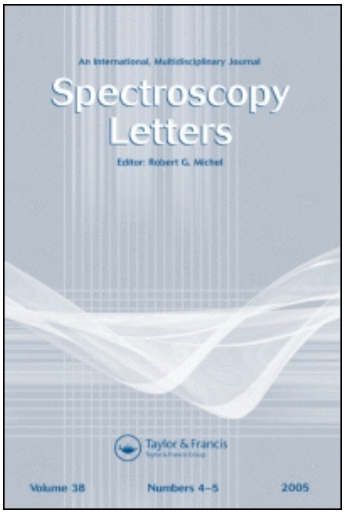

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

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Online publication date: 19 January 2010

To cite this Article Lanfranchi, Don Antoine , Vellutini, Muriel , Blanc, Marie-Cécile , Bradesi, Pascale , Casanova, Joseph and Tomi, Félix(2010) 'Enantiomeric Differentiation of Oxygenated Bicyclo[2.2.1]heptane Derivatives by ^{13}C NMR Spectroscopy Using $Yb(hfc)_3$', Spectroscopy Letters, 43: 1, 36 — 43
To link to this Article: DOI: 10.1080/00387010903261123
URL: http://dx.doi.org/10.1080/00387010903261123

Spectroscopy Letters, 43:36–43, 2010

ISSN: 0038-7010 print/1532-2289 online
DOI: 10.1080/00387010903261123

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ABSTRACT The ^{13}C NMR behavior of 10 oxygenated compounds (ketones, alcohols, acetates) bearing the bicyclo[2.2.1]heptane skeleton was examined in the presence of a chiral lanthanide shift reagent ($Yb(hfc)_3$). For each compound, we measured the lanthanide-induced shift (LIS) on the signals of the carbons and the splitting of signals, enabling the enantiomeric differentiation. The enantiomeric splitting was observed for the majority of signals in the spectrum of each compound.

KEYWORDS ^{13}C NMR, bicyclo[2.2.1]heptane derivatives, borneol, chiral lanthanide shift reagent, enantiomeric differentiation, Ytterbium

INTRODUCTION

Enantiomeric differentiation of monoterpenes and monoterpenoids, the major components of essential oils, is usually carried out by using chiral columns on gas chromatography (GC). Permethylated cyclodextrins are the most usual chiral phases and are efficient for most terpenoids. Otherwise, enantiomeric differentiation may be achieved by NMR. Various techniques based on the formation of diastereomeric entities, which give different spectral characteristics to both enantiomers of a compound, have been recently reviewed by Wenzel et al.[1] Among these, chiral lanthanide shift reagents (CLSR) form diastereoisomeric complexes in situ, held together by weak physical forces.

In our laboratories, ^{13}C-NMR chiral LSR has been successfully used for the differentiation of acyclic oxygenated mono-, sesqui-, and diterpenes;[2] oxygenated menthanes;[3] and olefinic mono- and sesquiterpene hydrocarbons.[4] The influence of various structural parameters, such as the stereochemistry of double bonds or substituents, on the amplitude of splitting of some signals has been discussed. Concerning bicyclic terpenoids, enantiomeric differentiation of camphor and bornyl acetate, the major components of the essential oil of *Lavandula stoechas*[5] and *Inula graveolens*,[6] respectively, has been achieved using CLSR.

Received 7 April 2009; accepted 25 July 2009.

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Many oxygenated monoterpenes bearing the bicyclo[2.2.1]heptane skeleton are useful in the flavor and fragrance industries.[7,8] But they are also of great interest for chemical research. For instance, camphor derivatives have found numerous applications in synthesis of enantiomerically pure natural compounds[9] and chiral ligands, which are very helpful in many fields of organic chemistry.[10]

In order to have a better insight on the splitting carbons of the bornane skeleton, we examined the behavior of various oxygenated substrates (ketones, alcohols, acetates) bearing the bicyclo[2.2.1]heptane framework. We describe the lanthanide-induced shift (LIS, $\Delta\delta$) for each carbon of each molecule and the splitting ($\Delta\Delta\delta$) of the signals of some carbons that enables the enantiomeric differentiation. Before the enantiomeric analysis, we assigned the chemical shift of all carbons using conventional 1D and 2D NMR spectra, particularly the combination of Nuclear Overhauser Effect Spectroscopy (NOESY) and Heteronuclear Single–Quantum Correlation (HSQC) spectra.

