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Artifact-free matrix-assisted laser desorption ionization time-of-flight mass spectra of *tert.*-butyldimethylsilyl ether derivatives of cyclodextrins used for the synthesis of single-isomer, chiral resolving agents for capillary electrophoresis

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Abstract

Artifact-free, high-resolution matrix-assisted laser desorption ionization (MALDI) time-of-flight mass spectra have been obtained for the labile, single-isomer, *tert.*-butyldimethylsilyl ether derivatives of α-, β- and γ-cyclodextrins by optimizing the MALDI sample preparation method. 2,5-Dihydroxybenzoic acid, a 3:1 mixture of 2,5-dihydroxybenzoic acid and 1-hydroxyisoquinoline, and 2,4,6-trihydroxyacetophenone were investigated as MALDI matrices with methanol and acetonitrile as matrix solvents. Partial-to-complete loss of the *tert.*-butyldimethylsilyl groups was observed when the commonly used 2,5-dihydroxybenzoic acid was the MALDI matrix and/or methanol was the solvent, both with and without trifluoroacetic acid as additive. Loss of the labile *tert.*-butyldimethylsilyl groups was avoided with 2,4,6-trihydroxyacetophenone as MALDI matrix and acetonitrile as matrix solvent. Good ion intensities were achieved for the $(M+Na)^+$ and $(M+K)^+$ quasimolecular ions in the positive-ion mode. Minor byproducts were observed in some of the samples and the information was used to aid the optimization of the synthetic work.

Keywords: Matrix-assisted laser desorption ionization mass spectrometry; Cyclodextrins; *tert.*-butyldimethylsilylcyclodextrins; Carbohydrates

1. Introduction

Native cyclodextrins (CDs), derivatized CDs, and, especially, regioselectively derivatized CDs have become important in biotechnology [1–3], drug delivery and formulation [4,5], flavor and fragrance chemistry [6], and organic synthesis [7]. Recent reviews have surveyed the use of regioselectively derivatized CDs in gas chromatography (GC) [8–10], high-performance liquid chromatography (HPLC) [11–13] and capillary electrophoresis (CE) [14–24]. Regioselectively methylated CDs proved valuable for enantiomer separations by GC [25–28], HPLC [29–32] and, especially, CE [33–38]. In the last year, single-isomer, regioselectively methylated and sulfated CDs, as well as regioselectively acetylated and sulfated CDs, were introduced for the CE separation of enantiomers [39–43].

High-resolution matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS) has been used to characterize nonionic carbohydrate derivatives (e.g., Refs. [44–59]). Sever-

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al MALDI matrices, including 4-hydroxy-α-cyanocinnamic acid [44,45], 2,5-dihydroxybenzoic acid [45,46], 2,4,6-trihydroxyacetophenone [47], β-carbolines [48,49], a 3:1 mixture of 2,5-dihydroxybenzoic acid and 1-hydroxyisoquinoline [50], and a binary liquid matrix, a mixture of *p*-nitroaniline and glycerol [51], proved successful for that purpose. For nonionic carbohydrate derivatives, cationization was reported to occur by the addition of alkali metal ions [52–54], divalent metal ions or trivalent metal ions [55]. Several papers reported the post-source-decay (PSD) mass spectra of glycosilated cyclodextrin derivatives and correlated their fragmentation patterns and ion intensities with the type of glycosidic bond [56–59].

Previous MALDI-TOF-MS studies dealt only with native CDs, simple alkylated CDs and hydroxypropylated CDs. However, most regioselectively alkylated and regioselectively acetylated CDs are produced by protecting-group chemistry through *tert.*-butyldimethylsilyl ether intermediates using Takeo et al.'s classical procedures [60]. Our initial attempts to obtain high-resolution MALDI-TOF mass spectra for the *tert.*-butyldimethylsilyl ether derivatives of cyclodextrins using the most common matrix, 2,5-dihydroxybenzoic acid, yielded poorly reproducible results and contradicted the HLPC, NMR and X-ray crystallographic results. Some of these problems were traced back to the marginal chemical stability of silylated CD intermediates. Since there were no publications dealing with the MALDI-TOF-MS behavior of regioselectively silylated CD intermediates, we decided to assess, with the use of single-isomer *tert.*-butyldimethylsilyl ether CDs, whether MALDI-TOF-MS can be used for their characterization and, if so, under what conditions.

