The Polyenoic Fatty Acids of Phospholipids and the Problem of Essential Fatty Acids

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A report will be given of the investigations carried out by the author's group during the last 40 years on the nature of the polyenoic fatty acids of phospholipids in animal organs. Isolation and analysis of the various compounds revealed that the complex fatty acid mixture in general consists of C_{20} and C_{22} polyenoates of the linoleate and linolenate types. Detailed examination of the metabolism of these acids has shown that they are synthesized from linoleate and linolenate or from the respective C_{16} polyenoates by chain elongation and dehydrogenation. New double bonds are introduced into the molecule towards the carboxyl group in a penta-2,4-dienyl sequence. It is only under certain abnormal conditions that the same enzymic apparatus converts oleate into a C_{20} trienoate of the oleate type. In general, however, the enzyme system is largely specific for linoleate and linolenate or polyenoates of these types as substrates, as has been shown in extensive experiments *in vivo* with polyenoates of different types.

In higher plants linoleate and linolenate are synthesized from oleate by a different enzyme system, which introduces the new double bonds in the opposite direction, i.e. towards the terminal methyl group.

The importance of these findings with respect to the role of essential fatty acids, particularly the problem whether not only the polyenoates of the linoleate type but also those of the linolenate type, both very similar in their metabolic behaviour, can serve as essential fatty acids, will be discussed.

The Biosynthesis of Unsaturated Fatty Acids

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Studies have been made of the effect of the configuration of the substrate molecule on the conversion of saturated into monoenoic fatty acids and of monoenoic into dienoic fatty acids. These data have allowed some preliminary suggestions to be made on the interaction between the protein and the substrate and how the position of the newly introduced double bond is controlled.

Biosynthesis of Unsaturated Fatty Acids by Higher-Plant Systems

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Mono- and poly-unsaturated fatty acids are found in all plant lipids. Although they are synthesized by aerobic pathways, little is known about their biosynthesis.

Whereas [^{14}C]acetate is readily incorporated by intact plant systems into C_{16} and C_{18} saturated, monounsaturated and polyunsaturated fatty acids, [^{14}C]palmitate and [^{14}C]stearate have failed to be converted into the corresponding polyunsaturated fatty acids.

In the sequence

we have examined step 1 and step 3 in some detail. Step 1 involves a special elongation enzyme system that differs from the pathway of biosynthesis *de novo* in that it is particularly sensitive to low concentrations of arsenite (Harwood & Stumpf, 1971). The arsenite effect can be observed in tissues *in vivo* as well as in systems *in vitro* without effecting the synthesis of C_{16} acids from acetate. Of interest is the potato fatty acid synthetase system, which produces C_{12} , C_{14} and C_{16} saturated fatty acids from acetyl-CoA and malonyl-CoA, which is not inhibited by arsenite (Huang & Stumpf, 1971). Further studies into this system will be discussed in detail.

System 3 has been explored in some detail (Vijay & Stumpf, 1971). It is highly specific, requiring oleoyl-CoA, NADH and molecular O_2 . The enzyme is microsomal and is found only in maturing *Carthamus tinctorius* seeds. It desaturates oleoyl-CoA specifically to linoleoyl-CoA, with both substrates rapidly being transferred to phosphatidylcholine. The evidence is very clear that the true substrate of desaturation is a CoA thiol ester and not phospholipid oxygen esters. Further details of this important system will be discussed.

Harwood, J. L. & Stumpf, P. K. (1971) *Arch. Biochem. Biophys.* **142**, 281

Huang, K. P. & Stumpf, P. K. (1971) *Arch. Biochem. Biophys.* **143**, 412

Vijay, I. & Stumpf, P. K. (1971) *J. Biol. Chem.* **246**, 2910