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Reference Data

Assignment of ^{1}H and ^{13}C NMR Signals of Eight Apocampholenic Derivatives

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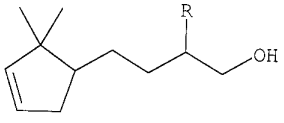
ABSTRACT: The ^{1}H and ^{13}C chemical shifts of four apocampholenic aldehydes and the corresponding alcohols are reported. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: NMR; ^{1}H NMR; ^{13}C NMR; sandalwood; apocampholenic derivatives

INTRODUCTION

In connection with investigations on sandalwood fragrances concerning structure–odour relationships, we have recently synthesized the apocampholenic compounds **1**–**8**. One of the analytical aims was the complete assignment of ^{1}H and ^{13}C chemical shifts.



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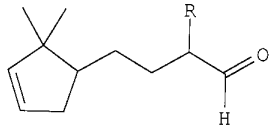
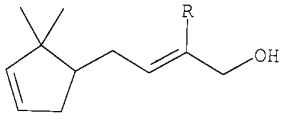
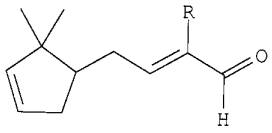


5: R = CH_3 **6**: R = C_2H_5



3: R = CH_3 **4**: R = C_2H_5



7: R = CH_3 **8**: R = C_2H_5

RESULTS AND DISCUSSION

We recorded standard ^{1}H, ^{13}C, ^{13}C APT (SEFT), ^{1}H,^{1}H-COSY and ^{13}C,^{1}H-COSY NMR spectra of all the compounds.

The ^{1}H spectra show signal splittings of higher order in most cases. We determined the center of the multiplets for the chemical shift values if the multiplets were not overlapped by other signals. Otherwise, the use of cross peaks for chemical shift determination made necessary by the complex nature of the spectra leads to a slightly reduced accuracy which we estimate to be about $\pm$0.01 ppm in the worst cases.

The chemical shifts are compiled for ^{1}H and ^{13}C in Tables 1 and 2, respectively. Scheme 1 shows the numbering of the atoms used in the tables (the numbering was chosen pragmatically and is not in accordance with systematic nomenclature).

It is remarkable that the resonance of C-2 of all compounds is shifted about 10 ppm towards lower field compared with a prediction from a database search (SPECINFO.[1]) The latter reports 36.2 ppm with a standard deviation of 5.5 ppm (the same value for **1**–**8** owing to the use of only four spheres of neighboring atoms) compared with the experimental values of 46.0 $\pm$ 0.2 ppm. Obviously the lack of NMR data for the exact or a similar molecular substructure in the SPECINFO database is the reason for the misleading prediction. The substructures in

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Table 1. Chemical shifts of all protons in **1**–**8** in ppm relative to the solvent ($CDCl_3$ = 7.26 ppm, corresponding to TMS = 0 ppm)[a]

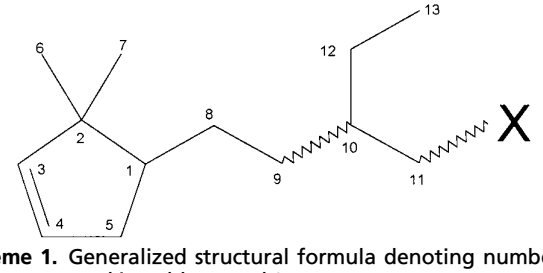
H	1	2	3	4	5	6	7	8
1	1.69	1.68	1.78	1.77	1.71	1.72	1.97	1.92
3	5.52	5.54	5.56	5.53	5.54	5.55	5.56	5.55
4	5.56	5.56	5.57	5.55	5.56	5.58	5.57	5.55
5	2.42	2.46	2.41	2.42	2.45	2.46	2.44	2.47
5′	1.92	1.93	1.98	1.96	1.95	1.96	2.02	2.01
6	1.05	1.05	1.07	1.06	1.05	1.06	1.11	1.09
7	0.79	0.80	0.85	0.84	0.80	0.81	0.90	0.88
8	1.53	1.47	2.17	2.20	1.79	1.45	2.49	2.45
8′	1.18	1.25	2.00	2.01	1.39	1.22	2.33	2.31
9	1.49	1.42	5.44	5.42	1.33	1.42	6.56	6.45
10	1.63	1.39	—	—	2.36	2.23	—	—
11	3.51	3.57	4.00	4.03	9.64	9.61	9.41	9.35
11′	3.43	3.57	4.00	4.04	—	—	—	—
12	—	1.29	—	2.13	—	1.70	—	2.26
12′	—	1.29	—	2.13	—	1.61	—	2.26
13	0.94	0.91	1.68	1.00	1.11	0.95	1.77	0.96

[a] For numbering, see Scheme 1.

