Effect of Cationization Reagents on the Matrix-Assisted Laser Desorption/Ionization Time-of-Flight Mass Spectrum of Chinese Gallotannins

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Received 15 June 2006; accepted 12 February 2007
DOI 10.1002/app.26373
Published online 4 April 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: In this study, Chinese gallotannins were characterized by MALDI-TOF MS, and effects of cationization reagents on the quality of spectra were investigated. The trideca- and tetradeca-galloyl glucoses were observed in Chinese gallotannins, which could not be detected in earlier studies. When Cs^+ was used as the cationization reagent, Chinese gallotannins gave a relatively simple MALDI-TOF spectrum, three series of quasimolecular ions $[M + Cs]^+$, $[M + 2Cs–H]^+$, and $[M + 3Cs–2H]^+$ and a series of metastable ion peaks with minimum abundance were detected. Selection of Na^+ as the cationization reagent, additional three series of ion peaks including two patterns from the fragmentation and complex 2M adducts $[2M + Na]^+$ can be distinguished. In the case of no deionization or addition of cationization reagent to the analyte/matrix, naturally abundant Na^+ and K^+ as the cationization reagent, $[M + Na]^+$ and $[M + K]^+$ molecular ions both appeared in the complicated spectrum. Therefore, we conclude that cationization reagents affect the MALDI-TOF MS spectrum of Chinese gallotannins significantly. J Appl Polym Sci 105: 859–864, 2007

Key words: cationization reagents; Chinese gallotannins; hydrolyzable tannins; MALDI-TOF MS

INTRODUCTION

Since matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) was introduced by Karas et al.,[1] it has become a powerful method for the characterization of both synthetic and natural polydispersity polymers.[1–11] Because of its soft ionization energy and high ion transmission yield, MALDI-TOF MS produces only a singly charged molecular ion for each parent molecule, unlike ESI-MS. In addition, it is highly contaminant tolerant and thus particularly suitable for directly studying complex mixtures.[12] These attributes allow the simultaneous determination of masses in complex mixtures of low and high molecular weight compounds.[13]

Individual oligomers of vegetable tannins are well resolved in MALDI-TOF MS spectra with their molecular weights determination in the analysis of condensed tannins recently.[2,12–22] When MALDI-TOF MS is used to characterize tannins, the mass spectrum tend to favor an association with naturally abundant Na^+ or K^+ over the formation of a protonated molecular ion $[M + H]^+$.[13,23] To promote the formation of single tannin-ion adducts, K^+, Na^+, Ag^+, or Cs^+ is usually added to the analyte/matrix and the adducts are detected positive. However, MALDI-TOF mass spectra of condensed tannins are notably affected by various added and naturally abundant ions. Except for the over-evaluation of hydroxyl substitution in flavan-3-ol oligomers due to the formation of both $[M + Na]^+$ and $[M + K]^+$ from one species.[23] Using MALDI-TOF with deionization and selection of Cs^+ as the cationization reagent rather than selection of Na^+, condensed tannin polymers of higher polymerization degree (PD) were observed. Meanwhile, the polymer with the highest intensity ion peak changed with the ion adducts used.[24]

Hydrolyzable tannins are structurally different from condensed tannins, which are derivatives of gallic acid (3,4,5-trihydroxyl benzoic acid). Gallic acid, associated with sugars, polyols, glycosides, and other phenols, typically with β-D-glucopyranose in ester form, and the galloyl groups may be further esterified or oxidatively crosslinked to yield more complex hydrolyzable tannins in plants.[25]

The MALDI-TOF MS provides a powerful tool for identifying polydisperse hydrolyzable tannins in mixtures.[3,19,26] However, our recent study revealed

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Contract grant sponsor: The National Natural Science Foundation of China; contract grant numbers: 40376026, 30530150, 30671646.
Contract grant sponsor: Program for Innovative Research Team in Science and Technology in Fujian Province University.

the fact that MS spectra of the same analyte contain different series of peaks in the presence of different cations at the time of the MALDI. In addition to the accurate molecular mass determination, the series of fragment ions and complex adducts were also observed in these spectra. The Chinese gallotannins without deionization or addition of Na^+ as cationization reagent for MALDI gave a relatively more complicated spectrum than those with addition of Cs^+ as cationization reagent.

