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Reversed phase ion-pair chromatographic separation of sugar alcohols by complexation with molybdate ion

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ABSTRACT

In this study, we developed a simple and sensitive reversed phase ion-pair chromatographic method for the analysis of C4-C6 sugar alcohols. The method is based on the on-line complexation of sugar alcohols with molybdate ion. The resulting dinuclear anionic complexes can be separated on a reversed-phase C18 column using tetrabutylammonium chloride as an ion-pairing reagent. The mobile phase (pH 3.1) consisted of 0.1 mM disodium molybdate, 1 mM hydrochloric acid and 0.4 mM tetrabutylammonium chloride – 10% v/v methanol. By complexing with molybdate ion, sugar alcohols can be detected by their UV absorption at 247 nm with high resolution and sensitivity. The quantification limits of the examined sugar alcohols calculated at S/N = 10 were 0.1 mM for erythritol and xylitol and 0.01 mM for arabitol, sorbitol, mannitol and dulcitol. The detector response was linear over three orders of magnitude of sugar alcohol concentration. The proposed method was successfully applied to measure sugar alcohols in health drinks, eyedrops and mouthwashes.

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1. Introduction

Sugar alcohols (SAs) are used in a variety of consumer products. One of their main uses is as sugar substitutes in reduced-sugar foods. Due to their outstanding thermal stability and ability to absorb moisture, they are also used as humectants, stabilizers, thickeners, anticaking agents and bulking agents in food, healthcare, cosmetic and pharmaceutical products. Hence, the determination of SAs in finished products is essential for quality control [1–3].

Being hydrophilic and having similar structures, SAs are difficult to separate by conventional reversed phase liquid chromatography (RPLC). Moreover, lacking chromophores, SAs are difficult to detect by ordinary ultraviolet (UV) detection. On the other hand, SAs can be sensitively determined by anion exchange chromatography coupled with pulsed amperometric detection (PAD) [4–7]. SAs can also be separated with ligand exchange chromatography [8–11] or hydrophilic interaction chromatography [12–20], and subsequently can be determined by refractive index detection (RID) [10,11], evaporative light scattering detection (ELSD) [9,13–19,21] or charged aerosol detection (CAD) [18,20]. However, these analytical methods require dedicated columns and instrumentations.

Some analytes coordinate with metal ions added to the mobile phase, which may influence their retention on the RPLC column as well as create absorption bands that can be detected with a UV detector. Amino acids can be separated by RPLC with UV detection using a mobile phase containing copper (II) ions (Cu(II)) [22]. Using RPLC and UV detection, we also separated organic acids [23] and alcohols [24] using a mobile phase containing Cu(II), and separated C6 SAs with a mobile phase containing molybdate ion (MoO_4^{2-}) [25], which forms a complex with polyhydroxy compounds [26–28].

Many carbohydrates, including SAs, form dinuclear anionic complexes with molybdate ion by four vicinal hydroxy groups in aqueous acidic solution [29,30]. However, RPLC columns retain only C6 SA complexes with molybdate ion, as complexes with C4-C5 SAs are hardly retained [25]. The RPLC separation of ionic compounds can be improved by adding amphiphilic ions, so-called ion-pairing reagents (IPRs), to the mobile phase, which enhance their retention by the hydrophobic stationary phase [31–33]. Here, we used this

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method, called reversed phase ion-pair chromatography (RPIPC), to simultaneously determine six SAs using on-line complexation with molybdate ion and UV detection. The SAs included C4 (erythrytol), C5 (xylitol and arabitol) and C6 (sorbitol, mannitol and dulcitol) SAs. We first selected the IPR and then investigated the optimum mobile phase composition to separate the SAs. The method was subsequently used to determine the SA contents in health drinks, eyedrops and mouthwashes.

2. Experimental

2.1. Chemicals

Mannitol, D-sorbitol, xylitol, D-arabitol, disodium molybdate(VI) dehydrate, tetramethylammonium chloride (TMACl) and tetraethylammonium chloride (TEACl) were obtained from Wako (Osaka, Japan). Tetrapropylammonium chloride (TProACl), and tetrapentylammonium chloride (TPenACl) were obtained from SIGMA-ALDRICH (St. Louis, MO, USA). Tetrabutylammonium chloride (TBACl) was obtained from ACROS (Fair Lawn, NJ, USA). Dulcitol, *meso*-erythritol and other chemicals (analytical grade) were purchased from Kanto (Tokyo, Japan). Water was purified with a Milli-Q Direct 8 (Millipore SAS, Molsheim, France). SA solutions were separately prepared as 0.25 M each stock solution. The stock solutions were stored at 4 °C and diluted before use.

