Nuclear Magnetic Resonance Spectroscopy, The Bandwidths of the Singlets in Gedunin and its Simple Derivatives

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RECENTLY, various workers[1] have discussed the relationship between the bandwidths of the absorption due to tertiary methyl groups and the stereochemistry of the groups. In this Communication, we report the relationship between the bandwidths of the absorption due to the H-15 and H-17 protons, and relevant features of the structure, of gedunin[2,3] (I) and some simple derivatives.[4] The Table shows both bandwidth (W_{H} is the bandwidth at half height, taken under conditions that give the W_{H} of the internal tetramethylsilane reference as 0·5—0·7 c./sec.) and the chemical shift (in p.p.m., δ scale), using deuterochloroform as solvent.

As can be seen, the bandwidth of the H-17 band is constant, within the limits 1·5—1·7, both in the twelve gedunin compounds, and in the four compounds related to *Cedrela odorata* substance B[5] (II). The relatively large value of this bandwidth is due to broadening by a measure of allylic coupling between the H-17 proton and the furan protons.

In contrast, the H-15 proton in the compounds with a 14,15-epoxide (compounds 1—6) has no proton to couple with on α- or β-carbon atoms, and consequently shows a significantly sharper absorption, the bandwidth being 0·7—0·85 c./sec. for these compounds. Elimination of the epoxide, giving a 14,15-double bond, generally causes slight

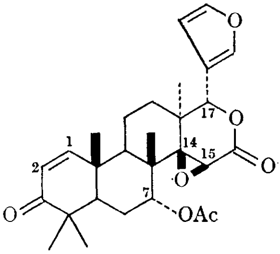
TABLE

	Compound	H-15		H-17		Reference
		δ	W_{H}	δ	W_{H}	
1.	Gedunin (I)	3·50	0·8	5·57	1·5	2, 3
2.	1,2-Dihydrogedunin	3·47	0·8	5·56	1·5	2
3.	7-Deacetylgedunin	3·96	0·85	5·60	1·5	3
4.	1,2-Dihydro-7-deacetylgedunin	3·95	0·85	5·60	1·6	6
5.	7-Deacetyl-7-oxogedunin	3·86	0·8	5·45	1·5	6
6.	1,2-Dihydro-7-deacetyl-7-oxogedunin	3·74	0·7	5·40	1·7	6
7.	14,15-Deoxygedunin	5·67	1·2	4·97	1·65	7
8.	1,2-Dihydro-14,15-deoxygedunin	5·65	1·0	4·93	1·7	7
9.	7-Deacetyl-14,15-deoxygedunin	5·91	1·4*	5·00	1·7	6
10.	1,2-Dihydro-7-deacetyl-14,15-deoxygedunin	5·88	1·1	4·97	1·7	—
11.	7-Deacetyl-7-oxo-14,15-deoxygedunin	6·62	0·9	5·00	1·7	8
12.	1,2-Dihydro-7-deacetyl-7-oxo-14,15-deoxygedunin	6·44	0·85	4·97	1·6	8
13.	*Cedrela odorata* substance B (= Mexicanolide) (II)	—	—	5·27	1·55	5
14.	Carapin (III)	5·79	3·4	5·08	1·6	9
15.	Khayasin (= low melting compound from *Khaya senegalensis*) (IV)	—	—	5·65	1·6	10
16.	*Cedrela odorata* substance C (V)	—	—	4·45	1·7	5

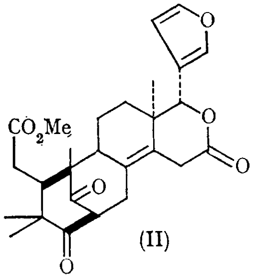
* overlaps H-2.

broadening of the H-15 absorption (compounds 7—12). The broadening is presumably due to interaction with protons that are β to the C-14 end of the double bond. Since the 7-oxo-derivatives (11 and 12) give slightly narrower absorption than the 7α-hydroxy- or -acetoxy-compounds, it would seem that the 7β-proton is primarily responsible for the broadening; this may be related to the near coplanarity of the atoms H-7β; C-7; C-8; C-14; C-15; H-15 in these compounds. The considerably increased width of the H-15 absorption in carapin (III) is due to coupling with the proton on C-8; in the gedunoid compounds (1—12) this proton is absent, a methyl group taking its place.

Thus we suggest that in a given group of closely related compounds, the bandwidth, as well as the chemical shifts, can be of use in correlating the n.m.r. spectrum with the structures of the compounds, for absorptions other than those due to tertiary methyl groups.



(I)



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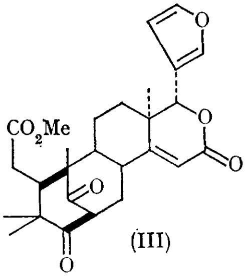

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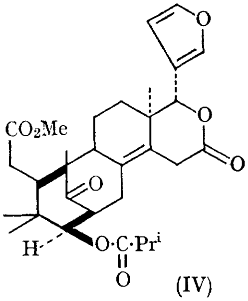

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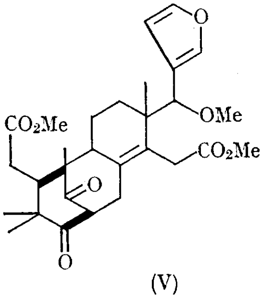

(V)

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