2. Experimental

2.1. Chemicals

The pure, stable, single-isomer heptakis(2-*O*-methyl)cyclomaltoheptaose (**1**), synthesized and analytically fully characterized in our laboratory [43], was used as internal standard for every *tert.*-butyldimethylsilyl CD derivative studied here. The single-isomer, *tert.*-butyldimethylsilyl ether CDs, hexakis(6 - *O* - *tert.* - butyldimethylsilyl)cyclomaltohexaose (**2**), heptakis(6-*O*-*tert.*-butyldimethylsilyl)cyclomaltoheptaose (**3**), octakis(6-*O*-*tert.*-butyldimethylsilyl)-cyclomaltooctaose (**4**), heptakis(2,6-di-*O*-*tert.*-butyldimethylsilyl)cyclomaltoheptaose (**5**), heptakis(2-*O*-triethylsilyl - 6 - *O* - *tert.* - butyldimethylsilyl)cyclomaltoheptaose (**6**), hexakis(2,3-di-*O*-acetyl-6-*O*-*tert.*-butyldimethylsilyl)cyclomaltohexaose (**7**), heptakis-(2,3-di - *O* - acetyl - 6 - *O* - *tert.* - butyldimethylsilyl)-cyclomaltoheptaose (**8**), octakis(2,3-di-*O*-acetyl-6-*O*-*tert.*-butyldimethylsilyl)cyclomaltooctaose (**9**), heptakis(2,3-di-*O*-methyl-6-*O*-*tert.*- butyldimethylsilyl)-cyclomaltoheptaose (**10**), heptakis(2-*O*-methyl-3,6-di - *O* - *tert.* - butyldimethylsilyl)cyclomaltoheptaose (**11**) and heptakis(2-*O*-methyl-3-*O*-triethylsilyl-6-*O*-*tert.*-butyldimethylsilyl)cyclomaltoheptaose (**12**), were synthesized in our laboratory using the modified procedures of Takeo et al. [60] and Icheln et al. [61], as described in Refs. [39–43]. They were analytically characterized by HPLC, ^{1}H and ^{13}C NMR spectroscopy, and for about half of the compounds, by X-ray crystallography. 2,5-Dihydroxybenzoic acid (DHB), 1-hydroxyisoquinoline (HIQ), and 2,4,6-trihydroxyacetophenone (THAP) — which were used as MALDI matrices — were obtained from Aldrich (Milwaukee, WI, USA) and used as received. The MALDI-TOF-MS calibration standard, substance P, was obtained from Sigma (St. Louis, MO, USA). HPLC-grade acetonitrile, dichloromethane, methanol, trifluoroacetic acid (TFA) and water were from EM Science (Gibbstown, NJ, USA).

2.2. Sample preparation and MALDI-TOF-MS measurements

High-resolution MALDI-TOF mass spectral data were obtained with a Voyager Elite XL TOF mass spectrometer, equipped with delayed extraction capability (PerSeptive Biosystems, Framingham, MA, USA), using the following instrument settings: nitrogen laser ($\lambda = 337$ nm), reflectron mode, 25 kV acceleration voltage, 70% grid voltage, 0.035% guide wire voltage and 180 μs delay time [62,63]. Generally, the mass spectra from 80 laser shots were averaged to achieve an adequate signal-to-noise ratio. The laser power setting was kept at a moderate level. One of the matrix ions and one of substance