2.2. Spectroscopic measurement

A Hitachi (Tokyo, Japan) U-3010 spectrophotometer, a double beam spectrometer, was used for measurements of absorption spectra of SAs. The spectra of SAs were measured from 220 to 370 nm by using a quartz cell of 10 mm path length. In the measurement of absorption spectra, 0.1 mM disodium molybdate added with 1 mM hydrochloric acid (Mb-HCl solution) was used as the reference.

2.3. Apparatus for HPLC

The HPLC system consisted of a Tosoh (Tokyo, Japan) CCPD pump, a Rheodyne (Cotati, CA, USA) manual injector, a Shimadzu (Kyoto, Japan) SPD-20A UV detector, a Shimadzu (Kyoto, Japan) CTO-10AC column oven, and a Shodex (Tokyo, Japan) DEGAS degasser.

2.4. Chromatographic conditions

SAs were separated by RPIPC with a 4.6 mm i.d. × 250 mm Inert-Sustain C18 column (GL Sciences, Tokyo, Japan) thermostated at 50 °C. The mobile phase consisted of Mb-HCl solution, 0.4 mM tetrabutylammonium chloride (pH 3.1) and 10% v/v methanol, and the flow rate was 0.8 mL per min. The injection volume was 10 μL and the detector wavelength was set at 247 nm.

2.5. Pretreatment of samples

Nine brands of health drinks, five brands of eyedrops, five brands of contact lens wetting solutions and four brands of mouthwashes were purchased from a local market.

Each sample was diluted 100 times with purified water and the diluent was passed through two solid phase extraction cartridges connected in series, an InertSep mini MA-1 anion exchange cartridge (GL Sciences, Tokyo, Japan) and an Oasis HLB multi-mode reversed-phase cartridge (Waters, Milford, MA, USA), which were preconditioned with 10 mL of methanol and 10 mL of purified water. The first nonbinding fractions (0–2 mL) were discarded and the next nonbinding fractions (2–3 mL) were collected. The filtered solution was further diluted if necessary and then immediately subjected to RPIPC. For recovery examination, a mixture (100 μL) of 0.1 M each of erythritol and xylitol and 0.01 M each of arabitol, sorbitol, mannitol and dulcitol was added to 9900 μL of 100 × dilutions of four samples (DR 6, DR 4, ED 1 and MW 1). Five replicates of these additive solutions were pretreated and analyzed in parallel.

3. Results and discussion

3.1. Absorption spectra of SAs with molybdate ion and IPRs in acidic solution

We previously reported that SAs had absorption maxima at 247 nm in Mb-HCl solution (pH 3.1) [25]. In the present study, we tested five tetraalkylammonium chlorides (TAACls) as IPRs. The TAACls (TMACl, TEACl, TProACl, TBACl and TPenACl) are defined in the legend of Fig. 1. We measured the absorption spectra of 0.1 mM mannitol in Mb-HCl solution containing 0.4 mM of each TAACl as well as various concentrations (0–0.8 mM) of TBACl. In all cases, mannitol showed the same spectrum having an absorption maximum at 247 nm (Fig. 1(A) (B)). These results suggested that the dinuclear anionic molybdate complex of mannitol may not form complexes with any of the TAACls. Both stoichiometric and non-stoichiometric models have been used to explain the retention of

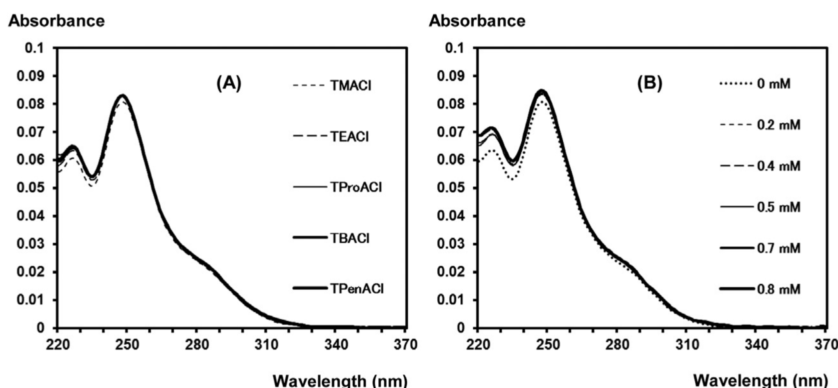

Fig. 1. UV spectra of 0.1 mM mannitol solutions containing 0.4 mM of each of five tetraalkylammonium chlorides (TMACl; tetramethylammonium chloride, TEACl; tetraethylammonium chloride, TProACl; tetrapropylammonium chloride, TBACl; tetrabutylammonium chloride, TPenACl; tetrapentylammonium chloride) (A) and with indicated concentrations of TBACl (B) in the presence of 0.1 mM disodium molybdate and 1 mM hydrochloric acid.

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