Tetrahedron: *Asymmetry* 20 (2009) 247–258

Contents lists available at ScienceDirect

Tetrahedron: *Asymmetry*

journal homepage: www.elsevier.com/locate/tetasy

Stereoselective synthesis of novel *N*-(α-L-arabinofuranos-1-yl)-L-amino acids

Ming Zhao, Yuji Wang, Caixia Huo, Chunyu Li, Xiaoyi Zhang, Li Peng, Shiqi Peng *

College of Pharmaceutical Sciences, Capital Medical University, Beijing 100069, PR China

ARTICLE INFO

Article history:
Received 15 December 2008
Accepted 13 January 2009
Available online 11 February 2009

ABSTRACT

In lead detoxification, the α-anomer of *N*-glycocyl-L-amino acid is more potent than its β-anomer. Here a six-step-reaction route for stereoselectively preparing *N*-(α-L-arabinose-1-yl)-L-amino acids is reported. Treating L-arabinose with acetic anhydride and sodium acetate provided 1,2,3,5-tetra-*O*-acetyl-L-arabinofuranose in 90% yield. After removing the 1-acetyl group, the thus formed 2,3,5-tri-*O*-acetyl-L-arabinofuranose and *N*-(2-nitrophenylsulfonyl)-L-amino acid *t*-butylesters were treated with triphenylphosphine to perform Mitsunobu dehydration and form 2,3,5-tri-*O*-acetyl-L-arabinofuranosyl-L-[*N*-(2-nitrophenylsulfonyl)]amino acid *t*-butylesters **2a–f**, and the ratios of their α- to β-anomer ranged from 8/1 to 9/1. Chromatographic separation provided epimerically pure **2a–f-α** and **2a–f-β**. In the presence of CF_3CO_2H, **2a–f-α** and **2a–f-β** were converted to α- and β-anomers of *N*-(2,3,5-tri-*O*-acetyl-L-arabinofuranosyl)-*N*-(2-nitrobenzenesulfonyl)-L-amino acids, **3a–f-α** and **3a–f-β**, in 87–92% yields. While in the presence of $NaOCH_3$, **3a–f-α** and **3a–f-β** were converted to α- and β-anomers of *N*-(L-arabinofuranosyl)-*N*-(2-nitrobenzenesulfonyl)-L-amino acids, **4a–f-α** and **4a–f-β**, in 90–96% yields. Treating **4a–f-α** and **4a–f-β** with *N*-ethyldiisopropylamine (DIPEA) and thiophenol, their 2-nitrophenylsulfonyl groups were removed, and the α- and β-anomers of *N*-(L-arabinose-1-yl)-L-amino acids were formed in 70–79% yields. The bioassay confirmed that the lead detoxification activity of the α-anomer was significantly higher than that of the β-anomer.

1. Introduction

Recently, the level of lead in air, water and soils has been increasing both in urban centers of industrialized countries and in developing countries.[1–5] Lead is a widespread toxic metal and accumulates inside human tissue, such as in bone, with a half-life time between 6 and 10 years,[4,6,7] and has been associated with many adverse effects such as hypertension, cognitive deficits, hyperthyroidism, osteoporosis, and skeletal diseases.[3–5,8] Lead exposure continues to be a major public health problem around the world, and there is an urgent need to find novel compounds for prevention of lead poisoning.[9–13]

In a previous investigation we pointed out that as the potential in lead detoxificators glycosylamino acids were cell membrane crossable and possess low toxicity,[14–16] In the evaluation of chelates of *N*-(1-deoxy-D-fructos-1-yl)-L-amino acids, the lead detoxification activity of *N*-(1-deoxy-α-D-fructos-1-yl)-L-phenyl alanine was significantly higher than that of its β-anomer. However, using the reported procedure, the α-anomer of *N*-(1-deoxy-D-fructos-1-yl)-L-amino acid was always obtained as a minor product.[16] Therefore, a synthetic method capable of stereoselectively forming the α-anomers is needed. Compared to D-glucose or D-fructose, recently L-arabinose was particularly used either as a pharmacophore of new bioactive compounds[17,18] or as a moiety of polymer chain of drug carrier,[19] and resulted in an increase in trans-membrane permeability. In this context, the present paper reports a stereoselective synthetic route of *N*-(α-L-arabinofuranos-1-yl)-L-amino acids. To verify their use, the lead detoxification activities of a pair of α- and β-anomers were premiliminarily evaluated on a mouse lead intoxication model.

2. Results and discussion

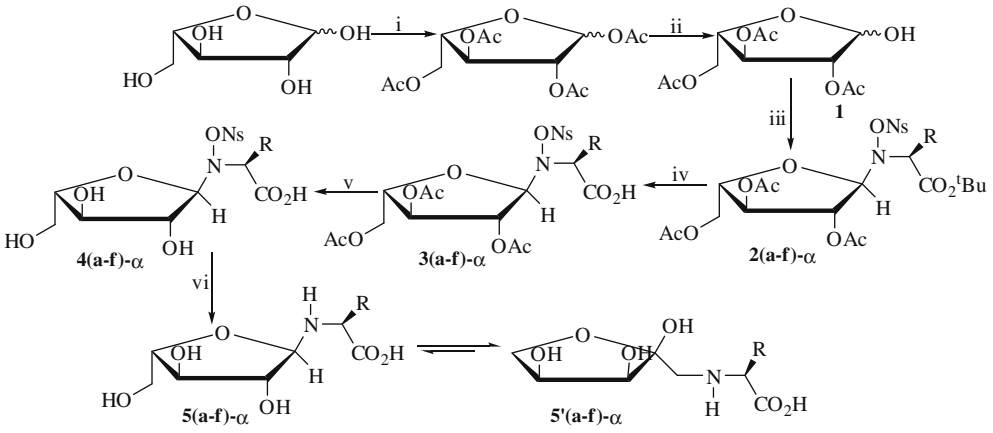
2.1. Preparing *N*-(α-L-arabinofuranos-1-yl)-L-amino acids

A stereoselective route of preparing epimerically pure *N*-(α-L-arabinofuranos-1-yl)-L-amino acids includes six reactions (Scheme 1). In the presence of acetic anhydride and sodium acetate, the acetylation of L-arabinose provided 1,2,3,5-tetra-*O*-acetyl-L-arabinofuranose in 90% yield. Treating 1,2,3,5-tetra-*O*-acetyl-L-arabinofuranose with ethyldiamine and glacial acetic acid, the 1-*O*-acetyl group was selectively removed and 2,3,5-tri-*O*-acetyl-L-arabinofuranose was obtained in 90% yield.

The second reaction step involves Mitsunobu dehydration of 2,3,5-tri-*O*-acetyl-L-arabinofuranose with *N*-(2-nitrophenylsulfonyl)-L-amino acid *t*-butylesters. In the presence of triphenylphosphine, 2,3,5-tri-*O*-acetyl-L-arabinofuranose and *N*-(2-nitro-phenylsulfonyl)-L-amino acid *t*-butylesters smoothly underwent Mitsunobu dehydration to form α- and β-anomers of 2,3,5-tri-*O*-acetyl-L-arabinofuranosyl-L-[*N*-(2-nitrophenylsulfonyl)]amino acid *t*-butylesters **2a–f** in good yield. The ratio of α- to β-anomers of

* Corresponding author. Tel./fax: +86 1083911528.
E-mail address: sqpeng@bjmu.edu.cn (S. Peng).

0957-4166/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetasy.2009.01.014

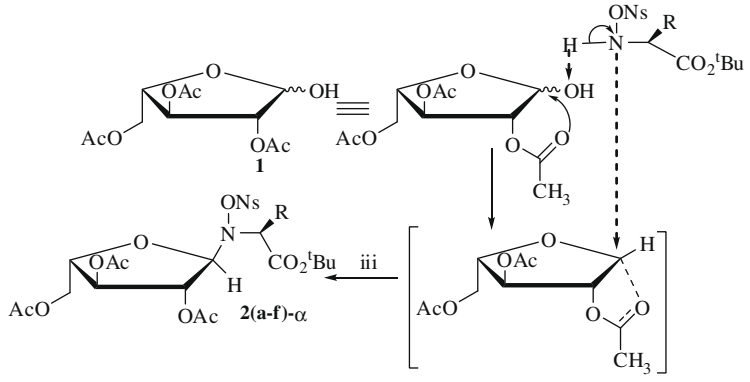


Scheme 1. Preparation of *N*-(α-L-arabinose-1-yl)-L-amino acids. (i) $(CH_3CO)_2O$, CH_3CO_2Na; (ii) ethylene diamine, glacial acetic acid; (iii) $(C_6H_5)_3P$, DIAD, *N*-(2-nitrophenylsulfonyl)-L-amino acid *t*-butylester, and chromatography; (iv) CF_3CO_2H; (v) $NaOCH_3/CH_3OH$; (vi) DIPEA, PhSH. In **2a** R = $CH_2CO_2{}^tBu$, **2b** R = $CH_2S{}^tBu$, **2c** R = $CH_2CH_2CO_2{}^tBu$, **2d** R_1 = $CH_2O{}^tBu$, **2e** R = $CH_2C_6H_5$, **2f** R = $CH(O{}^tBu)CH_3$, **3–5a** and **5a** R = CH_2CO_2H, **3–5b** and **5b** R = CH_2SH, (**3–5)c** and **5c** R = $CH_2CH_2CO_2H$, **3–5d** and **5d** R_1 = CH_2OH, **3–5e** and **5e** R = $CH_2C_6H_5$, **3–5f** and **5f** R = $CH(OH)CH_3$.

2a–f depended on both the dehydration temperature and time. Here the Mitsunobu dehydration was generally initiated at lower temperature and continued for several hours, during which the temperature was gradually raised to 20 °C. To get satisfactory yield and higher ratios of α- to β-anomer, a series of procedures were experienced, such as during 2 and 16 h the dehydration temperature was raised from −80 °C to 20 °C, during 8 h the dehydration temperature was raised from −60 °C to 20 °C, during 10 h the dehydration temperature was raised from −40 °C to 20 °C, and the hydration was carried out at 20 °C for 8 h. It was found that a suitable yield and higher ratio of α- to β-anomer could be obtained when the dehydration temperature was raised from −80 °C to 20 °C, and the dehydration time was 8 h. Using this procedure, the yields of **2a–f** ranged from 87% to 90% and the ratios of **2α** to **2β** ranged from 8:1 to 9:1. The rather high stereoselectivity of the Mitsunobu dehydration implies that *N*-(2-nitrophenylsulfonyl)-L-amino acid *t*-butylester approaches the C_1 preferably from the upside of the ring of 2,3,5-tri-*O*-acetyl-L-arabinofuranose and thus selectively forms the α-anomer. It could be considered that a neighboring group participation of acetyl group at C-2 was involved in the dehydration and was responsible for the stereoselectivity. As postulated in Scheme 2, the neighboring participation of the acetyl group in C-2 may lead to an intermediate having an additional 1,3-dioxalane ring which blocks the pathway of *N*-(2-nitrophenylsulfonyl)-L-amino acid *t*-butylester approaching the C_1 from the downside of the ring of 2,3,5-tri-*O*-acetyl-L-arabinofuranose.

After chromatographic separation, the epimerically pure **2a–f-α** and **2a–f-β** resulting from the Mitsunobu dehydration were obtained. Treating **2a–f-α** or **2a–f-β** with CF_3CO_2H, the third reaction step was carried out, their *t*-butylester groups were removed and **3a–f-α** or **3a–f-β** were obtained in 87–92% yields. In methanol **3a–f-α** or **3a–f-β** were treated with $NaOCH_3$ and their acetyl groups were removed. The fourth reaction step was performed and **4a–f-α** or **4a–f-β** were obtained in 90–96% yields. In the fifth reaction step, **4a–f-α** or **4a–f-β** were treated with DIPEA and thiophenol, their 2-nitrophenylsulfonyl groups were removed, and the final products *N*-(α-L-arabinofuranos-1-yl)-L-amino acids **5a–f-α** or *N*-(β-L-arabinofuranos-1-yl)-L-amino acids **5a–f-β** were formed in 70–79% yields.

To assign the anomeric configurations of **5a–f,** the chemical shifts of H-1 of anomeric pair of **4a–f** were compared. Based on the literature,[20] the anomer having a smaller δ value of H-1 was assigned as **4β**. On the contrary, the anomer having a larger δ value of H-1 was assigned as **4α**. These differences were also observed in the anomers of **5a–f**. The δ values of H-1 of **4a–f-α** ranged from 4.69 to 5.09 and the δ values of H-1 of **4a–f-β** ranged from 4.53 to 5.00 with the individual α-anomer having larger δ value for H-1 than the corresponding β-anomer. Though the anomeric configurations of **5a–f** were deduced from **4a–f**, similar differences were observed in the δ values of H-1 of **5a–f-α** and **5a–f-β**. The δ values of H-1 of **5a–f-α** ranged from 4.13 to 4.31 and the δ values of H-1 of **5a–f-β** ranged from 2.92 to 3.20 with the individual α-anomer having larger δ value for H-1 than the corresponding β-anomer.



Scheme 2. Supposed neighboring participation of acetyl group in C-2 for Mitsunobu dehydration.

2.2. Amadori rearrangement of *N*-(α-L-arabinofuranos-1-yl)-L-amino acids

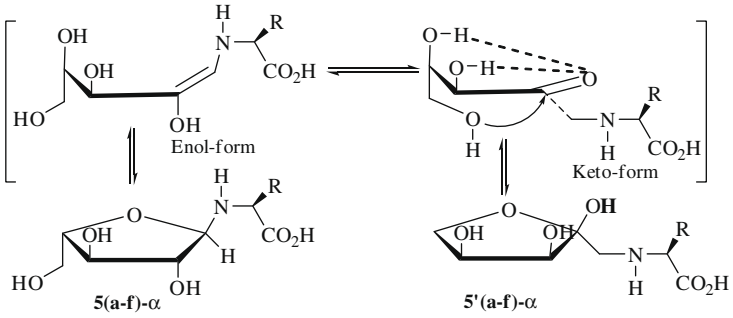
The sixth reaction step is Amadori rearrangement of *N*-(α-L-arabinofuranos-1-yl)-L-amino acids **5(a–f)-α**. HPLC analysis, LC-MS, and ^{1}H NMR spectra indicated that in aqueous solution, all **5a–f-α** underwent the Amadori rearrangement and *N*-(1-deoxy-β-L-araboketos-1-yl)-L-amino acids **5′a–f-α** occurred in tautomeric equilibrium.[21–24] In the determination of the products of the Amadori rearrangement of individual **5a–f-α**, HPLC analysis gave two peaks and ^{1}H NMR spectra exhibited two sets of signals corresponding to **5a–f-α** and **5′a–f-α**, of which the integrations indicated that the ratios of **5a–f-α** to **5′a–f-α** ranged from 1.0:2.0 to 1.0:3.0. Based on the facts that the ^{1}H NMR spectrum of individual anomers exhibited only two sets of signals, and the chemical shifts of the protons defined only **5a–f-α** and **5′a–f-α**, a tautomeric equilibrium involving ring opening, keto–enol tautomerism, and ring closure is proposed (Scheme 3). A similar Amadori rearrangement was also observed for *N*-(β-L-arabinose-1-yl)-L-amino acids **5a–f-β**, of which the tautomers were *N*-(1-deoxy-α-L-araboketos-1-yl)-L-amino acids **5′a–f-β**. In Scheme 3 the possible intramolecular hydrogen bonds between 2-OH, 3-OH, and the oxygen of the carbonyl group of the keto-form were indicated. The formation of these intramolecular hydrogen bonds led to five rings and six rings that blocked the pathway of 4-OH approaching the carbonyl group from the upside, and thus the rearrangement gave a single anomer.

2.3. Chemical shifts of ring protons of the tautomers in D_2O

The tautomerism of the anomers in D_2O was investigated with ^{1}H NMR. As mentioned above, individual α- or β-anomer of *N*-(L-arabinose-1-yl)-L-amino acid simply gave two sets of spectra, one set of major peaks and another set of minor peaks for tautomers **5a–f-α** and **5′a–f-α**, respectively. The assignment of the signals was performed with 2D spectroscopy (H/H-COSY, H/C-COSY), and the chemical shifts of the ring protons of **5(a–f)-α** and **5′(a–f)-β** are listed in Table 1. Based on the distinct chemical shifts of H-1 and H-2, their anomeric configuration could be simply assigned. According to the integration of ^{1}H signals, the ratios of **5α** to **5′α** ranged from 1.0:1.0 to 3.00:1.0. Similarly, the chemical shifts of the ring protons of **5a–f-β** and **5′a–f-β** were assigned, and are listed in Table 2. According to integration of ^{1}H signals, the ratios of **5β** to **5′β** also ranged from 1.0:1.0 to 3.0:1.0.