P's ions were used for external m/z calibration of the Voyager Elite XL mass spectrometer. The calibration curve was then single-point adjusted using the base isotope peak in the sodium quasimolecular ion cluster of the internal standard, heptakis(2-*O*-methyl)cyclomaltoheptaose (**1**), at $m/z = 1255.4690$. Compound **1** was selected as internal standard, because (i) it is structurally related to all the analytes, yet it cannot be formed in any of the reaction schemes used for the analytes, (ii) it has been analytically well characterized [43], (iii) it is available in high purity, and (iv) its m/z value does not overlap with any of the *tert.*-butyldimethylsilyl CDs.

The CD derivatives were applied onto the PTFE target stage using the dried droplet method [62]. Stock solutions (10 mg/mL) of the matrix components were prepared in methanol and acetonitrile. Initially, the matrix stock solutions also contained 0.1% TFA (see Results and discussion). The internal standard (**1**) and the CD derivatives ((**2**)–(**12**)) were dissolved, separately, in CH_2Cl_2 at a concentration of about 0.5 mg/mL. In order to obtain the dried droplet, 10 μL each of the matrix stock solution, the internal standard solution and the CD derivative solution were mixed, briefly homogenized by a vortex mixer, applied onto the PTFE target stage and allowed to dry.

3. Results and discussion

3.1. Acid-, solvent- and matrix-induced loss of the tert.-butyldimethylsilyl ether groups

When the common, 0.1% TFA-containing methanolic DHB matrix stock solution was used to prepare samples of the pure, single-isomer *tert.*-butyldimethylsilyl (TBS) CD derivatives for MALDI-TOF-MS, several peak clusters separated by $\Delta m/z = 114.09$ were observed in the spectra, all the way down to the unsubstituted, parent CD. The intensity of the peak clusters increased as their m/z values decreased, with the intensity of the unsubstituted parent CD being the highest. The $\Delta m/z = 114.09$ difference corresponds to the replacement of a TBS group with H. Since HPLC, ^{1}H NMR and ^{13}C NMR indicated that the TBS CD derivatives were single-isomer materials with greater than 95% purity, replacement of the TBS group with H had to occur either during the sample preparation step or the ionization step. Lowering the laser power did not eliminate or reduce the extent of TBS replacement by H. Since the *tert.*-butyldimethylsilyl ether group can be cleaved from the TBS CD derivatives by acids [64], the measurements were repeated with a DHB stock solution free of TFA. The extent to which TBS was replaced by H was greatly reduced. Therefore, TFA was eliminated from the matrix in all further measurements. The high-resolution MALDI-TOF mass spectrum of heptakis(2,3-di-*O*-acetyl-6-*O*-*tert.*-butyldimethylsilyl)cyclomaltoheptaose (**8**) obtained with DHB as matrix and methanol as matrix solvent is shown in Fig. 1. In addition to the Na^+ and K^+ quasimolecular ion clusters ($M+Na^+$ and $M+K^+$ at 2544.75 and 2559.71, respectively), one

