

Oxidative Degradation of Saturated Normal Long-chain Organic Compounds by Permanganate

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Recently we reported the extensive oxidative degradation of paraffin chains by potassium permanganate in acetic acid medium.^{1,2} This oxidative cleavage process has been used to localize deuterium atoms distributed in the carbon chain of catalytically deuterated methyl *cis*-9-octadecenoate,³ and to produce a homologous series of perdeuterated long-chain fatty acids or hydrocarbons.⁴ In order to study this oxidation more closely, we have investigated the reactions of a series of analogues of methyl octadecanoate labelled with deuterium and with carbon-13, and several saturated normal long-chain compounds with a constant number of carbon atoms and various functional groups.

In this note we wish to present the results of the degradative reaction carried out on docosane, docosanol-1, docosanoic acid and methyl docosanoate. All of these compounds were submitted to the reaction under the same conditions, which were described in an earlier report.¹ The carboxylic acids formed were converted into methyl esters which were analysed by gas-liquid chromatography and mass spectrometry.⁵ The percentages of methyl monocarboxylates and dimethyl dicarboxylates recorded are shown in Fig. 1.

Cleavage of the carbon chains by permanganate attack does not seem to occur haphazardly. The C(1)–C(2) link cleavage was strongly dependent upon the nature of the substituents at C(1) in docosanol and docosanoic acid, but this dependence was less pronounced in docosane and methyl docosanoate. The C(2)–C(3) bond was found to be more sensitive to oxidation and scission than the adjacent C(3)–C(4) bond in the alcohol, acid and ester. The carbon-carbon links situated at the central part of the chain were easily attacked by the oxidizing agent, and those at the end of the chain were less affected. Heneicosanedioic acid was found in all four oxidation-product mixtures. This proves, at least in the case of docosane, that a methyl group has undergone oxidation.

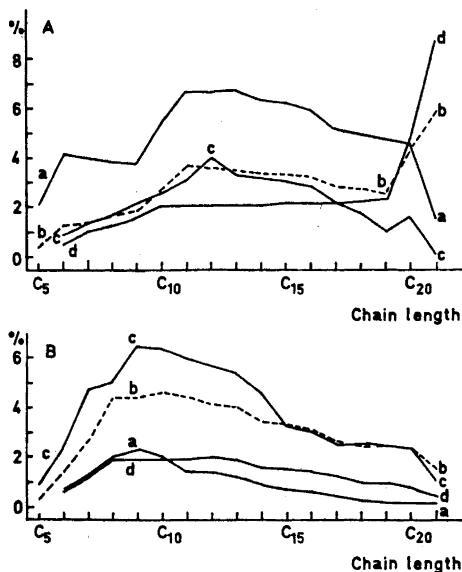


Fig. 1. Diagrams showing the percentages of methyl monocarboxylates (A) and dimethyl dicarboxylates (B) derived from the corresponding acids which were formed by permanganate oxidative degradations of docosane (a), docosanoic acid (b), methyl docosanoate (c) and docosanol-1 (d).

Full details of this work will be published later.

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1. Dinh-Nguyễn, Ng. and Raal, A. *Swed. Pat. Appl.* **16,972** (1968).
2. Dinh-Nguyễn, Ng. and Raal, A. *Acta Chem. Scand.* **23** (1969) 1442.
3. Dinh-Nguyễn, Ng. and Raal, A. *J. Res. Inst. Catalysis, Hokkaido Univ.* **17** (1969) 171.
4. The results of this synthesis are to be published.
5. Analyses performed with a combined gas chromatograph-mass spectrometer designed and constructed by S. Stållberg-Stenhagen. Cf. Stållberg-Stenhagen, S. and Stenhagen, E. In Burlingame, A. L. *Topics in organic mass spectrometry*, Wiley, New York 1970, p. 167.

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