2.4. Stereochemistry-dependent lead detoxification of *N*-(L-arabinose-1-yl)-L-amino acids

To evaluate lead detoxification activity, the mice loaded with lead were treated with **5a–f-α** and **5a–f-β**, the lead levels of kidney and femur of the mice after chelating treatment were measured (see Table 3). The data in Table 3 indicate that the kidney lead levels of the mice receiving 0.4 mmol/kg of **5a–f-α** and **5a–f-β** ranged from 3.36 ± 0.47 to 7.54 ± 0.44 and from 4.04 ± 0.50 to 9.13 ± 1.03 mg/g of kidney, respectively, all of them were significantly lower than that of the mice receiving NS (11.03 ± 1.72 mg/g of kidney, $p < 0.001$) and most of them were significantly lower than that of the mice receiving 0.4 mmol/kg of DL-penicillamine (9.46 ± 0.63 mg/g of kidney, $p < 0.05$–0.01). The femur lead levels of the mice receiving 0.4 mmol/kg of **5a–f-α** and **5a–f-β** ranged from 37.43 ± 1.68 to 40.43 ± 1.29 and from 39.10 ± 1.60 to 41.65 ± 1.16 mg/g of femur, respectively, all of them were significantly lower than that of the mice receiving NS (45.43 ± 2.89 mg/g of femur, $p < 0.001$) and most of them were significantly lower than that of the mice receiving 0.4 mmol/kg of DL-penicillamine (40.74 ± 1.19 mg/g of femur, $p < 0.05$–0.01). Thus both **5a–f-α** and **5a–f-β** effectively moved the lead accumulated in kidneys and femurs of the mice. Besides, the



Scheme 3. Supposed Amadori rearrangement of **5a–f-α** involving ring opening, keto–enol tautomerism, and ring closure.

Table 1
Chemical shifts (δ) of ring protons of **5a–f-α** and **5a–f-β** in D_2O

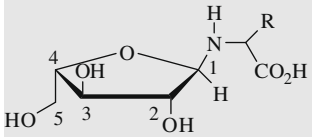
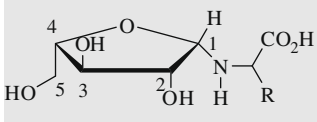
Ring proton		H-1	H-2	H-3	H-4	H-5a	H-5b
	**5a-α**	4.31	4.24	3.99	3.78	3.23	3.27
	5b-α	4.26	4.22	3.98	3.84	3.80	3.54
	5c-α	4.30	4.26	4.22	3.97	3.95	3.80
	5d-α	4.25	4.01	4.31	3.80	3.10	3.19
	5e-α	4.18	3.90	3.81	3.14	3.90	3.90
	5f-α	4.13	3.88	4.16	3.80	3.25	3.49
	**5a-β**	2.98	2.92	3.83	3.75	3.31	3.25
	5b-β	2.92	2.90	3.81	3.81	3.44	3.37
	5c-β	3.16	3.09	3.55	3.62	3.61	3.52
	5d-β	3.20	3.10	4.06	3.90	3.70	3.60
	5e-β	3.15	3.00	3.09	3.99	3.93	3.86
	5f-β	3.12	3.02	3.00	4.15	3.37	3.33

Table 2
Chemical shifts (δ) of ring protons of **5′a–f-α** and **5′a–f-β** in D_2O

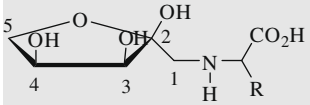
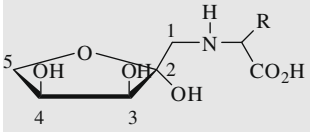
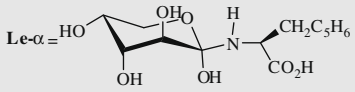
Ring proton		H-1a	H-1b	H-3	H-4	H-5a	H-5b
	**5′a-α**	3.35	3.15	4.14	4.37	4.07	3.82
	5′b-α	3.08	3.28	4.17	4.32	4.05	3.82
	5′c-α	3.25	3.15	4.14	4.37	4.06	3.83
	5′d-α	3.34	3.06	4.18	4.32	4.05	3.88
	5′e-α	3.25	2.98	4.08	4.25	3.98	3.67
	5′f-α	3.32	3.57	4.12	4.22	3.97	3.69
	**5′a-β**	3.30	3.12	3.70	3.85	3.64	3.39
	5′b-β	3.03	2.92	3.81	3.81	3.60	3.41
	5′c-β	3.16	3.09	3.65	3.65	3.55	3.40
	5′d-β	3.37	3.17	4.17	4.25	3.90	3.79
	5′e-β	3.16	3.15	4.04	4.22	3.86	3.65
	5′f-β	3.23	3.48	4.11	4.19	3.85	3.67

Table 3
Kidney and femur lead levels of mice after chelating treatment

Compound[a]		Kidney	Femur
NS		11.03 ± 1.72	45.43 ± 2.89
DL-PA		9.46 ± 0.63[d]	40.74 ± 1.19[f]
L-Arab		10.33 ± 2.54	43.22 ± 2.08
L-Asp		10.68 ± 2.02	45.66 ± 2.76
L-Cys		10.00 ± 2.69	43.59 ± 3.55
L-Glu		10.88 ± 2.87	44.02 ± 2.97
L-Ser		11.18 ± 2.27	45.28 ± 3.11
L-Phe		11.20 ± 1.98	43.95 ± 3.16
L-Thr		10.98 ± 1.95	44.88 ± 3.21
Le-α[16]		4.12 ± 0.48[b]	36.4 ± 3.62[f]
5a	**α**	7.43 ± 1.44[c]	39.00 ± 1.59[e]
	β	9.13 ± 1.03[d]	40.87 ± 1.64[f]
5b	**α**	3.36 ± 0.47[g]	37.43 ± 1.68[e]
	β	4.04 ± 0.50[b]	39.10 ± 1.60[f]
5c	**α**	6.48 ± 0.56[c]	39.08 ± 1.56[e]
	β	7.02 ± 0.52[b]	40.78 ± 1.34[f]
5d	**α**	6.52 ± 0.98[c]	39.34 ± 1.35[e]
	β	7.44 ± 0.81[b]	41.07 ± 1.21[f]
5e	**α**	7.54 ± 0.44[c]	39.85 ± 1.35[e]
	β	8.10 ± 0.40[b]	41.22 ± 1.31[f]
5f	**α**	6.76 ± 0.60[c]	40.43 ± 1.29[f]
	β	7.77 ± 0.51[b]	41.65 ± 1.16[f]



[a] Data are represented with microgram lead per gram tissue (X ± SE), DL-PA = DL-penicillamine, L-Arab = L-arabinose, NS = vehicle, $n = 10$, dose = 0.4 mmol/kg; L-arabinose, L-Asp, L-Cys, L-Glu, L-Phe, and L-Thr = reference compounds; kidney lead levels of mice after reference compound treatment ranged from 10.00 ± 2.69 to 11.20 ± 1.98, compared to NS $p > 0.05$; Femur lead levels of mice after reference compound treatment ranged from 43.22 ± 2.08 to 45.66 ± 2.76, compared to NS $p > 0.05$.

[b] Compared to NS and reference compounds $p < 0.001$, and to DL-penicillamine $p < 0.01$.

[c] Compared to NS, reference compounds, and DL-penicillamine $p < 0.001$, and to corresponding β-anomer $p < 0.05$.

[d] Compared to NS and reference compounds $p < 0.05$.

[e] Compared to NS and reference compounds $p < 0.001$, to DL-penicillamine and corresponding β-anomer $p < 0.05$.

[f] Compared to NS and reference compounds $p < 0.001$.

[g] Compared to NS, reference compounds, and DL-penicillamine $p < 0.001$, to corresponding β-anomer $p < 0.05$ and to **Le-α** $p < 0.01$.

lead levels of the kidneys and femurs of the mice receiving **5a–f-α** were significantly lower than that of the mice receiving **5a–f-β**, thus *N*-(L-arabinofuranos-1-yl)-L-amino acids obviously exhibited a stereo-chemistry-dependent lead detoxification. On the other hand, the kidney lead level of the mice receiving **5b-α**, the most potent compound of *N*-(L-arabinofuranos-1-yl)-L-amino acids, was 3.36 ± 0.47 mg/g of kidney and was significantly lower than that of the mice receiving **Le-α** [*N*-(1-deoxy-D-α-fructos-1-yl)-L-phenylalanine, 4.12 ± 0.483 mg/g of kidney, $p < 0.01$], the most potent compound of the reported *N*-(1-deoxy-D-fructos-1-yl)-L-amino acids, while the femur lead level of the mice receiving **5b-α** was 37.43 ± 1.68 mg/g of femur and was similar to that of the mice receiving **Le-α** (36.4 ± 3.622 mg/g of femur, $p > 0.05$).[16]

3. Conclusion

Using the six reaction step procedure, α-anomers of *N*-(L-arabinose-1-yl)-L-amino acids, the preferable anomers in lead detoxification, could be exclusively formed, which makes it possible to prepare individual *N*-(α-L-arabinose-1-yl)-L-amino acids as candidates for developing lead detoxification drugs. In aqueous solution, both α- and β-anomers of *N*-(L-arabinose-1-yl)-L-amino acids were in a tautomeric equilibrium with the α- and β-anomers of *N*-(1-deoxy-L-araboketos-1-yl)-L-amino acids. In this case the measured lead decorporation activity of each compound should be the contribution of both its tautomers.

4. Experimental

4.1. General

All the reactions were carried out under nitrogen (1 bar). ^1H (300 and 500 MHz) and ^{13}C (75 and 125 MHz) NMR spectra were recorded on Bruker AMX-300 and AMX-500 spectrometers for solution D_2O, DMSO-d_6, or $CDCl_3$ with tetramethyl-silane as internal standard. FAB/MS was determined on VG-ZAB-MS. Melting point was measured on an XT5 hot-stage microscope (Beijing keyi electro-optic factory) and uncorrected. Optical rotations were determined on a Schmidt and Haensch Polartronic D instrument at 20 °C. All L-amino acids and L-arabinose were purchased from China Biochemical Corp. 2-Nitrophenylsulfonyl chloride (*o*NsCl), Ph_3P, DIAD, trifluoroacetic acid (TFA), DIPEA, PhSH, and 2-nitrophenylsulfenyl chloride (NpsCl) were purchased from Aldrich. TLC was made with Qingdao silica gel GF_{254}. Chromatography was performed with Qingdao silica gel H_{60} or Sephadex-LH_{20}. All solvents were distilled and dried before use.

4.2. Chemical preparation

4.2.1. 2,3,5-Tri-*O*-acetyl–L-arabinose

The solution of 6.0 ml (90.0 mmol) of ethyldiamine, 5.3 ml (90.0 mmol) of glacial acetic acid, and 150 ml of anhydrous THF was stirred at room temperature for 0.5 h. To the solution, 15.9 g (50.0 mmol) of 1,2,3,5-tetra-*O*-acetyl-L-furanoarabinose was added, which was prepared from L-(+)-arabinose according to the

method described in the literature.[25] The reaction mixture was stirred at room temperature for 18 h and TLC analysis (petroleum ether:ethyl acetate, 2:1) indicated complete disappearance of 1,2,3,5-tetra-*O*-acetyl-L-furanoarabinose. The reaction mixture was evaporated under vacuum to remove the THF. The resulting residue was dissolved in ethyl acetate (200 ml) and the solution was washed successively with saturated NaCl solution, $NaHCO_3$ solution (5%), hydrochloric acid (5%), and saturated NaCl solution. The organic layer was dried over anhydrous $MgSO_4$. After filtration, the filtrate was evaporated under vacuum to give 12.4 g (90%) of the title compound as pale yellow syrup. FAB/MS (*m*/*e*): 277 $[M+H]^+$.

4.2.2. *N*-(2-Nitrobenzenesulfonyl)-L-aspartic acid di-*t*-butylester

The solution of 2.45 g (10 mmol) of L-aspartic acid di-*t*-butylester, which was prepared according to the method published in the literature,[26] 2 ml (15 mmol) of triethylamine, and 0.33 g (2 mmol) of 4-dimethylaminopyridine (DMAP) in 100 ml of anhydrous CH_2Cl_2 was stirred at room temperature for 15 min. The reaction mixture was cooled with ice bath to which 2.22 g (10 mmol) of oNsCl was added proportionally. The reaction mixture was stirred at room temperature for 3 h and TLC analysis (petroleum ether:ethyl acetate, 2:1) indicated complete disappearance of the starting materials. The reaction mixture was evaporated under vacuum to remove the CH_2Cl_2. The resulting residue was dissolved in 100 ml of ethyl acetate and the solution was washed successively with saturated NaCl solution, $KHSO_4$ solution (5%), and saturated NaCl solution. The organic layer was finally dried over anhydrous $MgSO_4$. After filtration, the filtrate was evaporated under vacuum and 3.87 g (90%) of the title compound was obtained as colorless solid. Mp 107–108 °C, FAB/MS (*m*/*e*): 431 $[M+H]^+$. Anal. Calcd for $C_{18}H_{26}O_8N_2S$: C, 50.20; H, 6.09; N, 6.51. Found: C, 50.40; H, 6.19; N, 6.38.

4.2.3. *N*-(2-Nitrobenzenesulfonyl)-*S*-*t*-butyl-L-cysteine *t*-butylester

Using the same procedure as that used for the preparation of *N*-(2-nitroben-zenesulfonyl)-L-aspartic acid *t*-butylester with 0.7 g (3 mmol) of *S*-*t*-butyl-L-cysteine *t*-butylester instead of L-aspartic acid *t*-butylester, 1.2 g (95%) of title compound was obtained as yellow powder. Mp 97–100 °C, ^1H NMR (500 MHz $CDCl_3$): δ = 8.13 (d, *J* = 10.0 Hz, 1H), 7.58 (m, 1H), 7.30 (m, 1H), 6.32 (d, *J* = 5.0 Hz, 1H), 4.32 (m, 1H), 3.56 (dd, *J* = 13.5 Hz, *J* = 5.5 Hz, 1H), 3.44 (dd, *J* = 13.5 Hz, *J* = 5.5 Hz, 1H), 1.3 (s, 18H); FAB/MS (*m*/*e*): 419 $[M+H]^+$. Anal. Calcd for $C_{17}H_{26}O_6N_2S_2$: C, 48.79; H, 6.26; N, 6.69. Found: C, 48.90; H, 6.40; N, 6.12.

4.2.4. *N*-(2-Nitrobenzenesulfonyl)-L-glutamic acid di-*t*-butylester

Using the same procedure as that used for the preparation of *N*-(2-nitrobenzenesulfonyl)-L-aspartic acid *t*-butylester with 3.0 g (10 mmol) of L-glutamate di-*t*-butylester hydrochloride instead of L-aspartic acid *t*-butylester, 4.0 g (90%) of title compound was obtained as colorless powder. Mp 101–103 °C, FAB/MS (*m*/*e*): 445 $[M+H]^+$. Anal. Calcd for $C_{19}H_{28}O_8N_2S$: C, 51.34; H, 6.35; N, 6.30. Found: C, 51.50; H, 6.60; N, 6.10.

4.2.5. *N*-(2-Nitrobenzenesulfonyl)-*O*-*t*-butyl-L-serine *t*-butylester

Using the same procedure as that used for the preparation of *N*-(2-nitrobenzenesulfonyl)-L-aspartic acid *t*-butylester with 2.5 g (10 mmol) of *O*-*t*-butyl-L-serine-*t*-butylester hydrochloride instead of L-aspartic acid *t*-butylester, 3.8 g (94%) of title compound was obtained as colorless powder. Mp 103–104 °C; ^1H NMR (300 MHz, $CDCl_3$) δ = 8.09 (d, *J* = 10.0 Hz, 1H), 7.94 (m, 1H), 7.74–7.77 (m, 2H), 6.37 (d, *J* = 5.0 Hz, 1H), 4.24 (m, 1H), 3.79 (dd, *J* = 8.5 Hz, *J* = 3.0 Hz, 1H), 3.61 (dd, *J* = 8.5 Hz, *J* = 3.0 Hz, 1H), 1.28 (s, 9H), 1.09 (s, 9H); FAB/MS (*m*/*e*) 403 $[M+H]^+$. Anal. Calcd for $C_{17}H_{26}O_7N_2S$: C, 50.74; H, 6.51; N, 6.96. Found: C, 51.01; H, 6.69; N, 6.72.

