Reference Data

Carbon-13 NMR Signals of Some Substituted Indanones, Tetralones and Benzo-α-pyrones, β-Substituted β-Phenylpropionic Acids and Related Compounds

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^{13}C spectral assignments for 3-methyl-1-indanone, 3-ethyl-1-indanone, 3-n-propyl-1-indanone, 3-phenyl-1-indanone, 3-phenyl-1-tetralone, 3- and/or 4-substituted benzo-α-pyrones and dihydrobenzo-α-pyrones, together with those for 3-phenylbutyric acid, 3-phenylvaleric acid, 3-phenylcaproic acid, 3,3-diphenylpropanoic acid, 3,4-diphenylbutyric acid, their 2-carboxy derivatives and the ethyl esters of the 2-carbethoxy derivatives are reported.

KEY WORDS Indanones Tetralones Benzo-α-pyrones Dihydrobenzo-α-pyrones β-Alkyl-β-phenylpropionic acids Ethyl β-alkyl-α-carbethoxy-β-phenylpropionates ^{13}C NMR spectral assignments

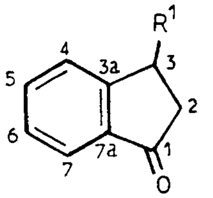
INTRODUCTION

Carbon-13 spectral assignments of some 3-substituted 1-indanones (**1**–**4**), 3-phenyl-1-tetralone (**6**), 3- and/or 4-substituted benzo-α-pyrones (**10**, **11**, **24**–**26**) and dihydrobenzo-α-pyrones (**8**, **9**, **12**–**23**), 3-substituted 3-phenylpropionic acids and closely related compounds (**28**–**43**), which were derived during our synthetic studies[1–4] on 3-alkylcoumarins and 4-alkylcoumarins, have been carried out.

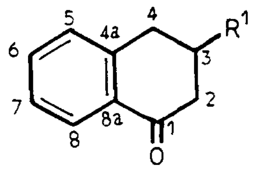
RESULTS AND DISCUSSION

The ^{13}C shift assignments of the above compounds are given in Tables 1 and 2. These were made from mutual chemical shift correlations between related compounds, the use of the spectra of suitable models (viz. **5**,[5] **7** [6] and **27** [7]) and consideration of the chemical shift changes expected for the replacement of an aliphatic hydrogen by a methyl group[8] and the substituent effect of a carbonyl moiety on the aromatic carbon shifts.[9]

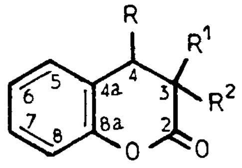
Conclusive carbon shift assignments for **3**, **4**, **6** and **7** were, however, achieved by appropriate two-dimensional ^{13}C–^{1}H hetero-



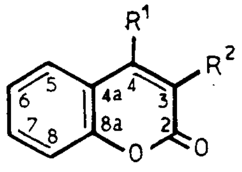
1–5



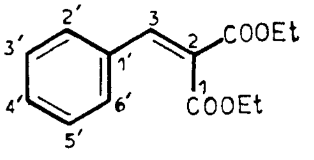
6, 7



8, 9, 12–23, 27



10, 11, 24–26



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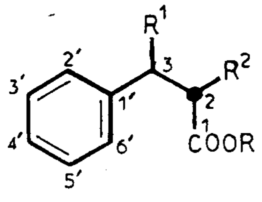
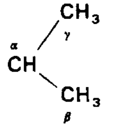


29–43

Compounds	R^1
1, 12, 19, 29, 34, 39	CH_3
2, 13, 20, 30, 35, 40	$\overset{\alpha}{C}H_2\overset{\beta}{C}H_3$
3, 10, 14, 21, 31, 36, 41	$\overset{\alpha}{C}H_2\overset{\beta}{C}H_2\overset{\gamma}{C}H_3$
4, 6, 11, 32, 37, 42	C_6H_5
5, 7–9, 18, 24–27	H
17, 33, 38, 43	$CH_2C_6H_5$
15, 23	$\overset{\alpha}{C}H_2\overset{\beta}{C}H{=}\overset{\gamma}{C}H_2$
16, 22	