The complex spectra of hydrolyzable tannins caused by inapposite cationization reagent for MALDI make it very difficult to interpret structural properties of complicated hydrolyzable tannins occurring in various plants. To obtain a quality MALDI-TOF MS spectrum and characterize complicated or unknown hydrolyzable tannins species effectively, the effects of coordinating metal ions and cautious selection of appropriate cation as cationization reagent for MALDI should be the prerequisite knowledge for the researchers.

In the present study, the simplest hydrolyzable tannins (Chinese gallotannins) were chosen and cation effects on the quality of MALDI-TOF MS spectra were investigated. Chinese gallotannins are biologically and commercially important and can provide a hint of the wide variety of hydrolyzable tannins and related materials in plants. The Chinese tannins/matrix mixtures were either deionized and spiked with a solution containing single cation (Na^+ or Cs^+) or applied directly to steel target.

MATERIALS AND METHODS

Samples

Chinese gallotannins (Analytical Reagent grade) were purchased from China National Pharmaceutical Group (Beijing, China).

Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry

Mass spectra of Chinese tannins were recorded using a Bruker Reflex III MALDI-TOF Mass Spectrometer (Bruker Daltonics, Bremen, Germany). The irradiation source was a pulsed nitrogen laser with a wavelength of 337 nm and with the duration of the laser pulse of 3 ns. In the positive reflection mode, an accelerating voltage of 20.0 kV and a reflection voltage of 23.0 kV were used. Spectra of the Chinese tannins were obtained from a sum of 100–150 shots and calibrated with AngiotensinII (1046.5 MW), Bombesin (1619.8), ACTHclip18–39 (2465.2 MW), and Somatostatin28 (3147.47 MW) as external standards.

MALDI-TOF MS sample preparation

2,5-Dihydroxy benzoic acid (DHB, 10 mg/mL 70% acetone solution) was used as a matrix based on the results from Pasch and Pizzi.[19] The Chinese gallotannins (10 mg/mL 70% acetone solution) were directly mixed with the matrix solution at a volumetric ratio of 1 : 6, or was deionized by weakly acidic cation-exchange resin (Amberlite IRP-64, about 50 mg in 1 mL analyte solution) or strong cation-exchange resin (Dowex 50 × 8 − 400, about 50 mg in 1 mL analyte solution)[23,27] and then mixed with the NaCl (2.6 mg/mL aqueous solution) or CsCl (7.6 mg/mL aqueous solution) solution at a volumetric ratio of 1 : 1. The analyte/cationization reagent solution was mixed with matrix solution at a volumetric ratio of 1 : 3 after the matrix solution was deionized by weak or strong acidic cation-exchange resin, respectively. The analyte/matrix solution was applied (1 μL) to steel target, dried at room temperature. The Amberlite IRP-64 cation-exchange resin and Dowex 50 × 8 − 400 cation-exchange resin, equilibrated in 70% acetone solution at room temperature, was used to deionize the analyte and matrix solution. The cationization reagent solution containing almost equally cations (0.045 mol/L) was mixed with the analyte solution to promote the formation of a single type of ion adduct ($[M + Na]^+$, or $[M + Cs]^+$).

RESULTS AND DISCUSSION

The Chinese gallotannins purchased from China National Pharmaceutical Group are the simplest hydrolyzable tannins, which are composed of mixtures of polygalloylglucoses having depsidically linked galloyl groups from sumac (*Rhus semialata*) galls [Fig. 1(A)]. Nishizawa et al.[28] described the Chinese gallotannins as mixtures mainly consisting of penta-undeca-galloylglucoses that have depside

