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^{13}C NMR OF SOME INSECT ATTRACTANTS AND RELATED COMPOUNDS

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Abstract—Ten insect attractants, a number of intermediates in their synthesis and some related compounds were characterized by their 13C NMR spectra. The chemical shifts of the allylic carbon atoms allowed neat distinction between *E* and *Z* isomers of alkenic compounds.

Recently, ^{13}C NMR characterization of the 4 geometrical isomers of 7,11-hexadecadien-1-yl acetate (sex attractant pheromone of the species *Pectinophora gossypiella* and *Sitotroga cerealella*) and of a number of intermediates in their synthesis was reported.[1] During our investigations concerning synthesis and applications of insect pheromones, ^{13}C NMR spectroscopy was also found particularly helpful in determinating the molecular structure of the biologically active final products and of the intermediate synthons. Thus practically complete characterization by ^{13}C NMR spectra could be achieved for 46 compounds, among which 10 are known to play a role in insect olfaction. Compound XI, also called "leaf alcohol", is a trail pheromone of *Kalotermes flavicollis*,[2] sorbic acid derivatives (XVI–XIX) are artificial food location attractants[3,4] for wasps of the *Vespula* family. Alkenols and their acetates are sex attractant pheromones of various lepidoptera: XXXII for *Anarsia lineatella*,[5] XXXV for *Trichoplusia ni*[6] and *Pseudoplusia includens*,[7] XXXVII and XXXVIII for *Grapholitha molesta*, *Grapholitha prunivora*,[8] XXXVIII for *Argyroploce leucotreta*,[9] XXXIX for *Paralobesia viteana*[10] and for *Eupoecilia* (*Clysia*) *ambiguella*,[11] XL for *Rhyacionia buoliana*,[12] XLI for *Carpocapsa* (*Laspeyresia*) *pomonella*[13,14] and XLVI for *Lymanthria dispar*[15] and *Lymanthria monacha*.[16] Compound XLII is an artificial sex attractant for *Pectinophora gossypiella*,[17] whereas XXXIII was reported[8] to be a synergist and XXXIV an inhibitor of the pheromone XXXVII–XXXVIII.

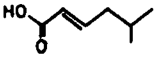
The assignments of the ^{13}C NMR chemical shifts measured for our compounds are included in Tables 1–6. Signals were assigned to individual carbon atoms empirically, by comparing logical series of related compounds and using literature data as indicated in Tables 1–6. The terminal functions and the multiple bonds offered valuable clues to interpretation. Thus for alkanols, alkenols and their O-substituted derivatives the terminal function (OH, OAc or O*t*-Bu) allowed unequivocal identification of the first three carbons of the adjacent *n*-alkane chain: C-1 is found at 62.3–63.2 ppm in the alcohols, shifted slightly upfield (61.0–62.2) in the *t*-butyl ethers and slightly downfield (64.2–65.1) in the acetates; C-2 appears at 32.6–33.2 in the alcohols, slightly upfield (30.4–31.0) in the *t*-butyl ethers and at even higher field (28.5–29.5) in the acetates; C-3 absorbs at 26.0–26.8 ppm, when there are no other groups influencing its shielding.

The sp^2-hybridized carbons of the double bonds as well as the sp-hybridized carbons of the triple bonds, although easily recognized as such by their large chemical shifts, afford signals of reduced interpretative value. Their unequivocal assignment is not always possible and in some cases even their observation as separate signals can be considered a resolution test (e.g. for compounds XXXVII, XXXVIII or XLI). For mono-enic compounds the signal at higher field was assigned to the carbon nearer to the terminal function, according to literature data.[28–30] The pattern of olefinic signals in the spectrum of 8,10-*E*,*E*-dodecadien-1-ol (XLI, Table 5) was compared to that observed[29] for methyl-9,11-*E*,*E*-

Table 1. ω-Halogenated alkane-1-ol derivatives. Assignments based upon Refs. 18–20

Compd. No.	Formula	δ ^{13}C (ppm) of carbons in position 1	2	3	4	5	6	1′	2′
I	$HO{-}(CH_2)_4{-}Cl$	62.3	30.0	29.4	45.3	—	—	—	—
II	$CH_3COO{-}(CH_2)_4Cl$	64.4	29.5	26.4	45.0	—	—	172.2	21.0
III	$CH_3COO{-}(CH_2)_4Br$	63.6	29.8	27.7	33.5	—	—	172.2	21.1
IV	$(CH_3)_3CO{-}(CH_2)_4Br$	61.0	29.7; 30.4		34.2	—	—	73.0	27.9
V	$(CH_3)_3CO{-}(CH_2)_5{-}CH_3$	62.2	31.0	26.2	32.1	22.9	14.1	—	—
VI	$HO{-}(CH_2)_6{-}Cl$	62.6	32.6	26.8	32.8	25.2	45.1	—	—
VII	$(CH_3)_3CO{-}(CH_2)_6{-}Cl$	61.7	31.0	27.2	33.2	26.0	45.2	73.0	28.0
VIII	$(CH_3)_3CO{-}(CH_2)_6{-}Br$	61.5	30.9	28.4	33.3	25.8	34.1	72.5	27.9