Compounds	R^2
8–17, 27, 39–43	H
18–23, 29–33	COOEt
34–38	COOH
24	CH_2CH_3
25	$CH(CH_3)_2$
26	$CH_2CH_2CH_3$

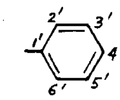
Compounds	R
12–23, 27, 34–43	H
29–33	$\overset{\alpha}{C}H_2\overset{\beta}{C}H_3$
8	$\overset{\alpha}{C}H_2\overset{\beta}{C}H_2\overset{\gamma}{C}H_3$
9	

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Table 1. ^{13}C NMR signals (ppm) for compounds 1–27

Compound	C-2	C-3	C-4	C-4a	C-5	C-6	C-7	C-8	C-8a	C-α	C-β	C-γ
1[a–c]	45.1	32.5	125.0		134.5	127.1	123.1			21.0		
2[a–c]	42.4	39.4	125.4		134.3	127.3	123.3			28.5	11.3	
3[a–c]	42.9	37.9	125.4		134.4	127.2	123.3			38.2	20.6	13.9
4[a–c]	46.7	44.5	126.7		134.9	127.7	123.3					
5[a–c]	36.0	25.6	126.6		134.3	127.0	123.3					
6[a,d]	45.7	40.8	37.3	143.1	128.5	133.5	126.4	126.9	131.9			
7[a]	39.0	23.1	29.5	144.3	128.5	133.1	126.4	127.0	132.5			
8	168.1	34.6	34.8	126.8	127.6	124.1	128.1	117.0	151.3	36.7	19.7	13.7
9[d]	167.2	36.6	40.6	125.7	128.6	124.4	128.2	116.9	151.6			
10	160.8	113.8	155.8	119.2	124.2	124.0	131.4	117.1	153.6	33.5	21.2	13.7
11[d]	160.5	115.0	155.5	118.8	126.8	124.0	131.7	117.1	154.0			
12	171.2	34.0	31.4	122.5	127.9[e]	124.0	127.7[e]	116.3	151.6	15.1		
13	170.4	40.3	28.5	122.4	127.9	123.9	127.9	116.2	151.4	22.6	10.9	
14	170.7	38.7	29.1	122.4	128.0	124.0	128.0	116.3	151.5	31.7	19.8	13.6
15	169.7	38.3	28.2	122.2	127.8	123.9	127.8	116.0	152.2	33.5	134.0	117.7
16	173.2	46.3	26.1	122.3	127.2	124.0	127.9	116.2	155.6	34.1	22.0	22.0
17[d]	170.2	40.6	28.0	122.2	128.0	124.1	128.0	116.3	151.5	35.4		
18[f–h]	167.2	46.0	26.9	120.5	127.9	124.4	128.3	116.3	151.1			
19[f–h]	167.4	49.0	34.8	120.9	127.7	124.0	128.1	115.8	151.1	20.2		
20[f–h]	167.0	53.4	32.1	121.3	128.1	124.2	128.2	116.0	151.0	27.1	8.8	
21[f–h]	167.4	53.3	32.7	121.5	128.2	124.4	128.4	116.2	151.0	36.3	17.9	14.2
22[f–h]	169.1	57.1	29.8	121.9	128.2	124.3	128.2	116.1	150.8	32.4	18.3	17.6
23[f–h]	168.9	52.8	32.0	121.0	128.1	124.2	128.0	115.9	150.8	38.0	131.7	119.6
24	165.6	130.9	137.3	119.5	127.0	124.1	130.3	116.3	152.4	23.8	12.1	
25	165.4	135.8	138.3	119.5	127.2	123.8	130.3	116.3	152.4	28.6	21.3	21.3
26	161.0	129.8	138.3	119.5	127.0	124.0	130.3	116.3	153.0	32.7	21.1	13.6
27	168.5	29.1	23.6	122.8	128.1	124.4	128.1	116.8	152.0			

[a] C-1 in **1–7** resonated at δ 205.8, 205.9, 206.2, 205.6, 206.2, 197.1 and 198.0, respectively.

[b] C-3a in **1–5** resonated at δ 159.6, 158.4, 158.8, 157.7 and 154.9, respectively.

