

**POLYAMINE ANALYSES OF SEED PLANT ORGANS OF CROPS,  
VEGETABLES AND FRUIT/FLOWERING TREES IN AGRICULTURE,  
AND FORESTRY PLANTS IN NATURAL ENVIRONMENTS: CO<sub>2</sub>  
CAPTURED BY POLYAMINES ARE USED FOR CARBON  
ASSIMILATION IN PLANT LEAVES**

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**ABSTRACT**

To determine taxonomically species-specific and organ-specific plant polyamines, cellular polyamines were acid-extracted from 95 seed plant organs, including agricultural, flowering and forestry products, and were quantitatively analyzed by high-performance liquid chromatography and high-performance gas chromatography. The distribution of 15 polyamines (e.g. diaminopropane, putrescine, cadaverine, norspermidine, spermidine, homospermidine, norspermine, spermine, thermospermine, aminopropylhomospermidine, canavamine, homospermine, caldopentamine, homocaldopentamine and agmatine) were shown in 55 plant species of Eudicots of Angiosperms, 15 species of Monocots of Angiosperms, and 9 species of Gymnosperms. Polyamine profiles are compared and considered among mangrove plants, parasitic plants, salt-tolerant plants, saprophytic plants, aquatic plants, and succulent plants, furthermore among the organs; root, stem, normal green leaf, fallen leaf, evergreen leaf, acupuncture leaf, flower, flower bud, fruit without seed, fruit skin, seed, seedling, sprout, tuber, skin of tuber, tuberous root, and skin of tuberous root. Over the past 40 years, we have analyzed 261 species of seed plants and their 1-5 organs in our 21 reports. Therefore, we have drawn four conclusions “Novel polyamines and polyamine derivatives in seed plants”, “Polyamine change in microbial symbiosis and infection in seed plants”, “Polyamines of seed plant organs as a food nutrient for human health”, and “Polyamines in CO<sub>2</sub> assimilation of photosynthetic plant cells”.

**Keywords:** Angiosperms, Gymnosperms, Polyamine analysis, Plant organ, Seed plant

## 1. INTRODUCTION

### 1.1 Characteristics of biogenic polyamines

High-basic and low-molecular biogenic polyamines (containing  $-\text{NH}_3^+$ ,  $=\text{NH}_2^+$ ,  $=\text{N}^+=$ ) ionically interact with biogenic acidic components such as ATP ( $-\text{H}_2\text{PO}_4^-$ ), Acetyl-CoA ( $-\text{H}_2\text{PO}_4^-$ ,  $-\text{COO}^-$ ), nucleic acids RNA and DNA ( $-\text{H}_2\text{PO}_4^-$ ), polyphosphoric acids ( $-\text{H}_2\text{PO}_4^-$ ), fatty acids ( $-\text{COO}^-$ ), amino acids ( $-\text{COO}^-$ ) and acidic polysaccharides ( $-\text{COO}^-$ ,  $-\text{HSO}_4^-$ ), for the protection of the biomolecules in biological cells of life. Polyamines can interact with nucleic acids and proteins through hydrogen bonds (N-H---N, N-H---O). Biogenic polyamines are needed as a controller of hydrogen ion concentration (pH) as a unique base in cells. Nucleobases (purines and pyrimidines) ( $-\text{NH}_3^+$ ,  $=\text{NH}_2^+$ ) are included in ATP and Acetyl-CoA as well as DNA and RNA. Therefore, more than 35 kinds of natural biogenic polyamines (linear diamines, triamines, tetra-amines, penta-amines and hexa-amines, and tertiary and quaternary branched triamines, tetra-amines and penta-amines, and guanidinoamines) have been found in life on the Earth. These polyamines have various respective functions in the adaptation to environment for cell growth, the differentiation of cells to multicellular organization, and fertilization of organisms (Hamana, 2002b, 2023, 2024; Hamana and Hayashi, 2025; Hamana and Hosoya, 2006; Hamana and Matsuzaki, 1992). Various biomolecules covalently binding with polyamines were found in microbes. It has been known that polyamines stimulate the incorporation of carbonic acid ( $\text{CO}_2 + \text{H}_2\text{O} = \text{HCO}_3^- + \text{H}^+$ ) into cells (Yasumoto et al., 2014, 2018; Kubota et al., 2024) and the binding of silicic acid ( $\text{H}_3\text{SiO}_4^-$ ) into biomolecules (Mizutani et al., 1998; Maddala et al., 2021). Silicon (Si) is a major element of the Earth's crust, therefore the biomineralization of Si is important for all organisms. Plant-specific carbonic acid assimilation through photosynthesis exposes terrestrial plants to light irradiation and heating. Polyamines can act as free radical scavengers in plant cells from oxidative damage by  $\text{O}_2^-$  radical (Das and Misra, 2004; Fujisawa and Kadoma, 2005). Polyamines are one of the most versatile compounds in plant cells as well as in human cells, and we humans are ingesting various seed plant organ-derived foods containing plant polyamines. Plant polyamines are important for carbon dioxide ( $\text{CO}_2$ ) assimilation into plants and to control global warming, ocean acidification, and the carbon cycle.

### 1.2 Development of biogenic polyamine analysis

Extraction methods of polyamines from plant organs and concentration and purification of polyamine fractions are a problem. Quantitatively chromatographic techniques for analyzing more than 35 kinds of polyamines are difficult. Chemically synthesized 35 polyamines are essential for chromatographic and mass-spectrometric polyamine analyses. Therefore, few studies on cellular polyamine distributions in various differentiated plant organs of taxonomically diverse seed plants have been reported, except for our studies. Using the excellent high-performance liquid

chromatography (HPLC), (standard) gas chromatography (GC), gas chromatography-mass spectrometry (GC-MS), and high-performance gas chromatography-mass spectrometry (HPGC-MS) developed to specialize for plant polyamine analysis (Figs. 1-3), we have analyzed simultaneously more than 35 kinds of normal linear and branched polyamines, as well as *N*-acethylpolyamines, *N*-methylpolyamines, 2-hydroxypolyamines and alkanolpolyamines. Except for a few commercially available diamines, linear triamines and linear tetra-amines (free, HCl salt or H<sub>3</sub>PO<sub>4</sub> salt), more than 30 polyamines and various polyamine derivatives (HCl salt or HClO<sub>4</sub> salt) as analytical standards were chemically synthesized in our laboratories (Furuchi et al., 2015; Niitsu et al., 1993, 2014). White powders of diamine carbonate were observed on the bottle mouth of the free diamines (Dap, Put, etc.) in our laboratories at room temperature. However, polyamine

- weak acid (H<sub>2</sub>CO<sub>3</sub>) salt is biologically important in photosynthetic plant cells.

### **1.3 History of polyamine analysis of seed plants**

A seed plant or spermatophyte is any plant that produces seeds. It is a category of embryophyte (i.e. land plant) that includes most of the familiar land plants, including the flowering plants (Angiosperms) and gymnosperms (Gymnosperms). By the transgenic studies of cellular polyamine synthetic and catabolic enzymes using a seed plant model *Brassica*, *Arabidopsis thaliana*, and a little of other seed plants, it has been proved that the common plant polyamines (e.g. diaminopropane (Dap) (3), putrescine (Put) (4), spermidine (Spd) (34), Spermine (Spm) (343) and thermospermine (TSpm) (334)) are involved in plant cell proliferation and differentiation and play a defensive role against various stresses and microbial infections (Chen et al., 2019; Hanzawa et al., 2002; Kusano et al., 2008; Minocha et al., 2014; Naka et al., 2010; Sheng et al., 2022; Takahashi and Kakehi, 2010; Takahashi and Motose 2021). Dap, Put and cadaverine (Cad) (5) (a diamine) and agmatine (Agm) (a guanidinoamine belonging to polyamines) are produced by the decarboxylation of diaminobutylic acid, ornithine, lysine and arginine, respectively and are precursor for triamine production. Dap is also produced from triamines and tetra-amines from polyamine oxidases (Salvi and Tavladoraki, 2020). Homospermidine (HSpd) (44) is generally found in plants and is believed to originate as a by-product of deoxyhypusine synthase and is a key intermediate in the biosynthesis of pyrrolizidine alkaloids (Ober et al., 2003; Zakaria et al., 2022). Furthermore, the transport system of the polyamines in plant cells has been studied (Fujita and Shinozaki, 2017; Stolarska et al., 2023).