MATERIALS AND METHODS

Materials

The chiral LSR, tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorato] ytterbium(III), known as (+) *Yb(hfc)*$_3$, was obtained from Aldrich and stored in a dessicator over silica gel. Chloroform-*d* was obtained from Euriso-top. Norcamphor **1**, *exo*- and *endo*-norborneols **2** and **3**, camphor **6**, isoborneol **7**, borneol **8**, isobornyl acetate **9** and bornyl acetate **10** were purchased from Aldrich. *Exo*- and *endo*-norbornyl acetates **4** and **5** were synthesized by acetylation ($AcCl/Et_3N/CH_2Cl_2$) of the corresponding alcohols.

Spectra

^{13}C-NMR spectra were recorded in deuterated chloroform on a Bruker AVANCE 400 Fourier Transform spectrometer (Bruker, Wissembourg, France) operating at 100.13 MHz for ^{13}C, equipped with a 5-mm probe with all shifts referred to internal tetramethylsilane (TMS). Spectra were recorded with the following parameters: pulse width (PW) 4 μs (flip angle 45°); acquisition time 2.7 s for a 128-K data table with a spectral width (SW) of 25000 Hz (250 ppm); CPD mode decoupling; and digital resolution 0.183-Hz per point. The number of accumulated scans ranged from 500 to 1000 for pure and reagent-added compounds. For enantiomeric differentiation, zero filling was applied before Fourier transformation.

Four to six equimolar increments of Yb(hfc)$_3$ were added to a 0.5-M solution of the substrate in $CDCl_3$, the molar ratio [Yb(hfc)$_3$]/[substrate] ranging from 0 to 0.3. The LSR was dissolved by shaking, and spectra were recorded at 25°C after dissolution.

RESULTS AND DISCUSSION

We investigated 10 oxygenated monoterpenes bearing the bicyclo[2.2.1]heptane skeleton using the chiral lanthanide shift reagent Yb(hfc)$_3$: norcamphor **1**, *exo*-norborneol **2**, *endo*-norborneol **3**, and the corresponding acetates **4** and **5**, camphor **6**, isoborneol **7**, borneol **8**, and their respective acetates **9** and **10** (Fig. 1). Regarding carbon numbering of the bornane skeleton, we followed the terpene nomenclature.[8] All the bornane compounds (ketones, alcohols, and acetates), norbornanone, and *exo*- and *endo*-norborneols were commercially available as racemic mixture and/or as enantiomerically pure compounds. *Exo*- and *endo*-norbornyl acetates were easily prepared by acetylation of the corresponding alcohols.

Chemical Shift Assignment

The chemical shift assignment of norcamphor **1**, *exo*-norborneol **2**, and *endo*-norborneol **3** was achieved in a conventional manner, taking into account the number of hydrogens linked to a given carbon (DEPT experiment) and the electronic and steric effects related to the nature and position of the function. They are in agreement with those reported by Kalinowski et al.[11] The chemical shift assignment of the *exo*-norbornyl acetate **4** and *endo*-norbornyl acetate **5** was obtained in a similar manner and considering the shielding and deshielding effects associated with the function, when moving from the alcohol to the acetate.

