and has an absolute value of 5.78 cps. This coupling interaction was verified by decoupling H_5 from other species and observing the collapse of the triplet of doublets at δ 2.87 to a doublet of doublets. The value of 5.78 cps falls in between 1.5 cps, found for coupling between the bridgehead protons in bicyclo[2.2.1]heptanes, and 18 cps, found for similar coupling in bicyclo[1.1.1]pentane.[2] Presumably, as the bridgeheads are brought closer together by decreasing the number of carbons in the intervening bridges, the interaction between bridgehead protons is enhanced.

Registry No.—Myrtenal, 564-94-3.

Acknowledgments.—The authors wish to acknowledge the invaluable assistance of Dr. Stanford Smith, Mr. Myron Delong, and Varian Associates Applications Laboratory, Pittsburgh, Pa. We would also like to thank Dr. Robert Bates for a copy of his manuscript on the nmr spectra of myrtenal, α-pinene, and verbenone prior to publication.[15]

(15) R. B. Bates and V. P. Thalacker, *J. Org. Chem.*, **33**, 1730 (1968).

Nuclear Magnetic Resonance Spectral Parameters in Bicyclo[3.1.1]heptanes. α-Pinene, Myrtenal, and Verbenone

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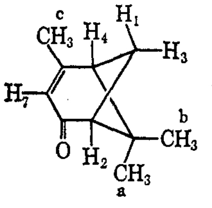
Nmr spectral parameters are derived for three bicyclo[3.3.1]heptane derivatives. As expected, the coupling constants vary little among the three compounds. A four-bond coupling constant of from +5.9 to +6.4 cps was observed between the bridgehead protons in these compounds, and two five-bond couplings of ±1.8 cps were found in α-pinene (III).

Among the bicyclo[3.1.1]heptanes are members of the pinene family of naturally occurring terpenoids. This paper concerns three of these compounds, verbenone (I), myrtenal (II), and α-pinene (III), the latter of which is the most abundant natural cyclobutane. A set of chemical shifts and coupling constants which fits the nmr spectrum of each of these compounds has been found and is given in Tables I and II. As is evident from Table II, the coupling constants hold very well from compound to compound in this series, and should prove useful in the analysis of other bicyclo[3.1.1]heptanes.

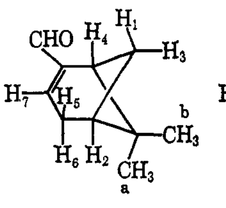
Table I

Chemical Shifts (τ) at 100 Mc

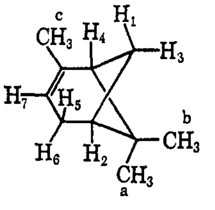
Proton	I	II	III
CH_3-a	9.00	9.26	9.16
CH_3-b	8.52	8.67	8.74
CH_3-c	8.00		8.35
H_1	7.94	8.96	8.84
H_2	7.38	7.80	7.92
H_3	7.22	7.51	7.66
H_4	7.60	7.12	8.06
H_5, H_6		7.43	7.79, 7.81
H_7	4.27	3.29	4.88
CHO		0.48	



I



II



III

Table II

Coupling Constants (in Cycles per Second)

	I	II	III
J_{12}	0.32[a]	0.3	0.3
J_{13}	−9.08[a]	−8.9	−8.5
J_{14}	0.04[a]		
J_{23}	5.53[a]	5.9	5.7
J_{24}	6.50[a,b]	5.9[c,b]	5.9[b]
J_{25}		3.0	2.8
J_{26}		3.0	2.8
J_{27}	1.41[a,b]	1.4[d]	1.4[d]
J_{34}	5.90[a]	5.7	5.7
J_{37}	0.11[a]		
J_{47}	1.32[a,b]	1.4[c,b]	1.4[b]
J_{56}		*d*	*d*
J_{57}		3.0	2.8
J_{67}		3.0	2.8
$J_{\text{C-5}}$			1.8[b]
$J_{\text{C-6}}$			1.8[b]
$J_{\text{C-7}}$	−1.5		−1.5

[a] Results from least-squares refinement using LAOCOON II, part II. [b] Sign based on calculations by M. Barfield and J. Reed, private communications, University of Arizona, 1967. [c] Sign verified by spin tickling. [d] Spectrum insensitive to this constant.

The nmr spectra of related compounds containing cyclobutane rings, including bicyclo[2.1.1]hexanes,[1] bicyclo[1.1.1]pentanes,[2] and tricyclo[1.1.1.0^{4,5}]pentanes,[3] have previously been analyzed. Bicyclo[2.2.1]heptanes, isomeric with the [3.1.1]heptanes, have been studied extensively.[4] In some of these compounds, long-range couplings (through more than three bonds) have been observed.[5] Some progress has been made in developing the theory of long-range coupling,[6] but a thorough understanding awaits the measurement of more such couplings in compounds of known molecular geometry such as the ones reported herein.