We comprehensively and systematically have examined endogenous cellular polyamines in the roots, leaves, pods, flowers and seeds of vegetables belonging to the orders *Brassicales* and *Solanales* (Hamana et al., 2015, 2017; Niitsu et al., 2014), in the osmotic-resistant bodies of aquatic plants (Hamana et al., 1994, 1998, 2000), and in the seeds, seedlings (or sprouts), roots and leaves of agricultural crop plants belonging to the families *Fabaceae* (formerly *Leguminosae*) (Hamana and Matsuzaki, 1985b, 1993; Hamana et al., 1991, 1992a, 1992b, 1992c, 1996, 2019; Matsuzaki

et al., 1990a, 1990b; Otsuka et al., 2005) and *Poaceae* (formerly *Gramineae*) (Hamana et al., 1994). We attempted first to analyze cellular polyamines in mosses (Bryophyta), ferns (Pteridophyta) and some gymnosperms (Hamana and Matsuzaki, 1985a) and recently extended our analysis to *Roseales* and *Fagales* organ polyamines (Hamana et al., 2025) in our 20 previous reports.

#### **1.4 Poupous of the present polyamine analysis of seed polyamines**

We reported here the distributions of the 15 normal linear polyamines; Dap (5), Put (4), cadaverine (Cad) (5), norspermidine (NSpd) (33), Spd (34), HSpd (44), norspermine (NSpm) (333), Spm (343), TSpM (334), aminopropylhomospermidine (APHSpd) (344), canavamine (Can) (434), homospermine (HSpm) (444), caldopentamine (CPen) (3333), homocaldopentamine (HCPen) (3334) and Agm (Tables 1-3), detected in the additional 95 plant organs of agricultural crops (4 species), vegetables (13 species), fruit trees (7 species), flowering trees (4 species), forestry plants (18 species) and related plant organs previously analyzed, within the seed plants (Spermatophyte) belonging to angiosperms (Phylum Angiospermae) and gymnosperms (Phylum Gymnospermae), as shown in Tables 1-3. Polyamine distributions in taxonomically related plant organs previously reported are cited in Tables. Following our three recent reports in this journal, *Int. J. Agri. Environ. Res.* (Hamana et al., 2017, 2019, 2025), we present our fourth/final report, as a review of seed plant polyamine analysis, and expect plant polyamine analysis in agriculture, forestry and environmental research in Asia.

## **2. MATERIALS AND METHODS**

### **2.1 Cultivation and collection of plant organs**

Although seed plants are distributed and cultivated in various environments on the Earth, we focused on collecting additional 95 plant organs of crops, vegetables, fruit trees, flowering plants and forestry plants, available in Japan. Although these additional plant organs in the present study are cultivated or collected as agricultural, floral, and forestry products in Japan, these polyamine analyses are provided and contributed to global applicability of the findings for species-specific and organ-specific polyamines. Seedlings or young trees of strawberry, mangrove, moringa, ice plant, fish mint, tea-plant, and olive were purchased from nursery companies located in various places in Japan and cultivated in Hamana home garden, Maebashi, Gunma, Japan. Organs of cherry (Japanese national flower), rose (Gunma prefectural flower), azalea (Maebashi City flower), pin oak, camellia, saprophyte, persimmon, maple, chinaberry, mistletoe, artichoke, and oyster plant were collected in Hamana home forest, Tsumagoi, Gunma, Japan. Apple fruits, kiwifruits, lotus roots, buckwheat seeds and *Brassica* plants (grown in Gunma), powder of tea leaves (made in Shizuoka, Japan) and powder of *Eucommia* leaves (made in Nagano, Japan), sea asparagus (made in J.O.R. Farm, Israel) and dried rooibos leaves (Rooibos tea) (made in South

Africa) were purchased from food markets in Maebashi. Seedlings of konjac plants (a Gunma specialty), aloe plants, taro plants, and ginger plants of Monocots were purchased in Maebashi and then cultivated in Hamana home garden. Brown rice, seed powder of barley and banana fruit (produced by Banana Freaks Maebashi, Maebashi) were purchased from food markets in Maebashi. Rice bran and pickled rice bran (fermented for 2 months) were produced from brown rice. Organs of conifers of Gymnosperms were collected in Hamana home forest. Ginkgo organs were collected in the garden of Maebashi Institute of Technology, Maebashi. Root samples of tree plants were collected from the seedlings/young trees cultivated in the home garden and home forest. Seeds were water-cultured axenically to obtain buds, sprouts and seedlings (these three are not accurately differentiated in our studies).

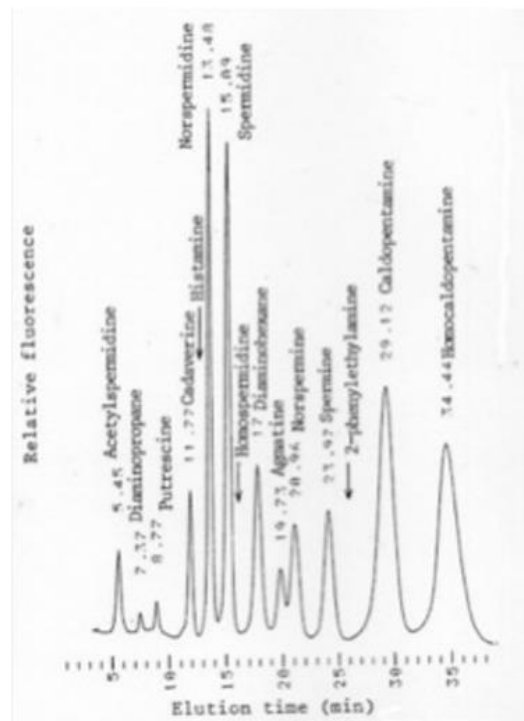
## **2.2 Polyamine analysis**

### **2.2.1 Polyamine fractions**

After washing and weighting, plant organs (10-100g) were homogenized in the same weight of 10% (1.0M) perchloric acid (PCA) by a mixer and a sonicator. After three extractions with 5% PCA by centrifugation and filtration, the supernatant of the PCA extract was applied to a column (3cm I.D. × 1cm) of a cation-exchange resin (-SO<sub>3</sub><sup>-</sup>), DOWEX W50x8, and then polyamines were concentrated by the eluted with 6M HCl from the column. After evaporating, dissolving in water, and then neutralizing, the supernatant of the polyamine fraction was subjected to a column of cation-exchange carboxymethyl-cellulose (-COO<sup>-</sup>), Whatman CM23 (3cm I.D. × 1cm). Polyamines were eluted with 1 M HCl from the column and evaporated as polyamine · HCl.

