# CAROTENOIDS

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Edited by

OTTO ISLER

Chemical Research Department
F. Hoffmann-La Roche & Co. Ltd., Basle, Switzerland

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# I. Introduction

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## A. General Remarks

The brightly coloured carotenoid pigments have aroused the curiosity of scientists since the beginning of organic chemistry. Indeed some of the oldest studies were published during the early 19th century. Research on carotenoids can be separated into four broad periods according to the selection of problems and the methods of attacking them. During the 19th century, the emphasis was on isolation of the pigments and their characterization by measurements of light absorption. The second period (1900–1927) centred on the determination of empirical formulae and on tentative efforts to discover a role in photosynthesis. The third period (1928–1949) was dominated by the provitamin A concept, by establishing structural formulae and developing synthetic methods. The latest period (1950 to the present) has seen an exponential increase in the number of known carotenoids accompanied by notable advances in total synthesis and in the determination of absolute configurations.

The recent explosive growth in knowledge has in no small part been due to new separation methods (e.g. thin layer chromatography) whereby the number of individual carotenoids has increased from about 80 in 1948 to the present total of more than 300. Moreover, techniques of structure determination have changed fundamentally so that today spectroscopic measurements such as proton magnetic resonance and mass spectra have become factors of prime importance. Partial and total syntheses are usually effected and serve to confirm the structures.

Great advances, especially in stereochemistry, have been made in recent years (e.g. in X-ray crystallography and optical rotatory dispersion combined with structural chemical correlations) and have reached a climax in the complete elucidation of the absolute configuration of many carotenoids. This progress has for the first time been summarized (Chapter V).

The present monograph is to be regarded as arising from and developing the standard work 'Carotenoids' of Karrer and Jucker [1]. It also serves in part as an extension of Goodwin's 'The Comparative Biochemistry of the Carotenoids' [2], a work shortly to appear in its second edition. In 1962, Zechmeister published his specialized monograph '*Cis–trans* Isomeric Carotenoids, Vitamins A and Arylpolyenes' [3], which remains indispensable in its field.

When Karrer and Jucker planned their survey, it was natural simply to proceed from one compound to another. Today the multiplicity of carotenoids makes it imperative to deal with related members of subgroups. This is reflected in the separate chapters, whether the emphasis is on natural occurrence, structure or synthesis.

The very rapid growth in the number of known carotenoids and in the pertinent literature has made it necessary to summarize the information in a new way. A characteristic of the book of Karrer and Jucker was that it noted all the then-known carotenoids and recounted their history and properties. Today, a more selective function is exercised by a 'Subcommittee on Carotenoids' of the U.S. National Academy of Sciences, which publishes at intervals 'Specifications and Criteria' of selected carotenoids [4]. In the present work, all the carotenoids described up to mid-1970 have been listed, and the information about them has been displayed and its provenance indicated, according to a systematic procedure (Chapter XII).

## B. Historical Development

The 19th century saw the accumulation of information on the occurrence and detection of carotenoids [cf. 5–7]. The isolation of carotene by Wackenroder in 1831 [6] and the naming of the yellow pigment of autumn leaves as xanthophyll by Berzelius in 1837 [7] are worthy of mention. In 1902, Kohl published [8] a monograph with about 800 literature references, but despite this very few pure crystalline pigments were then known.

Between 1900 and 1927, Tswett and the Willstätter School worked out procedures for the separation and purification of carotene, lycopene, xanthophyll (lutein), fucoxanthin and bixin, and this was followed by success in determining many empirical formulae. Tswett [9] invented column chromatography for the separation of leaf pigments into chlorophylls, xanthophylls (oxygen containing carotenoids) and carotenes (less strongly adsorbed). To him must be credited the concept of a carotenoid family. Willstätter and Mieg recognized in 1907 [10] a formal connection between carotenoids and isoprene. The monographs of Willstätter and Stoll [11] on chlorophyll in 1913 and on the assimilation of carbon dioxide in 1918 still merit study, although in the light of subsequent developments their hypotheses concerning the roles of carotenoids and chlorophylls in photosynthesis were less than adequate.

In 1922 Palmer contributed to the American Chemical Society Monograph Series a volume on carotenoids and related pigments [12], which presented to chemists and biologists a wealth of challenging information which no doubt stimulated wide interest in the topic and revealed how much had yet to be done.

Investigations of structure by the schools of Karrer, Kuhn, Zechmeister and Heilbron began to appear in 1928. The polyene concept was first advanced by Zechmeister, and the occurrence of conjugation in the chain of double bonds was shown spectroscopically to be necessary for colour in carotenoids (Kuhn). The isoprene rule (Ruzicka) had considerable influence on the process of postulating structures. In 1930–1931 Karrer recognized the symmetrical nature of the structures of β-carotene, lycopene and zeaxanthin, and the constitution of vitamin A was shown to be closely related to half the β-carotene molecule.

Indeed, as will be seen, β-carotene was shown to be the main precursor of vitamin A in the animal. This provitamin A concept was entirely new, and it proved to have great scientific and economic importance.