Identity of 'Nudic Acid B' and 'Diatretyne II'

In 1946 two crystalline acidic antibiotics ('nudic acids *A* and *B*') were isolated from the culture medium of the basidiomycete *Tricholoma nudum* (Bull.) Fr. and some preliminary work on their respective constitutions was carried out[1]. It has now been shown that 'nudic acid *B*' is identical with 'diatretyne II' (7-cyano-*trans*-hept-2-en-4 : 6-diynoic acid (I)), which is produced by another fungus, *Clitocybe diatreta*[2], and which has been obtained synthetically (Ashworth, Jones, Mansfield, Schlögl, Thompson and Whiting, unpublished work).

$$HOOC—CH=CH—C\equiv C—C\equiv C—C\equiv N$$

I

A sample of the original 'nudic acid *B*' (10 mgm.) was used for establishing the identity. This had been stored in darkness for ten years without any special precautions against decomposition and had gone black due to surface polymerization. However, when the sample (10 mgm.) was esterified with 3 per cent methanolic sulphuric acid the methyl ester (5 mgm.) was obtained, which was shown to be identical with synthetic material (mixed melting point (102–104° C.), ultra-violet and infra-red absorption spectra).

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Structure of Conjugated Methyl Linoleate Hydroperoxide

Attempts to find the position of the hydroperoxide group of methyl linoleate hydroperoxide by permanganate oxidation of esters and ethers of the hydroxy component which is produced by reducing the hydroperoxide with stannous chloride have not been successful. Recently, it has been reported that the hydroxy component formed by reduction of the hydroperoxide can be dehydrated[1]. This reaction has been confirmed, but it has been found that a more complete conversion occurs when the reaction mixture is boiled for half an hour in an atmosphere of nitrogen.

A peroxide mixture obtained from partially autoxidized methyl linoleate by partition between petrol ether (boiling point 40°–60°) and 95 per cent methanol was reduced to the hydroxy component by stannous chloride. The component, having an absorption band at λ232 mμ (E(1%, 1 cm.) 238) and therefore containing only a proportion of conjugated diene, was dehydrated by boiling methanolic sulphuric acid (5 per cent). Most of the diene was converted to a conjugated triene. This component was separated from the rest of the material, which appeared to be a hydroxy mono ethenoid compound, and the free acid was finally obtained in the pure state by crystallization from acetone at − 60° and petrol ether at 0°.

This compound appeared to be identical with β-elæostearic acid spectroscopically, with maxima at 258 mμ (E(1%, 1 cm.) 1,570), 268·5 mμ (E(1%, 1 cm.) 2,110) and 280 mμ (E(1%, 1 cm.) 1,650); compare β-elæostearic acid (melting point 69°) with maxima at 259 mμ (E(1%, 1 cm.) 1,550), 268·5 mμ (E(1%, 1 cm.) 2,115) and 279·5 mμ (E(1%, 1 cm.) 1,650) prepared according to the method of Hilditch[2]. However, its melting point (58·5°–66°) indicated that it was impure and probably a mixture of two very similar inseparable acids.

Sufficient of the acid has been prepared to enable the position of the double bond nearest to the carboxyl to be determined by permanganate oxidation. The dibasic acids thus obtained have been separated and identified chromatographically as azelaic and suberic acids. Crystalline specimens of the acids melted at 105° and 141° respectively, that is, a little lower than the figures quoted in the literature, but no lower than samples available at the time, and there was no depression when like samples were mixed. However, *p*-bromophenacyl esters were prepared which had the accepted melting points, namely, 130·5° and 144° respectively, with no depression when the specimens were mixed with authentic samples of the esters.

The conjugated triene obtained by dehydration of the hydroxy compound was therefore a mixture of 9,11,13- and 8,10,12-octadecatrienoic acids, and the hydroxy compound was consequently a mixture of 9-hydroxy, 10,12-octadecadienoic and 13-hydroxy, 9,11-octadecadienoic acids. It is assumed that the original hydroperoxide groups occupied the same position as the hydroxyl groups obtained on reduction.

A more detailed account of this work, which is part of the programme of the Food Investigation Organization of the Department of Scientific and Industrial Research, will be published elsewhere.

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Mucopolysaccharides of Human Nuclei Pulposi

No detailed investigation of the mucopolysaccharide component of nuclei pulposi has been reported, but the combined results of several groups of workers[1–3] suggest that more than one type of mucopolysaccharide is present. The presence of at least three mucopolysaccharides in human nuclei pulposi is now reported, together with a simple method for their partial separation.

Nuclei pulposi, from the last five lumbar disks of a subject aged seventy, were subjected to graded extraction as follows. The material was minced, suspended in water, and pulverized in a blendor. The suspension was filtered and the filtrate, after deproteinization by Sevag's method, furnished fraction *A*. A second fraction (*B*) was isolated by shaking the insoluble residue remaining after aqueous extraction with 10 per cent calcium chloride solution at room temperature, and afterwards deproteinizing. Under alkaline conditions (0·5 per cent aqueous potassium hydroxide) further polysaccharide was extracted which yielded the largest deproteinized fraction (*C*).

Chromatographic investigation of hydrolysates of fraction *A* indicated that major constituent sugars were glucosamine and galactose, which suggested that