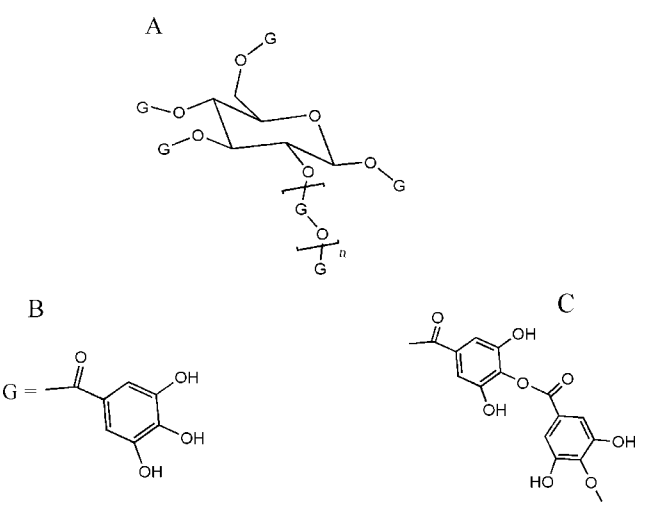

Figure 1 (A) The general structure of Chinese gallotannins, G: galloyl, and *n*: the number of depside bonds; The position of the additional galloyl residue on the penta-galloyl glucose core is not immobile; (B) galloyl; (C) *m*- or *p*-depside bonds.

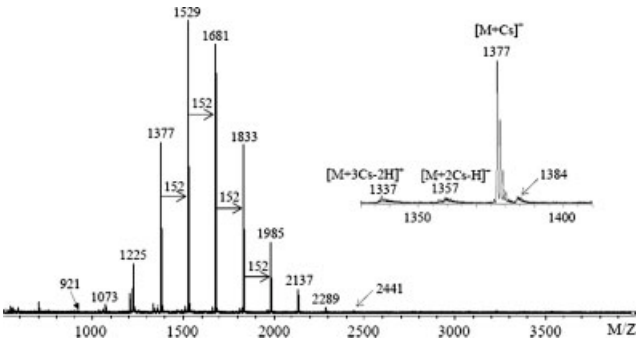

Figure 2 The MALDI-TOF positive reflection mode mass spectrum of the Chinese gallotannins in the case of deionization and selection of Cs^+ as the cationization reagent for MALDI. In the low mass region, mono-tri-galloyl glucoses were not presence of definite peaks corresponding to calculations (465, 617, and 769, respectively).

galloyl groups [Fig. 1(C)] randomly distributed at the C-2, C-3, and C-4 positions on a penta-*O*-galloyl-β-D-glucose core. Although the commercial Chinese gallotannins have a nominal molecular weight for this tannic acid, the preparations are mixtures of heterogeneous galloyl esters. MALDI-TOF MS enables us to distinguish molecular weight differences due to the extent of galloyl [Fig. 1(B)], but it lacks the ability to assign specific stereochemistry to the polygalloylglucose molecule.

Following the deionization of analyte/matrix mixture with the strong cation-exchange resin (Dowex $50 \times 8 - 400$), cesium chloride as a cationization reagent for MALDI (Di + Cs^+) was added to Chinese gallotannins/matrix solution. Chinese gallotannins gave a high quality MALDI-TOF spectrum (Fig. 2). Table I summarized the series of ions peaks for Chinese gallotannins obtained by Di + Cs^+. In the positive-ion mode, no protonated molecular ions were observed in MALDI-TOF MS by Di + Cs^+. Instead, a dominant series of $[M + Cs]^+$ molecular ion species was detected. The spectrum showed the polygalloyl ester chains extending up to 2441.3 Da, and a series of major $[M + Cs]^+$ molecular ion peaks exhibiting a mass increment of 152.0 Da, corresponding to the structure of polygallic tannins with repeat unit galloyl [Fig. 1(B)].

According to the structures described by Nishizawa et al.,[28] the expected molecular weights from Chinese gallotannins were calculated based on the equation $M + Cs^+ = 132.9 + 180.1 + 152.0 \times n$ (I), where $m/z = 180.1$ corresponds to the molecular weight of one glucose core, $m/z = 152.0$ represents one galloyl group [Fig. 1(B)], $m/z = 132.9$ is Cs^+ in the adducts $[M + Cs]^+$, and n is the number of galloyl groups that were esterified to a core glucose or *m*- and *p*-depsidically linked [Fig. 1(C)] to the 1,2,3,4,6-penta-*O*-galloyl-β-D-glucose core [Fig. 1(A)].

