Carbon-13 Nuclear Magnetic Resonance Spectra of Pinane Monoterpenoids

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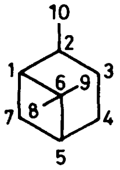
The carbon-13 n.m.r. spectra of 52 pinane monoterpenoids are reported under identical standard conditions and assignments made using deuterium labelling studies, carbon–hydrogen coupling information, chemical shift comparisons, and ytterbium-induced shift studies. The assignments of many previously reported spectra are shown to be in error.

Carbon-13 n.m.r. spectroscopy has become established as a standard tool for the molecular structure determination of both naturally occurring and synthetic organic compounds. Monoterpenes have been extensively studied by this technique and are included in most standard texts on ^{13}C n.m.r.[1 3] and in published compendia of spectra.[4 7] However, in spite of the simplicity of their spectra (a maximum of ten signals in the proton-decoupled spectra) the bicyclo[3.1.1]heptane (pinane) group of monoterpenes has been the subject of a large number of conflicting spectral assignments in the literature. This is typified by the case of *cis*-pinane for which the first four reported[8 11] spectral assignments all conflict with one another and agree in no more than three of the ten signal assignments. The reasons for the many incorrect literature assignments are numerous as will be discussed below. In addition a number of incorrect and misprinted chemical shift values have been reported, many of which are unfortunately still being quoted and used to help in the assignment of other spectra. The situation is further complicated by the fact that many ^{13}C n.m.r. reports,[8,11 16] including one recent comprehensive study,[11] have not employed the standard pinane numbering[17] (Figure) which itself has led to misunderstanding. The confused[18] state of the ^{13}C n.m.r. literature for pinane derivatives is exemplified by three recent reassignments for α-pinene,[16,19,20] the most common of all monoterpenes.

The aim of the present study is to provide definitive assignments of the spectra of naturally occurring pinane monoterpenes and selected model compounds (many for the first time) and to signal the many literature errors. The correct assignments of these spectra, all recorded under identical standard conditions (solvent $CDCl_3$; internal standard $SiMe_4$), are important since they facilitate the structure determination and spectral assignment of the higher terpenoids which contain a pinane substructure, as well as synthetic pinane derivatives.

Results and Discussion

A number of experimental techniques have been employed to assist with the correct assignments of the ^{13}C n.m.r. spectra of pinane monoterpenoids reported in this and previous studies. Of primary importance for distinguishing between carbon signals is the information provided by carbon–hydrogen coupling. One-bond carbon–hydrogen coupling ($^1J_{CH}$) information, from fully coupled, off-resonance decoupled or gated spin-echo spectra, immediately allows distinction between carbons of varying hydrogen substitution, although it is worth noting that a number of incorrect literature assignments have curiously been reported for carbons of incorrect hydrogen multiplicity. In addition the magnitude of $^1J_{CH}$ values can allow distinction between carbons of the same multiplicity in pinanes, due to the greater percentage *s*-character of the C–H bonds of the cyclobutane ring.[10,16,21,22] Long-range carbon–hydrogen coupling can also provide useful information for assignment purposes, as for example in α-pinene where $^3J_{CH}$ coupling distinguishes C-9 from C-10.[16]



