

CORRELATION OF METHYL SIGNALS IN  $\beta$ -HYDROXYOLEANENES

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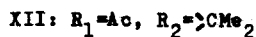
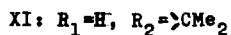
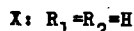
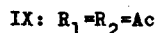
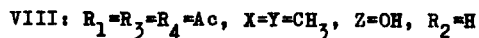
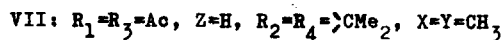
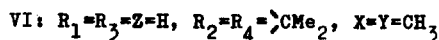
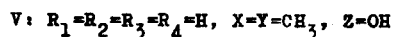
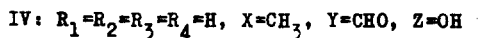
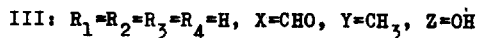
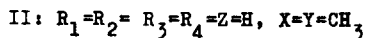
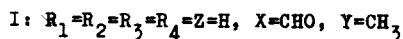
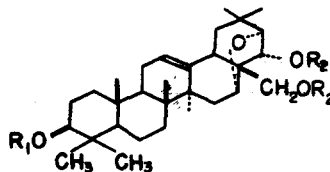
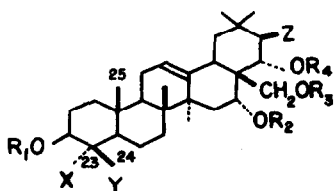
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Although the methyl region of the NMR spectra of the pentacyclic triterpenes has not been used for structural studies, a correlation of these signals with structure, once established, would be a very useful aid to the study of unknown triterpenoids, because eight methyl groups, or their biogenetic equivalents, are located throughout the carbon skeleton and any structural modification should cause systematic changes in some of the methyl chemical shifts, as has been found with the steroids (1). Although several papers (2) attempted to make this correlation in various type of triterpenoids, no discrimination was achieved between the signals due to the 23-, 24- and 25-methyl groups. The assignment of the methyl signals in the spectrum of olean-12-ene, reported by Karliner and Djerassi (3) also contained assumptions with respect to these three methyl groups and, furthermore, is not of great use in the structural study of natural triterpenoids which almost always carry a hydroxyl group at the  $\beta$ -position. During our structural studies on camelliagenins (4), theasapogenols (5) and barrigenols (6), we have noticed regular changes in the methyl signals on going from the  $\beta$ -hydroxyl to the  $\beta$ -acetoxy, as has been observed in the case of other types of triterpenoid (2), and from this, we have tentatively assigned the three signals appearing at 0.78-0.79 ppm, 0.91-0.94 ppm and 0.97-0.99 ppm in  $\beta$ -hydroxy compounds, and at 0.85-0.87 ppm, 0.85-0.88 ppm and 0.95-0.98 ppm in  $\beta$ -acetoxy compounds, to the methyl groups in question. In order to unambiguously assign these three methyl groups in the more common naturally-occurring  $\beta$ -hydroxyolean-12-enes and ultimately to establish the effect of substitution on these methyl signals, we have prepared and measured the NMR spectra of three  $\beta$ -hydroxyoleanenes and their acetates, each of which has been selectively deuterated at either 23- or 24-position.

Camelliagenin B (I) (4) was converted into its ethanedithioacetal which, without



Suffix "a" and "b" in the text refers to the 23-d<sub>2</sub> and 24-d<sub>2</sub> compounds, respectively.

