Reports

Beta-Carotene: Thermal Degradation

Abstract. *Thermal treatment of crystalline β-carotene (240°C in a vacuum) results in the formation of a volatile fraction containing chiefly aromatic hydrocarbons such as toluene,* m- *and* p-*xylene, 2,6-dimethylnaphthalene, and ionene. These compounds have been identified by means of gas-liquid chromatography, infrared spectroscopy, and, in the case of ionene, by additional nuclear magnetic resonance and mass spectroscopy. The principal degradation product is a yellowish-brown, glutinous mass which can be separated by means of preparative thin-layer chromatography in a number of fractions different in molecular weight. The structure of these fractions is not yet clear.*

Ionene (1,1,6-trimethyl-1,2,3,4-tetrahydronaphthalene) as a thermal degradation product of β-carotene has been reported by Day and Erdman (*1*). The thermal degradation was accomplished by maintaining a 1 percent benzene solution of β-carotene for 72 hours at 188°C.

This report on the thermal degradation of crystalline β-carotene offers an interesting comparison to the results of Day and Erdman (*1*). For the purpose of degradation β-carotene (Hoffmann-La Roche, Basel) is melted under a high vacuum in a glass apparatus. Degradation itself is effected by fairly prolonged heating at 240°C, while the volatile degradation products condense in a receiver cooled with liquid nitrogen. The quantity of volatile products obtained is equivalent to 15 to 20 percent of the original material.

A gas-liquid chromatogram of the volatile fraction reveals a large number of components, four of which are present in appreciable quantities. For a long time toluene, *m*-xylene, and 2,6-dimethylnaphthalene have been known to be formed during the thermal degradation of carotene (*2*). In our investigations they could be identified in the mixture by gas-liquid chromatography. However, the chief peak in the gas-liquid chromatogram of the mixture was caused by an unknown component, which was isolated by fractional distillation with a Jantzen concentric tube rectification column (Ringspaltsäule) (bp 69-70°C, 0.8 mm-Hg). Analysis of the fraction by nuclear magnetic resonance and mass spectroscopy (carried out at the Unilever Research Laboratory, Vlaardingen, Netherlands) and infrared spectroscopy indicated that it consisted of ionene with an infrared spectrum identical with that given by Stoll and co-workers (*3*). A molecular weight determination by Rast's method (*4*) gave a value of 167.3 (the theoretical value is 174.27).

I also identified *p*-xylene, hitherto unknown as a component of the volatile products of carotene degradation: investigation of the xylene fraction by gas-liquid chromatography showed only one peak. Under the conditions used (20 percent Apiezon L on Celite 545, mesh 100; 20 percent Reoplex on Celite 545, mesh 100) *m*- and *p*-xylene have the same retention volume, which is different from that of *o*-xylene. The peak of the xylene fraction was identical with that of *m*- or *p*-xylene or both. The infrared spectrum of the fraction did not show the spectrum of pure *m*-xylene or that of pure *p*-xylene. Additional bands at 8.95 and 12.5 μ in the spectrum of *m*-xylene made it probable that the xylene fraction contained *p*-xylene. A comparison with the infrared spectrum of a mixture of *m*-xylene with 15 percent by volume *p*-xylene provided the proof (see Figs. 1 and 2). Toluene and 2,6-dimethylnaphthalene were also identified by means of infrared spectra after isolation. Approximately 4 percent toluene, 5 percent *m*- and *p*-xylene, 83 percent ionene, and 8 percent 2,6-dimethylnaphthalene were present in the mixture; these amounts differ from those quoted by Day and Erdman (*1*).

The principal thermal degradation product of β-carotene (about 80 percent) is a yellowish-brown, nonvolatile, glutinous mass, on which the molecular weight, the ultraviolet, infrared, and visible spectra were determined. The average molecular weight of the solid degradation product is 550 to 580, measured, in chloroform, by means of a Mechrolab osmometer, model 301A. The adsorption spectrum of the substance reveals a weak maximum at 255 mμ (in petroleum ether). The infrared spectrum has few characteristic features; compared with that of β-carotene it shows a marked decrease in size of the band at 10.35 μ (*trans*-double bond). No conclusions could be drawn concerning aromatic compounds.

On hydrogenation the substance takes up about 2 moles of hydrogen. Fractionation by means of thin-layer chromatography (*5*) was achieved on Kieselgel G (Merck, Darmstadt) in layers 1-mm thick and plates with an area of 20 by 30 cm; the chromatogram was developed with petroleum ether. Twelve fractions were obtained and isolated. Prolonged contact of the yellowish-brown substance or its fractions with air causes oxidation. The oxidation products, however, are insoluble in

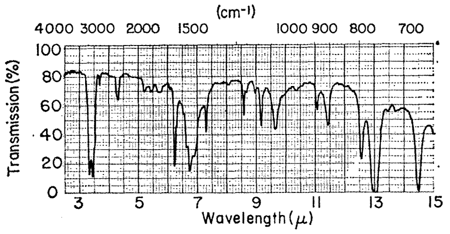

Fig. 1. Infrared spectrum of the xylene fraction of the volatile degradation products of β-carotene. Ordinate, transmission (%); abscissa, wavelength (μ).

