, 6H, (CH ₃) ₂ C<); 1.55 (t, 3H, J=7Hz, CH ₃ CH ₂ -); 2.03-2.23 (m, 4H, -CH ₂ CHCH ₂ -); 2.91 (qt, 1H, J=8Hz, H at C-3); 4.39 (q, 2H, J=7Hz, CH ₃ CH ₂ -); 5.86 (d, 1H, J=16Hz, -CH=CH-CO-); 7.40 (dd, 1H, -CH _c CH _b =CH _a -, J _{ab} =16Hz, J _{bc} =8Hz)	3005 (m), 2980 (m), 2940 (s), 2865 (m), 1715 (vs), 1645 (s), 1445 (s), 1370 and 1355 (s), 985 (s)	C ₁₃ H ₂₀ O ₂ (208.30) Calcd: 71.70, 10.94 Found: 71.23, 11.02
24	1.22 (2s, 6H, (CH ₃) ₂ C<); 1.54 (t, 3H, J=7Hz, CH ₃ CH ₂ O-); 4.36 (q, 2H, J=7Hz, CH ₃ CH ₂ -)	3010 (m), 2990 (s), 2935 (vs), 2870 (s), 1735 (vs), 1150 (s)	C ₁₃ H ₂₂ O ₂ (210.32) Calcd: 70.92, 11.90 Found: 71.22, 11.75
25	1.24 (s, 6H, (CH ₃) ₂ C<); 1.97-2.23 (m, 4H, -CH ₂ CHCH ₂ -); 3.20 (s, 1H, -OH); 3.77 (t, 2H, J=6Hz, -CH ₂ OH)	3340 (s), 3005 (m), 2920 (s), 2860 (m), 1450 and 1375 (w), 1050 (m)	C ₁₁ H ₂₀ O (168.28) Calcd: 78.51, 11.98 Found: 78.29, 12.11

(30 ml). The reaction mixture was refluxed up to the moment when TLC control did not show the presence of the substrate, and then quenched with distilled water. The precipitate was filtered off, the organic layers were separated, and the water layer was extracted three times with diethyl ether. The organic layers were combined, and after drying the solvent (MgSO₄) was removed and the crude product was distilled *in vacuo*.

GENERAL PROCEDURE FOR THE HYDROGENATION REACTION

The unsaturated compound (0.025 mole) was dissolved in methanol (50 ml) and hydrogenated in the presence of nickel-Raney prepared in a standard manner from 1.30 g Ni-Al alloy. When TLC control showed absence of the unsaturated substrate, the catalyst was filtered off, the solvent was evaporated, and the crude product was distilled *in vacuo*.

Spectral data and elemental analysis of all compounds that possessed olfactory properties are presented in Table II.

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