Along with the tetra-galloyl glucoses, the penta-, hexa-, and extending up to tetradeca-galloyl glucoses in Chinese gallotannins were detected with peaks of 921.2, 1073.3, 1225.2, 1377.3, 1529.3, 1681.3, 1833.3, 1985.3, 2137.3, 2289.3, and 2443.3 Da, respectively (Fig. 2 and Table I). The octa-galloyl glucose has the highest intensity in MALDI-TOF. This distribution of the Chinese gallotannins characterized by MALDI-TOF was similar to that reported by Nishizawa et al.[28] However, the trideca- and tetradeca-galloyl glucose, with low intensity being obtained with MALDI-TOF in the present study, was not reported in their earlier study due to a minimal amount of trideca-galloyl glucoses in the Chinese gallotannin mix-

TABLE I
The Series of Ions Peaks in the MALDI TOF Spectrum of Chinese Gallotannins Using Cs^+ as the Cationization Reagent

	$[M + Cs]^+$		$[M + 2Cs–H]^+$		$[M + 3Cs–2H]^+$		
G*n*	Calculated	Observed	Calculated	Observed	Calculated	Observed	$[M + Cs]^+ + 7$ Da
G1	465.0	N	596.9	N	728.8	N	N
G2	617.0	N	748.9	N	880.8	N	N
G3	769.0	N	900.9	N	1032.8	N	N
G4	921.0	921.2	1052.9	N	1184.8	N	N
G5	1073.0	1073.3	1204.9	1205.4	1336.8	1337.3	N
G6	1225.0	1225.2	1356.9	1357.0	1488.8	1489.2	1232.8
G7	1377.0	1377.3	1508.9	1509.0	1640.8	N	1384.4
G8	1529.0	1529.3	1660.9	1661.0	1792.8	N	1536.3
G9	1681.0	1681.3	1812.9	1813.0	1944.8	N	N
G10	1833.0	1833.3	1964.9	1965.1	2096.8	N	N
G11	1985.0	1985.3	2116.9	N	2248.8	N	N
G12	2137.0	2137.3	2268.9	N	2400.8	N	N
G13[a]	2289.0	2289.3	2420.9	N	2552.8	N	N
G14[a]	2441.0	2441.3	2572.9	N	2704.8	N	N

Note that the repeat unit in tannic acid is 152.0 Da; G*n* corresponds to the polygalloylglucoses consisting of a glucose core and various galloyl groups; N, no observed peaks corresponding to those calculated ones.

[a] The trideca- and tetradeca-galloyl glucose could not be detected in an earlier study by Nishizawa et al.[28]

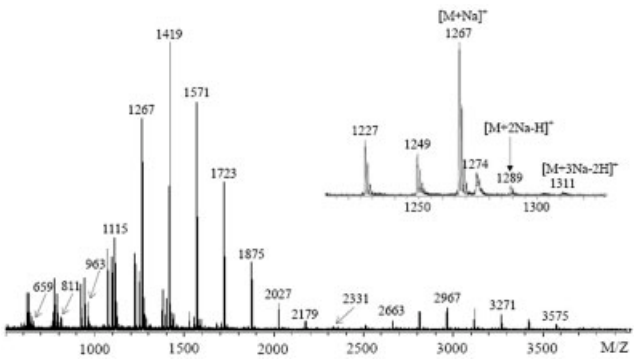

Figure 3 The MALDI-TOF positive reflection mode mass spectrum of the Chinese gallotannins in the case of deionization and selection of Na^+ as the cationization reagent for MALDI.

ture.[28] Calculated spectrum peaks (465.0, 617.0, 769.0 Da) of the mono-trigalloyl glucoses were not observed in this commercial Chinese gallotannins.