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(1) J. Meinwald and A. Lewis, *J. Amer. Chem. Soc.*, **83**, 2769 (1961); K. B. Wiberg, B. R. Lowry, and B. J. Nist, *ibid.*, **84**, 1594 (1962).

(2) K. Wiberg, *et al.*, *Tetrahedron*, **21**, 2749 (1965).

(3) S. Masamune, *J. Amer. Chem. Soc.*, **86**, 735 (1964).

(4) K. C. Ramey, D. C. Lini, R. M. Moriarty, H. Gopal, and H. G. Welsh, *ibid.*, **89**, 2401 (1967), and references therein.

(5) S. Sternhell, *Rev. Pure Appl. Chem.*, **14**, 15 (1964).

(6) (a) M. Barfield, *J. Chem. Phys.*, **41**, 3825 (1964); (b) *ibid.*, **46**, 811 (1967).

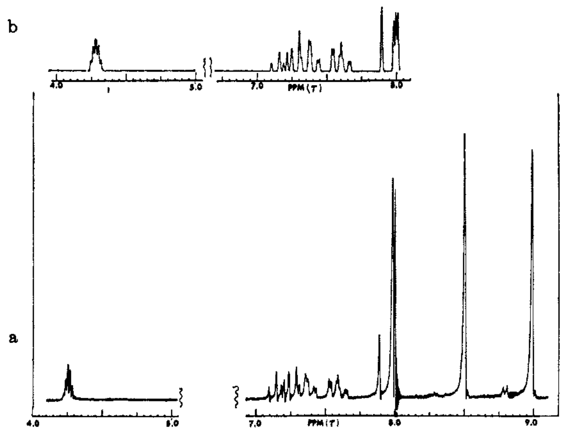

Figure 1.—100-Mc nmr spectra of verbenone (I): (a) experimental in $DCCl_3$; (b) computer simulated.

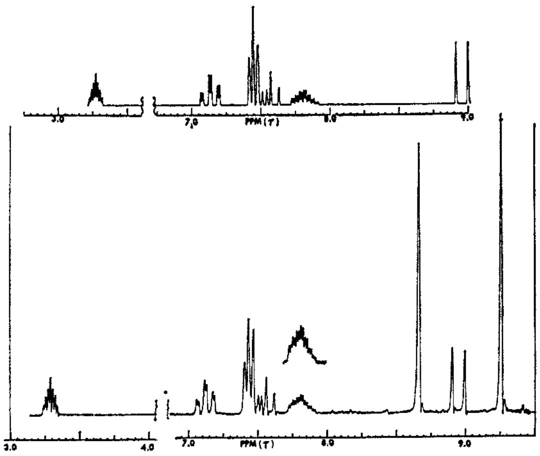

Figure 2.—100-Mc nmr spectra of myrtenal (II): (a) experimental in $DCCl_3$; (b) computer simulated.

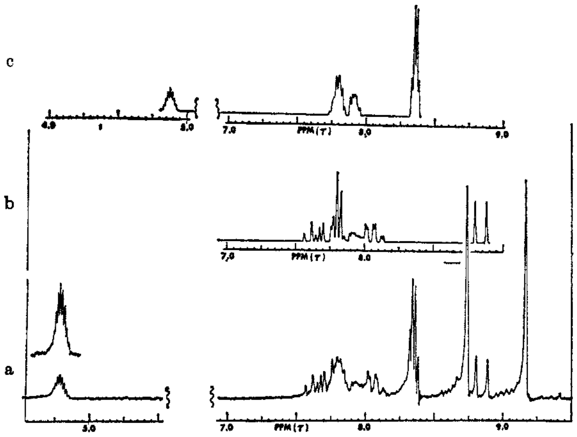

Figure 3.—100-Mc nmr spectra of α-pinene (III): (a) experimental in $DCCl_3$; (b and c) computer simulated.

Experimental Section

The experimental spectra were run on 10% solutions in $DCCl_3$ with Varian A-60 and HA-100 instruments; probable errors are 0.02 ppm for chemical shifts and 0.1 cps for coupling constants. The theoretical spectra were calculated using the LAOCOON II program of Castellano and Bothner-By,[7] modified for use on an IBM 7072 computer equipped with an XY plotter. The calculated parameters for compound I were obtained by leasts-quares refinement using part II of LAOCOON II. α-Pinene (III) was used as obtained from the Aldrich Chemical Co., myrtenal (II) was obtained from the Glidden Co., and verbenone (I) was prepared according to the procedure of Dupont, *et al.*[8]

Results and Discussion

The observed 100-Mc spectra are shown in Figures 1a, 2a, and 3a, and the corresponding spectra calculated using the parameters in Tables I and II are shown in Figures 1b, 2b, and 3b.