Table 2. Chemical shifts of all carbons in **1**–**8** in ppm relative to the solvent ($CDCl_3$ = 77.04 ppm, corresponding to TMS = 0 ppm)[a]

C	1	2	3	4	5	6	7	8
1	49.6	49.5	49.1	49.4	49.3	49.2	48.3	48.6
2	45.8	45.9	45.8	45.9	45.9	45.9	45.9	46.1
3	142.9	142.9	142.6	142.7	142.9	142.9	142.3	142.4
4	127.0	127.0	127.0	127.0	126.9	126.8	126.6	126.8
5	38.0	38.0	37.8	37.8	37.9	37.8	37.6	37.7
6	28.1	28.2	28.1	28.1	28.1	28.1	27.9	28.0
7	21.8	21.9	21.8	21.8	21.8	21.8	21.8	21.9
8	27.2	27.0	27.9	27.6	27.2	27.2	29.5	29.3
9	32.6	29.7	125.9	126.0	30.1	27.9	154.4	154.4
10	36.3	42.4	134.6	140.7	46.7	53.8	139.4	145.4
11	68.2	65.2	68.8	66.9	205.3	205.6	195.1	195.1
12	—	23.6	—	21.1	—	22.0	—	17.3
13	16.8	11.2	13.7	13.1	13.6	11.5	9.1	13.2

[a] For numbering, see Scheme 1.



Scheme 1. Generalized structural formula denoting numbering of C atoms used in Tables 1 and 2.

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the database which are neighbored (neighbored HOSE codes) give 44.8 ± 0.1 ppm (nine lines) and 34.0 ± 0.2 ppm (two lines), leading to the unexpected mean value of 36.2. ppm mentioned above (commented upon by SPECINFO as 'data originate from interpolation between preceding and subsequent code').

An ^{1}H NOE difference spectrum for **1** indicates that the methyl group at C-2 at lower field (denoted C-6) is in a *trans* position and that at higher field (C-7) is in a *cis* position with respect to the side-chain on C-1.

No further stereochemical considerations were made. Each product consists mainly of one stereoisomer (80–90%); exceptions are **1** and **5**, where the main portion amounts only to 60%.

EXPERIMENTAL

Compounds

The compounds studied were 2-methyl-4-(2,2-dimethylcyclopent-3-en-1-yl)butan-1-ol (**1**), 2-ethyl-4-(2,2-dimethylcyclopent-3-en-1-yl)butan-1-ol (**2**), 2-methyl-4-(2,2-dimethylcyclopent-3-en-1-yl)but-2-enol (**3**), 2-ethyl-4-(2,2-dimethylcyclopent-3-en-1-yl)but-2-enol (**4**), 2-methyl-4-(2,2-dimethylcyclopent-3-en-1-yl)butanal (**5**), 2-ethyl-4-(2,2-dimethylcyclopent-3-en-1-yl)butanal (**6**), 2-methyl-4-(2,2-dimethylcyclopent-3-en-1-yl)but-2-enal (**7**), 2-ethyl-4-(2,2-dimethylcyclopent-3-en-1-yl)but-2-enal (**8**).

Syntheses

In order to produce apocampholenic compounds, we synthesized apocampholenic aldehyde from myrtenal via apopinene and apopinene epoxide.[2–7] Aldol condensation with propanal and butanal gave the aldehydes **7** and **8** and reduction with $LiAlH_4$ afforded the allylic alcohols **3** and **4**.[8,9]

The aldehydes **5** and **6** were obtained by reduction of **7** and **8** with sodium in liquid ammonia[10] and the alcohols **1** and **2** by further reduction with $LiAlH_4$.

NMR spectra

All spectra were recorded on a Unity-400 spectrometer from Varian operating at 400 MHz (^{1}H) and 100 MHz (^{13}C) at 26 °C and were processed using a SPARC IPX workstation running VNMR software (version 4.1) from Varian.

The ^{1}H spectra were taken with a 5 mm broadband probe designed for indirect detection and the ^{13}C spectra with a normal 5 mm broadband probe. The concentrations were about 5 mg for ^{1}H NMR and 50 mg for ^{13}C NMR in 0.7 ml of $CDCl_3$ (deuterium lock). The solvent served as spectrum reference ($CDCl_3$ = 7.26 ppm for ^{1}H and 77.04 ppm for ^{13}C). All shifts listed in the tables are rounded to 0.01 ppm for ^{1}H and 0.1 ppm for ^{13}C.

Typical recording data for ^{1}H were flip angle 60° (4.5μs), acquisition time 3.8 s, spectral width 5600 Hz (14 ppm), number of scans 32, 41 900 data points for FID and 64K data points for Fourier transformation (digital resolution 0.17 Hz per point), Lorentzian broadening 0.2 Hz. Typical recording data for ^{13}C were flip angle 45° (4.5 μs), acquisition time 1.2 s, relaxation delay 3 s, spectral width 25 000 Hz (250 ppm), number of scans 400–1000, WALTZ-16 decoupling of ^{1}H, 60 000 data points for FID and 64K data points for Fourier transformation (digital resolution 4.24 Hz per point), Lorentzian broadening 2 Hz.

Typical data for APT (attached proton test, SEFT): were similar to those for decoupled ^{13}C spectra with echo delay 7.5 ms.

Typical data for H,H-COSY (90° COSY or 45° COSY in magnitude mode) were: acquisition time 0.247 s (1K data points), relaxation delay 1 s, number of scans 8–16, number of increments 128–350 (depending on the spectral width to set the digital resolution around 6 Hz per point), zero filling to 2K data points and sine-bell resolution enhancement (sine-bell shift equal to half the acquisition time) in both dimensions.

Typical data for C,H-COSY (HETCOR direct detection, magnitude mode) were: acquisition time 0.05 s (2K data points), relaxation delay 1.5 s, number of increments 512, number of scans 80–200, zero filling to 4K points in F_2 and 2K points in F_1 and sine-bell resolution enhancement (sine-bell shift equal to half the aquisition time) in both dimensions.

All pulse sequences used were delivered by the Varian standard software.

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