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CONCERNING RING A OF CUCURBITACIN B

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THE nuclear magnetic resonance (NMR) spectra of compounds having an α,β-unsaturated ketone group with hydrogen on the β carbon atom show signals from 13 to 54 c.p.s. downfield from benzene at 40 Mc.,[1] which corresponds to the region between $\delta = 6.76$ and $\delta = 7.77$ as defined here.[2] The NMR spectra of diosphenols prepared by the air oxidation of an alkaline solution of dihydro- and dihydrodeacetoxycucurbitacin B,[3]

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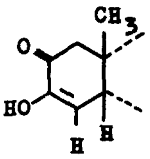
[1] J.N. Shoolery and Max T. Rogers, J. Am. Chem. Soc. 80, 5126 (1958).

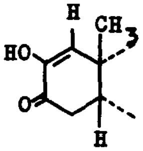
[2] All values reported here are at 60 Mc./sec. referred to tetramethylsilane in deuterochloroform solution. Chemical shifts are reported in parts per million according to the definition $\delta_i = 10^6(\nu_i - \nu_{ref.})/\nu_{ref.}$, which results in positive values of δ downfield from tetramethylsilane.

[3] A. Melera and C.R. Noller, manuscript submitted to J. Org. Chem. May 9, 1960.

which have hydroxyl on the α carbon atom of the α,β-unsaturated carbonyl grouping, lacked this peak and threw doubt on the presence of the diosphenol structure. Accordingly the two diosphenols having the partial structures I and II, and known respectively as forms A and B of 2,3-cholestanedione,[4] were prepared and their NMR spectra



I



II

determined. Neither compound gave a signal between $\delta = 6.76$ and $\delta = 7.77$. However, form B showed a single sharp peak at $\delta = 6.37$, indicating that the effect of the α hydroxyl group is to shift the signal arising from the β hydrogen to higher field strength. In form A this singlet is split into a sharp doublet centered at $\delta = 5.68$, which may be ascribed to the spin-spin interaction of the β proton with the proton on C-5, this proton being lacking in form B. The coupling constant is about 3 c.p.s. The diosphenols prepared from cucurbitacin B also show this doublet centered at $\delta = 5.97$. Hence, they also must have one hydrogen β and one

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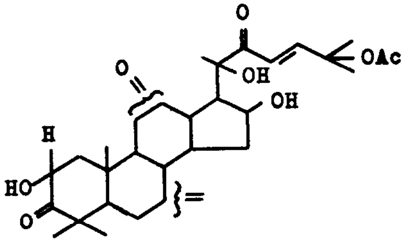
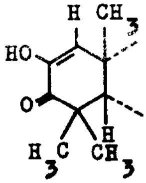
[4] E.T. Stiller and O. Rosenheim, J. Chem. Soc. 353 (1938); L. Ruzicka, P.A. Plattner, and M. Furrer, Helv. Chim. Acta **27**, 524 (1944).

hydrogen γ to the carbonyl group.

On the basis of the various structures (III) recently proposed for cucurbitacin B,[5] the diosphenols should have partial structure IV,



III



IV

but IV does not have the grouping required by the NMR spectra. Neither can the proper grouping be placed in any other position of the proposed carbon skeleton. If the structure of ring A is essentially correct as shown in III, the NMR spectra can be accommodated only if there is no angular methyl group at C-10.

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[5] D. Willner, P.R. Enslin, J.M. Hugo, and K.B. Norton, Chem. and Ind. (London) 951 (1959); D. Lavie and Y. Shvo, ibid. 403 (1960).