^{13}C Nuclear Magnetic Resonance Spectroscopy of Naturally Occurring Substances.[1] Camphor and Related Compounds

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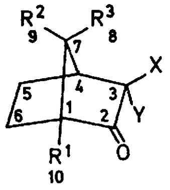
Summary All ^{13}C chemical shifts of camphor and other bicyclo[2,2,1]heptanones have been determined.

THE monoterpenic ketones camphor (VI) and fenchone (IX) as well as related bicyclo[2,2,1]heptan-2-ones have been analysed fully by ^{13}C n.m.r. spectroscopy. We now report the chemical shift values of each carbon site of nine ketones (see Table).

The spectra of carbon tetrachloride solutions, except for a chloroform solution of ketone (VIII), were determined at 15·074 MHz on a previously described instrument[2] and the δ values recorded in p.p.m. from carbon disulphide. The chemical shifts of the carbonyl groups were obtained by direct measurement of the internal standard and data on the remaining carbon centres on the basis of $\delta_{CS_2} = \delta_{CCl_4} + 96{\cdot}5 = \delta_{CHCl_3} + 115{\cdot}2$.

Noise resonance decoupled (n.r.d.) spectra[3] exhibited singlets per carbon units, while application of the noise off-resonance decoupling (n.o.r.d.) method[1] erased all signals except those of the quaternary carbon sites, C-1 of (V)—(IX), C-7 of (VI)—(VIII), and C-3 of (IX). All other carbon types were identified by the single frequency off-resonance decoupling technique.[4] The carbonyl and methyl groups were recognized by the low- and high-field



(I)	$R^1 = R^2 = R^3 = X = Y = H$
(II)	$R^1 = R^2 = R^3 = X = H$, $Y = Br$
(III)	$R^1 = R^2 = R^3 = Y = H$, $X = Br$
(IV)	$R^1 = R^2 = R^3 = X = H$, $Y = Me$
(V)	$R^1 = Me$, $R^2 = R^3 = X = Y = H$
(VI)	$R^1 = R^2 = R^3 = Me$, $X = Y = H$
(VII)	$R^1 = R^2 = R^3 = Me$, $X = H$, $Y = Br$
(VIII)	$R^1 = R^3 = Me$, $R^2 = CH_2Br$, $X = H$, $Y = Br$
(IX)	$R^1 = X = Y = Me$, $R^2 = R^3 = H$

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Ketones

	(I)	(II)	(III)	(IV)	(V)	(VI)	(VII)	(VIII)	(IX)
C-1	142·9	144·3	143·3	142·5	139·4	135·5	135·4	134·2	138·7
C-2	−21·3	−15·3	−15·8	−23·7	−22·3	−22·2	−16·8	−17·4	−26·6
C-3	147·5	136·6	142·4	144·4	147·5	149·3	138·6	140·1	145·4
C-4	156·9	149·9	147·7	151·8	158·4	149·3	142·7	144·7	147·0
C-5	168·1	169·4	168·4	171·3	163·5	165·1	169·6	170·4	167·2
C-6	164·8	167·1	165·9	166·9	161·1	162·4	161·8	162·1	160·5
C-7	154·8	157·2	157·2	155·3	148·6	145·9	146·7	142·4	150·7
C-8				181·8		173·0	172·3	175·3	170·6 (or 168·9)
C-9						172·5	172·3	153·3	168·9 (or 170·6)
C-10					178·7	182·8	182·5	182·3	177·5

positions of their signals, respectively.[5] Further analysis depended on deuteriation of specific centres and observation of the resultant ^{13}C–^{2}H coupling as well as utilization of known effects of substitution in alkanes[6] and cyclohexanes,[7] *i.e.* medium deshielding upon introduction of a single substituent at the centre under consideration (CH → CR), minor deshielding on *gem*-dimethyl substitution ($CH_2 \rightarrow CR_2$), major deshielding by substitution of a neighbouring site (CCH → CCR), and shielding as a consequence of substitution at the site one carbon further removed (CCCH → CCCR).

The signals of C-1 and C-3 of norbornanone (I) were expected[5] to be farthest downfield among those of the saturated carbon units. The C-3 signals of (I), (IV), (V), and (VI) were distinguished from their C-1 resonances by base-induced deuteriation, while the C-3 signals of all bromo-compounds were identified by their decoupling characteristics; *e.g.* proton decoupling with insufficient bandwidth leaving the downfield bromomethine ^{1}H n.m.r. signal uncovered led to ^{13}C signal broadening of C-3. Having thus ascertained the chemical shifts of C-1 and C-3 of eight ketones and having discovered little effect of C-3 substitution on the chemical shift of C-1, 1-methylnorbornanone (V) could serve as a model for differentiating C-1 from C-2 in fenchone (IX). While $\Delta\delta_{\mathrm{C-1}}$ was negligible, $\Delta\delta_{\mathrm{C-3}}$ showed the expected *gem*-dimethyl effect.[7] The only remaining methine in all ketones being C-4 permitted easy assignment of its chemical shift.

The strained one-carbon bridge of norbornane exhibits a ^{13}C n.m.r. signal *ca.* 9 p.p.m. downfield from that of the two-carbon bridge methylenes.[8] As this phenomenon was considered relevant for the ketones also, C-7 could be distinguished from the remaining methylene groups. Several expected substituent effects were noted,—deshielding by C-10 in (V)—(IX), *gem*-dimethyl deshielding in (VI) and (VII) similar to that experienced by C-3 in (IX), extra deshielding in (VIII) due to 9-bromosubstitution and, finally, shielding by 3-*exo*-substituents in (III) and (IX). Even 3-*endo*-substituents appear to have a shielding effect upon C-7.

Differentiation of the methyl groups of ketones (VI)—(IX) was based on model (V), substituent effects and the ^{13}C n.m.r. spectrum of 3-*endo*-9-dideuteriocamphor, prepared by the reduction of (VIII) with zinc in deuterioacetic acid.[9] Finally, assignment of the C-5 and C-6 signals was based on the supposition of trigonal C-2 having less steric effect on C-6 than C-3 on C-5, thus causing C-5 to be more shielded than C-6, and on 3-*endo*-substituents exerting a strong shielding effect on C-5.

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