4.2.6. *N*-(2-Nitrobenzenesulfonyl)-L-phenylalanine *t*-butylester

Using the same procedure as that used for the preparation of *N*-(2-nitrobenzenesulfonyl)-L-aspartic acid *t*-butylester with 2.6 g (10 mmol) of L-phenylalanine *t*-butylester hydrochloride instead of L-aspartic acid *t*-butylester, 3.7 g (92%) of title compound was obtained as a colorless powder. Mp 92–93 °C; FAB/MS (*m*/*e*) 407 $[M+H]^+$. Anal. Calcd for $C_{19}H_{22}O_6N_2S$: C, 56.15; H, 5.46; N, 6.89. Found: C, 56.40; H, 5.69; N, 6.65.

4.2.7. *N*-(2-Nitrobenzenesulfonyl)-L-*O*-*t*-butyl-theorine *t*-butylester

Using the same procedure as that used for the preparation of *N*-(2-nitrobenzenesulfonyl)-L-aspartic acid *t*-butylester with 2.2 g (10 mmol) of L-theorine *t*-butylester hydrochloride instead of L-aspartic acid *t*-butylester, 3.9 g (92 %) of title compound was obtained as colorless powder. Mp 95 °C; FAB/MS (*m*/*e*): 417 $[M+H]^+$. Anal. Calcd for $C_{18}H_{28}N_2SO_7$: C, 51.92; H, 6.80; N, 6.75. Found: C, 52.05; H, 6.98; N, 6.93.

4.2.8. General procedure for preparing α- and β-anomers of *N*-[2,3,5-tri-*O*-acetyl-L-arabinofuranos-1-yl]-*N*-(2-nitrophenylsulfonyl)-L-amino acid *t*-butyl-esters 2a–f

The solution of 0.6 g (2.0 mmol) of 2,3,5-tri-*O*-acetyl-L-arabinose, 0.5 g (2.0 mmol) of Ph_3P and 1.0 mmol of *N*-(2-nitrophenylsulfonyl)-L-amino acid *t*-butylester in 15 ml of anhydrous THF was cooled to −80 °C under the protection of argon. To this cooled solution, 0.4 ml (2.0 mmol) of DIAD was added immediately. The reaction mixture was stirred initially at −60 °C and then gradually warmed to 20 °C during 8 h, and TLC analysis (petroleum ether:-ethyl acetate, 2:1) indicated complete disappearance of *N*-(2-nitrophenylsulfonyl)-L-amino acid *t*-butylester. The reaction mixture was evaporated under vacuum to remove the THF. The resulting residue was purified and separated on chromatography (petroleum ether:ethyl acetate, 2:1) to give α- and β-anomers of **2a–f**.

4.2.8.1. Anomers of *N*-(2,3,5-tri-*O*-acetyl-L-arabinofuranos-1-yl)-*N*-(2-nitrobenzenesulfonyl)-L–aspartic acid di-t-butylester (2a-α and 2a-β). Using the general procedure for preparing α- and β-anomers of **2a–f** from 431 mg (1.0 mmol) of *N*-(2-nitrophenylsulfonyl)-L-aspartic acid di-*t*-butylester, 585 mg (85%) of **2a-α** and 69 mg (10%) of **2a-β** were obtained as colorless powder.

Compound **2a-α**: Mp 68–70 °C, $[\alpha]_D^{25} = +49.6$ (*c* 1.1, $CHCl_3$), ^1H NMR (500 MHz, $CDCl_3$): δ = 8.24 (d, *J* = 9.5 Hz, 1H), 7.69 (m, *J* = 9.2 Hz, 2H), 7.59 (m, *J* = 9.0 Hz, 1H), 5.22 (t, *J* = 6.5 Hz, 1H), 5.03 (dd, *J* = 10.0 Hz, *J* = 3.5 Hz, 1H), 4.94 (q, *J* = 13.5 Hz, 1H), 4.04 (dd, *J* = 13.0 Hz, *J* = 3.0 Hz, 1H), 3.69 (d, *J* = 13.5 Hz, 1H), 3.03 (m, *J* = 4.3 Hz, 1H), 2.75 (dd, *J* = 15.0 Hz, *J* = 4.5 Hz, 1H), 2.2 (s, 3H), 2.17 (s, 3H), 2.14 (m, *J* = 4.3 Hz, 2H), 2.00 (s, 3H), 1.45 (s, 9H), 1.32 (s, 9H). ^{13}C NMR (500 MHz, $CDCl_3$): δ = 171.5, 169.9, 169.2, 168.6, 167.7, 147.8, 133.5, 132.3, 131.8, 123.9, 87.9, 81.7, 73.8, 73.7, 69.0, 68.5, 68.4, 65.3, 38.8, 27.5, 27.2, 21.0, 20.8, 20.6, 20.1. FAB/MS (*m*/*e*): 689 $[M+H]^+$. Anal. Calcd for $C_{29}H_{40}O_{15}N_2S$: C, 50.58; H, 5.85; N, 4.07. Found: C, 50.44; H, 5.69; N, 3.99.

Compound **2a-β**: Mp 76–79 °C, $[\alpha]_D^{25} = +8.0$ (*c* 1.3, $CHCl_3$), ^1H NMR (500 MHz,$CDCl_3$): δ = 8.16 (dd, *J* = 5.8 Hz, *J* = 3.5 Hz, 1H), 7.58 (m, *J* = 6.2 Hz, 1H), 7.75 (m, *J* = 5.9 Hz, 2H), 5.51 (s, 1H), 5.29 (t, *J* = 5.5 Hz 1H), 5.21 (dd, *J* = 10.5 Hz, *J* = 2.5 Hz, 1H), 5.14 (m, *J* = 4.9 Hz, 1H), 4.97 (m, *J* = 5.2 Hz, 1H), 4.81 (s, 1H), 3.89 (dd, *J* = 10.5 Hz, *J* = 1.0 Hz, 1H), 3.93 (dd, *J* = 15.0 Hz, *J* = 5.5 Hz, 1H), 3.23 (dd, *J* = 17.0 Hz, *J* = 10.5 Hz, 1H), 2.22 (s, 9H), 1.46 (s, 9H), 1.32 (s, 9H). ^{13}C NMR (500 MHz, $CDCl_3$): δ = 170.40, 169.90,

169.50, 169.20, 167.90, 149.60, 134.70, 133.20, 132.60, 131.20, 123.80, 85.30, 83.90, 74.30, 74.00, 69.70, 67.50, 61.30, 55.90, 38.90, 27.90, 27.50, 20.60, 20.50, 20.49, 20.47. FAB/MS (*m*/*e*): 689 $[M+H]^+$. Anal. Calcd for $C_{29}H_{40}O_{15}N_2S$: C, 50.58; H, 5.85; N, 4.07. Found: C, 50.39; H, 5.73; N, 4.19.

4.2.8.2. Anomers of *N*-(2,3,5-tri-*O*-acetyl-L-arabinofuranos-1-yl)-*N*-(2-nitrobenzenesulfonyl)-*S*-*t*-butyl-L-cysteine *t*-butylester 2b-α and 2b-β. Using the general procedure for preparing α- and β-anomers of **2a–f** from 418 mg (1.0 mmol) of *N*-(2-nitrobenzenesulfonyl)-*S*-*t*-butyl-L-cysteine *t*-butylester, 548 mg (81%) of **2b-α** and 61 mg (9%) of **2b-β** were obtained as colorless powder.

Compound **2b-α**: Mp 66–67 °C, $[\alpha]_D^{25} = +50$ (*c* 1.1, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 8.26(d, *J* = 8.0 Hz, 1H), 7.69 (m, *J* = 7.6 Hz, 2H), 7.55 (d, *J* = 7.5 Hz, 1H), 5.26 (s, 1H), 5.04 (dd, *J* = 11.5 Hz, *J* = 3.5 Hz, 1H), 4.93 (m, *J* = 11.3 Hz, 2H), 4.43 (m, *J* = 10.6 Hz, 1H), 4.01 (d, *J* = 15.0 Hz, 1H), 3.65 (d, *J* = 10.0 Hz, 1H), 3.10 (t, *J* = 10.0 Hz, 1H), 2.76 (s, 1H), 2.11 (s, 9H), 1.23 (s, 9H), 1.34 (s, 9H). ^{13}C NMR (500 MHz,$CDCl_3$): δ = 170.3, 170.0, 168.6, 167.6, 148.8, 133.7, 132.9, 131.8, 131.0, 123.4, 85.3, 82.4, 72.2, 68.2, 67.8, 66.0, 60.0, 66.4, 42.9, 30.7, 27.4, 27.3, 21.8, 20.8, 20.7, 20.6, 20.5. FAB/MS (*m*/*e*): 677 $[M+H]^+$. Anal. Calcd for $C_{28}H_{40}O_{13}N_2S_2$: C, 49.69; H, 5.96; N, 4.14. Found: C, 49.81; H, 5.83; N, 4.02.

Compound **2b-β**: Mp 70–71 °C, $[\alpha]_D^{25} = +10$ (*c* 1.1, $CHCl_3$). ^1H NMR (500 MHz,$CDCl_3$): δ = 8.22 (m, *J* = 7.6 Hz, 1H), 7.74 (m, *J* = 7.2 Hz, 1H), 7.58 (m, *J* = 7.3 Hz, 2H), 5.55 (s, 1H), 5.32 (t, *J* = 7.0 Hz, 1H), 5.08 (m, *J* = 10.8 Hz, 1H), 4.83 (d, *J* = 3.5 Hz, 1H), 4.70 (dd, *J* = 8.8 Hz, *J* = 4.5 Hz, 1H), 3.94 (m, *J* = 3.8 Hz, 1H), 3.93 (d, *J* = 3.5 Hz, 1H), 3.45 (m, *J* = 9.2 Hz, 1H), 2.76 (dd, *J* = 15.0 Hz, *J* = 4.5 Hz, 1H), 2.10 (s, 9H), 1.31 (s, 9H),1.47 (s, 9H). ^{13}C NMR (500 MHz, $CDCl_3$): δ = 169.7, 169.2, 168.8, 168.3, 148.8, 134.3, 132.3, 131.9, 131.4, 123.5, 80.7, 83.3, 70.7, 66.5, 63.9, 61.8, 66.4, 42.6, 30.7, 30.4, 27.6, 21, 20. FAB/MS (*m*/*e*): 677 $[M+H]^+$. Anal. Calcd for $C_{28}H_{40}O_{13}N_2S_2$: C, 49.69; H, 5.96; N, 4.14. Found: C, 49.56; H, 6.01; N, 4.34.

4.2.8.3. Anomers of *N*-(2,3,5-tri-*O*-acetyl-α-L-arabinofuranos-1-yl)-*N*-(2-nitrobenzenesulfonyl)-L-glutamic acid di-t-butylester 2c-α and 2c-β. Using the general procedure for preparing α and β anomers of **2a–f** from 70 mg (1.0 mmol) of *N*-(2-nitrobenzenesulfonyl)-L-glutamic acid di-*t*-butylester, 597 mg (85%) of **2c-α** and 159 mg (10%) of **2c-β** were obtained as colorless powder.

Compound **2c-α**: Mp 73–75 °C, $[\alpha]_D^{25} = +45.0$ (*c* 1.2, $CHCl_3$), ^1H NMR (500 MHz,$CDCl_3$): δ = 8.24 (d, *J* = 8.0 Hz, 1H), 7.65 (m, *J* = 7.5 Hz, 2H), 7.52 (d, *J* = 7.5 Hz, 1H), 6.03 (s, 1H), 5.23 (s, 1H), 5.00 (dd, *J* = 9.5 Hz, *J* = 3.5 Hz, 1H), 4.79 (s, 1H), 4.48 (t, *J* = 15.0 Hz, 1H), 3.96 (dd, *J* = 13.5 Hz, *J* = 1.5 Hz, 1H), 3.59 (d, *J* = 13.0 Hz, 1H), 2.35 (m, *J* = 9.5 Hz, 2H), 2.10 (m, *J* = 8.9 Hz, 2H), 2.01 (s, 9H),1.19 (s, 9H) ,1.44 (s, 9H). ^{13}C NMR (500 MHz, $CDCl_3$): δ = 171.4, 170.0, 169.6, 169.1, 168.1, 148.6, 133.8, 133.2, 132.0, 131.2, 123.5, 85.1, 82.3, 81.5, 74.0, 72.3, 69.7, 67.5, 60.3, 39.2, 28.0, 27.5, 20.7, 20.6, 20.5, 20.4. FAB/MS (*m*/*e*): 703 $[M+H]^+$. Anal. Calcd for $C_{30}H_{42}O_{15}N_2S$: C, 51.28; H, 6.02; N, 3.99. Found: C, 51.19; H, 5.98; N, 4.01.

Compound **2c-β**: Mp 71–73 °C, $[\alpha]_D^{25} = 15.0$ (*c* 1.2, $CHCl_3$), ^1H NMR (500 MHz,$CDCl_3$): δ = 8.08 (m, *J* = 7.8 Hz, 1H), 7.71 (m, *J* = 7.7 Hz, 2H), 7.54 (m, *J* = 7.6 Hz, 1H), 5.5 (d, *J* = 1.5 Hz, 1H), 5.36 (s, 1H), 5.00 (m, *J* = 8.8 Hz, 1H), 4.92 (s, 1H), 4.62 (m, *J* = 9.0 Hz, 1H), 3.88 (m, *J* = 10.2 Hz, 2H), 2.45 (m, *J* = 8.7 Hz, 2H), 2.23 (m, *J* = 8.6 Hz, 2H), 1.96 (s, 9H), 1.42 (s, 18H). ^{13}C NMR (500 MHz, $CDCl_3$): δ = 171.1, 170.2, 170.0, 169.0, 168.5, 148.7, 134.0, 132.6, 131.9, 131.7, 123.1, 84.3, 82.1, 80.5, 73.2, 70.1, 68.5, 67.1, 61.0, 31.4, 27.80, 27.3, 27.1, 20.5, 20.4, 20.3. FAB/MS (*m*/*e*): 703 $[M+H]^+$. Anal. Calcd for $C_{30}H_{42}O_{15}N_2S$: C, 51.28; H, 6.02; N, 3.99. Found: C, 51.19; H, 6.01; N, 4.01.

4.2.8.4. Anomers of *N*-(2,3,5-tri-*O*-acetyl-L-arabinofuranos-1-yl)-*N*-(2-nitrobenzenesulfonyl)-L-*O*-t-butylserine-*t*-butylester 2d-α and 2d-β. Using the general procedure for preparing α- and β-anomers of **2a–f** from 402 mg (1.0 mmol) of *N*-(2-nitrobenzenesulfonyl)-*O*-*t*-butyl-L-serine *t*-butyl ester, 508 mg (77%) of **2d-α** and 66 mg (10%) of **2d-β** were obtained as colorless powder.

Compound **2d-α**: Mp 61–63 °C, $[\alpha]_D^{25} = +82.2$ (*c* 1.1, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ = 8.31 (d, *J* = 10 Hz, 1H), 7.64 (m, *J* = 8.7 Hz, 2H), 7.51 (d, *J* = 9.0 Hz,1H), 5.95 (s, 1H), 5.25 (s, 1H), 5.20 (d, *J* = 5.0 Hz, 1H), 4.99 (dd, *J* = 9.5 Hz, *J* = 3.5 Hz, 1H), 4.50 (m, *J* = 8.8 Hz, 1H), 4.02 (dd, *J* = 10.5 Hz, *J* = 1.0 Hz, 1H), 3.76 (m, *J* = 9.5 Hz, 2H), 3.64 (d, *J* = 14.5 Hz, 1H), 2.03 (s, 3H), 2.19 (s, 3H), 1.99 (s, 3H), 1.25 (s, 9H), 1.17 (s, 9H). ^{13}C NMR (500 MHz, $CDCl_3$): δ = 170.4, 170.1, 168.6, 167.7, 148.5, 133.5, 132.3, 131.1, 123.2, 81.7, 73.7, 86.6, 72.2, 68.5, 68.2, 67, 62.0, 60.6, 27.5, 27.2, 21.0, 20.8, 20.6. FAB/MS (*m*/*e*): 661 $[M+H]^+$. Anal. Calcd for $C_{28}H_{40}O_{14}N_2S$: C, 50.90; H, 6.10; N, 4.24. Found: C, 50.72; H, 6.21; N, 4.16.