The chemical shift assignment of carbons of camphor **6**, isoborneol **7**, and borneol **8** was first reported by Bohlmann et al.[12] Methyl carbons C8 and C9 (located at the bridge head C7), which exhibit very close chemical shifts, were differentiated by using LSR Eu(fod)$_3$, although LIS values were also

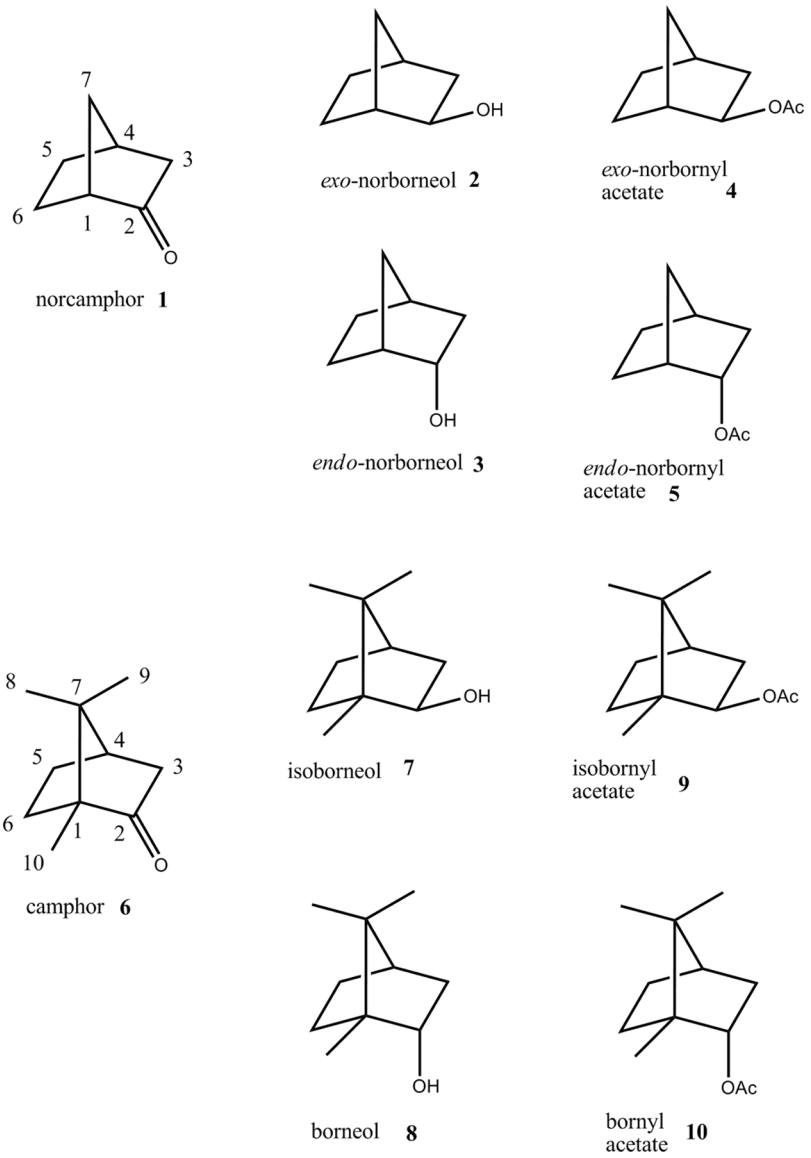

FIGURE 1 **Bicyclo[2.2.1]heptane compounds studied.**

close. Later, C8 and C9 carbons of camphor were unambiguously assigned by selective deuteration of carbon C8.[13]

In the present study, the chemical shifts of carbons C8 and C9 of isoborneol **7**, borneol **8**, isobornyl acetate **9,** and bornyl acetate **10** were differentiated by 2D NMR, by combination of NOESY and HSQC experiments. Observation of correlation plots in the NOESY spectrum between the methyl C9 and the *exo*-hydrogen brought by C3 for all molecules and between the methyl C9 and the *exo*-hydrogen brought by C2 for borneol **8** and bornyl acetate **10** enabled the assignment of hydrogens of C9. The corresponding carbons were assigned by examination of the correlation plots in the HSQC spectrum.

Definition of Investigated Parameters

The definition of investigated parameters and the experimental procedure were given in detail, exemplified and illustrated, in a previous work with the molecule of menthol.[3] They are summarized below.