Also of interest was the existence of peaks at 1205.4, 1357.0, 1509.0, 1661.0, 1813.0, and 1965.1 Da for Chinese gallotannins in the case of Di + Cs^+ (Fig. 2 and Table I). These had a subset of masses Δ20 Da lower than the predicted hexa-undeca-galloyl glucose adducts $[M + Cs]^+$, respectively. From the *m/z* values, it was found that ions were formed with the general compositions $[M + 2Cs–H]^+$ in this case. The quasimolecular ions were generated by simultaneous attachment of two Cs^+ and loss of a proton. One can proceed in this series with the peaks at 1337.3 and 1489.2 Da corresponding to the penta- and hexa-galloyl glucose triple adducts $[M + 3Cs–2H]^+$. The overall adducts remain singly charged. In this case, further complex adducts were not observed in the spectrum.

The relatively lower-intensity series of peaks 1232.8–1384.4–1536.3 Da was observed in the spectrum in the case of Di + Cs^+, which has a subset of masses 7 Da higher than the calculated hexa-octa-galloyl glucoses adducts $[M + Na]^+$. Given the inconstant mass increase from the predicted hexa-undeca-galloyl glucoses and the relative breadth of peaks, these peaks were likely to be contributed to metastable ions.

When the Chinese gallotannins/matrix mixture was deionized with the strong cation-exchange resin (Dowex 50 × 8 − 400) and then Na^+ was added to promote the formation of single ion adducts (Di + Na^+), the Cs^+ adduct peaks were replaced by sodium ion adducts ($[M + Na]^+$). In addition, no protonated molecular ions were observed (Fig. 3). In this case, the expected molecular weights from Chinese gallotannins were calculated based on the equation $M + Na^+ = 23.0 + 180.1 + 152.0 \times n$ (II). Here $m/z = 23.0$ is Na^+ in the adducts $[M + Na]^+$, differing form the $m/z = 132.9$, the molecular weight of Cs^+ in the adducts $[M + Cs]^+$ shown in expression (I). Tables II and III summarized the series of ions peaks for Chinese gallotannins obtained by Di + Na^+.

Figure 3 shows the MALDI-TOF mass spectrum of the Chinese gallotannins in the case of Di + Na^+. It can be seen from the spectrum and Table II that the tri-, tetra-, and extending up to tetradeca-galloyl glucoses have molecular weights of 659.4, 811.3, 963.3, 1115.2, 1267.2, 1419.2, 1571.2, 1723.2, 1875.2, 2027.2, 2179.2 and 2331.1 Da, which are consistent with those calculated molecular weights. The octa-galloyl

TABLE II
Six Main Series of Peaks Observed for Chinese Gallotannins in 300–2500 Da Range with MALDI-TOF by Deionization and Selection of Na^+ as the Cationization Reagent

	Calculated	Observed					
G*n*	$[M + Na]^+$	$[M + Na]^+$	$[M + 2Na–H]^+$	$[M + 3Na–2H]^+$	$[M–OH]^+$	$[M–OH+ Na–H]^+$	$[M + Na]^+ + 7–8$ Da
G1	355.1	N	N	N	N	N	N
G2	507.1	N	N	N	N	N	N
G3	659.1	659.4	N	N	619.3	N	N
G4	811.1	811.3	N	N	777.2	793.4	N
G5	963.1	963.3	985.3	N	923.2	945.3	971.4
G6	1115.1	1115.2	1137.3	N	1075.2	1097.3	1123.0
G7	1267.1	1267.2	1289.2	1311.4	1227.2	1249.3	1274.6
G8	1419.1	1419.2	1441.1	1463.2	1379.2	1401.3	1426.1
G9	1571.1	1571.2	1593.2	1615.2	1531.2	1553.2	1578.0
G10	1723.1	1723.2	1745.2	N	1683.3	1705.2	N
G11	1875.1	1875.2	N	N	1835.3	1857.2	N
G12	2027.1	2027.2	N	N	1987.2	N	N
G13[a]	2179.1	2179.2	N	N	N	N	N
G14[a]	2331.1	2331.1	N	N	N	N	N

G*n* corresponds to the polygalloylglucoses consisting of a glucose core and various galloyl groups. N no observed peaks corresponding to calculation.