Compound **2d-β**: Mp 58–62 °C, $[\alpha]_D^{25} = +7.0$ (*c* 1.2, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 8.51 (d, *J* = 7.5 Hz, 1H), 7.70 (m, *J* = 7.0 Hz, 2H), 7.65 (d, *J* = 6.8 Hz, 1H), 5.38 (m, (d, *J* = 5.2 Hz, 1H), 5.35 (s, 1H), 5.14 (m, *J* = 5.2 Hz, 1H), 4.98 (d, *J* = 4.0 Hz, 1H), 4.66 (m, *J* = 7.8 Hz, 1H), 4.04 (dd, *J* = 10.0 Hz, *J* = 5.0 Hz, 1H), 3.96 (dd, *J* = 10.8 Hz, *J* = 5.5 Hz, 1H), 3.74 (m, *J* = 8.2 Hz, 2H), 1.99 (s, 9H), 1.15 (s, 9H), 1.45 (s, 9H). $^{13}CNMR$ (500 MHz, $CDCl_3$): δ = 169.6, 168.9, 168.7, 168.6, 133.6, 131.8, 130.8, 124, 123.1, 81.3, 73.5, 83.3, 70.8, 66.4, 61.3, 64.0, 64.2, 61.4, 27.6, 27.4, 21.8, 21.1, 20.7, 20.6. FAB/MS (*m*/*e*): 661 $[M+H]^+$. Anal. Calcd for $C_{31}H_{44}O_{16}N_2S$: C, 50.90; H, 6.10; N, 4.24. Found: C, 50.70; H, 6.19; N, 4.16.

4.2.8.5. Anomers of *N*-(2,3,5-tri-*O*-acetyl-α-L-arabinofuranos-1-yl)-*N*-(2-nitrobenzenesulfonyl)-L-phenylalanine *t*-butylester 2e-α and 2e-β. Using the general procedure for preparing α- and β-anomers of **2a–f** from 406 mg (1.0 mmol) of *N*-(2-nitrobenzenesulfonyl)-L-phenylalanine *t*-butylester, 574 mg (81%) of **2e-α** and 66 mg (9%) of **2e-β** were obtained as colorless powder.

Compound **2e-α**: Mp 75–77 °C, $[\alpha]_D^{25} = +14.8$ (*c* 1.0, $CHCl_3$), ^1H NMR (500 MHz,$CDCl_3$): δ = 8.29 (dd, *J* = 4.2 Hz, *J* = 1.5 Hz, 1H), 7.55(d, *J* = 9.0 Hz, 1H), 7.67 (m, *J* = 8.7 Hz, 2H), 7.29 (t, *J* = 7.0 Hz, 1H), 7.28 (d, *J* = 7.2 Hz, 2H), 7.21 (t, *J* = 7.0 Hz, 2H), 6.01 (s, 1H), 5.30 (s, 1H), 5.11 (dd, *J* = 10.0 Hz, *J* = 3.5 Hz, 2H), 4.57 (m, *J* = 7.2 Hz, 1H), 4.04 (dd, *J* = 10.0 Hz, *J* = 2.0 Hz, 1H), 3.70 (d, *J* = 13.0 Hz, 1H), 3.23 (m, *J* = 7.8 Hz, 1H), 3.04 (m, *J* = 7.6 Hz, 1H), 2.10 (s, 9H), 1.26 (s, 9H). ^{13}C NMR (500 MHz, $CDCl_3$): δ = 170.2, 169.9, 168.7, 167.9, 148,8, 133.8, 131.5, 131.3, 131.2, 129.4, 129.0, 128.2, 126.7, 123.3, 81.6, 85.2, 72.0, 68.1, 67.5, 60.7, 66.2, 38.5, 27.1, 26.9, 21.6, 20.7, 20.5, 20.4. FAB/MS (*m*/*e*): 665 $[M+H]^+$. Anal. Calcd for $C_{30}H_{36}O_{13}N_2S$: C, 54.21; H, 5.46; N, 4.21. Found: C, 54.18; H, 5.28; N, 4.33.

Compound **2e-β**: Mp 68–70 °C, $[\alpha]_D^{25} = +44.4$ (*c* 1.1, $CHCl_3$), ^1H NMR (500 MHz, $CDCl_3$): δ = 8.17 (d, *J* = 8.0 Hz, 1H), 7.67 (m, *J* = 7.3 Hz, 2H), 7.59 (d, *J* = 7.5 Hz, 1H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.32 (d, *J* = 7.0 Hz, 2H), 7.30 (t, *J* = 7.2 Hz, 2H), 5.63 (s, 1H), 5.35 (t, *J* = 9.4 Hz, 1H), 5.20 (m, *J* = 8.6 Hz, 1H), 4.91 (m, *J* = 7.2 Hz, 2H), 3.97 (m, *J* = 7.1 Hz, 2H), 3.59 (dd, *J* = 13.5 Hz, *J* = 10.0 Hz, 1H), 3.13 (d, *J* = 13.5 Hz, 1H), 1.99 (s, 3H), 2.17 (s, 6H), 1.39 (s, 9H). ^{13}C NMR (500 MHz, $CDCl_3$): δ = 169.7, 169.2, 168.9, 168.3, 148.7, 139.3, 134.3, 132.3, 131.8, 131.2, 128.9, 128.1, 126.2, 123.4, 81.0, 82.7, 70.7, 66.4, 64.1, 64.0, 61.4, 39.2, 27.5, 20.5, 20.8. FAB/MS (*m*/*e*): 665 $[M+H]^+$. Anal. Calcd for $C_{30}H_{36}O_{13}N_2S$: C, 54.21; H, 5.46; N, 4.21. Found: C, 54.19; H, 5.38; N, 4.16.

4.2.8.6. Anomers of *N*-(2,3,5-tri-*O*-acetyl-α-L-arabinofuranos-1-yl)-*N*-(2-nitrobenzenesulfonyl)-L-*O*-*t*-butyltheorine *t*-butylester 2f-α and 2f-β. Using the general procedure for preparing α- and β-anomers of **2a–f** from 416 mg (1.0 mmol) of *N*-(2-nitro-

benzenesulfonyl)-L-*O*-*t*-butyl-theorine *t*-butylester, 519 mg (77%) of **2f-α** and 68 mg (10%) of **2f-β** were obtained as colorless powder.

Compound **2f-α**: Mp 77–79 °C, $[\alpha]_D^{25} = +6.0$ (*c* 1.0, $CHCl_3$), ^1H NMR (500 MHz, $CDCl_3$): δ = 8.38 (m, *J* = 8.0 Hz, 1H), 7.64 (m, *J* = 7.6 Hz, 2H), 7.54 (m, *J* = 7.3 Hz, 1H), 5.23 (d, *J* = 2.7 Hz, 1H), 4.92 (dd, *J* = 10.2 Hz, *J* = 3.3 Hz, 1H), 4.50 (d, *J* = 3.0 Hz, 1H), 4.33 (m, *J* = 8.2 Hz, 1H), 3.84 (d, *J* = 13.2 Hz, 2H), 3.62 (m, *J* = 9.6 Hz, 1H), 3.59 (m, *J* = 13.5 Hz, 1H), 2.21 (s, 9H), 2.09 (s, 9H), 1.74 (d, *J* = 6.0 Hz, 3H), 1.30 (s, 9H). ^{13}C NMR (500 MHz, $CDCl_3$): δ = 170.4, 170.1, 168.6, 167.3, 148.6, 134.6, 133.4, 132.8, 131.1, 123.4, 81.7, 74.1, 87.4, 73.2, 69.4, 65.2, 68.9, 67.1, 68.7, 31.6, 28.7, 27.8, 21.1, 21.0, 20.6, 19.4. FAB/MS (*m*/*e*): 675 $[M+H]^+$. Anal. Calcd for $C_{30}H_{36}O_{13}N_2S$: C, 51.62; H, 6.27; N, 4.15. Found: C, 51.59; H, 6.15; N, 4.21.

Compound **2f-β**: Mp 73–75 °C, $[\alpha]_D^{25} = +64.0$ (*c* 1.0, $CHCl_3$), ^1H NMR (300 MHz,$CDCl_3$): δ = 8.28 (m, *J* = 7.1 Hz, 1H), 7.72 (m, *J* = 6.9 Hz, 2H), 7.56 (m, *J* = 6.7 Hz, 1H), 5.27 (dd, *J* = 14.4 Hz, *J* = 5.0 Hz, 1H), 5.14 (d, *J* = 3.0 Hz, 1H), 4.50 (t, *J* = 16.2 Hz, 1H), 4.28 (m, *J* = 7.8 Hz, 1H), 3.97 (d, *J* = 8.1 Hz, 2H), 3.66 (m, *J* = 9.4 Hz, 1H), 3.61 (m, *J* = 12.5 Hz, 1H), 1.80 (d, *J* = 6.6 Hz, 3H), 2.13 (s, 9H), 2.02 (s, 9H), 1.37 (s, 9H). ^{13}C NMR (300 MHz, $CDCl_3$): δ = 169.7, 169.5, 168.8, 168.1, 148.0, 134.6, 133.4, 132.8, 131.0, 123.4, 81.7, 83.6, 74.4, 71.7, 70.1, 68.5, 67.0, 63.9, 64.6, 34.4, 29.1, 27.8, 21.6, 21.1, 21.0, 19.4. FAB/MS (*m*/*e*): 675 $[M+H]^+$. Anal. Calcd for $C_{30}H_{36}O_{13}N_2S$: C, 51.62; H, 6.27; N, 4.15. Found: C, 51.65; H, 6.33; N, 4.21.

4.2.9. General procedure for preparing α- and β-anomers of *N*-(2,3,5-tri-*O*-acetyl-L-arabinofuranos-1-yl)-*N*-(2-nitrobenzenesulfonyl)-L-amino acid (3a–f)

The solution of 1.0 mmol of epimerically pure *N*-(2,3,5-tri-*O*-acetyl-L-arabino-furanos-1-yl)-*N*-(2-nitrophenylsulfonyl)-L-amino acid *t*-butyl ester **2a–f-α** or **2a–f-β** and 5.5 ml of CF_3CO_2H was vigorously stirred at room temperature for 3 h, and TLC analysis (petroleum ether:ethyl acetate:glacial acetic acid, 2:1:0.2) indicated complete disappearance of **2a–f-α** or **2a–f-β**. The reaction mixture was evaporated under vacuum to remove the CF_3CO_2H. The residue was dissolved in acetone and evaporated under vacuum, which was repeated three times to remove the trace CF_3CO_2H. The residue was purified by chromatography (petroleum ether:ethyl acetate:glacial acetic acid, 1:1:0.2) to provide the corresponding **3a–f-α** or **3a–f-β**.

4.2.9.1. *N*-(2,3,5-Tri-*O*-acetyl-α-L-arabinofuranos-1-yl)-*N*-(2-nitrophenylsulfonyl)-L-aspartic acid 3a-α.

Using the general procedure for preparing α- and β-anomers of **3a–f** from 688 mg (1.0 mmol) of *N*-(2,3,5-tri-*O*-acetyl-α-D-arabinofuranos-1-yl)-*N*-(2-nitrobenzenesulfonyl)-L-aspartic acid di-*t*-butylester **2a-α**, 0.489 g (90%) of **3a-α** was obtained as colorless powder. Mp 110–113 °C, $[\alpha]_D^{25} = +25.3$ (*c* 1.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 8.72(s, 2H), 8.24 (d, *J* = 9.5 Hz, 1H), 7.69 (m, *J* = 8.6 Hz, 2H), 7.59 (m, *J* = 8.7 Hz, 1H), 5.23 (t, *J* = 6.5 Hz, 1H), 5.03 (dd, *J* = 10.0 Hz, *J* = 3.5 Hz, 1H), 4.94 (q, *J* = 13.5 Hz, 1H), 4.04 (dd, *J* = 13.0 Hz, *J* = 3.0 Hz, 1H), 3.69(d, *J* = 13.5 Hz, 1H), 3.03 (m, *J* = 4.9 Hz, 1H), 2.75 (dd, *J* = 15.0 Hz, *J* = 4.5 Hz, 1H), 2.20 (s, 3H), 2.17 (s, 3H), 2.14 (m, *J* = 5.9 Hz, 2H), 2.00 (s, 3H). FAB/MS (*m*/*e*): 577 $[M+H]^+$. Anal. Calcd for $C_{21}H_{24}O_{15}N_2S$: C, 43.75; H, 4.20; N, 4.86. Found: C, 43.68; H, 4.15 N, 4.69.

4.2.9.2. *N*-(2,3,5-Tri-*O*-acetyl-β-L-arabinofuranos-1-yl)-*N*-(2-nitrophenylsulfonyl)-L-aspartic acid 3a-β.

Using the general procedure for preparing α- and β-anomers of **3a–f** from 688 mg (1.0 mmol) of *N*-(2,3,5-tri-*O*-acetyl-β-D-arabinofuranos-1-yl)-*N*-(2-nitrobenzenesulfonyl)-L-aspartic acid di-*t*-butylester **2a-β**, 0.465 g (85%) of **3a-β** was obtained as colorless powder. Mp 125–128 °C, $[\alpha]_D^{25} = +5.8$ (*c* 1.1, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 8.59 (s, 2H,), 8.18 (d, *J* = 9.2 Hz, 1H), 7.48 (m, *J* = 8.2 Hz, 2H), 7.31 (m, *J* = 8.4 Hz, 1H), 5.20 (t, *J* = 6.3 Hz, 1H), 5.00 (dd, *J* = 10.0 Hz, *J* = 3.3 Hz, 1H), 4.86 (q, *J* = 13.2 Hz, 1H), 3.97 (dd, *J* = 13.0 Hz, *J* = 3.2 Hz, 1H), 3.70 (d, *J* = 13.2 Hz, 1H), 3.12 (m, *J* = 4.9 Hz, 1H), 2.72 (dd, *J* = 15.0 Hz, *J* = 4.3 Hz, 1H), 2.22 (s, 3H), 2.19 (s, 3H), 2.12 (m, *J* = 5.7 Hz, 2H), 2.02 (s, 3H). FAB/MS (*m*/*e*): 577 $[M+H]^+$. Anal. Calcd for $C_{21}H_{24}O_{15}N_2S$: C, 43.75; H, 4.20; N, 4.86. Found: C, 43.82; H, 4.30; N, 4.99.

4.2.9.3. *N*-(2,3,5-Tri-*O*-acetyl-α-L-arabinofuranos-1-yl)-*N*-(2-nitrobenzenesulfonyl)-S-t-butyl-L-cysteine 3b-α.

Using the general procedure for preparing α- and β-anomers of **3a–f** from 676 mg (1.0 mmol) of *N*-(2,3,5-tri-*O*-acetyl-α-L-arabinofuranos-1-yl)-*N*-(2-nitrobenzenesulfonyl)-*S*-*t*-butyl-L-cysteine *t*-butylester **2b-α**, 539 mg (87%) of **3b-α** was obtained as colorless powder. Mp 117–120 °C, $[\alpha]_D^{25} = +101.0$ (*c* 1.2, $CHCl_3$). ^1H NMR (500 MHz,$CDCl_3$): δ = 8.79 (s, 1H), 8.26 (d, *J* = 8.0 Hz, 1H), 7.70 (m, *J* = 7.5 Hz, 2H), 7.55 (d, *J* = 7.5 Hz, 1H), 5.26 (s , 1H), 5.00 (dd, *J* = 11.5 Hz, *J* = 3.5 Hz, 1H), 4.93 (m, *J* = 11.0 Hz, 2H), 4.43 (m, *J* = 10.2 Hz, 1H), 4.01 (d, *J* = 15.0 Hz, 1H), 3.65 (d, *J* = 10.0 Hz, 1H), 3.10 (t, *J* = 10.0 Hz, 1H), 2.76 (s, 1H), 2.12 (s, 9H), 1.34 (s, 9H); FAB/MS (*m*/*e*): 621 $[M+H]^+$. Anal. Calcd for $C_{24}H_{32}O_{13}N_2S_2$: C, 46.45; H, 5.20; N, 4.51. Found: C, 46.51; H, 5.07; N, 4.39.

