

Possible Precursor for 1-Methyl-4-isopropenylbenzene in Commercial Blackberry Flavor Essence

1-Methyl-4-isopropenylbenzene and *p*-cymen-8-ol were identified in commercial blackberry essence and evidence was obtained which shows that *p*-cymen-

8-ol is converted to 1-methyl-4-isopropenylbenzene by a heat-induced dehydration reaction.

Andersson *et al.* (1963) identified 1-methyl-4-isopropenylbenzene (I) in black currant leaves and later (Andersson and von Sydow, 1964) I and *p*-cymen-8-ol in black currants. In both studies steam distillation at atmospheric pressure was employed in essence recovery. Teranishi *et al.* (1963) indicated the presence of a compound in orange volatiles that was tentatively identified as I. Loori and Cover (1964) identified I in the oil of distilled Mexican lime. These workers showed the hydrocarbon could be formed under acidic conditions from citral but also concluded that heat treatment alone of citral at high temperatures for extended periods does not produce I. Nursten and Williams (1969a) found I in a commercial black currant distillate and suggested (1969b) heat-induced dehydration of terpene alcohols as a possible source. Recently, Heatherbell *et al.* (1971) demonstrated an increase in the amount of I due to retorting canned carrots. These investigators suggested *p*-cymene, dehydration of alcohols, degradation of carotenoids, and the C enamel coatings on the ends of the cans as possible sources of I.

Earlier our laboratory (Scanlan *et al.*, 1970) reported the identification of volatile compounds in a commercial blackberry essence. During the continuation of this work, I and *p*-cymen-8-ol have been identified in the blackberry essence. The purpose of this communication is to report our investigation of the heat-induced dehydration of *p*-cymen-8-ol to I (Figure 1).

EXPERIMENTAL

The commercial essence and procedures for essence extraction and tandem gas chromatographic-mass spectrometric (glc-ms) analysis for the identification of I and *p*-cymen-8-ol in commercial blackberry essence were as described previously by Scanlan *et al.* (1970).

Samples of *p*-cymen-8-ol were separated from the blackberry essence extract by glc on a Barber-Colman Series 5000 chromatograph and trapped in 12 in. \times 0.063 in. o.d. glass capillaries attached to a 8:1 (capillary:detector) effluent splitter. Gas chromatographic conditions were: sample size, 35 μ l; column, 12 ft \times 0.085 in. i.d. stainless steel packed with 5% butanediol succinate plus 0.05% Igepal CO-880 on 80-100 mesh AW-DMCS Chromosorb G; column temperature, 60° C for 2 min then programmed at 2° C/min to 200° C; injector, 200° C; detector, 240° C; flow rate, 28 ml of N₂ per

min at 100° C. The glc conditions for the analysis of heated *p*-cymen-8-ol were the same except the column temperature was 110° C for 9 min, then programmed at 10° C/min to 200° C.

Samples subjected to infrared analysis (ir) were also trapped as described above and analyzed as a thin film between two NaCl plates on a Beckman IR-5 infrared spectrophotometer equipped with a 5X beam condenser.

RESULTS AND DISCUSSION

The identity of I was established in the commercial blackberry essence by ms, ir, and glc relative retention data. The corresponding ms, ir, and glc retention data obtained from commercially available I was used as a basis for comparison in all cases. Mass spectrometry and ir were used to identify *p*-cymen-8-ol in the commercial blackberry essence and in both cases the spectra of Andersson and von Sydow (1964) were used for comparison.

In order to investigate the possible dehydration of *p*-cymen-8-ol to I, approximately 20 μ l of *p*-cymen-8-ol was gas chromatographically separated from the commercial blackberry essence, and trapped and heated to 175° C for 1 hr in a sealed glass capillary tube. The contents of the tube were then rechromatographed and the composition (based on peak area) was 87% I, 11% *p*-cymen-8-ol, and 2% unidentified. The identification of I in this experiment was based on matching relative retention times and infrared spectra. A second *p*-cymen-8-ol sample collected from the blackberry essence was reinjected into the glc without prior heating and based on peak area approximately 1% of the conversion of *p*-cymen-8-ol to I occurred in the glc, probably in the heated injection port.

It is difficult to equate directly the heat treatment studied in our experiment with the various heat treatments in commercial berry juice concentrators, or in retorting carrots. Nevertheless, our results point to *p*-cymen-8-ol as a direct precursor of I in heated foods.

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Marilyn Houchen¹
 Richard A. Scanlan*
 Leonard M. Libbey
 Donald D. Bills

Department of Food Science
 and Technology
 Oregon State University
 Corvallis, Oregon 97331

Received for review April 26, 1971. Accepted June 21, 1971.
 Technical Paper No. 3084, Oregon Agricultural Experiment Station.
¹ Data from thesis in partial fulfillment of requirements of undergraduate honors program.

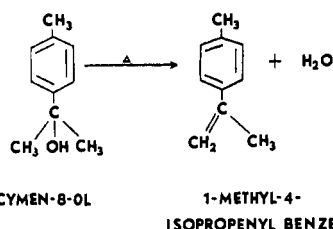


Figure 1. Dehydration of *p*-cymen-8-ol to 1-methyl-4-isopropenylbenzene