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CARBON-13 NMR SPECTRA OF *ent*-BEYERANE AND *ent*-BEYERENE DERIVATIVES

C. von Carstenn-Lichterfelde, C. Pascual* and J. Pons
Facultad de Ciencias. Universidad Autónoma de Madrid. Canto Blanco. Madrid-34.
and
Rosa Ma. Rabanal, B. Rodríguez and S. Valverde*
Instituto de Química Orgánica (C.S.I.C.), Juan de la Cierva 3, Madrid-6. Spain.

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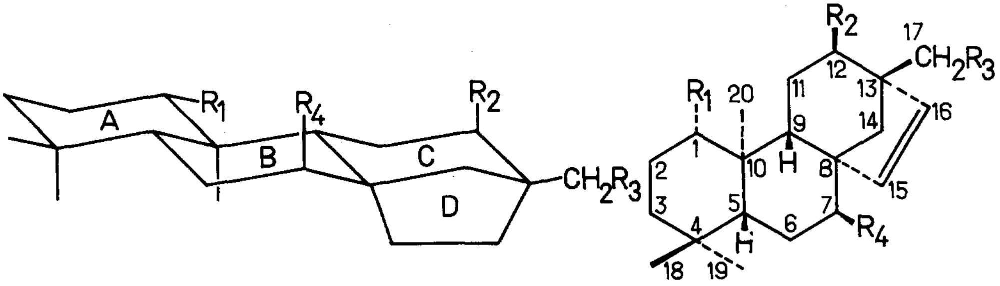
The tetracyclic diterpenoids are quite widespread in nature. Their biogenesis takes place through the cyclization of suitably oriented pimaradienes[1]. As an aid to the structural determination of new compounds of this type, we have analysed the ^{13}C NMR spectra of a series of compounds with the *ent*-beyerane skeleton[2], which also provide a model for the study of steric effects in fairly rigid bridged polycyclic compounds. In this communication we are presenting some preliminary results.



(1) $R_1 = R_2 = R_3 = R_4 = H$

(2) $R_1 = H$; $R_2 = R_3 = R_4 = OAc$

(3) $R_1 = R_4 = H$; $R_2 = R_3 = OAc$

(4) $R_1 = H$; $R_2 = R_3 = R_4 = OAc$

(5) $R_4 = H$; $R_1 = R_2 = R_3 = OAc$

The ^{13}C NMR signals were assigned by means of single-frequency off-resonance decoupling techniques[3], by applying known chemical shift rules such as acetylation shifts and steric γ and δ effects[3,4], and by comparing the spectra of pairs of compounds. Table 1 gives a list of the ^{13}C chemical shifts, δ_C, assigned.

Table 1. Carbon-13 Chemical Shifts of *ent*-Beyerane (*1*,*2*) and *ent*-Beyerene (*3*-*5*) Derivatives.[a]

Carbon atom	(*1*)	(*2*)	(*3*)	(*4*)	(*5*)
C-1	39.7	39.3	38.8	38.6	81.5
C-2	18.5	18.2	18.4	18.3	24.9
C-3	42.0	41.8[b]	41.9	41.9	39.2
C-4	33.1	32.5	33.1	32.5	32.9
C-5	56.5	47.7	55.8	47.8	54.9
C-6	20.4[b]	25.0[c]	20.0	25.2[d]	19.7
C-7	41.2[c]	78.8	36.4	75.2	36.6
C-8	44.9	47.4[d]	48.3	52.0[e]	48.6
C-9	56.9	48.5	49.3	44.9	49.2
C-10	37.6	37.3	36.9	36.9	41.6
C-11	20.2[b]	25.1[c]	26.4	26.1[d]	28.7
C-12	40.0[c]	72.4	68.9	68.4	68.8
C-13	39.2	46.3[d]	50.8	51.1[e]	50.5
C-14	57.7	41.6[b]	49.2	44.9	48.9
C-15	33.6	32.2	139.3	136.6	138.8
C-16	37.6	30.4	131.4	133.1	131.9
C-17	27.1	67.5	65.5	65.2	65.3
C-18	33.7	33.3	33.5	33.2	32.9
C-19	21.9	21.6	21.8	21.6	21.5
C-20	15.1	14.7	14.2	13.7	10.5

[a] The spectra were taken in $CDCl_3$ on a VARIAN XL-100-15-FT spectrometer. All carbon-13 chemical shifts are given in ppm relative to TMS.

