

DISSERTATIONES

DCC-7 (Univ. Zagreb)

547.979.8.07:543.854.1

**Synthetic Studies in the Carotenoide Series.
Synthesis of 15, 15'-Dihydro- β -carotene**

A. Markovac-Prpić

*Research Department, »Pliva« Pharmaceutical and Chemical Works,
Zagreb, Croatia, Yugoslavia*

In the course of the studies on the preparation of carotenoids more saturated than β -carotene, 15,15'-dihydro- β -carotene has been prepared using the following reaction scheme: $C_{14} + C_{12} + C_{14} = C_{40}$. The central C_{12} -component was 3,8-dimethyl-3,8-dihydroxy-decadiyne-(1,9) (I), which was prepared from octanedione-(2,7) and lithium acetylide in liquid ammonia. Phenyl-lithium condensation of I with two moles of 4-[2',6',6'-trimethyl-cyclohexene-(1')-yl]-2-methyl-butene-(2)-al-(1) (II) gave 1,18-bis-[2',6',6'-trimethyl-cyclohexene-(1')-yl]-3,7,12,16-tetramethyl-4,7,12,15-tetrahydroxy-octadecadiene-(1,17)-diyne-(5,13) (C_{40} -tetraol III). As a by-product 14-[2',6',6'-trimethyl-cyclohexene-(1')-yl]-3,8,12-trimethyl-4,7,12-trihydroxy-tetradecaene-(13)-diyne-(1,9) (C_{26} -triol IV) was obtained. From the crude reaction mixture compounds III and IV were isolated using absorption chromatography technique. The structures of C_{40} -tetraol III and C_{26} -triol IV were proved by spectroscopic and analytical methods. The stepwise dehydration of C_{40} -tetraol III with *p*-toluene-sulphonic acid gave the mixture of C_{40} -hydrocarbons, from which 1,18-bis-[2',6',6'-trimethyl-cyclohexene-(1')-yl]-3,7,12,16-tetramethyl-octadecahexaene-(1,3,7,11,15,17)-diyne-(5,13) (V) was isolated by the use of absorption chromatography technique. The ultraviolet spectrum and a perhydrogenation test of this compound were in agreement with the proposed structure. Using Lindlar catalyst compound V was partially hydrogenated to give a

mixture of hydrocarbons, which was repeatedly chromatographed on aluminum oxide of the different activity. Several orange-yellow zones were obtained, and from one of these zones 15,15'-dihydro- β -carotene (VI) was isolated as a glassy orange-yellow solid, which gave characteristic blue-violet color with the Carr-Price reagent. The ultraviolet spectrum of 15,15'-dihydro- β -carotene was very similar with the spectrum of vitamin A, showing maximum at 2880 Å and 3400 Å with $E_{1\text{ cm}}^{1\%}$ value of 720 and 1990 respectively.

An attempt was made to prepare 4-[2',6',6'-trimethyl-cyclohexene-(1')-yl]-2-methyl-butene-3-al-(1) (II) from the β -cyclocitral and triphenyl-(2-carbomethoxy-propyl)-phosphonium bromide using the Wittig reaction, but it was found that a β -elimination occurred rather than the normal Wittig reaction.

Parts of this Dissertation will be published: *Croat. Chem. Acta* 32 (1960).

Examinats: Prof. V. Hahn, Prof. K. Balenović, Prof. M. Proštenik, Dr. P. Mildner.

Oral Examination: February 19, 1960; *Degree Conferred:* April 11, 1960. Dissertation deposited at the University Library, Zagreb.

(91 pages, 13 figures, 80 references)

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I. Markovac-Prpić A.

II. Research Department, »Pliva« Pharmaceutical and Chemical Works, Zagreb, Croatia, Yugoslavia

Carotenoide

1,18-Bis-[2',6',6'-trimethyl-cyclohexene-(1')-yl]-3,7,12,16-tetramethyl-octadecahexane-(1,3,7,11,15,17)-diyne-(5,13)

—, octadecaoctaene-(1,3,7,11,15,17)

—, 4,7,12,15-tetrahydroxy-, octadecadiene-(1,17),diyne-(5,13) and tetraacetate

—, octadecatetraene-(1,5,15,17)

14-[2',6',6'-trimethyl-cyclohexene-(1')-yl]-3,8,12-trimethyl-4,7,12-trihydroxy-tetradecaene-(13)-diyne-(1,9)

11,11'-Dehydro-15,15'-dihydro- β -carotene

15,15'-Dihydro- β -carotene

3,8-Dihydroxy-3,8-dimethyl-decadiyne-(1,9) and bis (*p*-nitrobenzoate

Lindlar Catalyst