Chemical Shifts.—The simplest case, that of I, will be considered first. In the spectrum (Figure 1a), methyl groups a and b appear as sharp singlets at τ 9.00 and 8.52, respectively. The assignment of the higher field resonance to a is based on its position above the π cloud of the olefinic double bond; the contribution from π electrons to shielding of groups situated above the plane of the double bond is well known.[9] The olefinic methyl absorbs at τ 8.00 and the olefinic proton at 4.27. The doublet centered at τ 7.94 (one line obscured by the olefinic methyl absorption) is assigned to proton H_1 because of the relationship of this proton to the olefinic double bond. The six-line pattern at 7.22 is due to H_3, since of the remaining three protons, only H_3 should be split by three protons with couplings 5.5 cps or larger. A decision as to which of H_2 and H_4 gives rise to which of the "triplets" at τ 7.60 and 7.38 is difficult, and a tenuous assignment of the lower field peaks to H_2 was made because it was thought that this proton should be deshielded more by the carbonyl than H_4 would be by the carbon–carbon double bond.

The assignments of chemical shifts (Table I) for II (Figure 2a) and III (Figure 3a) are based primarily on the ones discussed above for I. The most striking difference is the large upfield shift (1 ppm) observed for H_1 in going from I to II and III. This difference should result from the sp^2 hybridization of the carbonyl carbon in the former compound as compared to the sp^3 hybridization of the corresponding carbon in the other compounds, but it is not clear how much of the extra shielding in II and III is due simply to the presence of the H_5–C bond, how much to the difference in the field around the π system, and how much to a slight change in conformation which could put H_1 closer to the π system in II and III. Whatever the reason for this difference is, the methyl group (CH_3-a) corresponding to H_1 undergoes parallel but smaller shifts in going from I to II and III.

Part of the six-line pattern due to H_3 is easily discernible in the spectra of II and III at τ 7.51 and 7.66, respectively. The "triplet" pattern at 7.60 in I due to H_4 should change little among the three compounds, except for the chemical shift, and is observed at τ 7.12 in II and 8.06 in III. These large differences in the chemical shift of H_4 can be rationalized in terms of the anisotropic magnetic fields around the unsaturated systems. H_2, unlike H_4, should show greater multiplicity in II and III than in I owing to the introduction of H_5 and H_6. H_2 clearly absorbs at τ 7.80 in II, and, since it should have about the same chemical shift and splitting pattern in II and III, apparently gives rise to the partially obscured absorption centered at τ 7.92 in the spectrum of III.

The remaining absorption centered at τ 7.43 in II and 7.80 in III must be due to H_5 and H_6. In each compound H_5 and H_6 should have very nearly the same chemical shift because of their very similar environments; this is observed to be the case.

Coupling Constants.—Coupling constants (Table II) were estimated for I and then improved using a least-squares refinement program. Using the values thus obtained as starting points, the coupling constants for II and III were determined by trial and error.

H_1 appears in all cases as a doublet with a separation of 8.5–9.1 cps. This separation also occurs in the H_3 pattern and therefore represents J_{13}. It is somewhat larger than the corresponding coupling in bicyclo[2.1.1]hexane.[1] Using a plot of geminal J_{HH} *vs.* H–C–H angle for other systems,[10] our finding of J_{13} = 8.5–9.1 cps predicts a bond angle of ~113°. This geminal

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(7) S. Castellano and A. A. Bothner-By, *J. Chem. Phys.*, **41**, 3863 (1964).

(8) G. Dupont, R. Dulou, and O. Mondou, *Bull. Soc. Chim. Fr.*, 60 (1953).

(9) L. M. Jackman, "Applications of Nuclear Magnetic Resonance in Organic Chemistry," Pergamon Press Inc., New York, N. Y., 1959, p 129.

(10) H. S. Gutowsky, M. Karplus, and D. M. Grant, *J. Chem. Phys.*, **31**, 1278 (1959).

coupling constant is assigned as negative by analogy with related systems.[11]

The very small coupling between H_1 and the remaining protons on the four-membered ring is no doubt due to the unfavorable dihedral angle. The Karplus equation[12] for vicinal cases gives poor agreement when applied to small strained ring systems,[13] and so it would be dangerous to deduce dihedral angles in this case.