4.2.9.4. *N*-(2,3,5-Tri-*O*-acetyl-β-L-arabinofuranos-1-yl)-*N*-[2-nitrobenzenesulfonyl]-S-t-butyl-L-cysteine 3b-β.

Using the general procedure for preparing α- and β-anomers of **3a–f** from 676 mg (1.0 mmol) of *N*-(2,3,5-tri-*O*-acetyl-β-L-arabinofuranos-1-yl)-*N*-(2-nitrobenzenesulfonyl)-*S*-*t*-butyl-L-cysteine *t*-butylester **2b-β**, 558 mg (90%) of **3b-β** was obtained as colorless powder. Mp 102–104 °C, $[\alpha]_D^{25} = +48.0$ (*c* 1.3, $CHCl_3$). ^1H NMR (500 MHz,$CDCl_3$): δ = 8.60 (s, 1H), 8.20 (d, *J* = 8.1 Hz, 1H), 7.55 (m, *J* = 7.3 Hz, 2H), 7.42 (d, *J* = 7.3 Hz, 1H), 5.17 (s , 1H), 4.89 (dd, *J* = 11.2 Hz, *J* = 3.3 Hz, 1H), 4.78 (m, *J* = 11.2 Hz, 2H), 4.36 (m, *J* = 10.0 Hz, 1H), 3.92 (d, *J* = 15.1 Hz, 1H), 3.90 (d, *J* = 10.2 Hz, 1H), 3.01 (t, *J* = 10.2 Hz, 1H), 2.70 (s, 1H), 2.10 (s, 9H), 1.32 (s, 9H); FAB/MS (*m*/*e*): 621 $[M+H]^+$. Anal. Calcd for $C_{24}H_{32}O_{13}N_2S_2$: C, 46.45; H, 5.20; N, 4.51. Found: C, 46.34; H, 5.31; N, 4.42.

4.2.9.5. *N*-(2,3,5-Tri-*O*-acetyl-α-L-arabinofuranos-1-yl)-*N*-(2-nitrobenzenesulfonyl)-L-glutamic acid 3c-α.

Using the general procedure for preparing α- and β-anomers of **3a–f** from 702 mg (1.0 mmol) of *N*-(2,3,5-tri-*O*-acetyl-α-L-arabinofuranos-1-yl)-*N*-(2-nitrobenzenesulfonyl)-L-glutamic acid di-*t*-butylester **2c-α**, 531 mg (90%) of **3c-α** was obtained as colorless powder. Mp 117–119 °C, $[\alpha]_D^{25} = +94.0$ (*c* 1.1, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 8.97 (s, 2H), 8.24 (d, *J* = 8.0 Hz, 1H), 7.65 (m, *J* = 7.5 Hz, 2H), 7.51 (d, *J* = 7.5 Hz, 1H), 5.97 (s, 1H), 5.13 (s, 1H), 5.00 (dd, *J* = 9.5 Hz, *J* = 3.5 Hz, 1H), 4.70 (s, 1H), 4.41 (t, *J* = 15.0 Hz, 1H), 3.96 (dd, *J* = 13.5 Hz, *J* = 1.5 Hz, 1H), 3.59 (d, *J* = 13.0 Hz, 1H), 2.55 (m, *J* = 9.5 Hz, 2H), 2.10 (m, *J* = 8.9 Hz, 2H), 2.11 (s, 9H). FAB/MS (*m*/*e*): 591 $[M+H]^+$. Anal Calcd for $C_{22}H_{26}O_{15}N_2S$: C, 44.75; H, 4.44; N, 4.74. Found: C, 44.68; H, 4.51; N, 4.79.

4.2.9.6. *N*-(2,3,5-Tri-*O*-acetyl-β-L-arabinofuranos-1-yl)-*N*-(2-nitrobenzenesulfonyl)-L-glutamic acid 3c-β.

Using the general procedure for preparing α- and β-anomers of **3a–f** from 702 mg (1.0 mmol) of *N*-(2,3,5-tri-*O*-acetyl-β-L-arabinofuranos-1-yl)-*N*-(2-nitrobenzenesulfonyl)-L-glutamic acid di-*t*-butylester **2c-β**, 507 mg (86%) of **3c-β** was obtained as colorless powder. Mp 128–130 °C, $[\alpha]_D^{25} = +45.5$ (*c* 1.1, $CHCl_3$), ^1H NMR (500 MHz, $CDCl_3$): δ = 8.69 (s, 2H), 8.06 (d, *J* = 8.2 Hz, 1H), 7.51 (m, *J* = 7.3 Hz, 2H), 7.39 (d, *J* = 7.3 Hz, 1H), 5.88 (s, 1H), 5.02 (s, 1H), 4.87 (dd, *J* = 9.2 Hz, *J* = 3.4 Hz, 1H), 4.66 (s, 1H), 4.22 (t, *J* = 15.1 Hz, 1H), 3.81(dd, *J* = 13.2 Hz, *J* = 1.8 Hz, 1H), 3.46 (d, *J* = 13.2 Hz, 1H), 2.42 (m, *J* = 9.3 Hz, 2H), 2.13 (m, *J* = 8.7 Hz, 2H), 2.14 (s, 9H). FAB/MS

(*m*/*e*): 591 $[M+H]^+$. Anal Calcd for $C_{22}H_{26}O_{15}N_2S$: C, 44.75; H, 4.44; N, 4.74. Found: C, 44.83; H, 4.56; N, 4.60.

4.2.9.7. *N*-(2,3,5-Tri-*O*-acetyl-α-L-arabinofuranos-1-yl)-*N*-(2-nitrobenzenesulfonyl)-L-serine 3d-α. Using the general procedure for preparing α- and β-anomers of **3a–f** from 660 mg (1.0 mmol) of *N*-(2,3,5-tri-*O*-acetyl-α-L-arabinofuranos-1-yl)-*N*-(2-nitrobenzenesulfonyl)-L-*O*-*t*-butyl-serine *t*-butylester **2d-α**, 503 mg (88%) of **3d-α** was obtained as colorless powder. Mp 106–109 °C, $[\alpha]_D^{25} = +83.2$ (*c* 1.2, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): $\delta = 8.89$ (s, 1H), 8.31 (d, $J = 10.0$ Hz, 1H), 7.64 (m, $J = 8.7$ Hz, 2H), 7.51 (d, $J = 9.0$ Hz,1H), 5.95 (s, 1H), 5.25 (s, 1H), 5.20 (d, $J = 5.0$ Hz, 1H), 4.99 (dd, $J = 3.5$ Hz, $J = 9.5$ Hz, 1H), 4.50 (m, $J = 8.8$ Hz, 1H), 4.01 (dd, $J = 10.5$ Hz, $J = 1.0$ Hz, 1H), 3.76 (m, $J = 9.5$ Hz, 2H), 3.64 (d, $J = 14.5$ Hz, 1H), 1.99 (s, 3H), 2.03 (s, 3H), 2.19 (s, 3H). FAB/MS (*m*/*e*): 549 $[M+H]^+$. Anal Calcd for $C_{20}H_{24}O_{14}N_2S$: C, 43.80; H, 4.41; N, 5.11. Found: C, 43.67; H, 4.19; N, 4.89.

4.2.9.8. *N*-(2,3,5-Tri-*O*-acetyl-β-L-arabinofuranos-1-yl)-*N*-(2-nitrobenzenesulfonyl)-L-serine 3d-β. Using the general procedure for preparing α- and β-anomers of **3a–f** from 660 mg (1.0 mmol) of *N*-(2,3,5-tri-*O*-acetyl-β-L-arabinofuranos-1-yl)-*N*-(2-nitrobenzenesulfonyl)-L-*O*-*t*-butyl-serine *t*-butylester **2d-β**, 466 mg (85%) of **3d-β** was obtained as colorless powder. Mp 112–114 °C, $[\alpha]_D^{25} = +40.9$ (*c* 1.1, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): $\delta = 8.66$ (s, 1H), 8.20 (d, $J = 10.1$ Hz, 1H), 7.52 (m, $J = 8.5$ Hz, 2H), 7.38 (d, $J = 8.8$ Hz,1H), 5.85 (s, 1H), 5.11 (s, 1H), 5.00 (d, $J = 5.2$ Hz, 1H), 4.76 (dd, $J = 3.6$ Hz, $J = 9.5$ Hz, 1H), 4.34 (m, $J = 8.6$ Hz, 1H), 4.24 (dd, $J = 10.2$ Hz, $J = 1.0$ Hz, 1H), 3.62 (m, $J = 9.4$ Hz, 2H), 3.53 (d, $J = 14.0$ Hz, 1H), 2.18 (s, 3H), 2.08 (s, 3H), 2.01 (s, 3H). FAB/MS (*m*/*e*): 549 $[M+H]^+$. Anal. Calcd for $C_{20}H_{24}O_{14}N_2S$: C. 43.80; H. 4.41; N. 5.11. Found: C, 43.93; H, 4.58; N, 5.25.

4.2.9.9. *N*-(2,3,5-Tri-*O*-acetyl-α-L-arabinofurano-1-syl)-*N*-(2-nitrobenzenesulfonyl)-L-phenylalanine 3e-α. Using the general procedure for preparing α- and β-anomers of **3a–f** from 664 mg (1.0 mmol) of *N*-(2,3,5-tri-*O*-acetyl-α-L-arabinofuranos-1-yl)-*N*-(2-nitrobenzenesulfonyl)-L-phenylalanine *t*-butylester **2e-α**, 565 mg (93%) of **3e-α** was obtained as colorless powder. Mp 117–119 °C, $[\alpha]_D^{25} = +85.2$ (*c* 1.1, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): $\delta = 8.69$ (s, 1H), 8.29 (dd, $J = 1.5$ Hz, $J = 4.2$ Hz, 1H), 7.70 (m, $J = 7.2$ Hz, 2H), 7.55 (d, $J = 7.6$ Hz, 1H), 7.31 (t, $J = 7.0$ Hz, 1H), 7.29 (d, $J = 7.2$ Hz, 2H), 7.22 (t, $J = 7.0$ Hz, 2H), 5.99 (s, 1H), 5.29 (s, 1H), 5.11 (dd, $J = 10.0$ Hz, $J = 3.5$ Hz, 2H), 4.54 (m, $J = 7.0$ Hz, 1H), 4.04 (dd, $J = 10.0$ Hz, $J = 2.0$ Hz, 1H), 3.70 (d, $J = 13.0$ Hz, 1H), 3.23 (m, $J = 7.8$ Hz, 1H), 3.04 (m, $J = 7.6$ Hz, 1H), 2.10 (m, 9H). FAB/MS (*m*/*e*): 609 $[M+H]^+$. Anal. Calcd for $C_{26}H_{28}O_{13}N_2S$: C, 51.31; H, 4.64; N, 4.60. Found: C, 51.19; H, 4.51; N, 4.38.

4.2.9.10. *N*-(2,3,5-Tri-*O*-acetyl-β-L-arabinofuranos-1-yl)-*N*-(2-nitrobenzenesulfonyl)-L-phenylalanine 3e-β. Using the general procedure for preparing α- and β-anomers of **3a–f** from 664 mg (1.0 mmol) of *N*-(2,3,5-tri-*O*-acetyl-β-L-arabinofuranos-1-yl)-*N*-(2-nitrobenzenesulfonyl)-L-phenylalanine *t*-butylester **2e-β**, 523 mg (86%) of **3e-β** was obtained as colorless powder. Mp 130–132 °C, $[\alpha]_D^{25} = +50.8$ (*c* 1.1, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): $\delta = 8.51$ (s, 1H), 8.12 (dd, $J = 1.7$ Hz, $J = 4.4$ Hz, 1H), 7.51 (m, $J = 7.0$ Hz, 2H), 7.40 (d, $J = 7.2$ Hz, 1H), 7.24 (t, $J = 7.2$ Hz, 1H), 7.14 (d, $J = 7.0$ Hz, 2H), 7.03 (t, $J = 7.2$ Hz, 2H), 5.80 (s, 1H), 5.12 (s, 1H), 4.97 (dd, $J = 10.1$ Hz, $J = 3.6$ Hz, 2H), 4.39 (m, $J = 7.2$ Hz, 1H), 4.15 (dd, $J = 10.2$ Hz, $J = 2.0$ Hz, 1H), 3.55 (d, $J = 13.0$ Hz, 1H), 3.14 (m, $J = 7.7$ Hz, 1H), 2.94 (m, $J = 7.2$ Hz, 1H), 2.12 (m, 9H). FAB/MS (*m*/*e*): 609 $[M+H]^+$. Anal. Calcd for $C_{26}H_{28}O_{13}N_2S$: C, 51.31; H, 4.64; N, 4.60. Found: C, 51.47; H, 4.59; N, 4.73.

4.2.9.11. *N*-(2,3,5-Tri-*O*-acetyl-α-L-arabinofuranos-1-yl)-*N*-(2-nitrobenzenesulfonyl)-L-threonine 3f-α. Using the general procedure for preparing α- and β-anomers of **3a–f** from 674 mg (1.0 mmol) of *N*-(2,3,5-tri-*O*-acetyl-α-L-arabinofuranos-1-yl)-*N*-(2-nitrobenzenesulfonyl)-L-*O*-*t*-butyl-theonine *t*-butylester **2f-α**, 556 mg (95%) of **3f-α** was obtained as colorless powder. Mp 103–105 °C, $[\alpha]_D^{25} = +67.0$ (*c* 1.2, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): $\delta = 8.65$ (s, 1H), 8.38 (m, $J = 8.0$ Hz, 1H), 7.64 (m, $J = 7.6$ Hz, 2H), 7.54 (m, $J = 7.3$ Hz, 1H), 6.18 (t, $J = 19.5$ Hz, 1H), 5.41 (d, $J = 12.0$ Hz, 1H), 5.34 (d, $J = 2.7$ Hz, 1H), 4.92 (dd, $J = 10.2$ Hz, $J = 3.3$ Hz, 1H), 4.50 (d, $J = 3.0$ Hz, 1H), 4.33 (m, $J = 8.2$ Hz, 1H), 3.84 (d, $J = 13.2$ Hz, 1H), 3.59 (d, $J = 13.5$ Hz, 1H), 2.01 (s, 3H), 2.09 (s, 3H), 2.21 (s, 3H), 1.34 (d, $J = 6.0$ Hz, 3H). FAB/MS (*m*/*e*): 549$[M+H]^+$. Anal. Calcd for $C_{21}H_{26}O_{14}N_2S$: C, 56.93; H, 4.78; N, 5.11. Found: C, 56.78; H, 4.58; N, 5.23.

4.2.9.12. *N*-(2,3,5-Tri-*O*-acetyl-β-L-arabinofuranos-1-yl)-*N*-(2-nitrobenzenesulfonyl)-L-threonine 3f-β. Using the general procedure for preparing α- and β-anomers of **3a–f** from 674 mg (1.0 mmol) of *N*-(2,3,5-tri-*O*-acetyl-β-L-arabinofuranos-1-yl)-*N*-(2-nitrobenzenesulfonyl)-L-*O*-*t*-butyl-threonine *t*-butylester **2f-β**, 482 mg (88%) of **3f-β** was obtained as colorless powder. Mp 115–117 °C, $[\alpha]_D^{25} = +40.3$ (*c* 1.1, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): $\delta = 8.47$ (s, 1H), 8.20 (m, $J = 8.1$ Hz, 1H), 7.52 (m, $J = 7.4$ Hz, 2H), 7.43 (m, $J = 7.2$ Hz, 1H), 6.04 (t, $J = 19.2$ Hz, 1H), 5.25 (d, $J = 12.2$ Hz, 1H), 5.17 (d, $J = 2.9$ Hz, 1H), 4.77 (dd, $J = 10.0$ Hz, $J = 3.5$ Hz, 1H), 4.38 (d, $J = 3.2$ Hz, 1H), 4.27 (m, $J = 8.4$ Hz, 1H), 3.96 (d, $J = 13.0$ Hz, 1H), 3.68 (d, $J = 13.0$ Hz, 1H), 2.24 (s, 3H), 2.04 (s, 3H), 2.12 (s, 3H), 1.32 (d, $J = 6.2$ Hz, 3H). FAB/MS (*m*/*e*): 549 $[M+H]^+$. Anal. Calcd for $C_{21}H_{26}O_{14}N_2S$: C, 56.93; H, 4.78; N, 5.11. Found: C, 56.80; H, 4.89; N, 5.00.