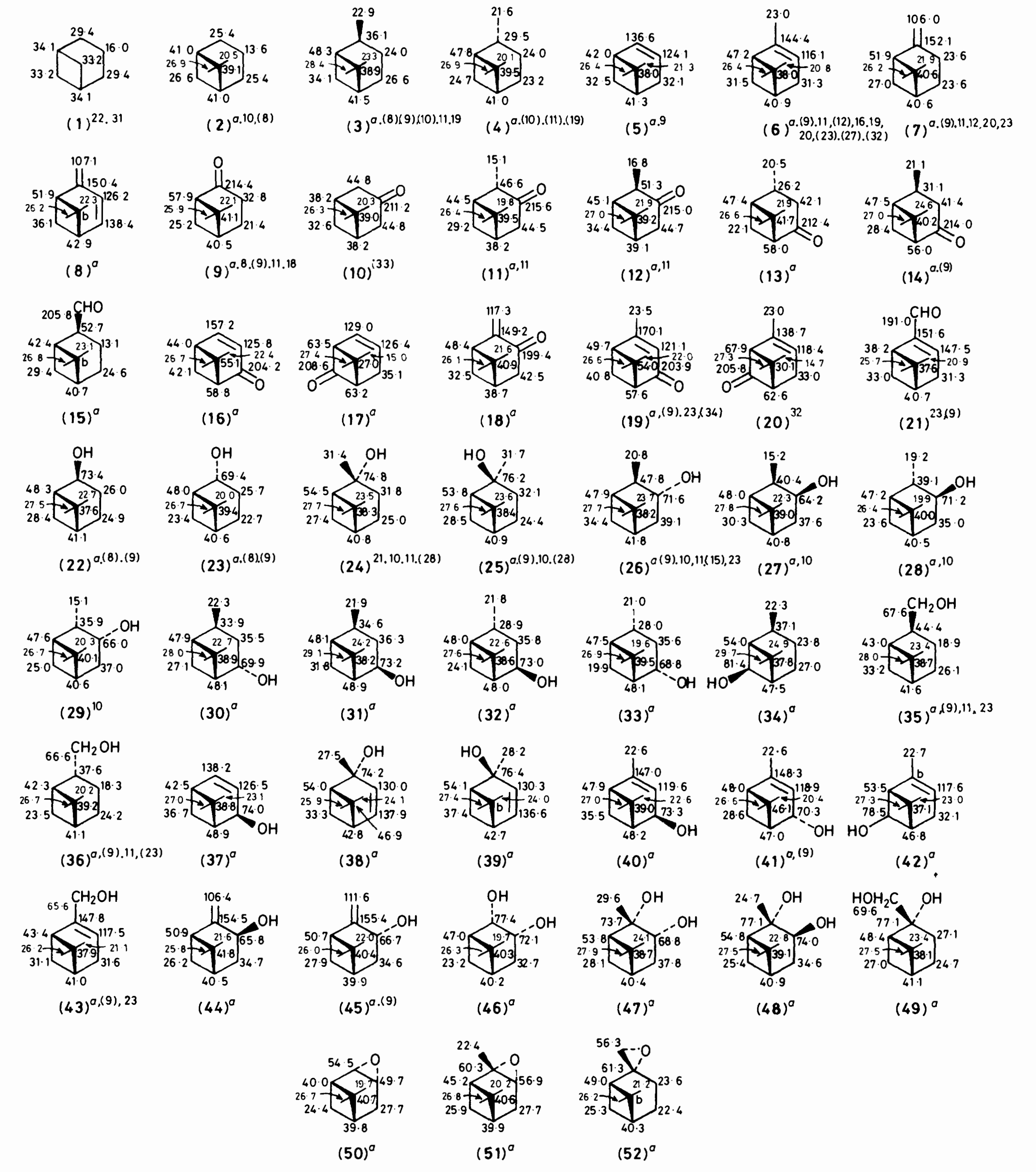
Numbering of the pinane carbon skeleton

Lanthanide shift reagents have been extensively used to assign ^{13}C n.m.r. spectra of pinanes.[10,23] However, in the case of europium shift reagents this has unfortunately led to a number of incorrect assignments due to the presence of competing upfield contact shifts.[24] For this reason the ytterbium shift reagent $Yb(fod)_3$, which does not produce contact shifts,[25] has been used in the present study. Silver–lanthanide shifts[26] have also been used to assign the spectra of pinane alkenes.[16]

Isotopic labelling is extremely useful for aiding signal assignments. Spectral data of both ^{13}C[20] and ^2H[10,11,19,27] labelled pinanes have been reported. Comparison of the spectra of naturally occurring pinanes with those of analogues prepared by derivatisation of functional groups often provides helpful assignment information.[10,11,28,29] A number of assignment errors in the literature have resulted from the assumed additivity of substituent effects. However, such additivity is not always valid due to variations in substituent effects resulting from changes in the conformation of the pinane skeleton with varying substitution. Indeed substituent effects can depend on the degree of β-substitution, as has been shown to be the case for norbornyl derivatives.[30]

Inspection of the many conflicting spectral assignments of pinanes in the literature reveals the existence of three recurring assignment problems: C-1 *versus* C-5, C-4 *versus* C-7, and C-9 *versus* C-10. For each of these pairs the carbons are of the same multiplicity in coupled (or partially coupled) spectra. C-1 and C-5 can often be distinguished by the effects of proximate substituents and use of shift reagents. Distinction between C-4 and C-7 is possible by comparison of $^1J_{CH}$ values. Long-range carbon–hydrogen coupling can be used to distinguish between C-9 and C-10, although isotopic labelling or shift reagents is often necessary.