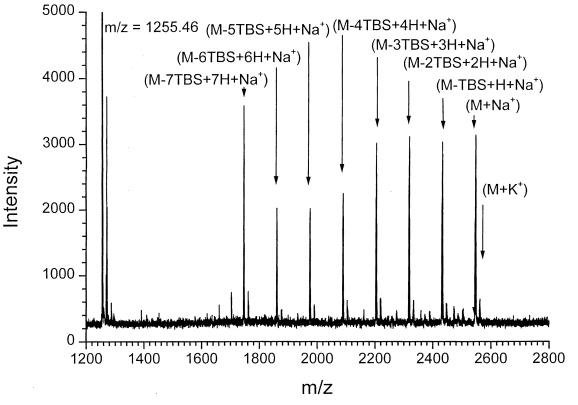

Fig. 1. High-resolution MALDI-TOF mass spectrum of heptakis(2,3-di-*O*-acetyl-6-*O*-*tert.*-butyldimethylsilyl)cyclomaltoheptaose (**8**) in DHB matrix using methanol as matrix solvent. Calculated and measured base-isotope m/z values: Na^+ quasimolecular ion cluster, $m/z_{calc} = 2544.11$, $m/z_{meas} = 2544.75$; K^+ quasimolecular ion cluster, $m/z_{calc} = 2560.09$, $m/z_{meas} = 2559.71$. (M-TBS+H+Na^+) ion cluster, $m/z_{calc} = 2430.03$, $m/z_{meas} = 2429.78$; (M-2TBS+2H+Na^+) ion cluster, $m/z_{calc} = 2315.94$, $m/z_{meas} = 2315.74$; (M-3TBS+3H+Na^+) ion cluster, $m/z_{calc} = 2201.85$, $m/z_{meas} = 2201.69$; (M-4TBS+4H+Na^+) ion cluster, $m/z_{calc} = 2087.77$, $m/z_{meas} = 2087.65$. (M-5TBS+5H+Na^+) ion cluster, $m/z_{calc} = 1973.68$, $m/z_{meas} = 1973.57$; (M-6TBS+6H+Na^+) ion cluster, $m/z_{calc} = 1859.59$, $m/z_{meas} = 1859.51$; (M-7TBS+7H+Na^+) ion cluster, $m/z_{calc} = 1745.51$, $m/z_{meas} = 1745.42$. The peak cluster at $m/z = 1255.47$ is that of the sodium adduct of the internal standard (**1**).

can also observe both the Na^+ and K^+ ion clusters of a CD derivative that has (i) one fewer TBS group than the target molecule, (M-TBS + H + Na^+), (ii) two fewer TBS groups than the target molecule, (M-2TBS + 2H + Na^+), (iii) three fewer TBS groups than the target molecule, (M-3TBS + 3H + Na^+), etc., all the way down to the CD derivative with no TBS groups (M-7TBS + 7H + Na^+). The peak cluster at $m/z = 1255.47$ is that of the sodium adduct of the internal standard (**1**).

When the methanolic DHB solution was replaced with an acetonitrile DHB solution, the extent of TBS replacement by H was further reduced. Thus, it was concluded that nonprotic acetonitrile was preferable to the protic solvent, methanol. Next, the effects of different MALDI matrices were investigated to see if the extent of TBS replacement by H could be reduced even further. When pure DHB was replaced with a 3:1 mixture of DHB and HIQ [50], only a small improvement was observed. When pure DHB was replaced with THAP, a much weaker acid than DHB, all TBS replacement was eliminated as shown in Fig. 2 for compound **8**.

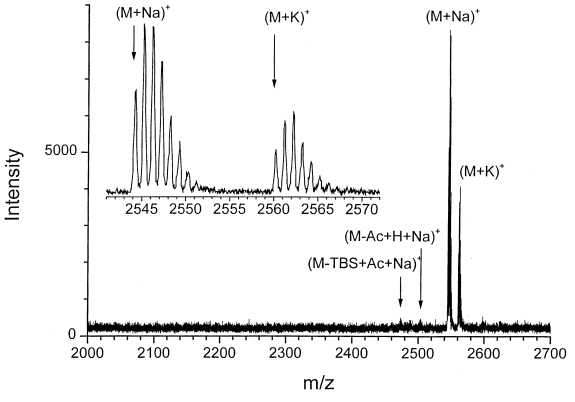

Fig. 2. High-resolution MALDI-TOF mass spectrum of heptakis(2,3-di-*O*-acetyl-6-*O*-*tert*.-butyldimethylsilyl)cycloma ltoheptaose (**8**) in THAP as matrix using acetonitrile as matrix solvent. Calculated and measured base isotope m/z values: Na^+ quasimolecular ion cluster, $m/z_{calc} = 2544.11$, $m/z_{meas} = 2544.26$; K^+ quasimolecular ion cluster, $m/z_{calc} = 2560.09$, $m/z_{meas} = 2560.22$. Note the presence of an ion corresponding to m/z of the sodium adduct of an underacetylated byproduct, (M-Ac + H + $Na)^+$, and the sodium adduct of an undersilylated, overacetylated byproduct, (M-TBS + Ac + $Na)^+$.

