

CARBON-13 NMR SPECTRA OF STACHENOL AND RELATED DERIVATIVES

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A recent investigation of the heartwood constituents of Androstachys johnsonii Prain yielded several novel tetracyclic diterpenes,² together with the known diterpene stachenol (1).³ The availability of a number of stachene and ent-atisene derivatives prompted us to undertake a ¹³C NMR study of these compounds. The data obtained will aid in determining new structures of this type, and provide confirmation for the structure assigned to compound (12),⁴ a novel C-16-hydroxy-ent-atisene.

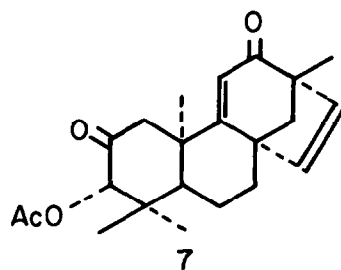
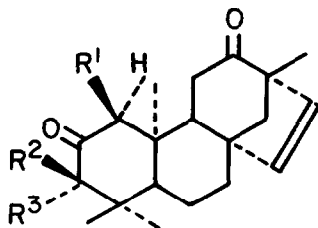
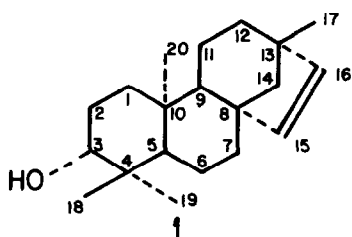
Although single frequency off-resonance proton decoupled (SFORD) spectra revealed in most instances the number of attached protons, inversion-recovery spectra were also recorded. With the concentration used (0.63 M in CDCl₃) the pulse sequence (10 sec-180°-0.8 sec-90°)_N gave spectra with clear distinction between CH₂, CH, and C allowing a more confident decision on carbon type. The methyl carbon relaxation times vary widely with C-20 consistently having the longest T₁, C-18 the shortest, and C-17 and C-19 intermediate values. Assignments were further based on comparison of pairs of compounds, consideration of β- and γ-hydroxy substituent effects,⁵ acetylation shifts, literature data on related structures,⁶ and general chemical shift arguments. The spectra of the product formed on acid catalysed deuteration of (2) distinguished between the closely spaced C-7 and C-11 resonances, and these assignments are carried over to the compounds with the same C-ring substitution viz. (3), (4), (5) and (6). Yb(fod)₃ induced shifts of the resonances of (1) gave unambiguous assignments for all carbons save C-15 and C-16 which are equally shifted. In the ¹H spectrum of (7) H-15 and H-16 are well separated and the residual splittings in the ¹³C SFORD spectrum show that the lowest field carbon is directly bonded to the lowest field proton. This proton has been assigned as H-15.⁴