Table 2. Alkenols and alkenoic acids. Assignments based upon Refs. 21–24

Compd. No.	Formula	$\delta_{^{13}C}$ (ppm) of carbons in position 1	2	3	4	5	6
IX*		59.5	133.0		59.5	—	—
X		58.5	134.5	128.5	21.0	14.5	—
XI		62.4	31.0	135.3	125.3	20.5	14.2
XII		62.0	36.0	135.0	125.0	26.1	13.8
XIII		179.4	37.9	120.3	137.2	25.5	13.5
XIV		173.4	122.5	151.8	41.4	27.7	22.5
XV		180.9	34.6	22.8	38.5	27.9	22.5

*In D_2O solution, against external TMS.

Table 3. Sorbic acid derivatives. Assignments based upon Refs. 21–25

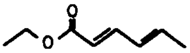
Compd. No.	Formula	$\delta_{^{13}C}$ (ppm) of carbons in position 1	2	3	4	5	6	1′	2′
XVI		173.4	119.0	147.6	130.0	141.0	19.0	—	—
XVII		166.8	119.4	144.6	129.6	138.6	18.6	60.0	14.1
XVIII		63.0		130.0; 131.7; 132.1			18.0		
XIX		65.2	135.4	124.5	131.2; 131.7		18.0	171.3	20.8

Table 4. Alkynes and their Hg salts. Assignments based upon Refs. 19, 26

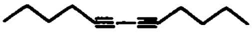
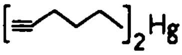
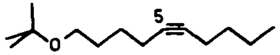
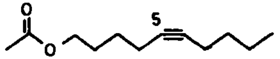
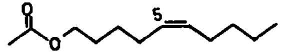
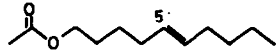
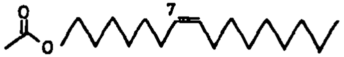
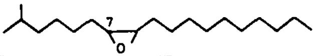
Compd. No.	Formula	$\delta_{^{13}C}$ (ppm) of carbons in position 1	2	3	4	5	6	7	8	9	10	11	12
XX		68.4	84.5	20.5	22.0	13.4	—	—	—	—	—	—	—
XXI		109.0; 111.2		21.8	22.3	13.7	—	—	—	—	—	—	—
XXII		68.4	84.9	18.3	30.9	21.9	13.5	—	—	—	—	—	—
XXIII		13.7	22.2	31.0	18.6	82.8				18.6	31.0	22.2	13.7
XXIV		109.0; 111.0		19.2	30.8	21.8	13.5	—	—	—	—	—	—
XXV		68.5	85.0	18.6	28.9	30.0	29.2	29.5	30.0	29.7	32.3	23.0	14.2
XXVI		108.5; 111.0		19.6	29.1	29.8	29.1	29.3	29.8	29.5	32.1	22.8	14.2

Table 5. Alkanols, alkenols, alkynols and their acetates. Assignments based upon refs. 1, 16–20, 26–35

Compd. No.	Formula	$\delta_{^{13}\mathrm{C}}$ (ppm) of carbons in position													
		1	2	3	4	5	6	7	8	9	10	11	12	1′	2′
XXVII		63.0	33.2	26.2	29.9	30.0	30.05	29.75	32.4	23.0	14.3	—	—	—	—
XXVIII		65.1	29.0	26.2	29.7	29.9		29.7	32.3	22.9	14.1	—	—	172.8	21.0
XXIX		61.5	30.4	26.5	19.0	80.9; 81.2		18.8	31.8	22.3	13.8	—	—	73.0	28.0
XXX		64.4	28.3	27.0	18.7	79.7; 81.2		18.7	31.8	22.2	13.7	—	—	171.6	21.0
XXXI		64.8	28.6	26.4	27.1	130.2	131.4	27.3	32.3	22.6	14.1	—	—	172.2	21.0
XXXII		64.8	28.5	26.2	32.5	130.2	131.7	32.6	32.2	22.4	14.1	—	—	171.6	21.1
XXXIII		63.2	33.2	26.2	29.9	30.1				29.8	32.4	23.0	14.2	—	—
XXXIV		64.8	29.0	26.3	29.7	30.0				29.7	32.3	22.9	14.2	172.2	21.1
XXXV		64.6	28.9	26.1	29.9	29.2	27.2	131.4	131.5	27.4	32.3	22.6	14.1	171.6	21.2
XXXVI		64.2	29.0	26.2	29.0; 29.1; 29.5			18.9	79.8		21.0	22.9	13.6	171.3	21.0
XXXVII		64.8	28.8	26.0	29.8	29.4		27.3	129.6	129.8	29.3	23.0	13.8	171.6	21.0
XXXVIII		64.8	28.8	26.1	29.7	29.3	29.2	32.8	130.6	130.8	35.0	22.9	13.7	171.0	21.1
XXXIX		65.2	29.0	26.2	29.8	29.6		30.1	27.4	130.7	132.9	20.8	14.5	173.0	21.1
XL		64.5	28.9	26.1	29.9	29.3; 29.5; 29.6			32.8	129.0	131.4	25.8	14.1	170.7	20.9
XLI		63.0	33.1	26.0	29.4	29.6		32.8	132.8	131.3	127.5	133.0	18.1	—	—
XLII*		64.8	28.9	26.1	29.9	29.2	27.4	129.9	130.5	27.5	29.6; 29.9; 30.1			171.6	21.1