[c] C-7a in **1–5** resonated at δ 136.2, 136.9, 136.6, 136.7 and 136.9, respectively.

[d] Other resonances were at δ 143.2 (C-1′), 126.7 (C-2′,6′), 128.5 (C-3′,5′) and 126.4 (C-4′) in **6**; 140.2 (C-1′), 127.4 (C-2′,6′), 128.9 (C-3′,5′) and 127.5 (C-4′) in **9**; 135.1 (C-1′), 128.3 (C-2′,6′), 128.7 (C-3′,5′) and 129.5 (C-4′) in **11**; 137.8 (C-1′), 129.9 (C-2′,6′), 128.5 (C-3′,5′) and 126.6 (C-4′) in **17**; 143.6 (C-1′), 127.5 (C-2′, 6′), 128.8 (C-3′, 5′) and 126.8 (C-4′) in **4**.

[e] Signals are interchangeable.

[f] *C*OOEt in **18–23** resonated at δ 164.4, 170.0, 169.4, 169.7, 169.1 and 166.4, respectively.

[g] OCH_2CH_3 in **18–23** resonated at δ 61.7, 61.4, 61.5, 61.7, 61.6 and 61.6, respectively.

[h] OCH_2CH_3 in **18–23** resonated at δ 13.6, 13.2, 13.5, 13.6 and 13.4, respectively.

nuclear correlation experiments[10] (see Table 3). This indirectly allowed the specific assignments of the carbon resonances for **5**,[5] which were compatible with the assignments made from consideration of the substituent parameters for a carbonyl moiety[9] and the spectrum of indane.[11]

EXPERIMENTAL

The ^{13}C (75.47 MHz) NMR spectra of **1–11**, **26** and **28–43** were recorded on a Bruker AM 300L spectrometer equipped with an Aspect 3000 computer and an array processor, using the DISNMR program version 870101.1. The compounds were submitted to composite pulse decoupling and DEPT sequences to establish the carbon shifts and the degree of protonation. The spectra were recorded in a 5-mm $^{13}C/^1H$ dual-probe head using $CDCl_3$ as solvent (DMSO-d_6 for **34–38**) and internal lock. The concentration of all solutions was *ca.* 2–5%. The chemical shifts reported are in δ (ppm) downfield from TMS. $CDCl_3$ or the DMSO-d_6 signal served as the internal standard in carbon spectral measurements; $\delta_{TMS} = \delta_{CDCl_3} + 76.9$ ppm $= \delta_{DMSO\text{-}d_6} + 39.6$ ppm. The carbon spectra were recorded with a pulse of *ca.* 65° flip angle and about a 3 s delay between pulses, and the FIDs were acquired over 200 ppm (230 ppm for **1–7**) and 32K data points. The ^1H (80 MHz) and ^{13}C (20 MHz) NMR spectra of **12–25** were recorded on a Varian CFT-20 NMR spectrometer using 16K data points and ^{13}C multiplicities were determined by the SFORD technique. Two-dimensional X–H correlation (^{13}C–^1H) spectra were obtained using the INEPT sequence. The FIDs were acquired over 4096 data points and 17241 Hz for each of 128 values of evolution time. The second-dimension sweep width was ±1497 Hz. The raw data were processed using a sine-bell window function in both dimensions in the magnitude mode.

The compounds employed were characterized from their elemental and spectral analyses and have mostly been reported elsewhere.[1–3] Treatment of 3-carbethoxy-3,4-dihydrocourmarin in *t*-BuOH with *t*-BuOK followed by addition of *n*-PrI, *i*-PrBr or allyl bromide, as in Ref. 1, yielded[4] **21**, **22** and **23**, respectively, in 75–85% yield. Compound **21**: viscous oil; ν_{max} (neat), 1770, 1740, 1230, 1140, 755 cm^{-1}; ^1H NMR, 0.99 (3H, t, $J = 6.8$ Hz, H_3-γ), 1.06 (3H, t, $J = 7.2$ Hz, OCH_2CH_3), 1.47 (2H, m, H_2-β), 1.94 (2H, m, H_2-α), 2.97 and 3.32 (1H each, d, $J = 15.2$ Hz, H_2-4), 4.04 (2H, q, $J = 7.2$ Hz, OCH_2CH_3), 6.98–7.30 (4H, m, Ar-Hs). Compound **22**: m.p. 72 °C; ν_{max} (KBr), 1760, 1730, 1220, 1145, 745 cm^{-1}; ^1H NMR, 1.00 (3H, t,