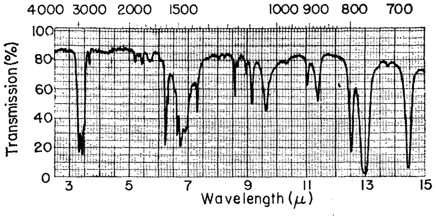

Fig. 2. Infrared spectrum of a mixture of *m*-xylene with 15 percent (by volume) *p*-xylene. Ordinate, transmission (%); abscissa, wavelength (μ).

Table 1. Molecular weights after fractionation of the nonvolatile degradation product of β-carotene by means of thin-layer chromatography.

Fraction	R_F	Molecular weight
1	0.9	384 ± 1
2		476 ± 8
3		590 ± 6
4		442 ± 20
5		462 ± 5
6		431 ± 3
7		517 ± 13
8		580 ± 16
9		622 ± 12
10		731 ± 36
11		762 ± 23
12	0.08	983 ± 24

petroleum ether and do not move either with the solvent used for developing the thin-layer chromatogram or during elution of the fractions from the silica gel.

The molecular weights of the fractions were determined in chloroform with a Mechrolab osmometer (Table 1). From the determination of the iodine values by Kaufmann's micromethod (*6*) it is possible to calculate that the fractions contain between two and five double bonds.

The results indicate that the mechanism of degradation of β-carotene without solvent is evidently the same as that in solution, the same volatile products being identifiable in each case. Whereas toluene, *m*- and *p*-xylene, and 2,6-dimethylnaphthalene are formed by cyclization of the polyene chain, the β-ionone ring is involved in the formation of ionene. This was confirmed by experiments which were carried out on canthaxanthin, a carotenoid with a carbonyl group in positions 4 and 4′ of the β-ionone rings. After comparable thermal degradation no ionene could be identified among the volatile decomposition products.

Nothing is yet known about the structure of the high-molecular-weight, nonvolatile products derived from the thermal degradation of β-carotene, either as the crystalline substance at 240°C or in the benzene solution at 188°C.

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Periodic Phenomena Observed with Spherical Particles in Horizontal Pipes

Abstract. *A thin layer of spherical particles resting on the bottom of a round pipe was observed to form into essentially equally spaced clumps or islands at fluid velocities only slightly greater than those required to initiate particle movement. This phenomenon appeared to be similar to dune formation in open channels since the ratio of the square of the stream velocity,* U, *and the product of the gravitational constant,* g_L, *and the island wavelength,* λ, *was correlated by the same function of island height and velocity, particle diameter, and fluid depth regardless of whether the flow was through a closed conduit or an open channel.*

During studies of the transport of suspensions of spherical particles in round horizontal pipes by flowing water (*1*), it was observed (*2*) that if the fluid velocity was adjusted to a value only slightly greater than that required to initiate particle movement, then the particles grouped into clumps or islands within seconds to minutes after the flow rate had been adjusted. The clumps of particles were spaced periodically along the bottom of the pipe and moved slowly downstream. Although the formation of periodic sand dunes or ripples commonly occurs during sediment transport in flow in which there is a free surface (*3–5*) (streams and flumes), it is apparently not widely known that such a phenomenon can occur in horizontal round pipes full of running water. In 1953 a theory of dune formation in an open channel was proposed which required the existence of water waves on a free fluid surface (*6*). In those few instances in which the occurrence of dunes in pipe flow has been mentioned, little or no data were reported on dune characteristics or flow conditions (*7*). Because of the paucity of experimental data and the opportunity afforded for clarification of the mechanism of dune formation, an extensive study was made over a range of pipe diameters (D) from 2.5 to 10 cm, mean particle diameters (D_p) from 50 to 565 μ, and particle densities (ρ_p) of 2.65 and 1.09 g/cm^3 in equipment described previously (*1*). The advantage of using a round pipe rather than a flat-bed flume is that the island train formed in a pipe possesses well-defined, easily measured characteristics in contrast to the rather chaotic conditions often observed in flumes.

Typical shapes for the clumps or islands are shown in Fig. 1. In this figure the islands of island train I were formed by the use of glass beads 565 μ in diameter. The mean wavelength was 10 cm and the mean island velocity (u_I) was 1.23 cm/sec when the mean stream velocity was 45.2 cm/sec. The islands of island train II were formed when glass beads 50 μ in diameter were used. The mean wavelength was 4.68 cm and the mean island velocity was 0.045 cm/sec when the mean stream velocity was 33 cm/sec.

In the early phases of the study, it was observed that the islands occurred only over a rather narrow range in mean stream velocities with a slight dependence on pipe diameter. (The mean stream velocity was always based on the pipe diameter). For example, this range was found to be roughly from 15 to 45 cm/sec for 100 μ glass beads and from 30 to 65 cm/sec for 565 μ glass beads; it was extremely difficult to form islands with glass beads greater than 750 μ in diameter. The range of flow conditions for which island formation was observed has been described in detail (*8*). Despite the narrow range in mean stream velocities, the island velocity u_I varied over a 500-fold range being roughly proportional to the fifth power of the mean stream velocity as observed by Liu (*4*) for ripple motion in open channel flow. In all cases the island velocity was less than 5 percent of the mean stream velocity.

Comparison of the data for the configuration of islands formed in closed pipes with values—obtained from the literature—for dunes in open flumes,