### **2.2.2 HPLC analysis**

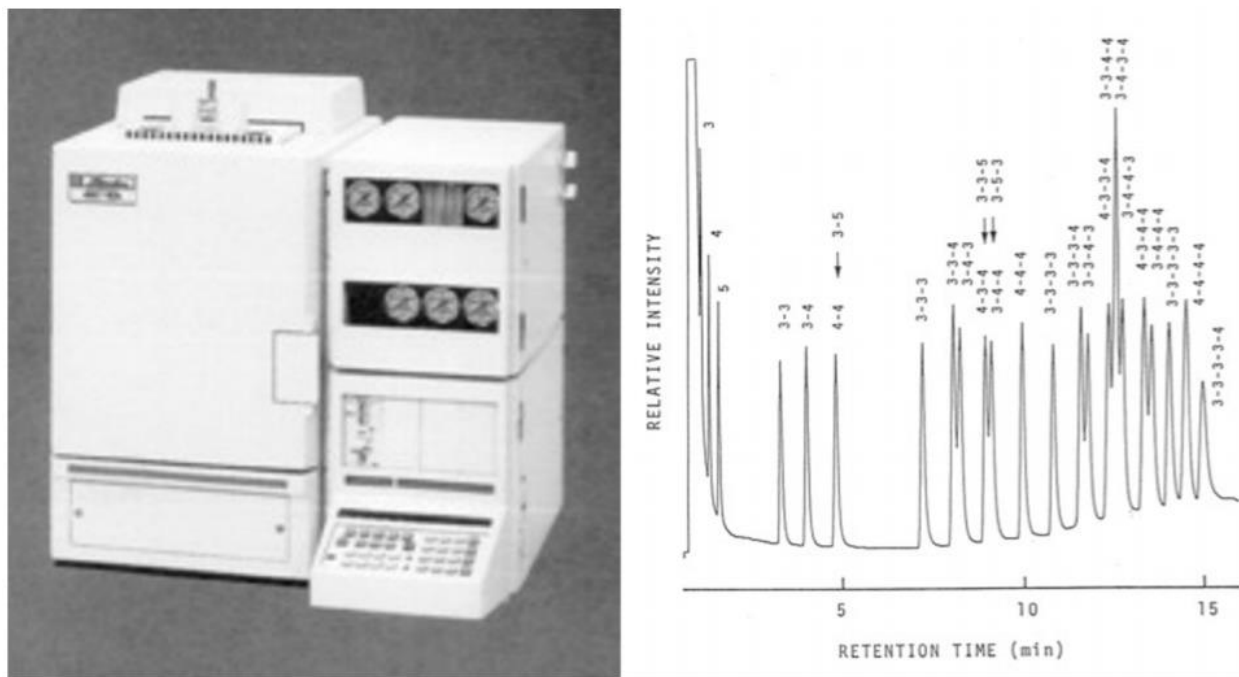
HPLC of the concentrated/purified polyamine fraction by a high-speed, high-pressure elution have been performed on a Hitachi L6000 (Tokyo, Japan) using a column of cation-exchange resin, Hitachi 2619F (=Hitachi 2720) (4mm I.D. × 50mm) (Fig. 1) (Hamana, 2002a; Hamana et al., 2015). HPLC on a Kyowa Seimitsu K-101AS (Tokyo, Japan) using a column of cation-exchange resin (62210F, 4.8 mm I.D. × 8cm) (Kyowa Seimitsu) had been used in our initial studies.



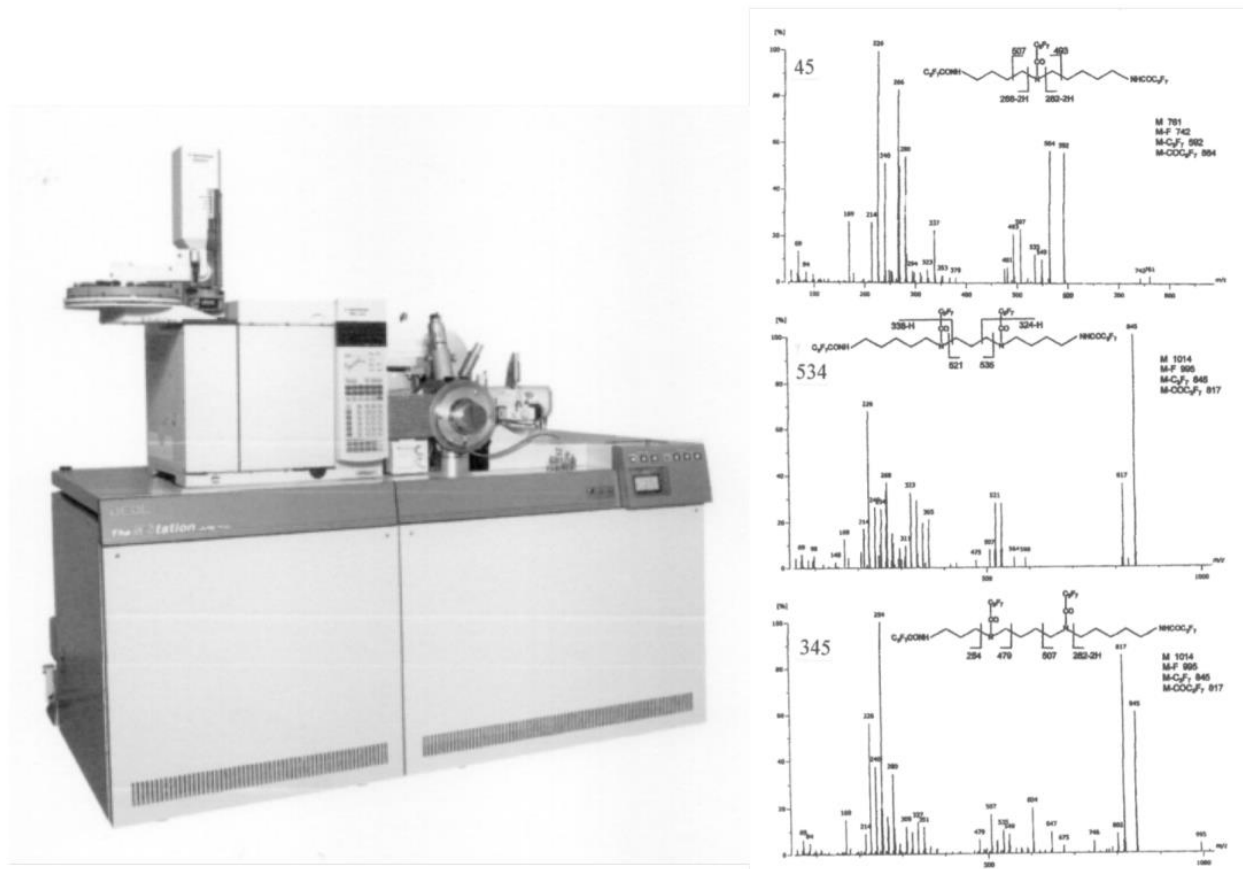
**Fig. 1: HPLC elution chart of 12 standard polyamines (1-1,000 pmol) (Right) (Hamana, 2002a) by Hitachi L6000 (Left) constructed in Maebashi Institute of Technology (Hamana and Hayashi, 2025).**

### 2.2.3 GC and HPGC-MS analyses

After heptafluorobutyrylation of the polyamine fraction, (standard) GC on a SHIMADZU GC-9A (Kyoto, Japan) equipped with a packed column (3% SE-30/Chromosorb WHP, 3mm I.D. × 2.1 m) (Gasukuro Kogyo) (Fig. 2) or HPGC on a SHIMADZU GC-17A equipped with a long capillary column (0.32mm I.D. × 30m) of Inert Cap 1MS (GL Sciences, Tokyo, Japan) had been performed (Niitsu et al., 1993; Hamana et al., 2005). Furthermore, (standard) GC-MS on a JEOL JMS-DX 300 (Tokyo, Japan) equipped with the packed column or HPGC-MS on a JEOL JMS-700 equipped with the long capillary column, were performed (Fig. 3) (Niitsu et al., 1993, 2014; Furuchi et al., 2015; Hamana et al., 2015, 2019).