The addition of the chiral lanthanide shift reagent [CLSR, (+)Yb(hfc)$_3$] to a racemic oxygenated derivative induces two effects: (1) the LIS ($\Delta\delta$) of most (if not all) carbons of the molecule and (2) the splitting ($\Delta\Delta\delta$) of the signals of some carbons. The magnitude of each effect should be considered independently.

The LIS ($\Delta\delta$) in NMR is usually defined as the sum of terms arising from Fermi contact ($\Delta\delta_{FC}$) and pseudocontact ($\Delta\delta_{PC}$, dipolar effect).[14] It is a function of

the interaction between Yb^{3+} and the functional group of the substrate and of the ratio [Yb(hfc)$_3$]/[substrate]. Therefore, the LIS of each carbon of a given molecule depends on the one hand on the number of bonds between that carbon and the binding function and on the other hand on the through-space distance to Yb^{3+}. Conversely, the splitting of the signals ($\Delta\Delta\delta$) of some carbons of a molecule depends of the through-space position of that carbon (distance between Yb^{3+} and C and angle between the z axis and Yb-C vector) with respect to the chiral camphorato moieties linked to Yb^{3+}. The $\Delta\Delta\delta$ values are also dependent on the difference in complex formation constants between the diastereoisomeric complexes.

When (+)Yb(hfc)$_3$, used as CLSR, was added to the racemic oxygenated bicyclo[2.2.1]heptane, both phenomena occurred, the signals of all carbons were deshielded, and the signals of some (if not all) carbons were split (Fig. 2).

In order to present comparable results for the whole set of molecules, we follow the scheme developed by Rothchild et al.[15] and successfully used by us in previous studies.[3,4]

1. The chemical shift of a split signal of a carbon is obtained by taking the mean value (δ_m) of the chemical shifts of both enantiomers. The $\Delta\delta$ is accordingly calculated by comparing that mean value with the chemical shift in the experiment carried out without LSR: $\Delta\delta = \delta_m - \delta$. The splitting value ($\Delta\Delta\delta$) represents the difference between the chemical shifts of both enantiomers.
2. LIS values ($\Delta\delta$) and splitting values ($\Delta\Delta\delta$) are presented as the slopes of the straight lines obtained by plotting $\Delta\delta$ or $\Delta\Delta\delta$ values, measured after adding five equimolar fractions of CLSR, against the molar ratio [Yb(hfc)$_3$]/[substrate]. That ratio reached 0.25 at the end of the experiment. Usually at this low molar ratio, the variation of $\Delta\delta$ and $\Delta\Delta\delta$ follow linearity,[16] therefore giving lines with defined slope.
3. The LIS values ($\Delta\delta$) and splitting values ($\Delta\Delta\delta$) were normalized, according to Rothchild et al.[15] who have previously described the advantages of such a procedure. Therefore, for each molecule, the value 10.00 was attributed to the highest $\Delta\delta$ slope and $\Delta\Delta\delta$ slope (except for C2; see below), and the other values were proportionally calculated, leading to $\Delta\delta_N$ and $\Delta\Delta\delta_N$, respectively.