3.2. Detection of the presence of possible synthetic byproducts in tert.-butyldimethylsilyl ether derivatives of cyclodextrins

Therefore, the MALDI-TOF mass spectra of compounds **2**–**12** were obtained with THAP as matrix and acetonitrile as solvent to characterize the *tert*.-butyldimethylsilyl ether CDs. The calculated and measured m/z values for the base isotope peaks of the Na^+ and K^+ quasimolecular ion clusters are listed in Table 1. In addition, these artifact-free mass spectra allowed us to detect the presence of minor byproducts in the synthetic targets and tentatively assign a logical composition to them. For example, Fig. 3 shows the high-resolution MALDI-TOF mass spectrum of heptakis(2,3-di-*O*-methyl-6-*O*-*tert*.-butyldimethylsilyl)cyclomaltoheptaose (**10**) that was obtained with THAP as matrix and acetonitrile as matrix solvent. In addition to the expected Na^+ and K^+ quasimolecular ion clusters of the target molecule at $m/z_{meas} = 2152.24$ and 2168.22, respectively, one can observe the ions corresponding to a minor byproduct, the undersilylated (six TBS groups instead of the expected seven) and overmethylated (15 methyl groups instead of the expected 14) CD derivative, (M-TBS + Me + $Na)^+$. Similarly, Fig. 4 shows the high-resolution MALDI-TOF mass spectrum of heptakis(2-*O*-methyl-3,6-di-*O*-*tert*.-butyldimethylsilyl)cyclomaltoheptaose (**11**) that was ob-

Table 1
Calculated and measured m/z values for the Na^+ and K^+ quasimolecular ions of compounds **1**–**12**

Compound	Na^+ cluster		K^+ cluster	
	m/z_{calc}	m/z_{meas}	m/z_{calc}	m/z_{meas}
1	1255.46	1255.46	1271.44	1271.45
2	1679.83	1679.98	1695.80	1696.03
3	1955.96	1956.16	1971.94	1972.16
4	2232.10	2232.28	2248.08	2248.26
5	2754.57	2754.81	2770.54	2770.78
6	2754.57	2754.76	2770.54	2770.71
7	2183.95	2183.69	2199.93	2199.65
8	2544.11	2544.26	2560.09	2560.22
9	2904.27	2904.43	2920.25	2920.41
10	2152.18	2152.24	2168.16	2168.22
11	2852.68	2852.89	2868.65	2868.89
12	2852.68	2852.86	2868.65	2868.83

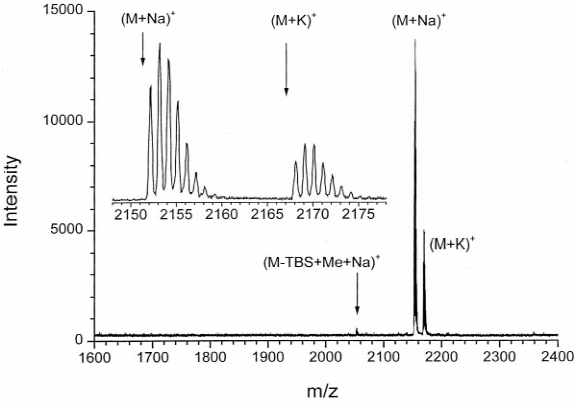

Fig. 3. High-resolution MALDI-TOF mass spectrum of heptakis(2,3-di-*O*-methyl-6-*O*-*tert*.-butyldimethylsilyl)cyclomaltoheptaose (**10**) in THAP as matrix using acetonitrile as matrix solvent. Calculated and measured base-isotope m/z values: Na^+ quasimolecular ion cluster, $m/z_{calc} = 2152.18$, $m/z_{meas} = 2152.24$; K^+ quasimolecular ion cluster, $m/z_{calc} = 2168.16$, $m/z_{meas} = 2168.22$. Note the presence of an ion corresponding to m/z of the sodium adduct of an undersilylated, overmethylated byproduct, $(M\text{-}TBS + Me + Na)^+$.