[a] The trideca- and tetradeca-galloyl glucose could not be detected in an earlier study by Nishizawa et al.[28]

TABLE III
The Series of Peaks Observed for Chinese Gallotannins in 2500–4000 Da Range with MALDI-TOF by Deionization and Selection of Na^+ as the Cationization Reagent

$[2M + Na]^+$	Calculated	Observed
$[Gn + Gm + Na]^+$; $n + m = 15$	2511.2	2511.3
$[Gn + Gm + Na]^+$; $n + m = 16$	2663.2	2663.2
$[Gn + Gm + Na]^+$; $n + m = 17$	2815.2	2815.2
$[Gn + Gm + Na]^+$; $n + m = 18$	2967.2	2967.2
$[Gn + Gm + Na]^+$; $n + m = 19$	3119.2	3119.1
$[Gn + Gm + Na]^+$; $n + m = 20$	3271.2	3271.1
$[Gn + Gm + Na]^+$; $n + m = 21$	3423.2	3423.1
$[Gn + Gm + Na]^+$; $n + m = 22$	3575.2	3575.0

G*n* or G*m* corresponds to the polygalloylglucoses consisting of a glucose core and various galloyl groups; *n* or *m* is the number of galloyl groups in the polygalloylglucoses oligermers, where $3 \leq n \leq 14$, $3 \leq m \leq 14$.

glucose appears to have the highest intensity in MALDI-TOF. Compared with the absence of definite peaks corresponding to those by calculated in the case of Di + Cs^+, the tri-galloyl glucoses can be obtained with relatively low intensity sodium adduct ions ($[M + Na]^+$). To identify small amount of oligomers of low molecular weight in Chinese gallotannins using MALDI-TOF MS, Na^+ is a relatively better cationization reagent than Cs^+. The distribution of tetra-, tetradeca-galloyl glucoses in the spectrum shown in Figure 3 is similar to that in the spectrum by Di + Cs^+.

In addition to the series of quasimolecular ions $[M + 2Na–H]^+$ and $[M + 3Na–2H]^+$ and the metastable ion peaks at 971.4, 1123.0, 1274.6, 1426.1, and 1578.0 Da in MALDI-TOF by Di + Na^+ as these patterns described in the case of Di + Cs^+, other three patterns can be distinguished. These series of peaks also show the polygalloyl ester chains and exhibit the same mass increment of 152.0 Da (Tables II and III). First, we found a series of peaks 619.3–771.2–923.2–1075.2–1227.2–1379.2–1531.2–1683.3–1835.3–1987.2 Da, which is 40 Da lower than tri-dodeca-galloyl glucoses adducts $[M + Na]^+$ calculated by the equation. The masses of the series of peaks can be presented by an equation of (M–OH). The ions seemed to be generated by loss of a —OH from the tri-dodeca-galloyl glucoses, respectively. One can proceed in this series with the second series of peaks 793.4–945.3–1097.3–1249.3–1401.3–1553.2–1705.2–1857.2 Da corresponding to the tetra- and undeca-galloyl glucose forming with the formula of $[M–OH + Na–H]^+$. These complex adducts ions appeared a subset of masses 18 Da lower than the calculated penta-nona-galloyl glucoses adducts $[M + Na]^+$ in the MALDI-TOF spectrum.

The last and most interesting pattern is the series of 2511.3–2663.2–2815.2–2967.2–3119.1–3271.1–3423.1–3575.0 Da in the high mass region (Table III), which also show the polygalloyl ester chains and exhibit the same mass increment of 152.0 Da. The masses of this series of peaks can be presented by the equation of (G*n* + G*m* + Na), where G*n* or G*m* corresponds to the polygalloylglucoses consisting of a glucose core and various galloyl groups, and *n* or *m* is the number of galloyl groups in the polygalloylglucoses oligomers. It is therefore clearly demonstrated that the series of ions appearing in the high mass region were formed with the formula of $[2M + Na]^+$, i.e., the peaks at 3119.1 being contributed to the complex adducts $[G9 + G10 + Na]^+$ and so on. These patterns of polygalloyl glucoses adducts $[2M + Cs]^+$ were also obtained in MALDI-TOF by Di + Cs^+ in very low intensity.