From the appearance of the absorptions for H_2, H_3, and H_4 in I, it is apparent that J_{23}, J_{24}, and J_{34} are all about 6 cps. Starting with each of these couplings as 6 cps and iterating gave the values shown in Table II for I. The signs of the vicinal couplings J_{23} and J_{34} are undoubtedly positive,[14,15] but the sign of the large four-bond coupling, J_{24}, remained to be found. Barfield[6a,16] summarized the available data on four-bond couplings and came to the conclusion that large couplings of this type are positive. That J_{24} is positive in the present case was verified in two ways. First, by calculating and then plotting the 60-Mc spectrum for II, changing only the sign of J_{24}, a noticeable change in the spectrum is observed. The difference, as might be expected, was much less noticeable at 100 Mc. The calculated spectrum for J_{24} positive matched the observed spectrum much more closely. A second test of the sign of J_{24} was accomplished by spin-tickling experiments.[15] Irradiation at the low-field line of the H_4 triplet caused distortion of the low-field side of the H_2 absorption, indicating J_{24} and J_{34} to have the same sign.

Long-range coupling has been reported by some to require a near planar arrangement of the protons for detectable couplings, while a recent article[4] has observed that planarity of the system may not be dominant in determining the size of coupling over four bonds. In this series, the coupling through four saturated bonds (J_{24}) is large even though models show that the system is not planar.

Our finding of 5.9–6.4 cps for the bridgehead–bridgehead coupling constant (J_{24}) in these bicyclo[3.1.1]heptanes compares with values of 18 cps for [1.1.1][2] and 1.5 cps for [2.2.1][4] systems. Surprisingly, a value for the [2.1.1] system, probably the only other bicyclic system which has a long-range bridgehead–bridgehead coupling constant over 1.5 cps, has not been reported. The [2.1.1] constant is probably between the [1.1.1] and [3.1.1] values, and should be much closer to the latter value since the number of four-bond paths seems to be dominant in determining the magnitude of these couplings.

J_{24} is smaller for II and III by 0.6 cps, whereas J_{23} increases by 0.2–0.4 cps. The removal of the carbonyl from the ring system and the resulting hybridization change from sp^2 to sp^3 is probably responsible for these coupling changes.

J_{27} and J_{47} are observable four-bond couplings ranging in magnitude from 1.3–1.5 cps, and were calculated[15] to be positive. By spin tickling, J_{27} and J_{47} were shown to have the same sign as J_{23}. In all three compounds J_{27} and J_{47} are through at least one sp^2-hybridized carbon, and the atoms are rigidly arranged in the "W" shape, which seems to provide maximum coupling.[17]

The values of 2.8–3.0 cps for the vicinal couplings J_{25}, J_{26}, J_{57}, and J_{67} in II and III conform with expectation for dihedral angles of 60°.[12]

The aldehydic proton of II is a sharp singlet at τ 0.48. This is consistent with the results reported by others[5] for aldehydes in which the carbonyl group is able to become coplanar with an α,β double bond. The olefinic methyl appears as a doublet ($J = -1.5$ cps) in I and a 1:3:3:1 quartet ($J \sim \pm 1.5$ cps) in III. J_{C-7} accounts for the splitting in I, but two additional couplings to the vinyl methyl in III are required. These additional couplings are almost undoubtedly five-bond couplings with H_5 and H_6. This coupling is confirmed by the close agreement between the H_5, H_6, and vinyl methyl absorbances in the observed (Figure 3a) and calculated spectra (Figure 3c; for this comparison, the seven-spin system, vinyl methyl, H_2, H_5, H_6, and H_7, was used).

Some of the coupling constants found above by calculations were confirmed by decoupling experiments. Thus, decoupling of II gave the following results. Irradiation at H_7 causes H_4 to become a triplet ($J = 5.8$ cps), H_2 to become seven peaks with an average distance of 3.0 cps, and H_5, H_6 to become a doublet ($J = 5.8$ cps). Irradiation at H_5, H_6 in III collapses the vinyl methyl absorption to a doublet ($J = 1.5$ cps).

Earlier workers[18] have assigned geminal coupling constants for protons on sp^3 carbon from -12.0 to -20.0 cps. Our results show that, in the case of II, J_{56} can be varied over a wide range (0 to -16 cps) with no appreciable effect on the calculated spectrum.

Registry No.—Verbenone, 80-57-9; myrtenal, 564-94-3; α-pinene, 80-56-8.

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(15) R. Freeman and W. A. Anderson, *ibid.*, **37**, 2053 (1962).

(16) See footnote *b*, Table II.

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(18) M. Barfield and D. M. Grant, *J. Amer. Chem. Soc.*, **85**, 1899 (1963), and references therein.

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