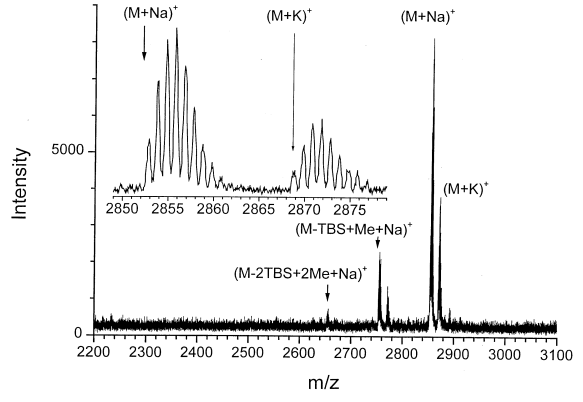

Fig. 4. High-resolution MALDI-TOF mass spectrum of heptakis(2-*O*-methyl-3,6-di-*O*-*tert*.-butyldimethylsilyl)cyclomaltoheptaose (**11**) in THAP as matrix using acetonitrile as matrix solvent. Calculated and measured base isotope m/z values: Na^+ quasimolecular ion cluster, $m/z_{calc} = 2852.68$, $m/z_{meas} = 2852.89$; K^+ quasimolecular ion cluster, $m/z_{calc} = 2868.65$, $m/z_{meas} = 2868.89$. Note the presence of ions corresponding to m/z of the sodium adducts of undersilylated, overmethylated byproducts, $(M\text{-}TBS + Me + Na)^+$ and $(M\text{-}2TBS + 2Me + Na)^+$, as well as an unknown contaminant.

tained with THAP as matrix and acetonitrile as matrix solvent. In addition to the expected Na^+ and K^+ quasimolecular ion clusters of the target molecule at $m/z_{meas} = 2852.89$ and 2868.89, respectively, one can observe the ions corresponding to two minor byproducts, the mono-undersilylated (13 TBS groups instead of the expected 14) and mono-overmethylated (eight methyl groups instead of the expected seven) CD derivative, $(M\text{-}TBS + Me + Na)^+$, and the bis-undersilylated (12 TBS groups instead of the expected 14) and bis-overmethylated (nine methyl groups instead of the expected seven) CD derivative, $(M\text{-}2TBS + 2Me + Na)^+$. This information helped the optimization of the respective synthetic procedures.

4. Conclusions

The mass spectra of 11 single-isomer, *tert*.-butyldimethylsilyl cyclodextrins were investigated by high-resolution MALDI-TOF-MS using three of the matrices recommended in the literature for the analysis of native and alkylated CD derivatives: 2,5-dihydroxybenzoic acid [45,46], a 3:1 mixture of 2,5-dihydroxybenzoic acid and 1-hydroxyisoquinoline [50], and 2,4,6-trihydroxyacetophenone [47]. The presence of TFA lead to a severe loss of *tert*.-butyldimethylsilyl groups. Methanol as matrix solvent or analyte solvent also lead to a pronounced loss of the *tert*.-butyldimethylsilyl groups. THAP as matrix and acetonitrile as matrix solvent could be used to obtain artifact-free mass spectra and accurate m/z values for the sodium and potassium quasimolecular ion clusters of **2**–**12**. The spectra could be used to detect the presence, and infer the likely structure, of minor byproducts that originate from the synthetic procedures.

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