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Vapor pressures and vaporization enthalpies of a series of esters used in flavors by correlation gas chromatography

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ABSTRACT

The vaporization enthalpies of a series of esters used commercially as flavor ingredients are reported as are their vapor pressures over the temperature range T/K = (298.15 to T_B). Vaporization enthalpies and vapor pressures at T = 298.15 K ($\Delta_l^g H_m$(298.15)/kJ · mol^{-1}, p/Pa) for 3-methyl-2-butenyl acetate (47.8 ± 1.5, 468 ± 7.2), *trans trans* 2,4-hexadienyl acetate (54.7 ± 1.4, 89 ± 1.5), ethyl 2-methylpentanoate (48.4 ± 1.5, 410 ± 42), *cis* 3-hexenyl propionate (55.7 ± 1.0, 66.2 ± 3), allyl hexanoate (55.2 ± 1.6, 81.9 ± 10), pentyl butyrate (53.6 ± 0.6, 109 ± 1.1), isoamyl isobutyrate (51.7 ± 1.6, 180 ± 20), phenethyl acetate (61.3 ± 1.3, 13.2 ± 0.2), *cis*-3-hexenyl butyrate (59.9 ± 1.7, 25.7 ± 2.2), *cis* 3-hexenyl 2-methylbutyrate (61.5 ± 0.6, 15.3 ± 1), ethyl cinnamate (70.4 ± 1.4, 1.5 ± 0.03), phenethyl propionate (65.6 ± 1.6, 4.8 ± 0.09), *cis*-5-octenyl propionate (65.3 ± 1.6, 7.0 ± 0.1), heptyl butyrate (65.1 ± 1.1, 7.8 ± 0.05), phenethyl butyrate (69.7 ± 1.4, 1.9 ± 0.4), linalyl acetate (62.5 ± 0.6, 12.2 ± 0.2), citronellyl acetate (67.8 ± 1.8, 4.0 ± 0.4), and phenethyl hexanoate (78.8 ± 1.5, 0.23 ± 0.005) have been evaluated by correlation gas chromatography experiments. The vaporization enthalpies of the esters studied are reproduced within ±2.0 kJ · mol^{-1} using a simple additivity scheme. Constants for a third order polynomial are reported which reproduces vapor pressures and predicts normal boiling temperatures to within T = 3.0 K.

1. Introduction

Simple esters derived from small fatty acids and a variety of small alcohols are important ingredients found in numerous flavors. Their vapor pressures are an important property that governs both their olfactory properties as well as their useful shelf life. This work examines a series of esters and reports both their vapor pressures and vaporization enthalpies as evaluated by correlation gas chromatography. The esters evaluated include 3-methyl-2-butenyl acetate, *trans trans* 2,4-hexadienyl acetate, (*dl*)-ethyl 2-methylpentanoate, *cis* 3-hexenyl propionate, 2-propenyl hexanoate, pentyl butyrate, phenethyl acetate, *cis*-3-hexenyl butyrate, (*dl*)-*cis* 3-hexenyl 2-methylbutyrate, ethyl cinnamate, phenethyl propionate, *cis*-5-octenyl propionate, heptyl butyrate, phenethyl butyrate, (*dl*)-linalyl acetate (3-acetoxy-3, 6-dimethyl-1,6-octadiene), (*dl*)-citronellyl acetate (1-acetoxy-3, 6-dimethyl-1,6-octadiene), and phenethyl hexanoate. All of these esters are GRAS chemicals (Generally Recognized As Safe) as recognized by the US Federal Food, Drug and Cosmetic Act) [1] and are found in numerous consumer foods and beverages. The structures of the esters examined as well as the materials used as standards are illustrated in figure 1.

2. Experimental

2.1. Compounds and purity controls

Table 1 lists the origin and purity of both targets and standards. Several of the esters examined are chiral. However there does not seem to be any olfactory information available on the individual enantiomers and all potentially chiral substances are assumed to be racemic. Most materials were analyzed by gas chromatography either to evaluate the chemical composition or to confirm it. Since some of the products are produced by natural processes, the following describes the additional characterization that was performed.

The *cis* 3-hexenyl propionate and the corresponding butyrate (both mass fraction 0.98) are reported by the supplier as a mixture of isomers. Analysis by gas chromatography of *cis* 3-hexenyl propionate separated three minor peaks, the largest having a mass fraction of 0.005. The H NMR spectrum did not suggest the presence of any other isomers. The main peak for *cis* 3-hexenyl butyrate (mass fraction 0.90) was closely flanked by three peaks with shorter retention times and two with longer retention times. The most abundant minor peak amounted to a mass fraction of 0.046. The vinyl region of all three esters was virtually identical in the H NMR spectra.