The ^{13}C n.m.r. chemical shifts of pinanes shown in the Scheme are all for $CDCl_3$ solutions and referenced with respect to internal tetramethylsilane. In each case the quoted chemical shift values are those of the first named reference (generally this work) and references in parentheses indicate incorrect assignments and/or misprinted chemical shifts in that reference. Some small variations amongst the chemical shift values in the Scheme and literature chemical shifts exist and these are undoubtedly due to solvent and/or concentration effects.



Scheme. Carbon-13 n.m.r. chemical shifts of pinane monoterpenoids. The shift values are those of the first named reference. References in parentheses are to incorrectly assigned spectra or incorrect chemical shifts. [a] This work. [b] Not measured

Hydrocarbons.—The only ambiguity in the assignment of the parent hydrocarbon norpinane (**1**) is distinction between C-2, -4 and C-6, -7 which was resolved[22] on the basis of $^1J_{CH}$ values; 128 and 136 Hz, respectively. Conflicting reports of the chemical shift for C-3 of apopinane (**2**) have appeared.[8,10] We confirm the value of 13.6 p.p.m. The varying assignments for *cis*-pinane (**3**) have been resolved by deuterium labelling,[19] $^1J_{CH}$ values,[10] and substituent effects.[11] Two complementary deuterium labelling studies[11,19] suggest that all previous assignments of the methylene carbons of *trans*-pinane (**4**) are incorrect. Recent C–H coupling,[16] ^{13}C[20] and ^2H[19,27] labelling, and shift reagent[16] studies leave little doubt about the

Relative ytterbium-induced shifts [a]

Substrate	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10
(22)	43	100	48	24	22	*b*	19	15	32	
(23)	50	100	52	34	24	*b*	24	11	12	
(31)	21	22	50	100	46	*b*	20	14	29	14
(32)	22	23	46	100	44	*b*	19	14	30	11
(35)	20	35	20	9	9	*b*	10	7	9	100
(36)	28	46	26	13	13	*b*	17	8	10	100
(40)	21	29	47	100	43	*b*	20	13	30	13
(41)	22	*b*	47	100	46	20	33	10	10	11
(51)	41	100	99	40	27	23	33	11	18	45
(52)	46	100	44	19	18	*b*	22	10	16	100

[a] The largest induced shift has been assigned a value of 100. See Experimental section. [b] Not measured.

correct assignments for the α- and β-pinenes (**6**) and (**7**). The assignments for apopinene (**5**) and verbenene (**8**) are straightforward.

Carbonyl Compounds.—Our assignments for nopinone (**9**) agree with all four previous reports[8,11,18] with one exception,[9] in which the carbonyl chemical shift is quoted incorrectly as δ 181.3 p.p.m. The same authors[9] report the carbonyl chemical shift of isoverbanone (**14**) as δ 187.1 p.p.m. These values presumably correspond to fold-back signals[3] in spectra recorded with an insufficiently wide spectral window. The spectra of the isomeric pinocamphones (**11**) and (**12**) have recently been assigned by chemical shift comparison with other pinanes.[11] We have confirmed these assignmtnts by base-catalysed incorporation of deuterium at each of the two carbons adjacent to the carbonyl carbon. This resulted in C–^{2}H coupling in the signals due to C-2 and C-4 and broadening of the signals due to C-1, -5, -7, and -10. The *gem*-dimethyl carbon signals were not affected. Of the isomeric verbanones (**13**) and (**14**), only (**14**) has previously been reported[9] with C-3 and -7 incorrectly assigned, as has been pointed out by Thomas and his co-workers.[18] *cis*-Myrtenal (**15**), apoverbanone (**16**), apochrysanthenone (**17**), and pinocarvone (**18**) are all reported here for the first time and all readily assigned using gated spin-echo spectra. Conflicting assignments for C-9 and -10 of verbenone (**19**) have been reported.[9,23,34] Examination of the fine structure in the fully coupled spectrum shows that the signal at δ 22.0 p.p.m. exhibits three-bond coupling to five protons whereas the carbon resonating at δ 23.5 p.p.m. shows long-range coupling to only two protons, which therefore identifies them as C-9 and -10 respectively. For myrtenal (**21**), europium-induced shifts[23] and comparison with the spectrum of the 1,3-dithiane derivative[35] resolves the conflicting assignments[9,23] for C-1 and -5.