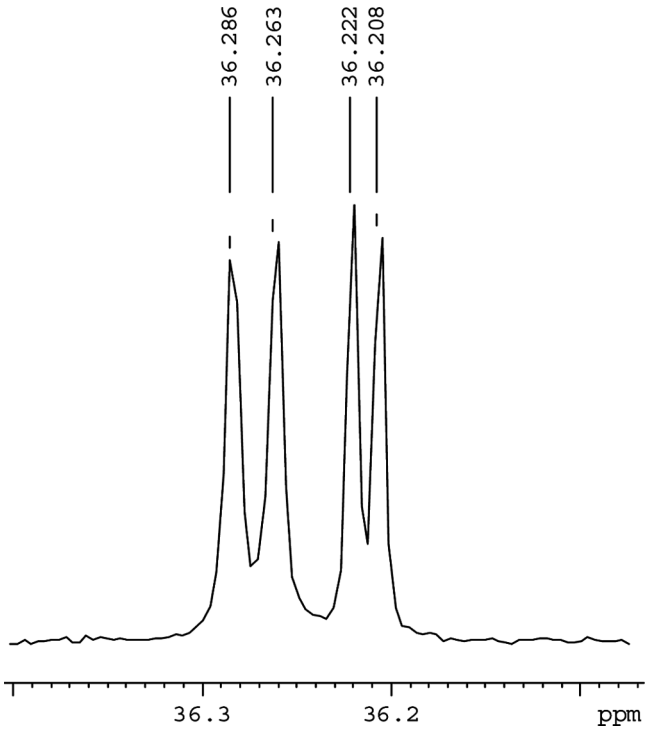

FIGURE 2 **^{13}C-NMR partial spectra (C4 and C7) of a mixture of *exo*-norbornyl acetate with Yb(hfc)$_3$ in $CDCl_3$, with molar ratio [Yb(hfc)$_3$]/[exobornyle acetate] = 0.15.**

Lanthanide Induced Chemical Shifts (LIS, $\Delta\delta_N$)

As expected, the largest LISs were observed for the signals of carbons C2 bearing the oxygenated function for all the molecules. However, for some compounds, the signal of C2 splits after the first addition of CLSR and broadens in the subsequent experiments. Therefore, it was not always possible to measure the $\Delta\delta$ and $\Delta\Delta\delta$ values and then to draw the straight lines $\Delta\delta$ and $\Delta\Delta\delta$ against the molar ratio [Yb(hfc)$_3$]/[substrate]. So, the highest normalized value (10.00) was systematically attributed to the carbon exhibiting the more deshielded signal (LIS, $\Delta\delta_N$) or the more split signal ($\Delta\Delta\delta_N$).

Ketones

The largest LISs were observed for carbons in β position, C3 and C1 (norcamphor **1**, $\Delta\delta_N = 10.00$ and 9.97; camphor **6**, $\Delta\delta_N = 10.00$ and 9.84) (Tables 1 and 2). Comparing the LIS for carbons C4, C6, C7, and C10 of camphor **6** in γ position (with respect to oxygen atom, we observe that the LISs of

TABLE 1 Chemical Shifts (δ, ppm), Numerical Values, After Normalization, of the Slope of the Lines i) $\Delta\delta = f$ ([(Yb(hfc)$_3$)]/[substrate]) ($\Delta\delta_N$) and $\Delta\Delta\delta = f$ ([(Yb(hfc)$_3$)]/[substrate]) ($\Delta\Delta\delta_N$), in $CDCl_3$, Corresponding to Each Nucleus of the Bicyclic Compounds **1–5**

	1 Norcamphor			2 *Exo*-norborneol			3 *Endo*-norborneol			4 *Exo*-norbornyl ac			5 *Endo*-norbornyl ac		
C	δ	$\Delta\delta_N$	$\Delta\Delta\delta_N$	δ	$\Delta\delta_N$	$\Delta\Delta\delta_N$	δ	$\Delta\delta_N$	$\Delta\Delta\delta_N$	δ*	$\Delta\delta_N$	$\Delta\Delta\delta_N$	δ*	$\Delta\delta_N$	$\Delta\Delta\delta_N$
1	49.86	9.97	3.54	44.26	9.89	6.22	42.51	9.82	**10.00 (0.15)**	41.43	9.38	3.59	40.23	**10.00 (1.80)**	2.22
2	218.26	§	§	74.86	§	§	73.00	§	§	77.62	§	§	75.75	§	§
3	45.26	**10.00 (1.80)**	**10.00 (0.15)**	42.28	**10.00 (3.98)**	**10.00 (0.19)**	39.46	**10.00 (4.15)**	4.81	39.63	**10.00 (2.24)**	**10.00 (0.05)**	37.32	9.43	**10.00 (0.05)**
4	35.32	1.81	3.81	35.41	5.72	2.46	37.17	5.45	3.82	35.40	4.82	3.07	36.50	4.41	3.11
5	27.19	1.39	2.90	28.12	3.52	1.86	28.96	5.27	4.24	28.16	2.62	–	29.35	4.39	–
6	24.19	2.08	3.81	24.42	4.24	1.34	19.92	7.53	5.50	24.35	3.62	–	20.96	6.59	2.89
7	37.70	1.86	2.50	34.39	7.08	4.18	37.60	4.91	3.71	35.26	5.89	4.87	36.86	3.93	0.89

§Signal of carbon C2 split quickly, and it was impossible to draw the slope.
*δ (ppm) of acyl group: **4** C=O (170.81) CH_3 (21.41); **5** C=O (171.27) CH_3 (21.20).

