

Procedure for Preparing Three β -apo-Carotenals from β -Carotene

A safe procedure is described for preparing three β -apo-carotenals by oxidation of β -carotene in presence of potassium permanganate and hydrogen

peroxide. The procedure does not require use of osmium tetroxide, so poisonous gases are not produced.

Karrer and Solmsen (1937) and Karrer *et al.* (1937) prepared β -apo-8'-carotenal and β -apo-12'-carotenal by oxidizing β -carotene with potassium permanganate. Goss and McFarlane (1947), and Wendler *et al.* (1950) oxidized β -carotene with hydrogen peroxide and osmium tetroxide, and found retinal. However, using hydrogen peroxide and osmium tetroxide Redfearn (1954) obtained retinal and β -apo-8'-, β -apo-10'-, and β -apo-12'-carotenals. The procedure presented here is safer than Redfearn's since osmium tetroxide, which produces poisonous gases, is not used.

MATERIALS AND METHODS

One hundred milliliters of benzene was mixed with 250 mg. of synthetic β -carotene in a 500-ml. boiling flask, 100 ml. of 1.3% potassium permanganate solution was added, and the mixture was stirred for 15 minutes. Then 10 ml. of 30% hydrogen peroxide was added dropwise with continuous stirring; stirring was continued for 10 minutes. Work was done in a darkened room at 25° C. behind a safety screen. The flask was stoppered tightly, wrapped as a safety precaution, and shaken for 2½ hours.

The emulsion of benzene, water, manganese dioxide, and oxidation products was filtered, and the precipitate was washed with benzene and hexane (1 to 1). The filtrate was transferred to a separatory funnel, the lower layer drained, and the supernatant washed by shaking five times with distilled water. The solution of products was filtered through anhydrous sodium sulfate, evaporated to dryness under reduced pressure and temperature of 60° to 70° C., and the residue was dissolved in hexane. The products were separated on a column of neutral alumina (Woelm), 5% H₂O content. Five bands were developed and eluted by increasing the concentration of ether in

hexane. Pigment of each band was evaporated to dryness under reduced pressure and temperature and was rechromatographed twice on acid alumina (Woelm), 5% H₂O content.

The absorption curve of each product dissolved in hexane was determined using a Beckman spectrophotometer. Thin-layer cochromatography on silicic acid also was used to identify β -apo-8'-carotenal and β -apo-12'-carotenal by comparing with known synthetic compounds. Chromatograms were developed with acetone in hexane. Chloroform solutions of the compounds were made to react with antimony trichloride for qualitative color tests. The number of conjugated double bonds was calculated by the equation, $\lambda^2 = An + B$, developed by Porter (1953) and also used by Redfearn (1954) for the β -apo-carotenal series.

RESULTS AND DISCUSSION

Compounds in bands 1 and 2, with maximum absorptions at 450 and 425 m μ , respectively, were probably β -carotene and a β -carotene isomer (Redfearn, 1954). Compounds in bands 3, 4, and 5 had maximum absorptions at 415, 435, and 455 m μ , respectively (Figure 1 and Table I). In cochromatography, the compound in band 3 and synthetic β -apo-12'-carotenal moved as a single spot, and the compound of band 5 and synthetic β -apo-8'-carotenal moved as a single spot. By cochromatography of the compound in band 4 with β -apo-8'-carotenal and β -apo-12'-carotenal, three spots were obtained. By number of conjugated double bonds, SbCl₃ color tests (Table I), absorption curves (Figure 1), and cochromatography, the compounds of bands 3, 4, and 5 were identified as β -apo-12'-, β -apo-10'-, and β -apo-8'-carotenals, respectively. Yields were 2.7, 3.3, and 4.6%, respectively.