Alcohols.—Conflicting chemical shifts and assignments have been reported[8,9] for the epimeric nopinols (**22**) and (**23**). Our assignments differ from all the previous reports and were made in the following way. Base-catalysed incorporation of deuterium into nopinone (**9**) and subsequent reduction with lithium aluminium hydride gave *trans*-3-deuterio-*cis*-nopinol, the ^{13}C n.m.r. spectrum of which possessed a small triplet at δ 25.7 p.p.m., thereby establishing the chemical shift of C-3 in (**22**). The spectrum of the deuteriated compound also showed broadening of the signals at δ 73.4 (C-2) and 24.9 p.p.m. which establishes the latter signal as that of C-4. These new assignments were confirmed by Yb(fod)$_3$ studies which show the expected order of induced shifts *viz* C-2 > C-1, C-3 > C-4—C-9. This reverses the assignment of C-3 and -7 from that given in both previous reports.[8,9] The spectrum of *trans*-nopinol (**23**) was assigned in a similar manner with the methylene carbon signal (at δ 25.7 p.p.m.) which experiences the greatest ytterbium-induced shift assigned to C-3. A previous report[8] interchanged C-3 and C-7 whilst another[9] assigned carbons to signals of the wrong multiplicity and apparently misprinted the chemical shift of C-3. Conflicting assignments for C-4 and C-7 in the isomeric pinanols (**24**) and (**25**) have been resolved[21] by consideration of $^1J_{CH}$ values obtained from broad-band decoupled spectra. Our assignments for the isomeric pinocampheols (**26**)—(**29**) are in general agreement with the literature values and consistent with previous shift reagent studies[10,23] of isopinocampheol (**26**).

The spectra of the four isomeric verbanols (**30**)—(**33**) have not previously been reported and our assignments are based on C–H couplings, ytterbium-induced shifts (Table), and extensive deuterium labelling experiments. Some literature assignments for the isomeric myrtanols (**35**) and (**36**) are grossly in error. We confirm the recent reassignments[11] of these spectra by Yb(fod)$_3$ shift studies (Table) where the following order of induced shifts is observed: C-10 > C-2 > C-1, C-3 > C-4—C-9.

The spectra of unsaturated pinenols are more readily assigned than the pinanols discussed above, due to the presence of the double bond. Despite this, several errors occur in the literature. Distinction between C-1 and -5 in *cis*-apoverbenol (**37**) was made by comparison with the spectra of (**5**) and (**22**). The spectra of the isomeric pinen-2-ols (**38**) and (**39**) are reported here for the first time. The bridgehead carbons, C-1 and -5, of the isomeric verbenols (**40**) and (**41**) were distinguished by ytterbium shifts (Table) and in the case of (**41**) by comparison with the spectrum of the corresponding acetate. The only previous assignment[9] for these signals is in error. The spectra of chrysanthenol (**42**) and myrtenol (**43**) are readily assigned, while to assign the spectra of the pinocarveols (**44**) and (**45**) comparison was made with the spectra of the corresponding acetate or *p*-nitrobenzoate. This corrects a previous[9] misprint in the chemical shift of C-7 in pinocarveol (**45**).

Diols and Epoxides.—The spectra of the diols (**46**)—(**49**), reported here for the first time, are readily assigned from the degree of hydrogen substitution and by comparison with the spectra described above. The spectra of the epoxides (**50**)—(**52**) were assigned in a similar manner, but making use of ytterbium-induced shifts to distinguish C-1 from C-5, C-4 from C-7, and C-9 from C-10 in (**51**) and C-3 from C-4 in (**52**).

