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CARBON-13 NMR SPECTRA OF SOME ent-ATISENE DERIVATIVES

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A recent investigation[1] of the roots of Margotia gummifera (Desf.) Lange yielded a novel tetracyclic diterpenoid, gummiferolic acid (1). The availability of a number of ent-atisene derivatives obtained from 1 prompted us to undertake a ^{13}C NMR study of these compounds.

Until now, only ^{13}C NMR data of some ent-atis-16-ene alkaloids[2] and two synthetic ent-atis-13-ene diterpenoids[3] have been reported. This paper presents (Table 1) the δ_C of the parent hydrocarbon ent-atis-16-ene (2), their C-7 and/or C-19 oxygenated derivatives 3-6 and the Δ^{15} isomer 7.

The spectra were determined in $CDCl_3$ solution at 25.19 MHz by using a pulsed Fourier transform system with proton noise-decoupling. The assignments were made with the aid of off-resonance-decoupled spectra and selective decoupling experiments, and further based on comparison of pairs of compounds, consideration of β, γ and δ substituent effects, acetylation shifts, general chemical shift arguments and literature data on related structures[2,3] and reported δ_C values of tri- and tetracyclic diterpenoids[4].

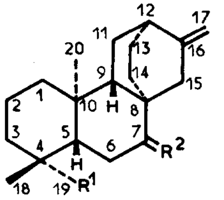
Inspection of Table 1 shows that there is a good agreement between the δ_C values of the ring A and C-6, C-7, C-18 and C-19 carbon atoms of all the compounds and those previously reported for ent-kaur-16-ene and ent-beyer-15-ene and their derivatives[4]. The chemical shifts of rings C and D carbon atoms (included C-8 and C-9) are also in agreement with the expected values obtained from ent-kaur-16-ene or ent-beyer-15-ene[4] taking into account the change of the bicyclo-[3.2.1]-octane moiety into the bicyclo-[2.2.2]-octane system[5] of the ent-atis-16-ene.

The diamagnetic shift ($\Delta\delta \simeq -3.6$ ppm) showed by the C-20 carbon atom of ent-atisene compounds with respect to similar ent-kaurene derivatives may be due to stereochemical perturbations exerted through space by the proximity of the C-13, C-14 bridge.

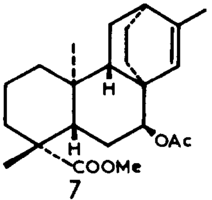
Finally, comparison of the δ_C values of compounds 6 and 7 accounts for the effects caused by the isomerization of the double bond.

Table 1. ^{13}C chemical shifts^{a} of compounds 2-7

	2	3	4	5	6	7
C-1	39.6^{b}	39.9^{b}	39.6	39.2^{b}	39.4	40.1
2	18.2	17.8	18.8	18.6	18.7	18.7
3	42.3	35.8	38.2	38.2	38.0	38.0
4	33.1	37.6	43.8	43.8	43.2	43.2
5	56.4	57.0	57.1	54.0	49.1	49.3
6	18.8	19.0	20.2	37.8	26.8^{b}	26.9^{b}
7	39.5^{b}	39.5^{b}	39.6	214.6	76.0	75.2
8	33.5	33.5	33.3	47.4	36.6	40.8
9	52.9	53.0	52.0	51.8	47.1	48.4
10	37.8	38.4	38.2	37.8	38.0	37.4
11	28.7	28.6^{c}	28.2^{b}	28.1^{c}	27.9^{c}	27.8
12	36.6	36.5	36.5	35.8	36.2	35.7
13^{d}	28.7	28.8^{c}	28.7^{b}	27.6^{c}	27.6^{c}	25.9^{b}
14^{d}	27.4	27.3	27.2	26.1	25.5^{b}	25.4^{b}
15	48.4	48.1	48.1	39.9^{b}	41.4	130.1
16	152.7	152.5	152.5	149.8	151.1	140.8
17	104.2	104.3	104.3	106.2	105.1	20.2
18	33.7	26.8	28.7	28.3	28.4	28.5
19	21.7	65.6	177.7	176.7	177.4	177.5
20	13.9	14.5	11.9	11.8	11.5	11.3
OMe	-	-	51.1	51.3	51.1	51.1
$\underline{C}H_3CO$	-	-	-	-	21.2	21.4
$CH_3\underline{C}O$	-	-	-	-	170.1	170.5



	R^1	R^2
1	COOH	O-angeloyl H
2	CH_3	H_2
3	CH_2OH	H_2
4	COOMe	H_2
5	COOMe	O
6	COOMe	OAc H



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[a] All ^{13}C chemical shifts are given in ppm relative to TMS.

[b,c] These assignments may be reversed, but those given here are considered to be most likely.

[d] These assignments for compounds 2-5 may be also interchanged. In this skeleton the effects caused on C-13 by the C-20 Me are presently difficult to determine.

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