**Fig. 2: GC retention chart of 24 standard polyamines (1 nmol) (Right) (Niitsu et al., 1993) by SHIMADZU GC-9A (Left) installed in Josai University. The photograph was provided from SHIMADZU Co. (Hamana and Hayashi, 2025). Abbreviations for polyamines in the GC charts are shown in Table 1.**



**Fig. 3: Mass spectrum (MS) of three standard polyamines in HPGC-MS (Right) (Hamana et al., 2018) by JEOL JMS-700 (Left) installed in Josai University. The photograph was provided from JEOL Co. (Hamana and Hayashi, 2025). Abbreviations for polyamines; 45, aminobutylcadaverine (ABCad); 534,  $N^1$ -aminopentylspermidine (AP1Spd); 345,  $N^8$ -aminopentylspermidine (AP8Spd). The three polyamines were not detected in the seed plants analyzed in our studies.**

#### 2.2.4 Calculation of polyamine concentration

The molar concentrations of endogenous polyamines per gram of wet weight of the organ ( $\mu\text{mol/g}$  wet weigh) were roughly estimated from the charts of the HPLC, GC-MS and HPGC-MS analyses of the polyamine extracts and are shown in Table 1. Although the numerical values of cellular polyamine concentrations per wet weight of starting plant organ samples depend on its moisture, the major and minor polyamine components are measurable, therefore polyamine distribution profiles specific to plant species and plant organs can be discussed without statistical analysis of polyamine concentrations. Since we spend a lot of time and effort to extraction, HPLC and GC/HPGC-MS of polyamines of a plant organ, we cannot repeat polyamine analysis for a plant



organ to obtain statistical validation in the present polyamine data for the 95 plant organs, as well as in our 20 previous reports.

**Table 1: Polyamine concentrations in plant organs in Eudicots of Angiosperms**

Plant species	Organs	References	Polyamines (μmol/g wet weight)														
			Dap	Put	Cad	NSpd	Spd	HSpd	NSpm	TSpm	Spm	AHSpd	Can	HSpm	CPen	HCPen	Agm
			3	4	5	33	34	44	333	334	343	344	434	444	3333	3334	
<b>Eudicots in Angiosperms</b>																	
<b>Rosids</b>																	
<b>Order Rosales</b>																	
<i>Cerasus sargentii</i> ( <i>Prunus sargentii</i> ) (Cherry)	root	Hamana <i>et al.</i> , 2025	-	0.02	-	-	0.56	0.20	-	0.02	0.14	-	-	-	-	-	
	stem	Hamana <i>et al.</i> , 2025	-	0.02	-	-	0.58	0.02	0.01	0.01	0.27	-	-	-	-	-	
	leaf		-	0.15	-	-	1.80	0.03	0.01	0.02	0.75	-	-	-	-	-	
	fallen red leaf		0.03	0.25	-	-	1.40	0.02	-	-	0.25	-	-	-	-	-	
	flower		-	-	-	-	0.75	-	-	0.01	0.15	-	-	-	-	-	
<i>Malus pumila</i> (Apple)	fruit		-	0.16	-	-	0.80	0.01	-	0.01	0.35	-	-	-	-	-	
	stem	Hamana <i>et al.</i> , 2025	0.10	0.10	-	-	0.72	0.10	-	-	0.03	-	-	-	-	-	
	fruit		-	0.45	-	-	0.75	-	-	-	0.12	-	-	-	-	-	
<i>Eriobotrya japonica</i> (Japanese loquat) "Biwa"	fruit skin		-	0.30	0.05	-	0.70	-	-	-	0.10	-	-	-	-	-	
	fruit	Hamana <i>et al.</i> , 2025	-	0.44	0.07	-	2.10	0.10	-	-	0.15	-	-	-	-	-	
	seed	Hamana <i>et al.</i> , 2025	-	0.17	0.02	-	1.60	0.02	-	-	0.27	-	-	-	-	-	
<i>Ficus carica</i> (Fig tree)	leaf	Hamana <i>et al.</i> , 2025	-	0.02	0.15	-	1.30	-	-	-	0.19	-	-	-	-	-	
	fruit	Hamana <i>et al.</i> , 2025	-	0.10	0.02	-	0.53	-	-	-	0.03	-	-	-	-	-	
<i>Fragaria ananassa</i> (Strawberry)	root	Hamana <i>et al.</i> , 2025	-	1.30	-	-	0.60	-	-	-	0.37	-	-	-	-	0.04	
	leaf		-	0.07	-	-	0.92	0.17	-	-	0.56	-	-	-	-	-	
	fruit		-	0.05	-	-	0.85	0.01	-	-	0.70	-	-	-	-	-	
<i>Morus alba</i> (Mulberry)	fruit		-	0.32	-	-	1.40	0.13	-	-	0.04	-	-	-	-	0.01	
	root	Hamana <i>et al.</i> , 2025	-	0.03	-	-	1.36	0.45	-	-	0.15	-	-	-	-	0.10	
	leaf	Hamana <i>et al.</i> , 2025	-	0.05	-	-	0.63	0.01	-	-	0.71	-	-	-	-	-	
<i>Morus bombycis</i> (Mulberry)	fallen leaf	Hamana <i>et al.</i> , 2025	-	0.10	-	-	0.88	-	-	-	0.15	-	-	-	-	-	
	fruit	Hamana <i>et al.</i> , 2025	-	0.30	-	-	1.50	-	-	-	0.20	-	-	-	-	-	
	root	Hamana <i>et al.</i> , 2025	-	0.25	-	-	0.65	0.25	-	-	0.03	-	-	-	-	0.02	
<i>Prunus mume</i> (Japanese apricot)	leaf	Hamana <i>et al.</i> , 2025	-	0.30	-	-	1.80	-	-	-	0.30	-	-	-	-	-	
	fallen leaf	Hamana <i>et al.</i> , 2025	-	0.04	-	-	0.55	-	-	-	0.03	-	-	-	-	-	
	fruit	Hamana <i>et al.</i> , 2025	-	0.80	0.10	-	0.25	-	-	-	0.10	-	-	-	-	-	
<i>Prunus persica</i> (Peach)	"Ume"	fruit	Hamana <i>et al.</i> , 2025	-	0.90	0.01	-	0.25	-	-	0.01	-	-	-	-	0.03	
<i>Prunus salicina</i> (Plum)	"Momo"	fruit	Hamana <i>et al.</i> , 2025	0.03	0.85	-	-	1.40	0.01	-	-	0.15	-	-	-	-	
<i>Prunus pyrifolia</i> (Nashi pear)	"Sumomo-soldum"	fruit	Hamana <i>et al.</i> , 2025	-	1.80	0.01	-	1.90	0.02	-	-	0.10	-	-	-	0.02	
<i>Pyrus pyrifolia</i> (Nashi pear)	"Nashi"	fruit	Hamana <i>et al.</i> , 2025	-	0.96	-	0.02	1.40	0.01	-	-	-	-	-	-	0.03	
	fruit skin	Hamana <i>et al.</i> , 2025	-	0.85	-	-	1.04	-	-	-	-	-	-	-	-	1.00	
<i>Rosa multiflora</i> (Multiflora rose) (Wild rose)	"Noibara" leaf		0.05	0.17	-	-	1.10	0.01	-	-	0.45	-	-	-	-	-	
	root		-	0.03	-	-	0.34	0.22	-	-	0.02	-	-	-	-	0.02	
	flower		-	0.25	-	-	0.65	-	-	-	0.20	-	-	-	-	0.07	
	fruit		-	0.10	-	-	1.40	0.04	-	-	0.45	-	-	-	-	0.50	
<b>Order Malpighiales</b>																	
<i>Bruguiera gymnorhiza</i>	"Ohirugi" [Mangrove plant] evergreen leaf		0.03	0.60	0.01	-	0.40	0.01	-	-	0.05	-	-	-	-	0.03	
	root		-	0.40	-	-	0.64	0.20	-	-	0.05	0.02	-	-	-	-	
<i>Kandelia obovata</i>	"Mehirugi" [Mangrove plant] evergreen leaf		-	0.85	0.02	-	0.80	0.02	-	-	0.10	-	-	-	-	0.02	
	root		-	0.50	-	-	1.80	0.35	-	-	0.03	0.02	-	-	-	0.01	
<i>Rhizophora mucronata</i>	"Yacayahirugi" [Mangrove plant] evergreen leaf		-	0.55	-	-	0.90	0.02	-	-	0.03	-	-	-	-	0.01	
	root		-	0.40	-	-	1.15	0.18	-	-	0.08	0.02	-	-	-	0.01	
<b>Order Fagales</b>																	
<i>Quercus serrata</i> (Pin oak)	"Konara" root		-	0.10	-	-	0.30	0.10	-	0.01	0.70	-	-	-	-	0.10	
	stem		-	0.40	-	-	0.75	-	0.01	0.01	0.70	-	-	-	-	0.02	
	stem		-	0.35	-	0.02	1.10	-	0.02	0.01	0.42	-	-	-	-	0.04	
	leaf		0.01	0.65	0.01	-	0.75	-	0.01	0.01	0.75	-	-	-	-	-	
	fallen red leaf		-	0.45	0.10	-	1.45	0.01	-	-	0.45	-	-	-	-	-	
	seed		-	0.55	-	-	2.20	-	-	-	0.35	-	-	-	-	-	
<b>Order Fabales</b>																	
<i>Aspalathus linearis</i> (Rooibos)	leaf [Rooibos tea]	Hamana <i>et al.</i> , 2019	-	0.04	0.02	-	1.05	0.01	0.13	0.06	0.75	-	-	-	0.01	0.03	-