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Table 2. ^{13}C NMR signals (ppm) for compounds 28–43

Compound	C-1	C-2	C-3	C-4	C-5	—COO—	C-1′,1″	C-2′,6′ C-2″,6″	C-3′,5′ C-3″,5″	C-4′,4″	OCH_2CH_3	OCH_2CH_3
28	166.2	126.3	141.7			163.8	132.8	129.2	128.5	130.2	61.3	13.6
											61.3	13.8
29	167.7	59.2	39.9	20.0		168.2	143.1	127.3	128.2	126.6	60.8	13.5
											61.2	13.9
30	167.6	58.5	47.1	26.8	11.5	168.3	140.6	128.0	128.2	126.6	60.8	13.4
											61.2	13.8
31	167.6	58.7	45.2	35.9	20.0	168.2	140.8	128.0	128.1	126.5	60.7	13.5
											61.1	13.8
32	167.5	57.4	51.1			167.5	141.3	127.7	128.4	126.7	61.3	13.6
							141.3	127.7	128.4	126.7	61.3	13.6
33	167.6	57.8	47.5	40.6		168.3	139.9	127.8	128.4	126.7	61.0	13.5
							138.8	127.9	129.1	125.9	61.5	14.0
34	170.2	59.6	40.0	21.2		170.8	144.7	128.1	129.1	127.3		
35	169.8	58.9	47.1	27.1	12.0	170.6	142.0	128.9	128.8	127.2		
36	169.3	58.7	44.7	35.9	19.9	170.0	142.0	128.3	128.5	126.6		
37	169.8	57.5	51.4			169.8	143.1	129.2	128.4	127.3		
							143.1	129.2	128.4	127.3		
38	169.1	58.1	46.9	39.8		169.9	140.7	128.0	128.7	126.5		
							139.5	127.9	128.9	125.9		
39	178.2	42.5	36.1	21.8			145.4	126.6	128.5	126.4		
40	178.6	41.0	43.4	29.0	11.7		143.5	127.4	128.3	126.4		
41	178.5	41.4	41.5	38.3	20.3		143.8	127.3	128.3	126.4		
42	177.9	40.3	46.5				143.1	127.5	128.5	126.5		
							143.1	127.5	128.5	126.5		
43	178.3	42.9	43.5	38.3			143.2	127.4	128.4	126.6		
							139.2	128.2	129.2	126.2		

$J = 7.1$ Hz, OCH_2CH_3), 1.09 and 1.15 [3H each, d, $J = 6.6$ Hz, $CH(CH_3)_2$], 2.48 (1H, q, $J = 6.6$ Hz, $CHMe_2$), 3.02 and 3.18 (1H each, d, $J = 15.1$ Hz, H_2-4), 4.00 (2H, q, $J = 7.2$ Hz, OCH_2CH_3), 6.92–7.20 (4H, m, Ar-Hs).

Compound **23**: oil; ν_{max} (neat), 1750, 1710, 1225, 900, 750 cm^{-1}; ^1H NMR, 1.01 (3H, t, $J = 7.2$ Hz, CH_2CH_3), 2.74 (2H, d, $J = 7.1$ Hz, H_2-α), 2.99 and 3.28 (1H each, d. $J = 15.8$ Hz, H_2-4), 4.02 (2H, q, $J = 7.2$ Hz, OCH_2CH_3), 5.22 (2H, m, H_2-γ), 5.74 (1H, m, H-β), 6.94–7.33 (4H, m, Ar-Hs).