*$\delta_{^{13}\mathrm{C}}$ of carbons in positions: 13 at 29.9; 14 at 32.2; 15 at 22.9 and 16 at 14.2 ppm.

Table 6. Isoheptyl bromide and 2-methyl-octadecane derivatives. Assignments based upon Refs. 18, 19, 26 and 32

Compd. No.	Formula	$\delta_{^{13}C}$ (ppm) of carbons in positions 1	2	3	4	5	6	7	8	9	16	17	18
XLIII		22.5	26.0	38.0	33.0	27.8	33.5	—	—	—	—	—	—
XLIV[a]		22.8	26.9	38.7	28.2		19.0	80.5		19.0	32.2	22.9	14.2
XLV[b]		22.95	27.55	39.0	28.5	[b]	27.7	131.0		27.7	32.5	23.1	14.3
XLVI[c]		22.8	26.9	39.0	29.6	27.6	28.2	57.3		28.2	32.2	22.9	14.2

[a] Carbons in positions 5, 10–15 included in a pattern of signals at 29.2, 29.5, 29.6, 29.7 and 29.9 ppm.

[b] Carbons in positions 5, 10–15 included in a pattern of signals at 29.9, 30.2, 30.3 and 30.6 ppm.

[c] Carbon in position 10 at 27.1; carbons in positions 11–15 at 29.9 ppm.

octadecadienoate and assigned accordingly. All these assignments are tentative and should be considered with reserve. The terminal alkynes shown in Table 4 allow easy assignment of their resonances; but this is not the case any more for their Hg salts. Valuable information is however obtained from the chemical shifts of the carbons in allylic (alpha) position to the multiple bonds. Carbons in alpha position to the triple bond are shifted upfield with about 11 ppm compared to an analogous *n*-alkane chain. Geometrical (*E*/*Z*) isomerism of alkene double bonds is a key feature of pheromone structure; the chemical shifts of the allylic carbons appear strikingly different in the two isomers and highly characteristic for the *E*- or *Z*-geometry. Thus allylic carbons in *E*-alkenes are shifted about 2–3 ppm downfield, whereas in *Z*-alkenes 2–3 ppm upfield with respect to the analogous saturated compound. This type of dependence of the allylic carbon chemical shift on the geometry of the alkene double bond was invariably observed on numerous olefinic compounds.[1,27–30,32,33] In fact, the end of the chain opposed to the oxygen function in compounds XXXV and respectively XXXIX afforded a chemical shift pattern closely matching that reported[27] for 3-*Z*-octene, whereas compound XL gave a pattern similar to that of 3-*E*-octene. Similarly, in compounds XXXVII and XXXVIII the chemical shifts assigned to carbons 8–12 are in good agreement with those reported[27] for 4-*Z*- and 4-*E*-octene respectively.

EXPERIMENTAL

All compounds were synthesized in our laboratory by methods which will be reported elsewhere. Samples used for ^{13}C-measurements were all found over 90% pure by GLC. The identity of the pheromone samples was checked (by GLC and/or ^{13}C NMR) in most cases against authentic specimens kindly supplied by workers of the US Department of Agriculture. A Bruker WP-60 FT-NMR instrument equipped with a 14.1 kG electromagnet (15.086 MHz for ^{13}C) was used for all measurements. $CDCl_3$ solutions containing 15–30% of sample were filled into standard 10 mm sample tubes. Chemical shifts were measured against internal TMS and are considered true within ±0.1 ppm. The chemical shifts measured for compound XXVII, Table 5, accorded well (generally within ±0.2 ppm) with those reported[20] in the literature, although different reference compounds were used.

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