Conclusions.—Of the 52 spectra assigned in this study, 25 have not previously been reported. Approximately half of the remainder have been shown to be incorrectly assigned in the literature. As a result some doubt is cast on conclusions of studies in which the ^{13}C n.m.r. assignments were of fundamental importance in the interpretation of results. For example, one study[9] used ^{13}C n.m.r. to probe the conformation of the pinane skeleton. In all but one of the 17 reported spectra assignments were in error or included incorrect chemical shift values.

The spectral assignments given in this study should prove useful for the spectroscopic identification of synthetic pinane derivatives[36–39] and higher terpenes which contain a pinane substructure.[13,40–42]

Experimental

The carbon-13 n.m.r. spectra were recorded with a Varian CFT-20 spectrometer for $CDCl_3$ solutions and referenced with respect to internal tetramethylsilane. Typically, 5 000 Hz spectral windows were examined using 8 000 data points and 0.8 s acquisition times. Ytterbium-induced shifts were determined by sequential addition of weighed amounts (*ca.* 10 mg) of $Yb(fod)_3$ (Aldrich) to a solution of the substrate (*ca.* 100 mg) in $CDCl_3$ and subsequent linear least-squares extrapolation to a normalised value of 100 for the largest induced shift. Good straight lines were obtained (typically $r^2 > 0.995$).

All the pinanes are known compounds. Samples of (**6**), (**7**), and (**19**) were commercially available. The following were prepared by the literature procedures: (**3**),[43] (**4**),[43] (**8**),[44] (**9**),[45] (**11**),[43] (**16**),[46] (**17**),[47] (**22**),[48] (**23**),[49] (**24**),[50] (**25**),[51] (**26**),[52] (**27**),[43] (**28**),[53] (**30**)—(**33**),[54] (**34**),[55] (**36**),[43] (**37**),[56] (**38**),[56] (**39**),[56] (**41**),[54] (**42**),[55] (**43**),[57] (**45**),[58] (**46**),[59] (**47**)—(**49**),[60] (**50**),[61] (**51**),[62] (**52**).[63] Hydrogenation of (**5**) gave (**2**)[10] and (**5**)[64] was prepared from (**9**) by the Shapiro reaction.[65] Pyridinium chlorochromate oxidation[66] of the corresponding alcohols afforded (**12**),[52] (**13**),[54] (**14**),[54] (**15**),[67] and (**18**)[58] whilst (**40**)[54] and (**44**)[58] were prepared by cerium chloride–sodium borohydride reduction[68] of the corresponding ketones. Deuterium labelling of ketones (**9**), (**11**), and (**12**) was effected by NaOD-catalysed exchange in D_2O–dioxane of the α-protons following a standard method.[69] Deuterium labelling of the verbanols (**30**)—(**33**) was carried out by catalytic reduction of verbenone with deuterium gas.[70]

Alcohol acetylation produced the following ^{13}C n.m.r. substituent shifts: (**41**): −0.3 (C-1), +2.1 (C-2), −3.6 (C-3), +3.5 (C-4), −2.6 (C-5), +0.1 (C-6), +0.8 (C-7), −0.1 (C-8), +0.1 (C-9), +0.2 (C-10); (**45**): +0.1 (C-1), −5.1 (C-2), +1.7 (C-3), −1.2 (C-4), −0.3 (C-5), +0.1 (C-6), 0.0 (C-7), −0.1 (C-8), 0.0 (C-9), +2.5 (C-10); (**46**): −2.6 (C-1), −0.1 (C-2), −1.4 (C-3), −1.6 (C-4), −0.5 (C-5), −0.3 (C-6), +0.6 (C-7), −0.4 (C-8), −0.1 (C-9). *para*-Nitrobenzoylation of (**44**) produced the following shifts: −0.1 (C-1), −5.4 (C-2), +3.6 (C-3), −2.9 (C-4), −0.4 (C-5), −0.1 (C-6), +0.5 (C-7), −0.1 (C-8), −0.2 (C-9), +1.7 (C-10).

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