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^{13}C NMR SPECTRA OF SOME D:A-FRIEDO-OLEANANES*

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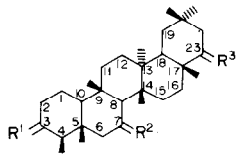
Key Word Index—D:A-Friedo-oleananes; friedelin; D:A-friedo-olean-7-one; putranjivadione; D:A-friedo-olean-22-one; D:A-friedo-olean-3,22-dione; *Salacia* triterpene R; ^{13}C NMR analysis.

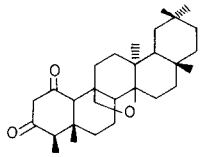
Abstract—The ^{13}C NMR signals of D:A-friedo-olean-7-one, putranjivadione, D:A-friedo-olean-22-one, D:A-friedo-olean-3,22-dione, and *Salacia* triterpene R have been assigned using off-resonance decoupling and lanthanide induced shift techniques. ^{13}C NMR data provide further evidence for the boat–boat conformation for the D and E rings of D:A-friedo-oleananes in solution.

INTRODUCTION

^{13}C NMR spectroscopy provides a valuable tool for the structural studies of natural products. Although a wide range of ^{13}C NMR data on triterpenes exists in the literature [2–7], very little information on the detailed analysis of the ^{13}C NMR spectra of D:A-friedo-oleananes is available [1, 8, 9]. The availability of a series of natural and synthetic D:A-friedo-oleananes and our continued interest in the application of ^{13}C NMR spectroscopy [1, 8] prompted us to conduct this study and we present now the ^{13}C NMR data of D:A-friedo-olean-7-one (**2**), putranjivadione (**3**), D:A-friedo-olean-22-one (**4**), D:A-friedo-olean-3,22-dione (**5**) and the *Salacia* triterpene R (**6**). Detailed analysis of the lanthanide induced shift (LIS) data for **2** provided further evidence for the boat–boat conformation for the D and E rings of D:A-friedo-oleananes in solution.



	R^1	R^2	R^3
1	O	H_2	H_2
2	H_2	O	H_2
3	O	O	H_2
4	H_2	H_2	O
5	O	H_2	O



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RESULTS AND DISCUSSION

The assignments for the ^{13}C NMR chemical shifts of the D:A-friedo-oleananes (Table 1) were made with the aid of proton-noise decoupled and off-resonance decoupled spectra, and further based on comparison of pairs of compounds, consideration of substituent and γ-gauche effects, general chemical shift arguments and literature data on related structures [1, 8–11].

Table 1. ^{13}C NMR chemical shifts [in δ-values (ppm) from TMS] of compounds **1**–**6**

	1*	**2**	**3**	**4**	**5**	**6**
C-1	22.3	21.1	21.8	20.8	22.3	202.6
C-2	41.5	27.0	41.0	27.5	41.5	60.5
C-3	213.0	30.2	210.9	31.1	212.6	203.7
C-4	58.2	46.3	57.9	46.3	58.3	59.2
C-5	42.1	44.1	47.1	37.6	42.1	37.5
C-6	41.3	58.0	57.0	41.5	41.3	38.5
C-7	18.2	212.4	210.4	18.2	18.1	17.0
C-8	53.1	63.9	63.6	51.9	51.8	45.2
C-9	37.4	43.5	42.5	37.2	37.6	37.1
C-10	59.5	60.6	59.1	61.0	59.7	69.0
C-11	35.6	35.7	35.6	35.6	35.7	35.8
C-12	32.4	32.0	31.9	30.2	30.2	26.5
C-13	38.3	39.4	39.5	38.7	38.6	38.1
C-14	39.7	37.6	37.6	39.6	39.7	40.0
C-15	30.5	30.7	30.0	30.4	30.4	34.7
C-16	36.0	36.2	36.4	27.2	27.1	36.8
C-17	30.0	30.2	34.7	45.1	45.0	30.8
C-18	42.8	42.0	41.9	48.1	48.1	44.0
C-19	35.3	35.1	35.0	34.8	34.8	35.4
C-20	28.1	28.2	28.2	31.4	31.5	28.3
C-21	32.8	33.0	32.9	49.7	49.6	32.5
C-22	39.2	38.9	38.8	217.3	217.3	38.9
C-23	6.8	13.8	7.0	13.6	6.8	7.5
C-24	14.6	15.1	15.3	15.1	14.7	15.7
C-25	17.9	19.6	19.4	18.0	18.1	67.1
C-26	18.6	18.4	18.4	18.4	18.3	19.3
C-27	20.3	19.6	19.6	18.5	18.5	69.9
C-28	32.1	32.3	32.3	34.0	34.0	30.0
C-29	31.8	31.7	31.7	31.1	31.1	31.4
C-30	35.0	34.7	34.7	35.1	35.1	35.1