	leaf [Rooibos tea]		0.05	0.25	-	-	1.20	0.03	0.32	-	0.18	-	-	-	-	-	0.35
	leaf [Rooibos tea]		0.04	0.12	-	-	0.75	0.01	0.05	-	0.10	-	-	-	-	-	0.10
<i>Glycine max</i> (Soy bean) (Soybean) "Daizu"	boiled soybean	Otsuka and Hamana, 2006	-	0.02	0.03	-	0.24	0.01	-	-	0.06	-	-	-	-	-	0.07
	fermented soybean ["Natto"]	Otsuka and Hamana, 2006	-	0.16	0.09	-	0.74	-	-	-	0.09	-	-	-	-	-	0.77
	seed	Otsuka et al., 2005	-	0.80	0.10	-	1.56	0.03	-	-	0.29	0.01	-	-	-	-	0.30
	immature seed	Hamana et al., 2019	-	0.17	-	^	1.07	-	0.01	0.03	0.87	-	-	-	-	-	-
<i>Phaseolus vulgaris</i> (Kidney bean)	seed	Otsuka et al., 2005	-	0.30	-	-	1.40	0.02	-	-	0.70	0.01	0.02	-	-	-	-
	seed	Hamana et al., 2019	-	0.06	-	-	1.07	0.05	-	-	1.05	0.03	-	-	-	-	-
<i>Visia sativa</i> (Vetch)	seed	Otsuka et al., 2005	-	0.20	0.03	-	0.80	0.04	-	-	0.40	0.01	-	0.03	-	-	-
<i>Vigna mungo</i> (Black gram)	seed	Otsuka et al., 2005	0.08	0.09	-	-	1.35	0.01	-	-	1.20	0.02	0.02	-	-	-	-
<b>Order Brassicales</b>																	
<b>Family Moringaceae</b>																	
<i>Moringa oleifera</i> (Moringa) (Horseradish tree)	leaf		-	0.25	-	-	0.50	-	-	-	0.25	-	-	-	-	-	-
	seed		-	0.15	-	-	1.02	-	-	-	0.10	-	-	-	-	-	-
<b>Family Brassicaceae</b>																	
<i>Brassica oleracea</i> var. <i>capitata</i> (Cabbage)	leaf	Hamana et al., 2015	-	0.64	-	-	1.33	0.02	-	0.02	0.16	-	-	-	-	-	0.03
	root	Hamana et al., 2015	-	0.07	-	-	0.70	0.02	-	-	0.02	-	-	-	-	-	0.28
<i>Brassica oleracea</i> var. <i>italica</i> (Broccoli)	leaf	Hamana et al., 2015	-	0.27	-	-	1.46	-	-	0.02	0.17	-	-	-	-	-	0.35
	flower bud	Hamana et al., 2015	0.02	0.36	-	-	1.57	-	-	0.05	0.22	-	-	-	-	-	2.82
	root	Hamana et al., 2015	-	0.03	-	-	0.63	0.03	-	0.01	0.12	-	-	-	-	-	0.25
	seed	Hamana et al., 2015	-	0.08	-	-	2.40	-	-	-	1.26	-	-	-	-	-	0.30
<i>Brassica oleracea</i> var. <i>botrytis</i> (Cauliflower)	flower bud	Hamana et al., 2015	0.06	0.38	-	-	1.62	0.01	-	0.08	0.42	-	-	-	-	-	0.31
<i>Brassica oleracea</i> var. <i>acephala</i> (Kale)	leaf		-	0.47	-	-	0.69	-	-	-	0.27	-	-	-	-	-	-
<i>Brassica oleracea</i> var. <i>gongylodes</i> (Kohlrabi) "Kabukanran"	stem		1.10	0.40	-	0.03	1.70	0.03	-	-	0.18	-	-	-	-	-	0.45
<i>Brassica rapa</i> var. <i>perviridis</i> (Japanese mustard spinach)	leaf	Hamana et al., 2015	-	0.46	-	-	0.75	0.01	-	0.04	0.21	-	-	-	-	-	0.01
"Komatsuna"	root	Hamana et al., 2015	0.01	0.18	-	-	1.19	0.08	-	0.07	0.32	-	-	-	-	-	0.08
	seed	Hamana et al., 2015	0.06	0.34	-	-	3.70	0.01	-	0.02	0.30	-	-	-	-	-	-
<i>Brassica rapa</i> var. <i>rapa</i> (Turnip) "Kabu"	stem (root in 2015)	Hamana et al., 2015	0.09	0.17	-	-	1.42	0.01	-	-	0.03	-	-	-	-	-	0.01
<i>Brassica rapa</i> var. <i>glabra</i> (Chinese cabbage) "Hakusai"	leaf		0.05	0.73	-	-	1.89	0.02	-	-	0.40	-	-	-	-	-	-
<i>Brassica napus</i> (Rapeseed) "Seiyou-aburana"	root	Hamana et al., 2015	-	0.18	-	-	1.12	-	-	0.02	0.10	-	-	-	-	-	-
	leaf	Hamana et al., 2015	-	0.25	-	-	2.10	-	-	0.04	0.45	-	-	-	-	-	0.08
	flower bud	Hamana et al., 2015	-	0.45	-	-	1.35	-	-	0.02	0.08	-	-	-	-	-	0.16
	flower	Hamana et al., 2015	0.02	0.45	-	-	0.96	-	-	0.01	0.04	-	-	-	-	-	0.13
	seed	Hamana et al., 2015	0.02	0.50	-	-	3.10	-	-	0.02	0.25	-	-	-	-	-	-
<i>Raphanus sativus</i> (Japanese radish) "Daikon"	root		-	0.50	-	-	0.32	-	-	-	0.06	-	-	-	-	-	0.50
<i>Nasturium officinales</i> (Watercress) (Cresson) "Kresson"	leaf	Hamana et al., 1994	-	0.30	-	-	1.90	0.01	-	0.01	0.08	-	-	-	-	-	0.01
	root	Hamana et al., 1994	-	0.10	-	-	0.80	0.01	-	-	0.04	-	-	-	-	-	0.01
	leaf		-	0.10	-	-	0.20	0.01	-	-	0.25	-	-	-	-	-	0.01
	root		-	0.02	-	-	0.50	0.01	-	-	0.20	-	-	-	-	-	-
<b>Order Solanales</b>																	
<i>Solanum tuberosum</i> (Poteto)	skin of tuber	Hamana et al., 2017	-	0.29	-	-	1.00	0.04	-	0.01	0.16	-	-	-	-	-	0.02
	peeled tuber	Hamana et al., 2017	-	0.36	-	-	0.85	0.02	-	0.02	0.12	-	-	-	-	-	0.02
<i>Ipomoea batatas</i> (Sweet potato)	skin of tuberous root	Hamana et al., 2017	-	1.13	-	-	1.46	0.08	-	0.05	1.08	-	-	-	-	-	-
	peeled tuberous root	Hamana et al., 2017	-	0.55	-	-	0.81	0.04	-	0.03	0.80	-	-	-	-	-	-
<b>Order Proteales</b>																	
<i>Nelumbo nucifera</i> (Lotus) "Hasu"	[Aquatic plant] leaf	Hamana et al., 1994	0.01	0.14	0.04	-	1.50	1.06	-	-	0.45	0.05	-	-	-	-	-
	root	Hamana et al., 1994	-	0.32	0.01	-	0.53	-	-	-	0.03	-	-	-	-	-	0.01
"Renkon"	root [lotus root]		-	0.55	0.03	-	1.60	0.12	-	-	0.12	-	-	-	-	-	0.18
<b>Order Sapindales</b>																	
<i>Acer palmatum</i> (Japanese maple) "Iroha-momigi"	leaf		0.20	0.40	-	-	1.90	0.18	-	-	0.60	-	-	-	-	-	-
<i>Melia azedarach</i> (Chinaberry) "Sendan"	fruit		-	0.51	-	-	0.39	-	-	-	0.02	-	-	-	-	-	-
<b>Order Santalales</b>																	
<i>Viscum album</i> (Mistletoe) "Yadorigi" [Parasitic plant]	evergreen leaf		-	0.56	-	-	1.80	-	-	-	0.50	-	-	-	-	-	-
	fruit		-	0.20	-	-	1.20	-	-	-	0.05	-	-	-	-	-	-
<b>Order Caryophyllales</b>																	
<i>Salicornia europaea</i> (Sea asparagus) [Salt-tolerant plant]	leaf and stem		-	0.10	0.02	-	1.65	0.03	-	-	0.06	-	-	-	-	-	0.02
( <i>Salicornia</i> ) (Sampfire) "Atsukeshisou"																	
<i>Mesembryanthemum crystallinum</i> [Salt-tolerant plant]	leaf		-	0.32	0.15	-	1.34	-	-	-	0.02	-	-	-	-	-	0.05