TABLE 2 Chemical Shifts (δ, ppm), Numerical Values, After Normalization, of the Slope of the Lines i) $\Delta\delta = f$ ([(Yb(hfc)$_3$)]/[substrate]) ($\Delta\delta_N$) and $\Delta\Delta\delta = f$ ([(Yb(hfc)$_3$)]/[substrate]) ($\Delta\Delta\delta_N$), in $CDCl_3$, Corresponding to Each Nucleus of the Bicyclic Compounds **6–10**

	6 camphor			7 isoborneol			8 borneol			9 isobornyl ac	10 bornyl ac				
C	δ	$\Delta\delta_N$	$\Delta\Delta\delta_N$	δ	$\Delta\delta_N$	$\Delta\Delta\delta_N$	δ	$\Delta\delta_N$	$\Delta\Delta\delta_N$	δ*	$\Delta\delta_N$	$\Delta\Delta\delta_N$	δ*	$\Delta\delta_N$	$\Delta\Delta\delta_N$
1	57.69	9.84	—	48.95	8.90	3.81	49.47	9.87	6.84	48.61	8.60	—	48.69	7.79	1.77
2	219.69	§	§	79.88	§	§	77.30	§	§	80.96	§	§	79.86	§	§
3	43.30	**10.00 (5.80)**	#	40.38	**10.00 (7.50)**	**10.00 (0.23)**	38.96	**10.00 (9.63)**	7.61	38.78	**10.00 (3.95)**	**10.00 (0.18)**	36.77	**10.00 (3.82)**	**10.00 (0.20)**
4	43.04	4.76	—	45.02	5.11	3.73	45.06	5.54	1.45	45.04	4.47	2.93	44.91	4.31	1.95
5	27.05	3.52	5.64	27.25	3.22	1.25	28.29	5.35	—	27.05	2.59	—	28.05	4.02	3.09
6	29.91	5.56	9.35	33.92	4.07	1.99	25.92	7.93	2.37	33.75	2.13	—	27.08	5.60	3.25
7	46.79	5.37	#	48.95	7.00	3.57	48.01	5.10	1.69	46.93	5.37	1.87	47.78	4.07	—
8	19.15	2.60	—	20.12	3.20	1.66	20.21	2.81	1.31	20.13	2.73	—	19.72	1.07	—
9	19.78	4.16	**10.00 (0.03)**	20.45	5.69	3.22	18.70	3.28	1.09	19.88	5.27	2.93	18.84	1.23	2.80
10	9.25	6.88	—	11.35	4.31	1.50	13.37	6.17	**10.00 (0.24)**	11.39	7.39	3.20	13.49	5.65	—

§The signal of carbon C2 split quickly, and it was impossible to drawn the slope needed for normalized data.
#Signals of carbons C3 and C7 split very lightly and only when the above ratio reached 0.25.
*δ (ppm) of acyl group: **9** C=O (170.67) CH_3 (21.32); **10** C=O (171.41) CH_3 (21.29).

C6 and C7 are comparable (5.56 and 5.37), while the LIS of C4 is lower (4.76), and that of C9 is higher (6.88). As expected, the LIS of methyl C9 (*syn* with respect to the keto function) is higher than that of methyl C8 (*anti* vs. the keto function): 4.16 versus 2.60. These observations are in agreement with the occurrence of through-space interactions.