4.2.10. General procedure for preparing α- and β-anomers of *N*-(L-arabinofuranos-1-yl)-*N*-(2-nitrophenylsulfonyl)-L-amino acids 4a–f

The solution of 1.0 mmol of α- and β-anomers of *N*-(2,3,5-tri-*O*-acetyl-L-arabinofuranos-1-yl)-*N*-(2-nitrophenylsulfonyl)-L-amino acid **3a–f** in 20 ml of anhydrous MeOH was treated at 0 °C with CH_3ONa (1.2 equiv, pH 9.5). The reaction mixture was stirred and gradually warmed to room temperature in 5 h and then TLC analysis (chloroform:methanol:water:glacial acetic acid, 3:1:0.15:0.1) indicated complete disappearance of **3a–f**. The reaction mixture was neutralized with Amberlite IRC 50 (H^+ form) and filtered. The filtrate was evaporated under vacuum to produce the corresponding α- and β-anomers of **4a–f**.

4.2.10.1. *N*-(α-L-Arabinofuranos-1-yl)-*N*-(2-nitrobenzenesulfonyl)-L-aspartic acid 4a-α. Using the general procedure for preparing α- and β-anomers of **4a–f** from 576 mg (1.0 mmol) of *N*-(2,3,5-tri-*O*-acetyl-α-L-arabinofuranos-1-yl)-*N*-(2-nitrophenylsulfonyl)-L-aspartic acid (**3a-α**), 432 mg (96%) of **4a-α** was obtained as pale yellow solid. Mp 128–130 °C, $[\alpha]_D^{25} = +97.0$ (*c* 1.1, CH_3OH). ^1H NMR (300 MHz, DMSO-d_6): $\delta = 10.31$ (s, 2H), 8.20 (d, $J = 7.20$ Hz, 1H), 7.86 (m, $J = 7.7$ Hz, 2H), 7.78 (m, $J = 7.9$ Hz, 1H), 4.74 (d, $J = 8.7$ Hz, 1H), 4.52 (m, $J = 8.3$ Hz, 1H), 4.21 (m, $J = 8.5$ Hz, 1H), 4.04 (t, $J = 6.4$ Hz, 1H), 3.92 (dd, $J = 6.3$ Hz, $J = 3.2$ Hz, 1H), 3.55 (d, $J = 12.9$ Hz, 1H), 3.52 (m, $J = 5.9$ Hz, 1H), 2.85 (s, 1H), 2.83 (s, 1H), 2.81 (s, 1H) 2.13 (d, $J = 5.7$ Hz, 2H). FAB/MS (*m*/*e*): 451 $[M+H]^+$. Anal. Calcd for $C_{15}H_{18}O_{12}N_2S$: C, 40.00; H, 4.03; N, 6.22. Found: C, 39.91; H, 3.92; N, 6.19.

4.2.10.2. *N*-(β-L-Arabinofuranos-1-yl)-*N*-(2-nitrobenzenesulfonyl)-L-aspartic acid 4a-β. Using the general procedure for preparing α- and β-anomers of **4a–f** from 576 mg (1.0 mmol) of *N*-(2,3,5-tri-*O*-acetyl-β-L-arabinofuranos-1-yl)-*N*-(2-nitrophenylsulfonyl)-L-aspartic acid **3a-β**, 405 mg (90%) of **4a-β** was obtained as pale

yellow solid. Mp 120–122 °C, $[\alpha]_D^{25} = +51.0$ (*c* 1.2, CH_3OH). ^1H NMR (300 MHz, DMSO-d_6): δ = 10.16 (s, 2H), 8.09 (d, *J* = 7.0 Hz, 1H), 7.71 (m, *J* = 7.5 Hz, 2H), 7.63 (m, *J* = 7.5 Hz, 1H), 4.61 (d, *J* = 8.5 Hz, 1H), 4.41 (m, *J* = 8.2 Hz, 1H), 4.18 (m, *J* = 8.3 Hz, 1H), 4.12 (t, *J* = 6.6 Hz, 1H), 3.80 (dd, *J* = 6.5 Hz, *J* = 3.2 Hz, 1H), 3.41 (d, *J* = 12.2 Hz, 1H), 3.37 (m, *J* = 5.8 Hz, 1H), 2.80 (s, 1H), 2.77 (s, 1H), 2.70 (s, 1H) 2.12 (d, *J* = 5.5 Hz, 2H). FAB/MS (*m*/*e*): 451 $[M+H]^+$. Anal. Calcd for $C_{15}H_{18}O_{12}N_2S$: C, 40.00; H, 4.03; N, 6.22. Found: C, 39.89; H, 4.20; N, 6.39.

4.2.10.3. *N*-(α-L-Arabinofuranos-1-yl)-*N*-(2-nitrobenzenesulfonyl)-*S*-*t*-butyl-L-cysteine 4b-α. Using the general procedure for preparing α- and β-anomers of **4a–f** from 620 mg (1.0 mmol) of *N*-(2,3,5-tri-*O*-acetyl-α-L-arabinofuranos-1-yl)-*N*-(2-nitrobenzenesulfonyl)-*S*-*t*-butyl-L-cysteine (**3b-α**), 459 mg (93%) of **4b-α** was obtained as colorless powder. Mp 127–129 °C, $[\alpha]_D^{25} = +90.0$ (*c* 1.2, CH_3OH). ^1H NMR (300 MHz, DMSO-d_6): δ = 10.01 (s, 1H), 8.26 (d, *J* = 7.2 Hz, 1H), 7.78 (m, *J* = 7.3 Hz, 2H), 7.65 (m, *J* = 7.3 Hz, 1H), 4.69 (d, *J* = 9.0 Hz, 1H), 4.56 (m, *J* = 6.7 Hz, 1H), 4.29 (m, *J* = 5.6 Hz, 1H), 4.11 (m, *J* = 7.6 Hz, 1H), 3.68 (d, *J* = 5.8 Hz, 2H), 3.41 (d, *J* = 11.2 Hz, 2H), 3.36 (m, *J* = 5.7 Hz, 1H), 2.86 (s, 1H), 2.84 (s, 1H), 2.82 (s, 1H), 1.69 (s, 9H). FAB/MS (*m*/*e*): 495 $[M+H]^+$. Anal. Calcd for $C_{18}H_{26}O_{10}N_2S_2$: C, 43.72; H, 5.30; N, 5.66. Found: C, 43.61; H, 5.19; N, 5.78.

4.2.10.4. *N*-(β-L-Arabinofuranos-1-yl)-*N*-(2-nitrobenzenesulfonyl)-*S*-*t*-butyl-L-cysteine 4b-β. Using the general procedure for preparing α- and β-anomers of **4a–f** from 620 mg (1.0 mmol) of *N*-(2,3,5-tri-*O*-acetyl-β-L-arabinofuranos-1-yl)-*N*-(2-nitrobenzenesulfonyl)-*S*-*t*-butyl-L-cysteine (**3b-β**), 435 mg (88%) of **4b-β** was obtained as colorless powder. Mp 120–122 °C, $[\alpha]_D^{25} = +44.6$ (*c* 1.1, CH_3OH). ^1H NMR (300 MHz, DMSO-d_6): δ = 9.95 (s, 1H), 8.12 (d, *J* = 7.4 Hz, 1H), 7.64 (m, *J* = 7.2 Hz, 2H), 7.42 (m, *J* = 7.2 Hz, 1H), 4.53 (d, *J* = 9.2 Hz, 1H), 4.38 (m, *J* = 6.5 Hz, 1H), 4.22 (m, *J* = 5.8 Hz, 1H), 4.18 (m, *J* = 7.6 Hz, 1H), 3.52 (d, *J* = 5.9 Hz, 2H), 3.38 (d, *J* = 11.0 Hz, 2H), 3.28 (m, *J* = 5.7 Hz, 1H), 2.80 (s, 1H), 2.77 (s, 1H), 2.70 (s, 1H), 1.66 (s, 9H). FAB/MS (*m*/*e*): 495 $[M+H]^+$. Anal. Calcd for $C_{18}H_{26}O_{10}N_2S_2$: C, 43.72; H, 5.30; N, 5.66. Found: C, 41.84; H, 5.21; N, 5.53.

4.2.10.5. *N*-(α-L-Arabinofuranos-1-yl)-*N*-(2-nitrobenzenesulfonyl)-L-glutamic acid 4c-α. Using the general procedure for preparing α- and β-anomers of **4a–f** from 590 mg (1.0 mmol) of *N*-(2,3,5-tri-*O*-acetyl-α-L-arabinofuranos-1-yl)-*N*-(2-nitrobenzenesulfonyl)-L-glutamic acid **3c-α**, 418 mg (90%) of **4c-α** was obtained as colorless powder. Mp 117–119 °C, $[\alpha]_D^{25} = +105.0$ (*c* 1.2, CH_3OH). ^1H NMR (300 MHz, DMSO-d_6): δ = 9.98 (s, 1H), 8.31 (d, *J* = 8.0 Hz, 1H), 7.48 (m, *J* = 7.6 Hz, 2H), 7.38 (d, *J* = 7.5 Hz, 1H), 4.93 (d, *J* = 9.0 Hz, 1H), 4.60 (m, *J* = 6.1 Hz, 1H), 4.71 (m, *J* = 5.8 Hz, 1H), 4.11 (d, *J* = 3.5 Hz, 1H), 3.79 (t, *J* = 10.1 Hz, 2H), 3.01 (m, 2H), 2.88 (s, 1H), 2.85 (s, 1H), 2.83 (s, 1H), 2.54 (t, *J* = 5.2 Hz, 2H), 1.69 (d, *J* = 4.9 Hz, 2H). FAB/MS (*m*/*e*): 465 $[M+H]^+$. Anal. Calcd for $C_{16}H_{20}O_{12}N_2S$: C, 41.38; H, 4.34; N, 6.03. Found: C, 41.55; H, 4.25; N, 5.89.

4.2.10.6. *N*-(β-L-Arabinofuranos-1-yl)-*N*-(2-nitrobenzenesulfonyl)-L-glutamic acid 4c-β. Using the general procedure for preparing α- and β-anomers of **4a–f** from 590 mg (1.0 mmol) of *N*-(2,3,5-tri-*O*-acetyl-β-L-arabinofuranos-1-yl)-*N*-(2-nitrobenzenesulfonyl)-L-glutamic acid **3c-β**, 394 mg (85%) of **4c-β** was obtained as colorless powder. Mp 122–124 °C, $[\alpha]_D^{25} = +60.1$ (*c* 1.2, CH_3OH). ^1H NMR (300 MHz, DMSO-d_6): δ = 9.90 (s, 1H), 8.20 (d, *J* = 8.1 Hz, 1H), 7.35 (m, *J* = 7.4 Hz, 2H), 7.24 (d, *J* = 7.2 Hz, 1H), 4.83 (d, *J* = 9.1 Hz, 1H), 4.48 (m, *J* = 6.2 Hz, 1H), 4.66 (m, *J* = 5.6 Hz, 1H), 4.20 (d, *J* = 3.6 Hz, 1H), 3.60 (t, *J* = 10.0 Hz, 2H), 2.96 (m, 2H), 2.84 (s, 1H), 2.77 (s, 1H), 2.70 (s, 1H), 2.52 (t, *J* = 5.2 Hz, 2H), 1.67 (d, *J* = 4.9 Hz, 2H). FAB/MS (*m*/*e*): 465 $[M+H]^+$. Anal. Calcd for $C_{16}H_{20}O_{12}N_2S$: C, 41.38; H, 4.34; N, 6.03. Found: C, 41.25; H, 4.47; N, 6.16.

4.2.10.7. *N*-(α-L-Arabinofuranos-1-yl)-*N*-(2-nitrobenzenesulfonyl)-L-serine 4d-α. Using the general procedure for preparing α- and β-anomers of **4a–f** from 548 mg (1.0 mmol) of *N*-(2,3,5-tri-*O*-acetyl-α-L-arabinofuranos-1-yl)-*N*-(2-nitrobenzenesulfonyl)-L-serine **3d-α**, 388 mg (92%) of **4d-α** was obtained as colorless powder. Mp 105–108 °C, $[\alpha]_D^{25} = +39.0$ (*c* 1.2, CH_3OH). ^1H NMR (300 MHz, DMSO-d_6): δ = 10.52 (s, 1H), 8.23 (d, *J* = 7.5 Hz, 1H), 7.92 (m, *J* = 7.6 Hz, 2H), 7.78 (d, *J* = 7.4 Hz, 1H), 4.71 (d, *J* = 9.0 Hz, 1H), 4.51 (m, *J* = 5.8 Hz, 1H), 4.48 (m, *J* = 6.3 Hz, 1H), 4.15 (m, *J* = 8.0 Hz, 1H), 3.99 (m, *J* = 10.5 Hz, 2H), 3.72 (d, *J* = 6.3 Hz, 2H), 3.69 (m, *J* = 6.3 Hz, 1H), 2.88 (s, 1H), 2.85 (s, 1H), 2.83 (s, 1H), 2.79 (s, 1H). FAB/MS (*m*/*e*): 423 $[M+H]^+$. Anal. Calcd for $C_{14}H_{18}O_{11}N_2S$: C, 39.81; H, 4.30; N, 6.63. Found: C, 39.61; H, 4.18; N, 6.41.

4.2.10.8. *N*-(β-L-Arabinofuranos-1-yl)-*N*-(2-nitrobenzenesulfonyl)-L-serine 4d-β. Using the general procedure for preparing α- and β-anomers of **4a–f** from 548 mg (1.0 mmol) of *N*-(2,3,5-tri-*O*-acetyl-β-L-arabinofuranos-1-yl)-*N*-(2-nitrobenzenesulfonyl)-L-serine **3d-β**, 359 mg (85%) of **4d-β** was obtained as colorless powder. Mp 121–123 °C, $[\alpha]_D^{25} = +25.2$ (*c* 1.2, CH_3OH). ^1H NMR (300 MHz, DMSO-d_6): δ = 10.33 (s, 1H), 8.09 (d, *J* = 7.2 Hz, 1H), 7.74 (m, *J* = 7.3 Hz, 2H), 7.62 (d, *J* = 7.2 Hz, 1H), 4.55 (d, *J* = 9.2 Hz, 1H), 4.37 (m, *J* = 5.9 Hz, 1H), 4.29 (m, *J* = 6.5 Hz, 1H), 4.22 (m, *J* = 8.41 Hz, 1H), 3.72 (m, *J* = 10.2 Hz, 2H), 3.61 (d, *J* = 6.5 Hz, 2H), 3.41 (m, *J* = 6.5 Hz, 1H), 2.80 (s, 1H), 2.78 (s, 1H), 2.77 (s, 1H), 2.75 (s, 1H). FAB/MS (*m*/*e*): 423 $[M+H]^+$. Anal. Calcd for $C_{14}H_{18}O_{11}N_2S$: C, 39.81; H, 4.30; N, 6.63. Found: C, 39.94; H, 4.44; N, 6.50.

4.2.10.9. *N*-(α-L-Arabinofuranos-1-yl)-*N*-(2-nitrophenylsulfonyl)-L-phenylalanine 4e-α. Using the general procedure for preparing α- and β-anomers of **4a–f** from 608 mg (1.0 mmol) of *N*-(2,3,5-tri-*O*-α-acetyl-L-arabinofuranos-1-yl)-*N*-(2-nitrophenylsulfonyl)-L-phenylalanine **3e-α**, 459 mg (93%) of **4e-α** was obtained as colorless powder. Mp 127–129 °C, $[\alpha]_D^{25} = +90.0$ (*c* 1.1, CH_3OH). ^1H NMR (500 MHz, DMSO-d_6): δ = 10.41 (s, 1H), 8.03 (d, *J* = 7.01 Hz, 1H), 7.65 (d, *J* = 7.6 Hz, 2H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.29 (m, *J* = 8.1 Hz, 1H), 7.21 (m, *J* = 8.2 Hz, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.15 (m, *J* = 7.6 Hz, 1H), 5.09 (d, *J* = 9.0 Hz, 1H), 4.60 (dd, *J* = 5.7 Hz, *J* = 3.4 Hz, 1H), 4.14 (d, *J* = 8.7 Hz, 1H), 4.02 (t, *J* = 6.5 Hz, 1H), 3.79 (d, *J* = 12.9 Hz, 2H), 3.71 (m, *J* = 5.9 Hz, 1H), 2.97 (d, *J* = 6.1 Hz, 2H), 2.89 (s, 1H), 2.87 (s, 1H), 2.80 (s, 1H). FAB/MS (*m*/*e*): 495 $[M+H]^+$. Anal. Calcd for $C_{18}H_{26}O_{10}N_2S_2$: C, 49.79; H, 4.60; N, 5.81. Found: C, 49.81; H, 4.62; N, 5.79.

