Long-chain αω-Dicarboxylic Acids from Spores of *Equisetum* spp.

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IT is commonly suggested[1] that lipids of biological origin have played a significant role in the formation of crude petroleum. We have examined the lipid constituents of certain "living fossil" plants in order to ascertain whether or not they show distinctive features, and report results of an examination of spores[2] of *Equisetum* species.

Sosa[3] isolated "equisetolic acid" from spores of *E. maximum* Lam. (*E. telmateia* Ehrh., the Giant Horsetail) and formulated it as a hydroxydicarboxylic acid $C_{35}H_{69}(OH)(CO_2H)_2$. We have isolated what appears to be the same substance from spores of *E. maximum* and of *E. arvense* (the Common Horsetail). The earlier evidence for a hydroxy-group has not been confirmed, and the i.r. spectrum of the dimethyl ester indicates that such a group is not present. Careful g.l.c. (2 ft × $\frac{1}{4}$ in., 5% Apiezon L on 80—100 mesh Gas-Chrom Z at 240°) of this "dimethyl ester," obtained by methylating the crude acid with diazomethane, gives two significant components. The major one is dimethyl triacontanedioate ($CO_2Me\cdot[CH_2]_{28}\cdot CO_2Me$), m.p. 84—85°, as indicated by its mass spectrum and a comparison (i.r., mixed g.l.c., mixed m.p.) with an authentic sample synthesised by anodic coupling.[4] The mass spectrum of the minor component (in amount about one twentieth that of the C_{30}-diester) indicates that it is dimethyl octacosanedioate. Reduction of the diesters to the hydrocarbons, followed by mixed g.l.c., confirms these conclusions.

The purity and quantity of triacontanedioic acid available from this source is remarkable (up to 1% of the air-dried weight).† Long-chain αω-dicarboxylic acids have

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† Moreover its occurrence in a genus which is the only survivor of what was, in earlier eras, a flourishing class,[5] leads to the possibility that long-chain αω-dicarboxylic acids may have taken part in hydrocarbon deposition. If so, the resulting deposits (*e.g.* crude petroleum) might well contain traces of the corresponding macrocyclic paraffins (C_{27} and C_{29} in the present example). Such components do not appear to have been noticed, however.

been reported infrequently as natural products, and neither octacosanedioic acid nor triacontanedioic acid appears to have been so encountered previously. It seems likely that the diacids reside at or near the surface of the spore (little or no extraction of chlorophyll from within the spore during extraction; microscopic examination).

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[1] B. T. Brooks, in "Chemistry of Petroleum Hydrocarbons," Reinhold, New York, 1954, vol. 1, ch. 6; J. E. Cooper, *Nature*, 1962, **193**, 744; R. L. Martin, J. C. Winters, and J. A. Williams, *ibid.*, 1963, **199**, 110.

[2] Fossil spores are known to be widely distributed in various sedimentary rocks. *cf.* L. R. Wilson, *J. Sedimentary Petrology*, 1948, **16**, 110

[3] A. Sosa, *Bull. Soc. Chim. biol.*, 1949, **31**, 57.

[4] D. A. Fairweather, *Proc. Roy. Soc. Edinburgh*, 1926, **46**, 71.

[5] A. S. Seward, "Fossil Plants," Cambridge, 1898, vol. 1, p. 242 *et seq.*; D. H. Scott, "Studies in Fossil Botany," Black, London, 1907, p. 15.