[b,c] Owing to the closeness of these values, these assignments may be reversed.

[d,e] These assignments may also be reversed, but those given here are considered to be most likely.

Inspection of Table 1 shows that there is a good agreement between the δ_C values of the ring A carbon atoms of compound *1* and those previously reported for pimaradienes[5]. It may also be noted that the operation of the *anti*-periplanar γ-effect[6] is clearly observable in the case of both the equatorial acetoxyl group on C-1 (*5*) and the axial acetoxyl group on C-7 (*2*,*4*). A small, but noticeable, *syn*-diaxial effect (downfield shift) may be seen when comparing the chemical shifts of C-20 in the saturated (*1* and *2*) and unsaturated (*3* and *4*) series. The signal due to C-11 of compound *5* appears ~2.5 ppm at lower field than in the two other *ent*-15-beyerene derivatives (*3* and *4*). This shift may be attributed to the presence of an equatorial acetoxyl group on C-1.

We have also applied the rules derived by Beierbeck and Saunders[7] to the tetracyclic hydrocarbon *1* and found a reasonable agreement between the calculated and the experimental δ_C values (see Table 2) for all the carbon atoms pertaining to rings A, B and C, except for C-8 and C-13 at the bridgehead of the bicyclic C-D ring system. These two carbon atoms are strongly deshielded with regard to the calculated values (δ_{C-8} exp.= 44.9 ; δ_{C-8} calc.= 31.3 ; δ_{C-13} exp.=39.2 ; δ_{C-13} calc.=29.6). These discrepancies can be attributed to the fact that the rules of Beierbeck and Saunders, which were derived for decalins and polycyclic hidrocarbons with six-membered rings in chair conformation,do not allow for the effect of the bridge carbon atoms C-15 and C-16. For the purpose of these calculations, this effect has been considered equivalent to that of two axially oriented methyl groups on C-8 and C-13.

Table 2. Experimental and calculated ^{13}C chemical shifts for *ent*-beyerane (*1*)

	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-9	C-10	C-11	C-12	C-14
δ_C calc.[7]	37.0	16.6	41.5	33.1	55.7	17.0	41.5	54.1	36.6	17.0	41.4	53.9
δ_C exp.	39.7	18.5	42.0	33.1	56.5	20.4	41.2	56.9	37.6	20.2	40.0	57.7

Table 3 shows the changes in the δ_C values, Δδ, of the carbon atoms in rings C and D caused by the introduction of a Δ^{15} in compound *2*. It also includes a comparison of these changes with those reported for the corresponding carbon atoms of bicyclo-[3.2.1]-octane and Δ^6-bicyclo-[3.2.1]-octane[8].

Table 3

	(4)	(2)	$\Delta\delta$	Δ^6-Bicyclo-[3.2.1]-octane [a]	Bicyclo-[3.2.1]-octane [a]	$\Delta\delta$
C-8	51.9	47.4	4.5	39.5	35.2	4.3
C-9	44.9	48.5	-3.6	25.2	32.8	-7.6
C-11	26.1	25.1	1.0	18.7	19.1	-0.4
C-12	68.4	72.4	-4.0	25.2	32.8	-7.6
C-13	51.1	46.3	4.8	39.5	35.2	4.3
C-14	44.9	41.6	3.3	45.1	39.7	5.4
C-15	136.6	32.2	104.4	132.1	28.9	103.2
C-16	133.1	30.4	102.7	132.1	28.9	103.2

[a] Data taken from ref. 8

The slight discrepancies between the variations $\Delta\delta$ in the two series of compounds possibly reflect small conformational differences between ring C in these tetracyclic *terpenoids and the corresponding ring in bicyclo-[3.2.1]-octane.*

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