4.2.10.10. *N*-(β-L-Arabinofuranos-1-yl)-N-(2-nitrophenylsulfonyl)-L-phenyl-alanine 4e-β. Using the general procedure for preparing α- and β-anomers of **4a–f** from 608 mg (1.0 mmol) of *N* -(2,3,5-tri-*O*-β-acetyl-L-arabinofuranos-1-yl)-*N*-(2-nitrophenylsulfonyl)-L-phenylalanine **3e-β**, 395 mg (80%) of **4e-β** was obtained as colorless powder. Mp 121–123 °C, $[\alpha]_D^{25} = +50.1$ (*c* 1.2, CH_3OH). ^1H NMR (500 MHz, DMSO-d_6): δ = 10.02 (s, 1H), 7.95 (d, *J* = 7.0 Hz, 1H), 7.48 (d, *J* = 7.4 Hz, 2H), 7.24 (t, *J* = 7.5 Hz, 2H), 7.17 (m, *J* = 8.0 Hz, 1H), 7.08 (m, *J* = 8.0 Hz, 1H), 7.04 (t, *J* = 7.4 Hz, 1H), 7.00 (m, *J* = 7.4 Hz, 1H), 5.00 (d, *J* = 9.1 Hz, 1H), 4.55 (dd, *J* = 5.5 Hz, *J* = 3.4 Hz, 1H), 4.09 (d, *J* = 8.5 Hz, 1H), 4.07 (t, *J* = 6.6 Hz, 1H), 3.65 (d, *J* = 12.6 Hz, 2H), 3.53 (m, *J* = 5.7 Hz, 1H), 2.84 (d, *J* = 6.0 Hz, 2H), 2.80 (s, 1H), 2.76 (s, 1H), 2.72 (s, 1H). FAB/MS (*m*/*e*): 495 $[M+H]^+$. Anal. Calcd for $C_{18}H_{26}O_{10}N_2S_2$: C, 49.79; H, 4.60; N, 5.81. Found: C, 49.66; H, 4.71; N, 5.95.

4.2.10.11. *N*-(α-L-Arabinofuranos-1-yl)-N-(2-nitrobenzenesulfonyl)-L-theonine 4f-α. Using the general procedure for preparing α- and β-anomers of **4a–f** from 548 mg (1.0 mmol) of *N*-(2,3,5-tri-*O*-acetyl-α-L-arabinofuranos-1-yl)-*N*-(2-nitrobenzene sulfonyl)-L-threonine **3f-α**, 414 mg (95%) of **4f-α** was obtained as colorless powder. Mp 119–120 °C, $[\alpha]_D^{25} = +87.0$ (*c* 1.2, CH_3OH). ^1H NMR (300 MHz, DMSO-d_6): δ = 10.33 (s, 1H), 8.30 (d, *J* = 7.2 Hz, 1H), 7.81 (m, *J* = 7.4 Hz, 2H), 7.77 (d, *J* = 7.5 Hz, 1H), 4.98 (d, *J* = 9.0 Hz, 1H), 4.82 (dd, *J* = 6.5 Hz, *J* = 4.5 Hz, 1H), 4.44 (m, *J* = 5.2 Hz, 1H), 4.28 (m, *J* = 6.2 Hz, 1H), 3.72 (m, *J* = 105 Hz, 2H), 3.68 (m, *J* = 5.7 Hz, 1H), 3.62 (d, *J* = 6.5 Hz, 1H), 2.87 (s, 1H), 2.86 (s, 1H), 2.84 (s, 1H), 2.80 (s, 1H), 1.84 (d, *J* = 4.6 Hz, 3H). FAB/MS (*m*/*e*): 437 $[M+H]^+$. Anal. Calcd for $C_{15}H_{20}O_{11}N_2S$: C, 41.29; H, 4.62; N, 6.42. Found: C, 41.16; H, 4.38; N, 6.28.

4.2.10.12. N-(β-L-Arabinofuranos-1-yl)-N-(2-nitrobenzenesulfonyl)-L-threonine 4f-β. Using the general procedure for preparing α- and β-anomers of **4a–f** from 548 mg (1.0 mmol) of *N*-(2,3,5-tri-*O*-acetyl-β-L-arabinofuranos-1-yl)-*N*-(2-nitrobenzenesulfonyl)-L-threonine **3f-β**, 392 mg (90%) of **4f-β** was obtained as colorless powder. Mp 111–113 °C, $[\alpha]_D^{25} = +50.7$ (*c* 1.2, CH_3OH). ^1H NMR (300 MHz, DMSO-d_6): δ = 10.00 (s, 1H), 8.21 (d, *J* = 7.4 Hz, 1H), 7.77 (m, *J* = 7.2 Hz, 2H), 7.62 (d, *J* = 7.3 Hz, 1H), 4.77 (d, *J* = 9.2 Hz, 1H), 4.64 (dd, *J* = 6.7 Hz, *J* = 4.5 Hz, 1H), 4.30 (m, *J* = 5.4 Hz, 1H), 4.15 (m, *J* = 6.4 Hz, 1H), 3.84 (m, *J* = 10.2 Hz, 2H), 3.60 (m, *J* = 5.5 Hz, 1H), 3.53 (d, *J* = 6.6 Hz, 1H), 2.83 (s, 1H), 2.80 (s, 1H), 2.77 (s, 1H), 2.75 (s, 1H), 1.82 (d, *J* = 4.8 Hz, 3H). FAB/MS (*m*/*e*): 437 $[M+H]^+$. Anal. Calcd for $C_{15}H_{20}O_{11}N_2S$: C, 41.29; H, 4.62; N, 6.42. Found: C, 41.35; H, 4.46; N, 6.63.

4.2.11. General procedure for preparing α- and β-anomers of *N*-(α-L-arabinofuranos-1-yl)-L-amino acid 5a–f

Under argon, the solution of 0.1 mmol of *N*-(L-arabinofuranos-1-yl)-*N*-(2-nitrophenylsulfonyl)-L-amino acid **4a–f**, 0.7 ml (4.0 mmol) of DIPEA, and 0.71 ml (7 mmol) of PhSH in 2 ml of anhydrous DMF was stirred at room temperature for 4–6 h, and TLC analysis (chloroform:methanol:water:glacial acetic acid, 1:1:0.2:0.1) indicated complete disappearance of **4a–f**. The reaction mixture was evaporated under vacuum to remove the DMF. The residue was extracted with water and the water layer was washed with ethyl acetate. The separated water layer was evaporated under vacuum. The resulting residue was purified by Sephadex LH-20 and eluted with ethanol (10%) to give the corresponding epimerically pure **5a–f**.

4.2.11.1. *N*-(α-L-Arabinofuranos-1-yl)-L-aspartic acid 5a-α. Using the general procedure for preparing α- and β-anomers of **5a–f** from 45 mg (0.1 mmol) of *N*-(α-L-arabinofuranos-1-yl)-*N*-(2-nitrophenylsulfonyl)-L-aspartic acid **4a-α**, 18.6 mg (70%) of **5a-α** was obtained as colorless powder. Mp 127–129 °C, $[\alpha]_D^{25} = +7.6$ (*c* 1.1, H_2O). ^1H NMR (500 MHz, D_2O): δ = 4.37 (m, *J* = 5.2 Hz, 1H), 4.14 (d, *J* = 5.0 Hz, 1H), 4.07 (dd, *J* = 12.5 Hz, *J* = 4.5 Hz, 1H), 3.35 (d, *J* = 12.5 Hz, 1H), 3.15 (d, *J* = 12.5 Hz, 1H), 3.82 (m, *J* = 4.9 Hz, 2H), 2.78 (m, *J* = 4.6 Hz, 2H). ^{13}CNMR (500 MHz, D_2O): δ = 177.0, 176.0, 97, 78, 71.8, 72.2, 61.4, 50.3, 36.1. FAB/MS (*m*/*e*): 266 $[M+H]^+$. Anal. Calcd for $C_9H_{15}O_8N$: C, 40.76; H, 5.70; N, 5.28. Found: C, 40.67; H, 5.62; N, 5.11.

4.2.11.2. *N*-(α-L-Arabinofuranos-1-yl)-L-aspartic acid 5a-β. Using the general procedure for preparing α- and β-anomers of **5a–f** from 45 mg (0.1 mmol) of *N*-(β-L-arabinofuranos-1-yl)-*N*-(2-nitrophenylsulfonyl)-L-aspartic acid (**4a-β**), 19.3 mg (73%) of **5a-β** was obtained as a colorless powder. Mp 102–104 °C, $[\alpha]_D^{25} = -20.9$ (*c* 1.1, H_2O). ^1H NMR (500 MHz, D_2O): δ = 4.30 (m, *J* = 5.2 Hz, 1H), 4.09 (d, *J* = 5.0 Hz, 1H), 4.00 (dd, *J* = 12.5 Hz, *J* = 4.5 Hz, 1H), 3.65 (d, *J* = 12.5 Hz, 1H), 3.62 (d, *J* = 12.5 Hz, 1H), 3.55 (m, *J* = 4.9 Hz, 2H), 2.76 (m, *J* = 4.6 Hz, 2H). ^{13}C NMR (500 MHz, D_2O): δ = 175.0, 173.0, 96, 77, 72.0, 71.1, 61.0, 50.0, 35.7. FAB/MS (*m*/*e*): 266 $[M+H]^+$. Anal. Calcd for $C_9H_{15}O_8N$: C, 40.76; H, 5.70; N, 5.28. Found: C, 40.88; H, 5.84; N, 5.40.

4.2.11.3. *N*-(α-L-Arabinofuranos-1-yl)-L-cysteine 5b-α. Under argon the solution of 91 mg (0.27 mmol) of *N*-(α-L-arabinofuranos-1-yl)-*S*-*t*-butyl-L-cysteine and 75 mg (0.4 mmol) of 2-nitrophenylsulfenyl chloride in 2 ml of glacial acetic acid was stirred at room temperature for 2 h, and TLC analysis (chloroform:methanol:water:glacial acetic acid, 1:1:0.2:0.1) indicated complete disappearance of *N*-(α-L-arabinofuranos-1-yl)-*S*-*t*-butyl-L-cysteine. The reaction mixture was evaporated under vacuum and the residue was dissolved in 3 ml of CH_3OH. The formed solution was cooled with ice bath and treated with 20 mg (0.54 mmol) of sodium borohydride. The reaction mixture was stirred at room temperature for 2 h and then evaporated under vacuum to remove the solvent. The residue was dissolved in water, washed with ethyl acetate, and the water phase was evaporated under vacuum. The residue was purified by Sephadex LH-20 and eluted with ethanol (10%). The collected fractions were combined, frozen, and lyophilized to provide 11 mg (43%) of the title compound as colorless powder. Mp 243 °C (decomp.), $[\alpha]_D^{25} = +38.1$ (*c* 1.1, H_2O). ^1H NMR (500 MHz, D_2O): δ = 4.32 (m, *J* = 5.4 Hz, 1H), 4.17 (d, *J* = 4.0 Hz, 1H), 4.05 (dd, *J* = 12.0 Hz, *J* = 4.0 Hz, 1H), 3.82 (dd, *J* = 12.5 Hz, *J* = 3.0 Hz, 1H), 3.81 (m, *J* = 4.7 Hz, 1H), 3.28 (d, *J* = 10.0 Hz, 1H), 3.08 (d, *J* = 10.0 Hz, 1H), 2.89 (m, *J* = 5.0 Hz, 2H). FAB/MS (*m*/*e*): 254 $[M+H]^+$. Anal. Calcd for $C_9H_{17}O_7NS$: C, 37.94; H, 5.70; N, 5.53. Found: C, 37.86; H, 5.89; N, 5.67.

4.2.11.4. *N*-(β-L-Arabinofuranos-1-yl)-L-cysteine 5b-β. Under argon, the solution of 91 mg (0.27 mmol) of *N*-(β-L-arabofuranos-1-yl)-*S*-*t*-butyl-L-cysteine and 75 mg (0.4 mmol) of 2-nitrophenylsulfenyl chloride in 2 ml of glacial acetic acid was stirred at room temperature for 2 h, and TLC analysis (chloroform:methanol:water: glacial acetic acid, 1:1:0.2:0.1) indicated complete disappearance of *N*-(β-L-arabofuranos-1-yl)-*S*-*t*-butyl-L-cysteine. The reaction mixture was evaporated under vacuum and the residue was dissolved in 3 ml of CH_3OH. The formed solution was cooled with ice bath and treated with 20 mg (0.54 mmol) of sodium borohydride. The reaction mixture was stirred at room temperature for 2 h and then evaporated under vacuum to remove the solvent. The residue was dissolved in water, washed with ethyl acetate, and the water phase was evaporated under vacuum. The residue was purified by Sephadex LH-20 and eluted with ethanol (10%). The collected fractions were combined, frozen, and lyophilized to provide 13 mg (50%) of the title compound as colorless powder. Mp 252 °C (decomp.), $[\alpha]_D^{25} = -16.0$ (*c* 1.1, H_2O). ^1H NMR (500 MHz, D_2O): δ = 4.25 (m, *J* = 5.6 Hz, 1H), 4.11 (d, *J* = 4.2 Hz, 1H), 3.97 (dd, *J* = 12.1 Hz, *J* = 4.2 Hz, 1H), 3.89 (dd, *J* = 12.5 Hz, *J* = 3.0 Hz, 1H), 3.66 (m, *J* = 4.9 Hz, 1H), 3.20 (d, *J* = 10.0 Hz, 1H), 3.01(d, *J* = 10.0 Hz, 1H), 2.80 (m, *J* = 5.0 Hz, 2H). FAB/MS (*m*/*e*): 254 $[M+H]^+$. Anal. Calcd for $C_9H_{17}O_7NS$: C, 37.94; H, 5.70; N, 5.53. Found: C, 37.81; H, 5.56; N, 5.37.

4.2.11.5. *N*-(α-L-Arabinofuranos-1-yl)-L-glutamic acid 5c-α. Using the general procedure for preparing α- and β-anomers of **5a–f** from 46.3 mg (0.1 mmol) of *N*-(α-L-arabinofuranos-1-yl)-*N*-(2-nitrobenzenesulfonyl)-L-glutamic acid (**4c-α**), 20.9 mg (75%) of **5c-α** was obtained as colorless powder. $[\alpha]_D^{25} = +10.0$ (*c* 1.2, H_2O). ^1H NMR (500 MHz, D_2O): δ = 4.31(dd, *J* = 8.7 Hz, *J* = 2.3 Hz, 1H), 4.25 (m, *J* = 2.2 Hz, 1H), 4.14 (d, *J* = 4.5 Hz, 1H), 3.97 (dd, *J* = 8.8 Hz, *J* = 2.6 Hz, 1H), 3.83 (dd, *J* = 9.8 Hz, *J* = 2.7 Hz, 1H), 3.80 (dd, *J* = 8.0 Hz, *J* = 2.4 Hz, 1H), 3.25 (d, *J* = 11.0 Hz, 1H), 3.15 (d, *J* = 10.5 Hz, 1H), 2.06 (m, *J* = 4.1 Hz, 2H), 1.74 (m, *J* = 4.0 Hz, 2H).

FAB/MS (*m*/*e*): 280 $[M+H]^+$. Anal. Calcd for $C_{10}H_{17}O_8N$: C, 43.01; H, 6.14; N, 5.02. Found: C, 42.88; H, 6.05; N, 5.13.

