^{13}C NMR Spectra of Natural Products

2†—Eudesmanolides

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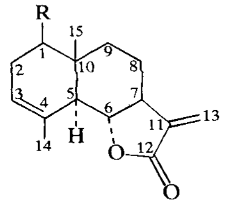
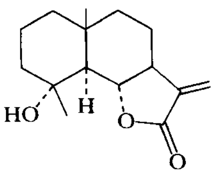
The ^{13}C NMR spectra of eight eudesmanolides have been measured and the chemical shifts assigned. Among the compounds studied are the naturally occurring α-cyclocostunolide, santamarin, arbsculin A and reynosin.

INTRODUCTION

As part of our programme on synthetic[1] and spectroscopic studies of sesquiterpene lactones,[2] we record in this paper the ^{13}C NMR spectra of a group of eudesmanolides including the naturally occurring α-cyclocostunolide (**1**), santamarin (**2**), arbusculin A (**4**) and reynosin (**7**).



1 R=H
2 R=OH
3 R=OAc



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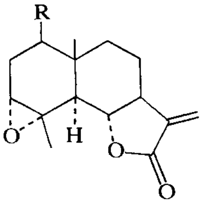

5 R=H
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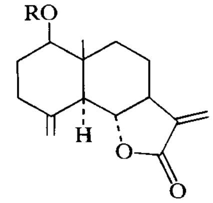

7 R=H
8 R=Ac

EXPERIMENTAL

The natural abundance ^{13}C NMR spectra were obtained in the PFT mode on a Varian XL-100-12 spectrometer operating at 25.2 MHz using 10% $CDCl_3$ solutions. An rf angle of 19 μs (45°) and an acquisition time of 0.65 s for a 6.5 KHz spectrum width were generally used for obtaining the spectra. Off-resonance decoupled spectra (SFORD) were obtained by irradiating 200 Hz upfield from TMS in the proton spectrum. The chemical shifts (relative to internal TMS) in the fully decoupled spectra are estimated to be accurate to ±0.1 ppm.

Compounds **1**, **2** and **7** were obtained and characterized as previously reported.[3,4] The acetates of **2** (**3**) and **7** (**8**) were obtained by the usual acetylation procedures while **5** and **6** resulted from the reaction of *m*-chloroperbenzoic acid with **1** and **2**, respectively. (The acetate **3** showed identical properties with those previously reported.[5] Compound **8**, obtained from **7**, displayed spectral properties in complete agreement with the proposed structure.) The properties of **1** & **2** were identical with those published.[6] Arbusculin A (**4**) was one of the components isolated by reaction of the oil of *E. elaeagnus* with dimethylamine followed by acid extraction, elimination, and silica gel chromatography of the resulting lactone fraction.[7] Its properties were identical with those recorded in Ref. 5.

Table 1. ^{13}C NMR chemical shifts of eudesmanolides (in ppm downfield from TMS)

Compound	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	C-12	C-13	C-14	C-15
1	37.8	22.9	122.3	132.9	51.3[a]	82.1	51.2[a]	21.5	39.2	36.0	139.3	170.8	116.3	23.7	17.4
2	75.1	32.8	121.2	133.3	51.1[a]	81.5	51.0[a]	21.2	34.3	40.9	138.9	170.6	116.6	23.3	11.1
3	76.6	29.4	120.6	133.1	50.8	81.0	50.8	21.0[b]	34.0	39.6	138.6	170.3[b]	117.0	23.2	12.3
4	40.9	19.4	42.8	71.5	57.8	81.3	50.7	21.9	40.0	37.5	138.3	169.6	117.5	24.2	19.7
5	34.6	21.0	60.1	57.4	53.1	81.1	50.9	21.4	38.5	34.9	138.7	170.3	116.8	21.9	17.8
6	72.5	31.1	60.8	57.1	52.6	80.9	50.4	21.0	34.4	40.3	138.7	170.1	116.8	21.7	11.8
7	78.1	31.3	35.7	142.4	53.0	79.6	49.6	21.5	33.6	43.0	139.1	170.5	117.0	110.5	11.7
8	79.1	27.7	35.2	141.7	52.9	79.1	49.3	21.2[b]	33.1	41.9	138.9	170.4[b]	117.1	110.9	12.7

[a] Assignments may be interchanged.
[b] Superposition of C-8 and C-12 with the methyl carbon and the carbonyl carbon of the acetate group, respectively.

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† For Part 1 see Ref. 2.

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RESULTS AND DISCUSSION

Table 1 shows the carbon assignments for all compounds included in this work. The shielding effects of the epoxide function, as well as the specific shifts induced upon acetylation of the equatorially oriented hydroxyl groups, are in complete agreement with the same effects reported for other series of compounds.[8,9]

It is of interest to note that while in a group of eudesmanolides related to santonin the chemical shift of C-15 is relatively unaffected by changes in either of the 6-membered rings, and it is always at lower field than C-14;[10] in the present series of compounds C-15 always appears at higher field than C-14. Since C-14 and C-15 are easily assigned by their residual coupling in the SFORD spectrum, their shifts can be considered of structural diagnostic value. [In the ^{1}H NMR spectra of all compounds studied the signal corresponding to the protons linked to C-14 always appeared at lower field (~1.5 ppm (**5** and **6**) and ~1.8 ppm (**1**, **2** and **3**)) than those at C-15 (~0.90 ppm), facilitating the assignments in the ^{13}C NMR spectra.]

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