*From ref. [9].

*Part 7 in the series "Studies on Terpenoids and Steroids" For Part 6 see ref. [1].

Proton-noise decoupled ^{13}C NMR spectra of D:A-friedo-olean-7-one (**2**) were also recorded with increasing amounts of $Eu(Fod)_3$. By extrapolation, the induced downfield shifts corresponding to a 1:1 mol ratio of the shift reagent–substrate was obtained to give a LIS value for individual carbons (Fig. 1). A low LIS value of δ1.7 for C-8 is due to a large contact contribution towards the shift [12].

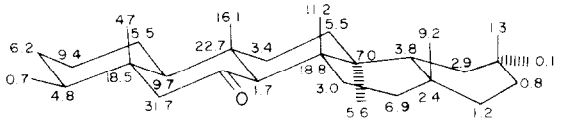

Fig. 1.

D:A-Friedo-oleananes are composed of five six-membered rings A–E. X-ray studies have indicated that rings A–C are in the chair conformation whereas rings D and E may take either chair–chair [13, 14] or boat–boat [15–17] conformations giving rise to folded and stretched forms, respectively. A recent ^1H NMR study using LIS and INDOR techniques has suggested the boat–boat conformation for the D and E rings of **1** in solution [18]. Our ^{13}C NMR LIS values show a better linear relationship with $1/r^3$ (where r is the distance from the carbonyl oxygen to the relevant carbon) when the D and E rings are in the boat–boat conformation rather than in the chair–chair conformation. Dreiding models show that the methyl carbons C-27 and C-30 are in close proximity when the D and E rings are chair–chair and would predict similar LIS values for these two carbons. On the contrary, C-27 and C-30 show markedly different LIS values and this can be attributed only to the boat–boat conformation of rings D and E.

EXPERIMENTAL

All ^{13}C NMR spectra were obtained on a JEOL FX-100 spectrometer operating at 25.05 MHz, using a pulse width of 5 μsec. Samples were made-up in $CDCl_3$ containing TMS as int. standard. The LIS expt was carried out by adding $Eu(fod)_3$ in three equal increments to a soln of **2**; the final molar ratio [$Eu(fod)_3$–sample] was 0.15. Chemical shifts are accurate to $\pm\delta$0.1 except for the carbonyl carbons where the error is $\pm$0.2 ppm.

Friedelin (**1**), putranjivadione (**3**) and *Salacia* triterpene R(**6**) used in this study were isolated from *Kokoona zeylanica* [19], *Putranjiva roxburghii* [20] and *Salacia prinoides* [21], respectively, following lit. procedures and their identities were confirmed by co-TLC and mmp determinations. D:A-Friedo-olean-7-one (**2**) was obtained from **3** by the method of ref. [20]. D:A-Friedo-olean-22-one (**4**) and D:A-friedo-olean-3,22-dione (**5**) were synthesized starting from 21α-hydroxy-D:A-friedo-olean-3-one [19] following unambiguous routes (unpublished results).

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