Table I. Properties of β -apo-Carotenals Prepared and Separated on Alumina Columns

Band No.	Character and Color on Column	Compound Identified	Eluent, Ether in Hexane, %	Conjugated Double Bonds, No.		Maximum Absorption in Hexane, m μ	Color with SbCl ₃ in CHCl ₃
				Calcd. ^a	Theoretical		
3	Broad, yellow orange band	β -apo-12'-Carotenal	10-12	7.1	7.0	415, slight inflexion at 390 and 435	Stable reddish brown
4	Narrow, intense reddish orange band	β -apo-10'-Carotenal	14-20	8.2	8.0	435, slight inflexion at 408 and 450	Stable blue
5	Narrow, mauve (purplish red) band	β -apo-8'-Carotenal	20-24	9.2	9.0	455, inflexion at 430 and 480	Stable blue

^a References: Porter, 1953; Redfearn, 1954.

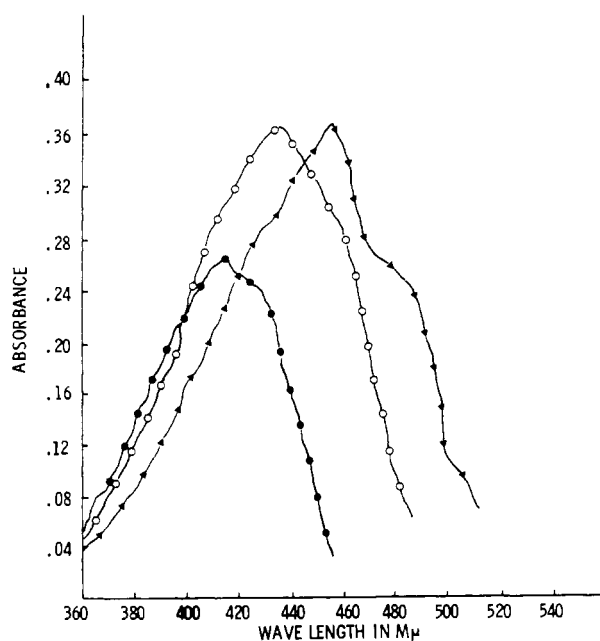


Figure 1. Absorption curves for β -apo-carotenals prepared

- β -apo-12'-Carotenal
- β -apo-10'-Carotenal
- ▲ β -apo-8'-Carotenal

Preparations of β -apo-carotenals by oxidation of β -carotene with the combination of potassium permanganate and hydrogen peroxide has not been reported in the literature, but the properties of products are in agreement with those of synthetic compounds reported by Glover (1959), and prepared by Rügge *et al.* (1959a, 1959b) (Table II). Absorbances at the maxima and shape of curves of β -apo-8'-carotenal and β -apo-10'-carotenal were in close agreement with those obtained by Redfearn (1954). Maximum absorption of β -apo-12'-carotenal was reported by Redfearn as 408 $m\mu$, instead of 415 $m\mu$, which might have been due to *cis* isomerization (Glover, 1959; Rügge *et al.*, 1959a, 1959b), but the trend of the curve was similar to that reported here. Karrer *et al.* (1937) reported the maximum absorption of β -apo-12'-carotenal at 442 $m\mu$ (diffused), which might have resulted from impurities.

Table II. Maximum Absorptions of β -apo-Carotenals

Reference	β -apo-8'-Carotenal, $m\mu$	β -apo-10'-Carotenal, $m\mu$	β -apo-12'-Carotenal, $m\mu$
Glover (1959)	454	432	414
Karrer <i>et al.</i> (1937)	450	...	442 (diffused)
Redfearn (1954)	454	432	408
Rügge <i>et al.</i> (1959a, 1959b)	457	435	415
This work	455	435	415

Potassium permanganate does not form gases poisonous to the body, so it is a safer oxidation reagent for preparing carotenals than is osmium tetroxide, which produces a highly toxic vapor (Merck, 1960) that should be avoided.

ACKNOWLEDGMENT

We thank Hoffmann-LaRoche, Inc., Nutley, N.J., for known samples of β -apo-8'- and β -apo-12'-carotenals.

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Received for review March 24, 1967. Accepted June 29, 1967.
 Contribution No. 67, Department of Biochemistry, Agricultural Experiment Station.