(Ice plant)	root		0.02	0.04	0.03	-	0.70	0.04	-	-	0.02	-	-	-	-	-	-	-
<i>Fagopyrum esculentum</i> (Buckwheat) "Soba"	seed		-	0.30	-	-	1.30	0.20	-	-	0.65	-	-	-	-	-	-	-
	seed	Hamana et al., 1994	-	0.32	0.09	-	0.95	0.05	-	-	0.30	-	-	-	-	-	-	0.01
<b>Order Piperales</b>																		
<i>Houttuynia cordata</i> (Fish mint) (Fish plant) "Dokudami"	leaf		-	0.25	0.05	0.02	0.75	0.20	-	-	0.25	0.02	-	0.02	-	-	-	-
	root		-	0.42	-	-	1.33	0.55	-	-	0.32	-	-	-	-	-	-	-
<b>Asterids</b>																		
<b>Order Ericales</b>																		
<b>Family Theaceae</b>																		
<i>Camellia sinensis</i> (Tea plant) "Chano-ki"	root		-	0.02	-	-	0.15	0.07	-	-	0.35	-	-	-	-	-	-	-
	evergreen leaf	"Yabukita-cha"	-	0.25	-	-	1.80	-	-	-	0.32	-	-	-	-	-	-	-
	leaf powder [Matcha powder]		-	0.35	-	-	1.60	-	-	-	0.53	-	-	-	-	-	-	-
	fruit peel (fruit skin)		-	0.12	-	-	0.60	-	-	-	0.02	-	-	-	-	-	-	-
	seed		-	0.02	-	-	0.90	-	-	-	0.10	-	-	-	-	-	-	-
<i>Camellia japonica</i> (Camellia) "Tsubaki"	seed	Hamana et al., 1994	0.25	1.25	0.19	-	2.21	0.18	-	-	0.30	-	-	-	-	-	-	0.03
	evergreen leaf		-	0.04	-	-	0.70	-	-	-	0.40	-	-	-	-	-	-	-
<b>Family Ericaceae</b>																		
<i>Rhododendron molle</i> (Japanese azalea) "Renge-tsutsuji"	leaf		-	0.24	-	-	0.65	-	-	-	0.10	-	-	-	-	-	-	-
	flower		-	0.29	-	-	0.43	-	-	-	0.02	-	-	-	-	-	-	-
<i>Pyrola japonica</i> "Ichiyakusou"	leaf		-	1.50	-	-	0.83	0.08	-	-	0.06	-	-	-	-	-	-	0.03
	root		-	0.06	-	-	0.75	0.13	-	-	0.06	-	-	-	-	-	-	0.05
<i>Monotropa hypopitys</i> "Shakujou-sou" [Saprophytic plant whole plant			-	0.16	-	-	0.45	-	-	-	0.12	-	-	-	-	-	-	-
<i>Monotropastrum humile</i> "Ginryou-sou" [Saprophytic plant whole plant			-	0.05	-	-	0.50	-	-	-	0.06	-	-	-	-	-	-	-
<b>Family Actinidiaceae</b>																		
<i>Actinidia deliciosa</i> (Kiwifruit)	fruit		-	1.40	-	-	1.40	0.08	-	-	0.34	-	-	-	-	-	-	0.01
<b>Family Ebenaceae</b>																		
<i>Diospyros kaki</i> (Kaki) (Persimmon) "Kakino-ki"	leaf		-	0.60	-	-	1.30	-	-	-	0.35	-	-	-	-	-	-	-
	fruit		-	0.10	-	-	0.70	-	-	-	0.22	-	-	-	-	-	-	-
<b>Order Garryales</b>																		
<i>Eucommia ulmoides</i> "Touchu"	leaf [Eucommia tea]		-	0.01	-	-	1.80	-	-	-	0.02	-	-	-	-	-	-	0.02
<b>Order Lamiales</b>																		
<i>Olea europaea</i> (Olive)	evergreen leaf		-	0.05	-	-	1.60	-	-	-	0.40	-	-	-	-	-	-	0.02
	fruit		-	0.51	-	-	1.25	-	-	-	0.35	-	-	-	-	-	-	0.02
<i>Osmunthus fragrans</i> (Fragrant orange-colored olive)	evergreen leaf		-	0.18	-	-	0.45	-	-	-	0.03	-	-	-	-	-	-	-
	fruit	"Kin-mokusei"	-	0.16	-	-	0.55	-	-	-	0.05	-	-	-	-	-	-	-
<b>Order Asterales</b>																		
<i>Helianthus tuberosus</i> (Jerusalem artichoke) "Kikuimo"	leaf		-	0.40	-	-	0.62	0.01	-	-	0.75	-	-	-	-	-	-	-
	tuber		-	0.35	-	-	0.90	0.01	-	-	0.17	-	-	-	-	-	-	-