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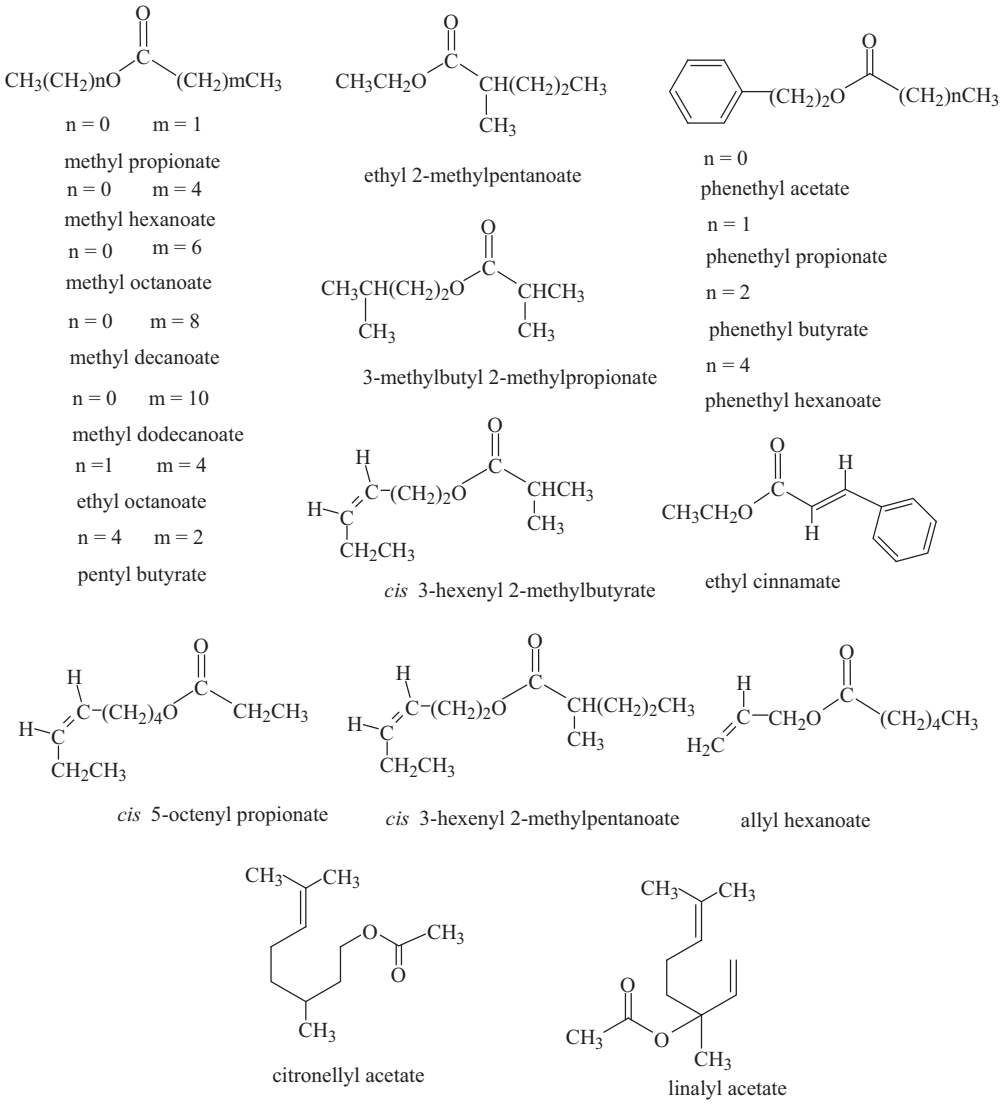

FIGURE 1. Structures of both the targets and standards studied.

Two peaks were observed in the gc of isoamyl isobutyrate. The major component amounted to a mass fraction of 0.7. The H NMR spectrum of the major component was consistent with its structure. Materials with a mass fraction $\geqslant$0.97 contained impurities with a mass fraction of 0.018 or less. Phenethyl butyrate (mass fraction 0.95) contained two minor components with retention times flanking the major component with trace amounts (<0.01) of several other compounds. Linalyl acetate (mass fraction: 0.81), in addition to the major isomer, contained four other minor components, two with shorter retention times and two with slightly longer retention times. The remaining impurities were present in trace amounts. Citronellyl acetate, contained five minor components, the largest amounting to a mass fraction of 0.11.

The CASRN number provided by Aldrich for *trans trans* 2,4-hexadienyl acetate conforms to an unspecified stereochemistry. The sample was analyzed by gas chromatography and one major sharp peak was observed corresponding to a mass balance of 0.988. The H NMR spectrum was consistent with the published spectrum for the *trans*, *trans* isomer available in SciFinder Scholar located using the chemical structure interface.

Chemical purity is usually not an issue with correlation gas chromatography since the chromatography generally separates the impurities. Only the major component was analyzed in this work. No effort was made to identify the minor components. Retention times do not appear to be significantly perturbed by the presence of other components. This is one of the major advantages of this technique, the ability to evaluate pure component properties of impure materials.

2.2. Methods

Measurements were performed either on an HP 5890 Gas Chromatograph or HP 5890 Series II system both equipped with FID detectors and running HP Chemstation. Chromatographs were recorded isothermally over a T = 30 K temperature range at T = 5 K intervals on a Supelco 15 m 0.32 mm, 1.0 μm thick SPB-5 capillary column using helium as the carrier gas at a split ratio of approximately 100/1. The temperature was controlled by the instrument and monitored independently on either a Vernier stainless steel temperature probe using a Go!Link USB interface running Logger Lite or a Fluke 50S K/J digital thermometer, depending on the instrument used. Both instrument were capable of maintaining the temperature to ±0.1 K. The solvent used was