Alcohols

For all alcohols, the highest LISs (except that of C2) were observed for carbons C1 and C3 in β position with respect to the oxygen atom. Otherwise, the LISs of carbons C4 and C7 of *exo*-norborneol **2**, 5.72 and 7.08, (both in γ position) are higher than that of C6 ($\Delta\delta_N = 4.24$). Conversely, opposite effects are observed for carbons in γ position of *endo*-norborneol **3**. Indeed, the LIS of carbon C6 is higher than that of C4 and C7. Moreover, it could be noticed that a through-space interaction is observed on the LIS of C5 (5.27 for **3** vs. 3.52 for **2**).

The LISs observed for the carbons of the bicyclic skeleton of isoborneol **7**, on the one hand, and borneol **8**, on the other hand, are quite similar to those discussed for *exo*-norborneol **2** and *endo*-norborneol **3**, respectively. Conversely, the LISs of methyl carbons C9 and C8, both in δ position with respect to the oxygen atom, exhibited quite different behaviors. In both cases, the LIS measured for C9 (*syn* with respect to the binding function) was higher than that measured for C8 (*anti* vs. the binding function). However, the LIS values of C9 and C8 are quite different for isoborneol **7** (5.69 vs. 3.20). Conversely, they are close for borneol **8** (3.28 vs. 2.81). As expected, these values demonstrated the occurrence of through-space interaction on C9, which is much more important in the case of isoborneol **7** (*exo* position of the oxygenated function) than in that of borneol **8**.

Acetates: The LISs measured for the carbons of the four acetates are in the same order of magnitude as those observed for the corresponding alcohols. So, we will focus only on the methyl groups C8 and C9. Once again, the behaviors of methyl groups are quite similar to those of alcohols. The LISs of carbons C8 and C9 are 2.73 and 5.27 for isobornyl acetate **9** and 1.07 and 1.23 for bornyl acetate **10**, respectively.

Enantiomeric Differentiation of Signals ($\Delta\Delta\delta_n$)

Ketones

The signals of all the carbons of norcamphor **1** split. The higher amplitude of splitting was observed for the functionalized carbon C2 (not reported). Quite different values of splitting were measured for carbons C3 and C1, both in β position (10.00 and 3.54, respectively). The splitting of carbons in γ position versus that of the oxygen atom is more important for C4 and C6 (both having $\Delta\Delta\delta_N = 3.81$) than for C7 (2.50), suggesting that the CLSR is preferentially positioned on the *endo* face of the molecule.

Concerning camphor **6**, splitting was not observed for the signals of all carbons. Indeed, the straight line $\Delta\Delta\delta = f$ [Yb(hfc)$_3$]/[substrate] was drawn for the signals of carbons C5, C6, and C9. The signals of carbons C3 and C7 split only when the above ratio reached 0.25. Conversely, signals of the bridgehead carbons C1 and C4 and those of methyls C8 and C10 are unsplit. The highest splitting values were measured for methylene C6 (9.35) and methyl C9 (10.00), located in γ position and δ position, respectively, from the oxygen atom. These values perfectly illustrated the influence of through-space interaction, the CLSR being equally oriented on the *endo* and *exo* faces of the molecule.

Alcohols

The signals of all the carbons of *exo*- and *endo*-norborneol (**2, 3**) split. The influence of the stereochemistry of the hydroxy function is particularly visible on signals of carbons C3 and C6 of **2** and **3**.

The behavior of isoborneol **7** (the signals of all carbons split) is comparable to that of *exo*-norborneol **2** for signals of carbons of the bicyclic skeleton, except for the signal of C1. Although the signals of the three methyl groups split, as expected, the splitting amplitude of the signal of methyl C9 (3.22), *syn* to the hydroxy function, was twice those of methyls C8 (1.66) and C10 (1.50).