Alphabetical abbreviations and numeric codes (number of methylene (CH<sub>2</sub>) groups between amino (NH<sub>2</sub>) or imino (NH) groups) of polyamines are used. Dap, diamino propane [NH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>NH<sub>2</sub>]; Put, putrescine [NH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>NH<sub>2</sub>]; Cad, cadaverine [NH<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub>NH<sub>2</sub>]; NSpd, norspermidine [NH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>NH(CH<sub>2</sub>)<sub>3</sub>NH<sub>2</sub>]; Spd, spermidine [NH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>NH(CH<sub>2</sub>)<sub>4</sub>NH<sub>2</sub>]; HSpd, homospermidine [NH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>NH(CH<sub>2</sub>)<sub>4</sub>NH<sub>2</sub>]; NSpm, norspermine [NH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>NH(CH<sub>2</sub>)<sub>3</sub>NH(CH<sub>2</sub>)<sub>3</sub>NH<sub>2</sub>]; TSpm, thermospermine [NH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>NH(CH<sub>2</sub>)<sub>3</sub>NH(CH<sub>2</sub>)<sub>4</sub>NH<sub>2</sub>]; Spm, spermine [NH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>NH(CH<sub>2</sub>)<sub>4</sub>NH(CH<sub>2</sub>)<sub>3</sub>NH<sub>2</sub>]; AHSpm, aminopropylhomospermidine [NH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>NH(CH<sub>2</sub>)<sub>4</sub>NH(CH<sub>2</sub>)<sub>4</sub>NH<sub>2</sub>]; Can, canavamine [NH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>NH(CH<sub>2</sub>)<sub>3</sub>NH(CH<sub>2</sub>)<sub>4</sub>NH<sub>2</sub>]; HSpn, homospermine [NH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>NH(CH<sub>2</sub>)<sub>4</sub>NH(CH<sub>2</sub>)<sub>4</sub>NH<sub>2</sub>]; CPen, caldopentamine [NH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>NH(CH<sub>2</sub>)<sub>3</sub>NH(CH<sub>2</sub>)<sub>3</sub>NH(CH<sub>2</sub>)<sub>3</sub>NH<sub>2</sub>]; HCPen, homocaldopentamine [NH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>NH(CH<sub>2</sub>)<sub>3</sub>NH(CH<sub>2</sub>)<sub>3</sub>NH(CH<sub>2</sub>)<sub>4</sub>NH<sub>2</sub>]; Agm, agmatine [NH<sub>2</sub>C(NH)NH(CH<sub>2</sub>)<sub>4</sub>NH<sub>2</sub>]. -, not detected (<0.005 μmol/g wet weight). (.), popular name. "", species or variety name in Japanese. Citations of our previous data from the References are shown and blanks are new data of this study or unpublished data previously analyzed.

### 3. RESULTS AND DISCUSSION

#### Polyamine distribution analysis of various organs of typical, characteristic or distinctive species in Angiosperms and Gymnosperms

Since the polyamines of the most of the 95 plant organs were analyzed by our HPLC only in the present study, quantitatively analyzing TSpm in the Spm peak on the HPLC charts was difficult. Previously published data and newly published data previously analyzed were determined by GC-

MS/HPGC-MS in addition to HPLC. Tertiary branched polyamines, *N*-methylpolyamines, 2-hydroxypolyamines and alkanolpolyamines were not detected in the 95 plant organs and are not shown in Tables. Species-specific and organ-specific polyamine distribution profiles and polyamine distributions for adapting for growth environment are shown in Table 1 (Rosids and Asterids of Eudicots in Angiosperms), Table 2 (Monocots in Angiosperms) and Table 3 (Gymnosperms) and are described in 1-14. Though polyamine distribution profiles did not chemotaxonomically depend on chemotaxonomic positions within seed plants, we don't really care about phylogenetic classification in detail, therefore orders are arranged within classes randomly in Tables. Unfortunately, cellular polyamines of citrus fruit tree of Rosids of Eudicots and cacti of the order *Caryophyllales* of Eudicots were not analyzed in the present study.

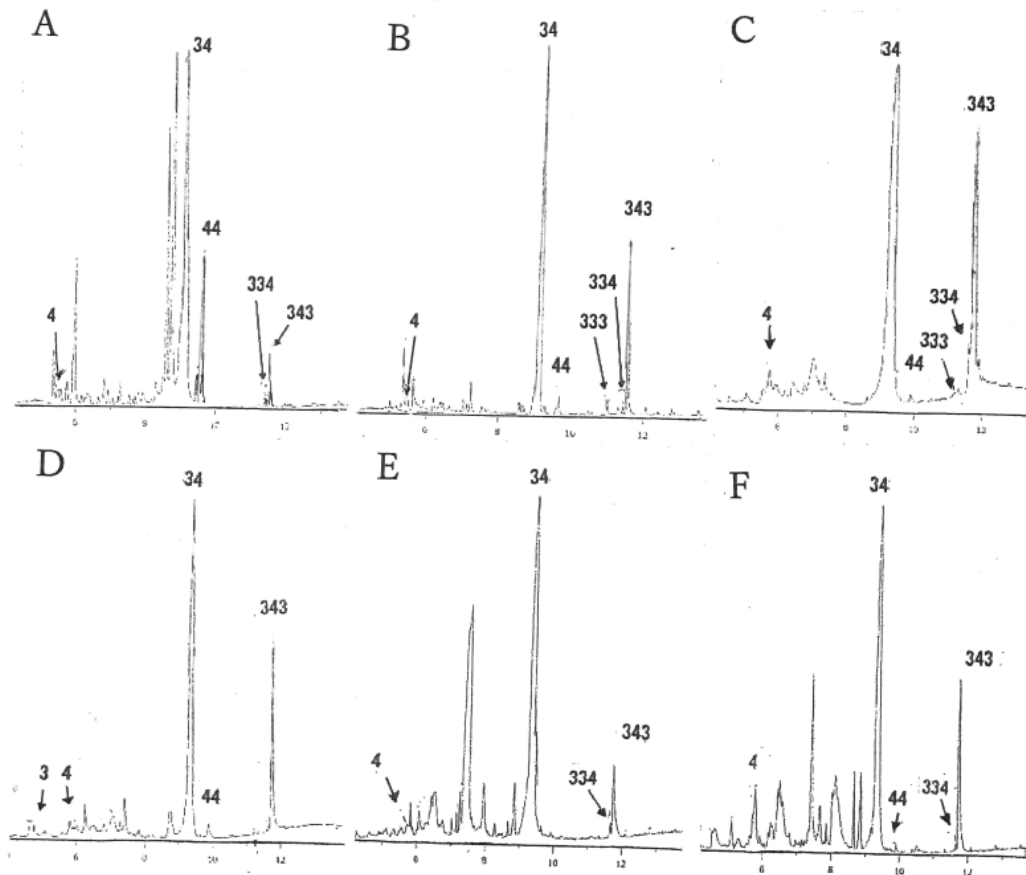
**Table 2: Polyamine concentrations in plant organs in Monocots of Angiosperms**