Table I Carbon-13 Chemical Shifts of Stachenol (1) and related compounds

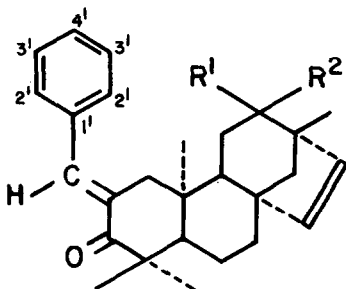
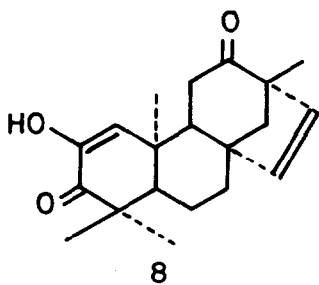
Carbon atom	(1)	(Yb ^c)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)
1	37.5	(0.19)	51.0	51.8	49.9	79.9	53.6 ^b	50.3	124.5	42.3	41.6	42.1	42.1
2	27.4	(0.49)	209.9	202.9	205.8	206.1	210.7	202.3	144.3	134.0	132.8	133.9	133.6
3	79.1	(1.00)	82.6	83.8	83.3	51.3	56.4 ^b	83.4	200.4	207.5	206.6	207.4	207.4
4	38.4	(0.46)	45.5	43.6	41.3	40.3	39.2	43.0	44.0	45.4	45.3	45.4	45.4
5	55.4	(0.21)	53.8	54.5 ^a	50.5	48.6 ^a	54.9 ^a	50.2	50.8	53.5	53.2	53.3	53.0
6	19.9	(0.13)	20.0	20.0	20.3	20.3	20.4	19.7	20.1	21.9	21.9	21.4	21.1
7	37.3	(0.08)	35.7	35.7	35.6	35.5	35.8	34.9	36.0	36.5	35.4	36.8	35.8
8	48.9	(0.06)	49.5	49.5	49.5	49.6	49.6	51.3	49.6	48.9	49.3	37.8	39.2
9	52.8	(0.10)	54.6	54.7 ^a	54.8	46.4 ^a	54.6 ^a	176.8	53.2	50.5	52.6	51.4	50.9
10	37.2	(0.16)	43.4	43.0	42.3	44.8	42.8	45.0	38.6	36.5	36.6	37.4	37.1
11	20.3	(0.06)	36.0	36.0	35.9	35.5	36.1	115.1	36.0	20.7	36.1	29.4	22.9
12	33.2	(0.03)	210.4	210.3	210.3	210.2	210.1	200.9	210.1	33.0	211.3	37.7	44.1
13	43.7	(0.03)	57.3	57.3	57.3	57.4	57.3	58.6	57.5	43.7	57.3	130.4	132.1
14	61.2	(0.03)	58.1	58.1	58.2	58.4	58.2	63.8	58.3	60.9	58.4	134.8	135.1
15	136.5	(0.05)	138.5	138.5	138.6	138.8	138.7	144.9	139.1	136.1	138.4	46.1	53.4
16	135.1	(0.05)	136.9	137.0	136.9	136.7	136.8	137.7	137.3	133.8	137.9	32.9	74.0
17	24.9	(0.02)	17.0	17.1	17.0	17.1	17.0	17.5	17.0	24.8	17.0	22.7	31.5
18	28.4	(0.30)	29.2	28.9	26.8	33.2	33.3	28.9	26.8	29.9	29.7	29.9	29.9
19	15.7	(0.33)	16.5	17.5	21.0	22.5	23.1	17.5	21.9	22.9	22.8	22.9	22.9
20	15.1	(0.13)	14.8	14.7	15.1	12.6	15.0	23.4	18.0	14.7	13.5	15.3	15.1
2'										128.3	128.6	128.3	128.3
3'&4'										130.2	130.1	130.2	130.1
1'										135.8	135.6	135.9	135.8
=CH										137.1	137.1	137.1	136.9
CH ₂ CO				170.3	169.7	169.4	170.1						
CH ₃ CO				20.5	20.7	20.7	20.5						

a, b Assignments may possibly be interchanged.

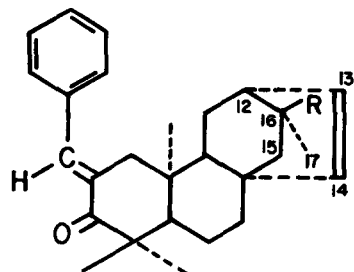
c Relative Yb(fod)₃ induced shifts.



- 2: $R^1 = R^2 = H; R^3 = OH$
- 3: $R^1 = R^2 = H; R^3 = OAc$
- 4: $R^1 = R^3 = H; R^2 = OAc$
- 5: $R^1 = OAc; R^2 = R^3 = H$
- 6: $R^1 = R^2 = R^3 = H$



- 9: $R^1 = R^2 = H$
- 10: $R^1 = R^2 = O$



- 11: $R = H$
- 12: $R = OH$

Table I lists the ^{13}C chemical shifts in CDCl_3 in ppm relative to TMS for compounds (1)-(12). The data were collected on a Varian CFT-20 spectrometer.

Compound (12) had been isolated from the reaction of benzaldehyde with the crude heartwood extract of Androstachys johnsonii. The proposed structure,⁴ suggested from physical and spectroscopic evidence, involved a novel C-16 hydroxylated-ent-atisene skeleton. For this reason (11) was prepared and the ^{13}C spectra of (11) and (12) compared. The ^{13}C data provide definite proof for the proposed structure, as evidenced by the shifts of the C-11, C-12, C-15, C-16 and C-17 resonances. This structure has recently been confirmed by X-ray crystallography.⁷

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