When moving to borneol **8**, once again, the stereochemistry of the hydroxy function plays a primary role. Indeed, if we neglect the splitting of signal of carbon C2, the largest amplitudes of splitting are observed for the methyl carbon C10 (10.00) in γ position of the binding function and then

for both carbons in β position, C3 (7.61) and C1 (6.84). However, it is an intriguing fact that the amplitude of splitting is higher ($\Delta\Delta\delta_N = 1.31$) for the signal of methyl C8 (unambiguously assigned by 2D NMR, NOESY, and HSQC experiments), linked to the methano bridge of the bicyclic skeleton and located in the opposite face of the molecule with respect to the oxygenated function, than for that of methyl C9 ($\Delta\Delta\delta_N = 1.09$) located in the same side of the molecule than the oxygenated function.

Acetates

In contrast with the behavior of the previously investigated alcohols, the signals of some carbons of the *exo*-norbornyl acetate **4,** the *endo*-norbornyl acetate **5**, the isobornyl acetate **9**, and the bornyl acetate **10** did not split: carbons C5 and C6 of **4** and **9**, carbon C1 of **9** (*exo* stereochemistry of the acetoxy group), carbon C5 of **5**, and carbons C8 and C10 of **10** (*endo* stereochemistry of the acetoxy group).

Concerning *exo*-norbornyl acetate **4**, the highest splitting values were observed for carbons C2 (linked to the binding function, not reported) and C3 (β position). In contrast, the signal of C7 (γ position, $\Delta\Delta\delta_N = 4.87$) is more split than those of C1 (β position, $\Delta\Delta\delta_N = 3.59$). Conversely, the signal of carbon C2 of *endo*-norbornyl acetate **5** split after the first addition of CLSR, and it was impossible to draw the slope. Therefore, the highest split value was measured for C3, while almost comparable split values were observed for carbons C1, C4, and C6. The signal of carbons C7 split only slightly in comparison with the same carbons in the corresponding alcohol **3**.

The signal of carbon C2 of isobornyl acetate **9** split quickly, and it was impossible to draw the slope. As expected, the highest splitting of signal was that of C3 (β position). The slopes of the straight lines corresponding to C4 and C10 (both in γ position) and C9 (in δ position) had the same order of magnitude (2.93–3.20), demonstrating the influence of the camphorato moiety through space. It could be noted that the signal of methyl C8 (*anti* stereochemistry vs. the binding function) was not split.

As already noted for borneol, a surprising behavior was observed for bornyl acetate **10.** Among the differences, it could be pointed out that the signal of methyl C8, which exhibited a fair splitting (1.31) in the case of borneol, is now unsplit. Conversely, the splitting value of carbon C9 is much more important for bornyl acetate **10** than borneol **8.** The splitting of signals of carbons in β position (C1, C3), were in the same range of magnitude in the case of borneol **8**. However, for its acetylated analog (bornyl acetate **10**), a striking difference was observed (10.00 for C3, and 1.77 for C1).

CONCLUSION

In contrast with acyclic terpenes and menthane derivatives, compounds bearing the bicyclo[2.2.1]-heptane skeleton cannot exhibit conformational equilibrium. The effects of CLSR on the signals of carbons (LIS and splitting) are more easily related to the through-space position of the CLSR : LISs (Δδ) are induced by the Yb^{3+}, while splitting (ΔΔδ) depends of the chiral camphorato moiety.

It appears that the LIS observed on the signals of carbons of norbornyl- or bornyl-oxygenated compounds depends overall on the number of bonds between that carbon and the binding function (Fermi contact). However, through-space interactions were also observed, depending on the *exo* or *endo* stereochemistry of the binding function (pseudocontact, dipolar effect).

The amplitude of the splitting of the signal of oxygenated bicyclo[2.2.1]heptane derivatives is also dependent on the stereochemistry of the binding function. The introduction of methyl groups, when moving from norbornyl framework to bornyl framework, also induces some differences. Indeed, various signals became unsplit, the approach of the chiral camphorato moiety being more difficult, due to the steric hindrance.

Although the enantiomeric ratio of an oxygenated monoterpene could be measured using chiral GC, the present method could be useful if a specific chromatography column is needed.[5,6]

ACKNOWLEDGMENTS

The authors are grateful to the Collectivité Territoriale de Corse (CTC) for financial support.

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