TABLE I. C-Methyl Signals in Camelliagenins and Barringtogenols (13)

Compd Nos.	Subst. at 3	-C-CH <sub>3</sub>						
		23	24	25	26	27	29	30
VI	OH	0.99	0.78	0.94	0.94	1.28	0.89	1.07
VIa	OH	—	0.78	0.94	0.94	1.28	0.89	1.07
XI	OH	1.01*	0.80	0.91	0.85	1.48	0.99	1.01*
XIa	OH	—	0.79	0.91	0.85	1.48	0.98	1.01
XIb	OH	1.01*	—	0.92	0.85	1.48	1.01*	1.01*
VII	OAc	0.86*	0.86*	0.96	0.94	1.26	0.90	1.05
VIIa	OAc	—	0.86	0.96	0.94	1.26	0.90	1.05
VIII	OAc	0.86*	0.86*	0.96	0.90	1.42	0.98*	0.98*
VIIIa	OAc	—	0.87	0.96	0.90	1.43	0.99*	0.99*
VIIIb	OAc	0.88	—	0.96	0.90	1.44	1.00*	1.00*
IX	OAc	0.87*	0.87*	0.94	0.87*	1.49	1.03	1.09
IXa	OAc	—	0.88*	0.95	0.88*	1.51	1.03	1.09
IXb	OAc	0.88*	—	0.95	0.88*	1.50	1.04	1.10
XII	OAc	0.87*	0.87*	0.93	0.87*	1.47	0.97	1.02
XIIa	OAc	—	0.87	0.94	0.85	1.48	0.98	1.01
XIIb	OAc	0.87	—	0.94	0.85	1.48	0.97	1.01

\* The values are not accurate because of overlapping.

purification, was then subjected to desulfurization using deuterium-containing Raney nickel (7) in deuteromethanol to give camelliagenin A 23-d<sub>2</sub> (IIa), m.p. 270-272° (8). Exactly the same reaction sequence was applied to theasapogenol E (III) (9) (camelliagenin E (5)) and camelliagenin D (IV) (5) to afford barringtogenol C 23-d<sub>2</sub> (Va), m.p. 281-283°, and 24-d<sub>2</sub> (Vb), m.p. 285-286°. These three deuterated compounds were further converted to derivatives with a greater solubility for the NMR measurement. Thus IIa was converted to the acetonide VIa, m.p. 274-275°, and the acetonide diacetate VIIa, m.p. 200-202°, whereas Va and Vb were converted to the following derivatives; the triacetates (VIIIa, m.p. 250-252°, VIIIb, m.p. 254-255°), the barringtogenol D triacetates (IXa, m.p. 227-230° and IXb, m.p. 229-231°), barringtogenol D (Xa, m.p. 269-272°, Xb, m.p. 272-274°), the barringtogenol D acetonides (XIa, m.p. 231-234°, XIb, m.p. 232-234°) and the acetonide acetates (XIIa, m.p. 228-231°, XIIb, m.p. 229-232°) (10), by well established procedures (11).

The C-methyl signals in the NMR spectra (12) of these deuterated compounds are listed in TABLE I (13) together with those of undeuterated compounds. It is clear from this table that the signals at 0.99-1.01 ppm and 0.86-0.87 ppm have disappeared or markedly decreased in the case of the 23-d<sub>2</sub> (a series) compounds with 3 $\beta$ -hydroxy and 3 $\beta$ -acetoxy groups, respectively, while in the case of the 24-d<sub>2</sub> (b series) compounds signals at 0.80 ppm and 0.86-0.87 ppm have, respectively, disappeared or largely decreased; thus the 23-, 24- and 25-methyl signals can be easily and unambiguously assigned in all these compounds. Our assignment is in agreement with that obtained recently by Tursch and others (14), from a careful examination of the chemical shift observed in a series of olean-12-enes and 4,4-dimethylsteroids. Furthermore, a comparison of our results with those of Tursch et al discloses that the chemical shifts of the 23-, 24- and 25-methyls are little affected by the presence of oxygen functions in the D and E rings; a result similar to that noted in the steroid (I). The assignment of these three methyl groups established in the present study can thus safely be extended to other triterpenoids (2) and the assignment given previously (2f) for the 30- and 31-methyl signals in lanostane derivatives should be reversed.

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- 12) All NMR spectra were measured at 60 Mc for deuteriochloroform solutions. Chemical shifts are expressed in p.p.m. from internal tetramethylsilane.
- 13) Assignment of the other methyl signals follows from our previous assignment (4,5,6) and will be discussed elsewhere.
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