

Volatile Tomato Constituents: Identification of 2,6-Dimethylundeca-2,6-dien-10-one

A major high boiling component of the steam volatile oil of tomatoes has been identified by mass and

infrared absorption spectrometry to be 2,6-dimethylundeca-2,6-dien-10-one.

A number of volatile tomato components have been identified (Pyne and Wick, 1965; Schormüller and Grosch, 1962, 1964, 1965; Spencer and Stanley, 1954). Because of the complexity and low concentration of the volatile tomato oil, identification has largely been confined to the lower boiling components. In the present work, the high resolution capability of capillary gas liquid chromatography (GLC) columns was used to isolate some of the higher boiling components in a relatively pure form, thus facilitating spectral characterization.

EXPERIMENTAL

Fresh California tomatoes (Type VF-145) were steam distilled under reduced pressure in a steam distillation-continuous extraction apparatus of the type described by Likens and Nickerson (1964). The steam distillation was conducted at 80 to 100 mm. of Hg (product temperature 45° to 50° C.) using hexane as the extracting solvent and ice-water cooled condensers. After removal of the hexane by distillation through low holdup columns, the steam volatile oil (of the order of 2 p.p.m. of the tomatoes) was resolved into its components on a 500-foot long by 0.03-inch I.D. stainless steel capillary GLC column coated with silicone SF96(100) containing 5% Igepal CO-880. The column was programmed from 50° to 175° C. non-linearly (ca. 1/2° per minute) over a 3 1/2-hour period. For mass spectral analyses, components leaving the column were introduced directly into a modified Consolidated 21-620 mass spectrometer through a Llewellyn-type molecular separator (Llewellyn, 1966). For infrared absorption spectral analyses components were collected from the column in 1.5-mm. glass capillary tubes and analyzed either in the pure form or in CCl₄ solution using ultra-micro cavity cells and a reflecting beam condenser.

RESULTS AND DISCUSSION

Most known major lower boiling components of the steam volatile tomato oil were eluted on the capillary GLC column after 80 minutes with 2-methylhept-2-ene-6-one being the last major lower boiling component. The largest GLC peak after this was eluted at 202 minutes. This component (ca. 8% of the oil) was found to have a mass spectrum with a molecular ion at 194 and major ions (above 40) in order of their intensity at 43, 41, 69, 93, 57, 55, 67, 136, 107, 109, 81, 68, 151, 125, 95, 83, and other important lower intensity ions at 176 and 161. Its infrared spectrum (neat) showed strong maxima at 3.37, 3.43, 3.5, 5.8; medium maxima at 7.0, 7.3, 7.4, 8.6, 9.1; and weak

maxima at 6.0, 7.1, 7.3, 8.0, 8.2, 9.5, 10.2, 12.1, 13.7 microns. This data indicated a C₁₃ methyl ketone with two tri (or tetra)-substituted double bonds. The mass and infrared spectra were found to be identical to those of a sample of 2,6-dimethylundeca-2,6-dien-10-one prepared according to the method of Carrol (1940) by the condensation of geranyl chloride with ethyl acetoacetate.

There are two possible cis-trans isomers for 2,6-dimethylundeca-2,6-dien-10-one. Both isomers were isolated from the condensation of linalool with ethyl acetoacetate (Carrol, 1940) and separated by gas chromatography. The isomer found in tomatoes has mass spectral and infrared data consistent with the geranyl form and not the neryl form.

Although 2,6-dimethylundeca-2,6-dien-10-one has been identified in lemon grass oil (Naves, 1931) and known for some time as an intermediate in synthetic and degradation work, it rarely has been found in natural products. This ketone is one isoprene unit greater than 2-methylhept-2-ene-6-one which was identified in tomatoes by Schormüller and Grosch (1964). In their current work the authors confirmed the presence of 2-methylhept-2-ene-6-one and most other volatile components previously reported. Additional compounds also identified were eugenol, deca-2,4-dienal and 2-heptenal, whose mass spectra were consistent with those of authentic samples.

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