2- and 4-Monoformyldeuteroporphyrin IX

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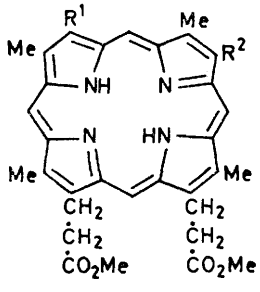
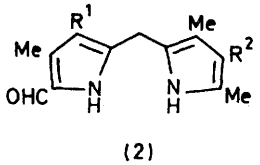
Summary Ring synthesised 2- and 4-acetyldeuteroporphyrin have been converted into the corresponding formyl derivatives and as a result the commonly accepted structural assignments for these formylporphyrins should be revised.

RECENTLY we reported[1] the synthesis of 2- and 4-acetyldeuteroporphyrin IX dimethyl ester [(**1a** and **b**) respectively] which allowed us to correct the structural assignments previously given to these compounds.[2] We had also shown[1] that our 4-acetyldeuteroporphyrin (**1b**) could be converted into pemptoporphyrin (**1c**). We now report that (**1a**) can be converted into isopemptoporphyrin (**1d**), identical with samples prepared independently in other laboratories.[3,4] Following the procedure of Sparatore and Mauzerall[5] we have oxidised (**1c**) and obtained 4-formyldeuteroporphyrin IX dimethyl ester (**1e**), m.p. 241—242°; oxidation of the isomer (**1d**) gave 2-formyldeuteroporphyrin IX dimethyl ester (**1f**), m.p. 266—268°. It has been considered in recent years[2,6] that the higher melting isomer was the 4-formyl derivative although Fischer and Beer[7] originally reported the m.p. of this isomer at 230°. We have been able to compare our products with those prepared by Brockmann *et al.*[2] by electrophilic substitution of deuteroporphyrin and find our 2-formyldeutereoporphyrin corresponds in all respects (m.p.; n.m.r.; i.r.) with the higher melting isomer of the German workers who, following Fischer and Wecker,[6] assigned this as the 4-isomer. Likewise, our 4-isomer is identical with the 2-isomer of Brockmann and his colleagues.

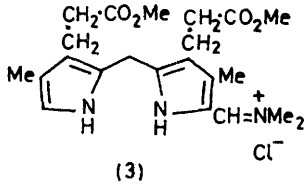


(1)

	R^1	R^2
a;	Ac	H
b;	H	Ac
c;	H	$CH=CH_2$
d;	$CH=CH_2$	H
e;	H	CHO
f;	CHO	H
g;	H	CO_2Me
h;	CO_2Me	Ac
i;	CO_2Me	H
j;	CO_2Me	$CH=CH_2$



(2)



(3)

	R^1	R^2
a;	H	CO_2Me
b;	CO_2Me	Ac

It would now seem that the generally accepted structures of the two formyldeuteroporphyrins should be revised.

To confirm our structural assignments further we have oxidised [2,7] our formyldeuteroporphyrins and, after methylation, obtained the corresponding methoxycarbonyl derivatives which were compared directly with porphyrins prepared by ring synthesis.

Condensation of (**2a**) with the imine salt[8] (**3**) gave a bilene which was cyclised[8] without isolation to give the porphyrin (**1g**), (14%), m.p. 214—216°, identical in all respects with the porphyrin obtained by oxidation of 4-formyldeuteroporphyrin. Similarly, (**2b**) and (**3**) yielded the porphyrin (**1h**), (11%), which was converted into (**1i**), m.p. 213—215°, by carrying out a Schumm melt[9] on the haematin derived from the vinylporphyrin (**1j**). The porphyrin (**1i**) was identical in all respects with the compound obtained by oxidation of 2-formyldeuteroporphyrin.

In view of the findings reported in this communication it is remarkable that Fischer arrived at the correct formulation for *Spirographis* porphyrin. Fischer and Wecker's[6] synthesis of this tetrapyrrole commenced from a monoformyldeuteroporphyrin, m.p. 255°, which at the time was thought to be relatively pure 4-formyldeuteroporphyrin. Reaction with methylmagnesium iodide gave the hydroxyethyl derivative which was then formylated; dehydration gave *Spirographis* porphyrin. The structure of *Spirographis* porphyrin cannot be in doubt since it has been synthesised independently by two other groups.[3,10] In view of the present work Fischer's preparation would seem to be fortuitous since the formyldeuteroporphyrin from which he started must have been largely the 2-isomer. It is true that the yield of *Spirographis* porphyrin obtained by Fischer was extremely low—from 2 g of the hydroxyethylporphyrin only 0·5 mg of the product was isolated.

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[1] P. S. Clezy, V. Diakiw, and N. W. Webb, *J.C.S. Chem. Comm.*, 1972, 413.
[2] H. Brockmann, K.-M. Bliesener, and H. H. Inhoffen, *Annalen*, 1968, **718**, 148.
[3] A. H. Jackson, G. W. Kenner, and J. Wass, *Chem. Comm.*, 1967, 1027.
[4] R. Grigg, A. W. Johnson, and M. Roche, *J. Chem. Soc.* (*C*), 1970, 1928.
[5] F. Sparatore and D. Mauzerall, *J. Org. Chem.*, 1960, **25**, 1073.
[6] H. Fischer and G. Wecker, *Z. physiol. Chem.*, 1941, **272**, 1.
[7] H. Fischer and L. Beer, *Z. physiol. Chem.*, 1936, **244**, 31.
[8] P. S. Clezy, A. J. Liepa, and N. W. Webb, *Austral. J. Chem.*, 1972, **25**, 1991.
[9] O. Schumm, *Z. physiol. Chem.*, 1928, **178**, 1.
[10] P. Bamfield, R. Grigg, A. W. Johnson, and R. W. Kenyon, *J. Chem. Soc.* (*C*), 1968, 1259.