Tetrahedron Letters No. 9, pp. 285-288, 1961. Pergamon Press Ltd. Printed in Great Britain.

A REVISED STRUCTURE FOR PTEROCARPIN

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(Received 11 May 1961)

THE recent isolation of the antifungal glucoside trifolirhizin and its aglycone from Trifolium pratense L.[1,2] and the methylation of the aglycone to pterocarpin has drawn our attention to the structure of the latter compound.

The subfamily Papilionatae is known as a rich source of isoflavanoid substances. A literature scrutiny of 2'-oxygenated isoflavanoids that have a dimethoxy or a methylenedioxy group in the B-ring revealed an interesting observation. All the investigated substances (rotenoid type compounds,[3,4] pachyrrhizin,[5] jamaicin,[6] erosnin,[7] sophorol[8]) except pterocarpin have the

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[*] Varian Associates, Palo Alto, California.

[1] P. K. Hietala, Ann.Acad.Sci.Fennicae, Series A II Chemica 100, 61 (1960).

[2] J. B. Bredenberg and P. K. Hietala, Acta Chem.Scand. 15, In press (1961).

[3] W. Karrer, Konstitution und Vorkommen der organischen Pflanzenstoffe references cited on pp. 572-579. Birkhäuser Verlag, Basel (1958).

[4] N. Finch and W. D. Ollis, Proc.Chem.Soc. 176 (1960).

[5] E. Simonitsch, M. Frei and H. Schmid, Monatsh. 88, 541 (1957).

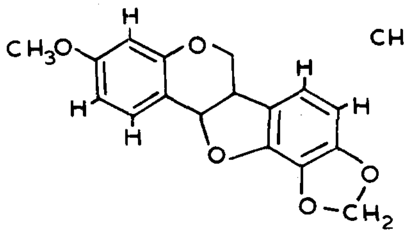
[6] O. A. Stamm, H. Schmid and J. Büchi, Helv.Chim.Acta 41, 2006 (1958).

[7] J. Eisenbeiss and H. Schmid, Helv.Chim.Acta 42, 61 (1959).

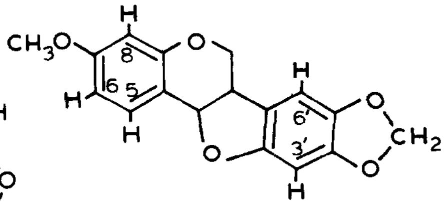
[8] H. Suginome, Tetrahedron Letters No. 19, 16 (1960).

oxygens in the 4',5'-positions. In the structure proposed for pterocarpin (I)[9,10] the oxygens are in the 3',4'-positions. This deviation from the biogenetically related compounds, particularly sophorol, made a reinvestigation of the structure necessary, especially as the evidence for the B-ring oxidation pattern[10] does not seem to be conclusive, since it rests on the comparison of the infrared spectra of a reaction product of pterocarpin with a synthetic compound.

An NMR spectrum of pterocarpin (Fig. 1) was taken in deuterated chloroform at 60 mc/sec, using a Varian Associates A-60 Spectrometer. It provides unequivocal proof of the superiority of structure II over structure I



I



II

Aromatic protons which are not adjacent to an oxygen will be found near the ordinary position for unsubstituted benzene, i.e. between δ = 7.3 and 7.4 p.p.m. (relative to tetramethylsilane).[11] If an aromatic proton is adjacent to one oxygen it will be shifted upfield to the region between δ = 6.7 and 6.8 p.p.m., while if it is adjacent to two oxygens

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[9] A. McGookin, A. Robertson and W. B. Whalley, J.Chem.Soc. 787 (1940).

[10] A. Robertson and W. B. Whalley, J.Chem.Soc. 1440 (1954).

[11] Chemical shifts, δ, were measured in parts per million relative to the reference tetramethylsilane taken as zero and were read directly from the pre-calibrated chart paper. Increasing shifts correspond to a larger degree of unshielding of the protons being observed.

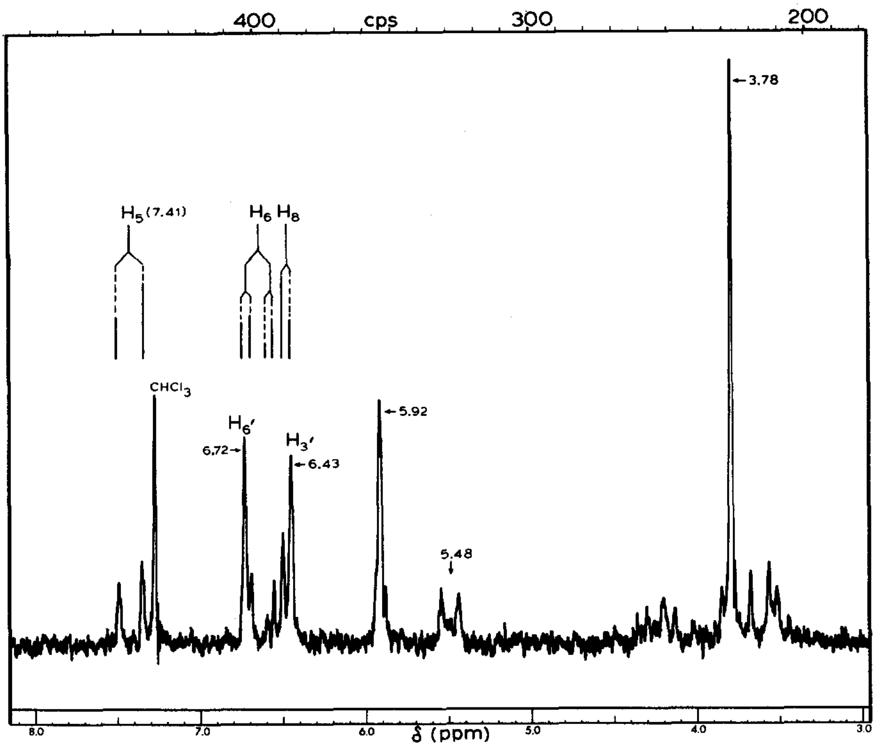

FIG. 1.

Nuclear magnetic resonance spectrum of pterocarpin.

it will be shifted to still higher magnetic field values (δ = 6.4 to 6.6).

A doublet centered at δ = 7.41 is found in the spectrum with a spin coupling of 9 cps, which shows that it must arise from a proton ortho to another aromatic proton. This can only be assigned as H_5. The remainder of the ABX pattern involving protons H_6 and H_8 is identified in Fig. 1 and accounts for the three protons of ring A. The remaining two strong peaks (at δ = 6.43 and 6.72) do not exhibit the spin-spin coupling which would be required for two aromatic protons ortho to one another. Furthermore, the chemical shifts correspond to one of these protons being adjacent to one oxygen and the other adjacent to two oxygens. The two strong peaks are therefore assigned to $H_{3'}$ and $H_{6'}$ which proves that the structure of pterocarpin is II.

Other assignments in the spectrum are as follows. The methylene dioxy peak falls at $\delta = 5.92$. The CH group attached to ring A is found as a doublet centered at $\delta = 5.48$. The remaining protons in the molecule yield a complex multiplet surrounding the methoxyl resonance.