Hydrolysis of **21–23** in refluxing 10% ethanolic NaOH, subsequent acidification with dilute HCl and further refluxing as in Ref. 1

Table 3. ^{13}C–^1H correlation data for compounds 3, 4, 6, and 7

	Proton(s) showing one-bond correlation[a]			Proton(s) showing long-range correlation[b]		
Carbon	3[c,d]	4[c,d]	7[e]	3[d]	4[d]	6[d]
C-1				H_2-2, H-7	H-3	
C-2	H_2-2	H_2-2	H_2-2			H_2-4
C-3	H-3	H-3	H_2-3		H-2′,6′	H_2-4
C-3a				H-5, H-7	H-5, H-7	
C-4	H-4	H-4	H_2-4	H-6	H-6	
C-4a						H_2-4, H-6, H-8
C-5	H-5	H-5	H-5	H-7	H-7	H_2-4, H-7
C-6	H-6	H-6	H-6	H-4	H-4	H-8
C-7	H-7	H-7	H-7	H-5	H-5	H-5
C-7a				H-4, H-6	H-4, H-6	
C-8			H-8			H-6
C-8a						H_2-4, H-5, H-7

[a] Optimized for $1/J = 0.0036$.

[b] Optimized for $1/J = 0.0714$.

[c] C-α, C-β and C-γ in 3 correlated with H_2-α, H_2-β and H_3-γ, respectively. C-2′,6′, C-3′,5′ and C-4′ in **4** correlated with H-2′,6′, H-3′,5′ and H-4′, respectively.

[d] ^1H signals are reported in Ref. 3. The resonance positions for H-3 and H_2-β in **3** and H-3 in **2** should read δ 3.37 (m) and 1.45 (m) and 3.31 (m), respectively.

[e] ^1H NMR signals ($CDCl_3$) for **7**: δ 2.13 (2H, m, H_2-3), 2.65 2H, t, $J = 6.6$ Hz, H_2-2), 2.96 (2H, t, $J = 6.1$ Hz, H_2-4), 7.24 (1H, br d, $J = 7.5$ Hz, H-5), 7.29 (1H, br dd, $J = 7.8$ Hz and 7.5 Hz, H-7), 7.46 (1H, ddd, $J = 7.5$ Hz, 7.5 Hz and 1.5 Hz, H-6), 8.02 (1H, dd, $J = 7.8$ Hz and 1.5 Hz, H-8).

gave[4] **14**, **16** and **15**, respectively, in 70–80% yield as oils. Compound **14**: ν_{max} (neat), 1760, 1220, 750 cm^{-1}; ^{1}H NMR, 0.95 (3H, t, $J = 7.2$ Hz, H_3-γ), 1.10–1.95 (4H, m, H_2-α and H_2-β), 2.78 (2H, m, H_2-4), 3.98 (1H, m, H-3), 6.90–7.35 (4H, m, Ar-Hs). Compound **15**: ν_{max} (neat), 1770, 1215, 1140, 910, 750 cm^{-1}; ^{1}H NMR, 2.20–3.07 (5H, m, H-3, H_2-4, H_2-α), 5.18 (2H, m, H_2-γ), 5.65 (1H, m, H-β), 6.90–7.32 (4H, m, Ar-Hs). Compound **16**: ν_{max} (neat), 1760, 1215, 740 cm^{-1}; ^{1}H NMR, 1.01 and 1.05 [3H each, d, $J = 7.0$ Hz, $CH(CH_3)_2$], 2.08 (1H, m, $CHCHMe_2$), 2.61 (1H, q, $J = 7.0$ Hz, H-3), 2.92 (2H, d, $J = 7.0$ Hz, H_2-4), 6.69–7.22 (4H, m, Ar-Hs).

Dehydrogenation of **15** and **16** with Pd–C (10%) in refluxing diphenyl ether followed by chromatography of the reaction mixture over silica gel as in Ref. 3 furnished[4] **26** [1] and **25**, respectively, in 60–65% yield. Compound **25**: amorphous; ν_{max} (KBr), 1700, 730 cm^{-1}; ^{1}H NMR, 1.26 [6H, d, $J = 6.8$ Hz, $CH(CH_3)_2$], 3.12 (1H, m, $CHMe_2$), 7.19–7.43 (4H, m, Ar-Hs), 7.44 (1H, s, H-4).

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