4.2.11.6. *N*-(β-L-Arabinofuranos-1-yl)-L-glutamic acid 5c-β. Using the general procedure for preparing α- and β-anomers of **5a–f** from 46.3 mg (0.1 mmol) of *N*-(β-L-arabinofuranos-1-yl)-*N*-(2-nitrobenzenesulfonyl)-L-glutamic acid **4c-β**, 19.5 mg (70%) of **5c-β** was obtained as colorless powder. $[\alpha]_D^{25} = -9.2$ (*c* 1.1, H_2O). ^1H NMR (500 MHz, D_2O): $\delta = 4.23$ (dd, $J = 8.5$ Hz, $J = 2.3$ Hz, 1H), 4.18 (m, $J = 2.5$ Hz, 1H), 4.06 (d, $J = 4.6$ Hz, 1H), 4.00 (dd, $J = 8.6$ Hz, $J = 2.6$ Hz, 1H), 3.71 (dd, $J = 9.6$ Hz, $J = 2.7$ Hz, 1H), 3.64 (dd, $J = 8.1$ Hz, $J = 2.4$ Hz, 1H), 3.17 (d, $J = 10.7$ Hz, 1H), 3.10 (d, $J = 10.6$ Hz, 1H), 2.00 (m, $J = 4.3$ Hz, 2H), 1.70 (m, $J = 4.1$ Hz, 2H). FAB/MS (*m*/*e*): 280 $[M+H]^+$. Anal. Calcd for $C_{10}H_{17}O_8N$: C, 43.01; H, 6.14; N, 5.02. Found: C, 43.13; H, 6.00; N, 4.98.

4.2.11.7. *N*-(α-L-Arabinofuranos-1-yl)-L-serine 5d-α. Using the general procedure for preparing α- and β-anomers of **5a–f** from 44.4 mg (0.1 mmol) of *N*-(α-L-arabinofuranos-1-yl)-*N*-(2-nitrobenzenesulfonyl)-L-serine (**4d-α**), 18.0 mg (76%) of **5d-α** was obtained as colorless powder. $[\alpha]_D^{25} = +20.0$ (*c* 1.1, H_2O), ^1H NMR (500 MHz, D_2O): $\delta = 4.30$(m, $J = 3.2$ Hz, 1H), 4.18 (d, $J = 4.6$ Hz, 1H), 4.05 (dd, $J = 10.2$ Hz, $J = 4.7$ Hz, 1H), 3.87 (dd, $J = 10.2$ Hz, $J = 5.7$ Hz, 1H), 3.83 (m, $J = 3.8$ Hz, 1H), 3.34 (d, $J = 10.2$ Hz, 1H), 3.06 (d, $J = 10.2$ Hz, 1H), 2.56 (m, $J = 3.9$ Hz, 2H), 1.71 (m, $J = 4.3$ Hz, 2H). FAB/MS (*m*/*e*): 238 $[M+H]^+$. Anal. Calcd for $C_8H_{15}O_7N$: C, 40.51; H, 6.37; N, 5.91. Found: C, 40.39; H, 6.19; N, 5.86.

4.2.11.8. *N*-(β-L-Arabinofuranos-1-yl)-L-serine 5d-β. Using the general procedure for preparing α- and β-anomers of **5a–f** from 44.4 mg (0.1 mmol) of *N*-(β-L-arabinofuranos-1-yl)-*N*-(2-nitrobenzenesulfonyl)-L-serine **4d-β**, 18.9 mg (80%) of **5d-β** was obtained as colorless powder. $[\alpha]_D^{25} = -19.0$ (*c* 1.1, H_2O). ^1H NMR (500 MHz, D_2O): $\delta = 4.22$ (m, $J = 3.4$ Hz, 1H), 4.10 (d, $J = 4.5$ Hz, 1H), 3.98 (dd, $J = 10.0$ Hz, $J = 4.7$ Hz, 1H), 3.92 (dd, $J = 10.0$ Hz, $J = 5.7$ Hz, 1H), 3.75 (m, $J = 3.9$ Hz, 1H), 3.26 (d, $J = 10.0$ Hz, 1H), 3.00 (d, $J = 10.0$ Hz, 1H), 2.50 (m, $J = 3.9$ Hz, 2H), 1.69 (m, $J = 4.3$ Hz, 2H). FAB/MS (*m*/*e*): 238 $[M+H]^+$. Anal. Calcd for $C_8H_{15}O_7N$: C, 40.51; H, 6.37; N, 5.91. Found: C, 40.64; H, 6.50; N, 5.83.

4.2.11.9. *N*-(α-L-Arabinofuranos-1-yl)-L-phenylalanine 5e-α. Using the general procedure for preparing α- and β-anomers of **5a–f** from 49.4 mg (0.1 mmol) of *N*-(α-L-arabinofuranos-1-yl)-*N*-(2-nitrophenylsulfonyl)-L-phenyl-alanine **4e-α**, 24.0 mg (79%) of **5e-α** was obtained as colorless powder. $[\alpha]_D^{25} = +6.7$ (*c* 1.2, H_2O), ^1H NMR (500 MHz, D_2O): $\delta = 7.30$ (d, $J = 7.2$ Hz, 2H), 7.22 (t, $J = 7.0$ Hz, 1H), 7.19 (t, $J = 7.3$ Hz, 1H), 4.32 (m, $J = 3.9$ Hz, 1H), 4.25 (m, $J = 3.8$ Hz, 1H), 4.08 (d, $J = 4.4$ Hz, 1H), 3.98 (dd, $J = 10.2$ Hz, $J = 2.7$ Hz, 1H), 3.86 (m, $J = 4.0$ Hz, 1H), 3.25 (d, $J = 10.5$ Hz, 1H), 3.19 (m, $J = 10.5$ Hz, 1H), 2.68 (m, $J = 4.5$ Hz, 2H), 1.71 (m, $J = 4.6$ Hz, 2H). FAB/MS (*m*/*e*): 298 $[M+H]^+$. Anal. Calcd for $C_{14}H_{19}O_6N$: C, 56.56; H, 6.44; N, 4.71. Found: C, 56.35; H, 6.65; N, 4.46.

4.2.11.10. *N*-(β-L-Arabinofuranos-1-yl)-L-phenylalanine 5e-β. Using the general procedure for preparing α- and β-anomers of **5a–f** from 49.4 mg (0.1 mmol) of *N*-(β-L-arabinofuranos-1-yl)-*N*-(2-nitrophenylsulfonyl)-L-phenyl-alanine **4e-β**, 20.7 mg (70%) of **5e-β** was obtained as colorless powder. $[\alpha]_D^{25} = -11.0$ (*c* 1.2, H_2O). ^1H NMR (500 MHz, D_2O): $\delta = 7.21$ (d, $J = 7.0$ Hz, 2H), 7.13 (t, $J = 7.1$ Hz, 1H), 7.04 (t, $J = 7.0$ Hz, 1H), 4.24 (m, $J = 3.8$ Hz, 1H), 4.19 (m, $J = 3.9$ Hz, 1H), 4.14 (d, $J = 4.2$ Hz, 1H), 3.78 (dd, $J = 10.0$ Hz, $J = 2.7$ Hz, 1H), 3.62 (m, $J = 4.2$ Hz, 1H), 3.17 (d, $J = 10.1$ Hz, 1H), 3.08 (m, $J = 10.2$ Hz, 1H), 2.64 (m, $J = 4.5$ Hz, 2H), 1.70 (m, $J = 4.6$ Hz, 2H). FAB/MS (*m*/*e*): 298 $[M+H]^+$. Anal. Calcd for $C_{14}H_{19}O_6N$: C, 56.56; H, 6.44; N, 4.71. Found: C, 56.72; H, 6.32; N, 4.83.

4.2.11.11. *N*-(α-L-Arabinofuranos-1-yl)-L-threonine 5f-α. Using the general procedure for preparing α- and β-anomers of **5a–f** from 43.5 mg (0.1 mmol) of *N*-(α-L-arabinofuranos-1-yl)-*N*-(2-nitrobenzenesulfonyl)-L-theorine **4f-α**, 19.0 mg (75%) of **5f-α** was obtained as colorless powder. $[\alpha]_D^{25} = +8.0$ (*c* 1.2, H_2O). ^1H NMR (500 MHz, D_2O): $\delta = 4.22$ (m, $J = 3.9$ Hz, 1H), 4.12 (d, $J = 6.5$ Hz, 1H), 4.08 (d, $J = 4.5$ Hz, 1H), 3.97 (dd, $J = 11.0$ Hz, $J = 3.0$ Hz, 1H), 3.82 (m, $J = 5.2$ Hz, 1H), 3.66 (m, $J = 6.4$ Hz, 1H), 3.27 (d, $J = 10.0$ Hz, 1H), 3.20 (d, $J = 10.0$ Hz, 1H), 2.54 (m, $J = 5.0$ Hz, 1H), 1.23 (d, $J = 6.7$ Hz, 3H). FAB/MS (*m*/*e*): 252 $[M+H]^+$. Anal. Calcd for $C_{14}H_{19}O_6N$: C, 43.03; H, 6.82; N, 5.58. Found: C, 42.88; H, 6.59; N, 5.46.

4.2.11.12. *N*-(β-L-Arabinofuranos-1-yl)-L-theorine 5f-β. Using the general procedure for preparing α- and β-anomers of **5a–f** from 43.5 mg (0.1 mmol) of *N*-(β-L-arabinofuranos-1-yl)-*N*-(2-nitrobenzenesulfonyl)-L-threonine (**4f-β**), 18.1 mg (72%) of **5f-β** was obtained as colorless powder. $[\alpha]_D^{25} = -9.0$ (*c* 1.1, H_2O). ^1H NMR (500 MHz, D_2O): $\delta = 4.18$ (m, $J = 3.8$ Hz, 1H), 4.16 (d, $J = 6.6$ Hz, 1H), 4.12 (d, $J = 4.7$ Hz, 1H), 3.85(dd, $J = 11.1$ Hz, $J = 3.0$ Hz, 1H), 3.78 (m, $J = 5.0$ Hz, 1H), 3.57 (m, $J = 6.5$ Hz, 1H), 3.19 (d, $J = 10.1$ Hz, 1H), 3.08 (d, $J = 10.1$ Hz, 1H), 2.51 (m, $J = 5.0$ Hz, 1H), 1.20 (d, $J = 6.7$ Hz, 3H). FAB/MS (*m*/*e*): 252 $[M+H]^+$. Anal. Calcd for $C_{14}H_{19}O_6N$: C, 43.03; H, 6.82; N, 5.58. Found: C, 43.15; H, 6.94; N, 5.70.

4.3. Animals

Male ICR mice (weighting 23 ± 2 g) were purchased from the Experimental Animal Center of Peking University. All the chemicals used in the animal experiments were purchased from Sigma Chemical Co. The study described herein was performed according to a protocol reviewed and approved by the ethics committee of Peking University. The committee assures that the welfare of the animals was maintained in accordance to the requirements of the animal welfare act and according to the guide for care and use of laboratory animals.

4.4. Lead decorporation assay[13]

Twenty groups (each 10) of mice were loaded with lead via ip injection of 8.2 mg/kg of $Pb(C_2H_3O_2)_2{\cdot}3H_2O$ in 0.5 ml of 0.9% saline (NS) per day for seven consecutive days. After a 2-day interval, one group served as the control and were given a daily injection of 0.5 ml of NS instead of **5a–f**; another seven groups served as the positive controls and was given a daily ip injection of 0.4 mmol/kg of D,L-penicillamine, L-arabinose, L-Asp, L-Cys L-Glu, L-Ser, L-Phe, and L-Thr in 0.2 ml of NS. The remaining twelve groups were given a daily ip injection (0.4 mmol/kg in 0.2 ml of NS) of **5a–f-α** and **5a–f-β** for five consecutive days. On each day, 2 h after the administration of the agents, the urine samples of each group were continually collected for 5 h. After administration of the agents, the fecal samples of each group were continually collected for 24 h. Twenty-four hours after the last administration of the agents, all the mice were sacrificed by diethyl ether anesthesia and dissected to immediately obtain kidney and left femur.

All the bio-samples were digested in $HClO_4$:HNO_3 (1:3) on a heating block, dried at 80 °C, redissolved in 1% nitric acid to determine lead content using a Varian Spectr AA-40 atomic absorption spectrometer in the graphite furnace. The variety of trace metals was determined by synchrotron X-ray fluorescence. All data are

expressed as means ± S.D. The statistical analysis of the data was carried out by using ANOVA test, $p < 0.05$ is considered significant.

Acknowledgments

This work was completed in the Beijing area major laboratory of peptide and small molecular drugs, supported by PHR (IHLB), the National Natural Scientific Foundation of China (30672513, 30801426), and the Beijing Municipal Commission of Education (KZ 200810025010).

References

1. Nriagu, J.; Afeiche, M.; Linder, A.; Arowolo, T.; Ana, G.; Sridhar, M. K. C.; Oloruntoba, E. O.; Obi, E.; Ebenebe, J. C.; Orisakwe, O. E.; Adesina, A. *Int. J. Hyg. Environ. Health* **2008**, *211*, 591–605.
2. Liu, Z. P. *Sci. Total Environ.* **2003**, *309*, 117–126.
3. Kachur, A. N.; Arzhanova, V. S.; Yelpatyevsky, P. V.; von Braun, M. C.; von Lindern, I. H. *Sci. Total Environ.* **2003**, *303*, 171–185.
4. Browne, D. R.; Husni, A.; Risk, M. J. *Sci. Total Environ.* **1999**, *227*, 145–154.
5. Hudson-Edwards, K. A.; Macklin, M. G. *J. Archaeol. Sci.* **1999**, *26*, 809–819.
6. Takser, L.; Mergler, D.; Lafond, J. *Neurotoxicol. Teratol.* **2005**, *27*, 505–508.
7. Patra, M.; Bhowmik, N.; Bandopadhyay, B.; Sharma, A. *Environ. Exp. Bot.* **2004**, *52*, 199–223.
8. Osterode, W.; Winker, R.; Bieglmayer, C.; Vierhapper, H. *Bone* **2004**, *35*, 942–947.
9. Andersen, O.; Nielsen, J. B.; Svendsen, P. *Toxicology* **1988B**, *52*, 65–79.
10. Liebelt, E. L.; Shannon, M. W. *Pediatr. Ann.* **1994**, *23*, 616–626.
11. Flora, S. J. S.; Kannan, G. M.; Pant, B. P. *Arch. Toxicol.* **2002**, *76*, 269–276.
12. Flora, S. J. S.; Bhattacharya, R.; Vijayaraghavan, R. *Fundam. Appl. Toxicol.* **1995**, *25*, 233–240.
13. Zheng, W.; Maiorino, R. M.; Brendel, K.; Aposhian, H. V. *Fundam. Appl. Toxicol.* **1990**, *14*, 598–607.
14. Wang, C.; Fang, Y.; Peng, S. *Chem. Res. Toxicol.* **1999**, *12*, 331–334.
15. Wang, C.; Zhao, M.; Yang, J.; Li, X. W.; Peng, S. *Toxicol. Appl. Pharmacol.* **2004**, *200*, 229–236.
16. Huo, C. X.; Wang, C.; Zhao, M.; Peng, S. *Chem. Res. Toxicol.* **2004**, *17*, 1112–1120.
17. Kline, T.; Trent, M. S.; Stead, M.; Lee, M. S.; Sousa, M. C.; Felise, H. B.; Nguyen, H. V.; Miller, S. I. *Bioorg. Med. Chem. Lett.* **2008**, *18*, 1507–1510.
18. Sanki, A. K.; Boucau, J.; Srivastava, P.; Adams, S. S.; Ronning, D. R.; Sucheck, S. J. *Bioorg. Med. Chem.* **2008**, *16*, 5672–5682.
19. Tanaka, T.; Fujishima, Y.; Hamano, S.; Kaneo, Y. *Eur. J. Pharm. Sci.* **2004**, *22*, 435–444.
20. Usul, T.; Tsushima, S.; Yamaoka, N.; Matsuda, K.; Tuzimura, K.; Hiroshi Sugiyama, H.; Seto, S.; Fujieda, K.; Miyajima, G. *Agric. Biol. Chem.* **1974**, *38*, 1409–1410.
21. Yaylayan, V. A.; Huyghues-Despointes, A. *Carbohydr. Res.* **1996**, *286*, 179–187.
22. Venkatraman, J.; Aggawal, K.; Balaram, P. *Chem. Biol.* **2001**, *8*, 611–625.
23. Harald, R.; Siyka, R.; Kurt, H. *Carbohydr. Res.* **1983**, *116*, 183–195.
24. Lederer, M. O.; Dreisbusch, C. M.; Bundschuh, R. M. *Carbohydr. Res.* **1997**, *301*, 111–121.
25. Yee, S. *Pharm. Res.* **1997**, *14*, 763–766.
26. Shaikh, A. R.; Ismael, M.; Carpio, C. A. D.; Tsuboi, H.; Koyama, M.; Endou, A.; Kubo, M.; Broclawikc, E.; Miyamoto, A. *Bioorg. Med. Chem. Lett.* **2006**, *16*, 5917–5925.