In the case of no deionization or addition of cation to the analyte/matrix (NDi + Cat), the six series of peaks described above (Di + Na^+) are also obtained using MALDI-TOF MS (Fig. 4). The spectrum shows that the $[M + Na]^+$ molecular ions are the most dominant pattern. The $[M + K]^+$ molecular ion peaks (979.1, 1131.1, 1283.1, 1435.1, 1587.1, 1739.2, and 1892.1 corresponding to penta-, hexa-, undeca-galloyl glucoses, respectively) are detected in this MALDI-TOF and have a relatively higher intensity because of abundant K^+ in the analyte or matrix without deionization. With MALDI as ionization technique for mass spectrometry, salt impurities from the matrix and analyte may result in extra alkali metal adducts appearing in the spectrum, in addition to the expected adducts ions. This is undesirable and can complicate the mass spectra. For this reason, the matrix and analyte should be deionized to simplify the result spectrum.

Deionization of Chinese gallotannins and matrix solution with the strong cation-exchange resin (Dowex 50 × 8 - 400) allowed to removing the salt impurities in the analyte and matrix including abundant Na^+ and K^+. The extra alkali metal adducts $[M + K]^+$ were not observed in the spectrum of Chinese gallotanins by Di + Na^+. However, the

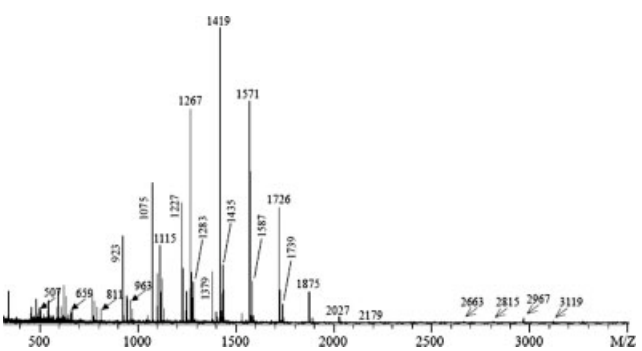

Figure 4 The MALDI-TOF positive reflection mode mass spectrum of the Chinese gallotannins in the case of no deionization or addition of cation to the matrix/analyte.

weak cation-exchange resin (Amberlite IRP-64) was used to remove the salt impurities from Chinese gallotannins and matrix solution, the $[M + K]^+$ molecular ion peaks can be detected distinctly in MALDI-TOF spectrum in the case of Di + Na^+ (1435.1,1587.1, and 1739.1 Da corresponding to octa-, nona-, and deca-galloyl glucoses). It can be seen from the result that the strong cation-exchange resin is a more sensitive reagent to remove the extra cations from Chinese gallotannins and matrix (DHB) than the weak cation-exchange resin.

CONCLUSIONS

Along with the tri-galloyl glucoses, the penta-, hexa-, and extending up to tetradeca-galloyl glucoses in Chinese gallotannins were detected by MALDI-TOF MS. MALDI-TOF of the Chinese gallotannins showed different series of peaks in the presence of different cations at the time of the MALDI. When Cs^+ was employed as the cationization reagent for MALDI, Chinese gallotannins gave a relatively simple MALDI-TOF spectrum. In addition to three series of quasimolecular ions $[M + Cs]^+$, $[M + 2Cs–H]^+$, and $[M + 3Cs–2H]^+$, a series of metastable ion peaks with minimum abundance was detected. In MALDI-TOF by selection of Na^+ as the cationization reagent, the series of quasimolecular ions $[M + Na]^+$, $[M + 2Na–H]^+$, $[M + 3Na–2H]^+$, and the metastable ions peaks were also observed. Furthermore, two patterns from the fragmentation of specific precursor peaks and complex 2M adducts $[2M + Na]^+$ could be distinguished. These three series of peaks were also detected in the case of no deionization or addition of cation to the analyte/matrix, where naturally abundant Na^+ or K^+ as the cationization reagent, $[M + K]^+$ molecular ions can be detected distinctly with relatively high intensity. To simplify the result spectrum, the strong cation-exchange resin should be selected as the deionization reagent to remove the extra cations from Chinese gallotannins and matrix (DHB) rather than the weakly cation-exchange resin.

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