Plant species	Organs	References	Polyamines (μmol/g wet weight)														
			Dap	Put	Cad	NSpd	Spd	HSpd	NSpm	TSpm	Spm	AHSpd	Can	HSpm	CPen	HCPen	Agm
			3	4	5	33	34	44	333	334	343	344	434	444	3333	3334	
<b>Monocots in Angiosperms</b>																	
<b>Order Poales</b>																	
<i>Hordeum vulgare</i> (Barley) "Ohmugi"	seed [Rolled barley]		0.05	0.12	-	-	1.05	-	-	-	0.80	-	-	-	-	-	
	seed	Hamana <i>et al.</i> , 1994	0.02	0.95	-	-	0.80	0.01	-	-	0.35	-	-	-	-	0.05	
	seedling	Hamana <i>et al.</i> , 1994	0.02	2.74	0.02	-	0.95	0.01	-	-	0.10	-	-	-	-	0.40	
<i>Oryza sativa</i> (Rice plant) "Ine" "Sasanishiki"	brown rice		0.01	0.09	-	-	0.33	0.01	-	-	0.84	-	-	-	-	-	
	rice bran		-	0.22	-	-	1.06	0.01	-	-	1.40	-	-	-	-	-	
	fermented rice bran		0.02	3.00	2.00	-	0.90	0.01	-	-	1.50	-	-	-	-	-	
	seed	Hamana <i>et al.</i> , 1994	-	0.35	0.25	-	0.25	0.01	-	-	0.04	-	-	-	-	0.15	
	seedling	Hamana <i>et al.</i> , 1994	-	1.65	0.13	-	1.07	-	-	-	0.07	-	-	-	-	0.37	
	leaf	Hamana <i>et al.</i> , 1994	-	0.10	-	-	0.86	0.02	-	-	0.42	-	-	-	-	-	
	root	Hamana <i>et al.</i> , 1994	-	0.20	0.01	-	0.45	0.04	-	-	0.13	-	-	-	-	-	
<i>Coix lacryma-jobi</i> (Pearl barley) "Hatoumugi"	seed	Hamana <i>et al.</i> , 1994	0.10	0.20	0.10	-	0.50	0.02	-	0.01	0.10	0.01	-	-	-	0.02	
<i>Panicum miliaceum</i> (Proso millet) "Kibi"	seed	Hamana <i>et al.</i> , 1994	0.08	0.80	0.02	-	0.45	0.01	-	-	0.25	0.01	-	-	-	-	
<i>Sorghum bicolor</i> (Great millet) "Morokoshi"	seed	Hamana <i>et al.</i> , 1994	0.07	0.45	0.10	-	2.04	0.02	-	-	0.09	0.01	-	-	-	-	
<i>Phleum pratense</i> (Timothy)	seed	Hamana <i>et al.</i> , 1994	0.08	0.20	-	-	0.50	0.01	-	-	0.04	0.01	-	-	-	-	
<i>Zea mays</i> (Corn) "Toumorokoshi"	seed	Hamana <i>et al.</i> , 1994	0.01	0.95	0.05	-	1.51	0.01	-	-	0.84	-	-	-	-	-	
	seedling	Hamana <i>et al.</i> , 1994	0.12	3.42	0.35	-	1.37	0.01	-	-	0.12	-	-	-	-	0.12	
<b>Order Alismatales</b>																	
<i>Spirodela polyrrhiza</i> (Duckweed) "Ukikusa"	leaf	Hamana <i>et al.</i> , 1994	0.10	0.42	-	-	0.90	0.04	0.02	-	0.06	-	-	-	0.01	-	0.02
	[Aquatic plant] root	Hamana <i>et al.</i> , 1994	0.26	1.99	-	-	1.90	0.32	0.01	-	0.01	-	-	-	-	-	
<i>Amorphophallus konjac</i> (Konjac) "Konjac"	leaf		-	0.10	0.06	-	1.80	0.35	-	-	0.34	-	-	-	-	-	
	tuber (corn)		0.01	0.48	-	-	0.65	0.02	-	-	0.06	-	-	-	-	-	
	flower		0.01	0.10	0.52	-	0.75	0.15	-	-	0.50	-	-	-	-	0.04	
<i>Colocasia esculenta</i> (Taro) "Satoimo"	leaf		0.35	0.50	0.01	-	1.13	-	-	-	-	-	-	-	-	0.02	
	tuber		-	0.35	-	-	1.27	0.05	-	-	0.10	-	-	-	-	0.05	
<b>Order Commelinales</b>																	
<i>Eichhornia crassipes</i> (Water hyacinth) "Hoteiaoi"	leaf	Hamana <i>et al.</i> , 1994	0.15	0.42	-	0.04	2.12	0.10	0.08	0.02	0.26	-	-	0.01	-	-	0.01
	[Aquatic plant] root	Hamana <i>et al.</i> , 1994	0.40	1.95	0.04	-	0.90	0.42	-	-	0.02	-	-	-	-	-	0.01
<i>Tradescantia ohiensis</i> (Spiderwort) (Oyster plant)root			0.02	0.22	-	-	0.82	0.10	-	-	0.09	-	-	-	-	-	
	"Murasaki-tsuyukusa" stem		0.31	0.35	-	-	0.06	-	-	-	0.02	-	-	-	-	-	
	leaf		0.55	0.85	0.02	-	0.22	-	-	-	0.07	-	-	-	-	-	
	flower		0.40	0.33	0.20	-	0.10	-	-	-	0.01	-	-	-	-	-	
<b>Order Asparagales</b>																	
<i>Aloe arborescens</i> (Aloe) "Kidachialoe" [succulen] leaf			-	0.05	-	-	0.63	0.02	-	-	0.07	-	-	-	-	-	0.02
<b>Order Zingiberales</b>																	
<i>Musa acuminata</i> 'Gros Michel' (Banana)	fruit		-	1.40	0.01	-	0.90	0.08	-	-	0.02	-	-	-	-	-	0.01
	root		-	0.67	-	-	0.74	0.04	-	-	0.02	-	-	-	-	-	-
<i>Zingiber officinale</i> (Ginger) "Shouga"	leaf		0.23	0.40	-	-	0.27	-	-	-	0.02	-	-	-	-	-	-
	flower		0.19	0.14	-	-	0.40	0.01	-	-	0.03	-	-	-	-	-	0.13

### **3.1 Organs of Eudicots (Rosids and Asterids) (Table 1.)**

Since the commercial cultivation of tea plants is thriving in Japan and that of rose and strawberry is prominent in Maebashi city, Gunma, these plant organs were included for analysis in the present study. Plant communities of *Cerasus sargentii* (cherry), *Rhododendron molle* (Japanese azalea), *Houttuynia cordata* (fish mint) and *Pyrola japonica* are protected in Hamana home forest, Tsumagoi, Gunma. *Helianthus tuberosus* is a naturalized plant in Japan and its tuber contains inulin. Therefore, polyamines of these plant organs were also analyzed in the present study. A part of polyamine analysis is described in 4. Organs of Asterids.

Polyamines of leaf, fallen red leaf, flower and fruit of cherry were additionally analyzed in the present study (Fig. 5). TSpM was detected in the leaf, flower, fruit as well as the root and stem but not in the fallen red leaf. HSpd was not detected in the flower. The polyamine profiles found in cherry organs is a typical polyamine profile in Rosids. In cherry, red fallen leaves contained lower levels of polyamines than green leaves, and flower lacked Put and HSpd. In wild rose root, high HSpd and low SpM levels were found. The rose flower lacked HSpd. The rose fruit contained a high concentration of Agm. In the fruit of strawberry, Put, Spd, HSpd, SpM and Agm were found. Fish mint contained high concentrations of HSpd in its leaf and root. This is the highest HSpd level observed alongside mulberry root among the seed plant roots analyzed in our studies. Furthermore, AHSpd (344) and HSpM (444) were detected in its leaf. In tea plant of Asterids, high Put, Spd and SpM levels were found in the leaves cultivated in Hamana home garden and similarly in the leaf powder as a food [Matcha powder] made in Shizuoka, Japan. The roots of the tea plant contained HSpd.



**Fig. 5: HPGC retention charts of cherry polyamines extracted from roots (A), stems (B), leaves (C), fallen red leaves (D), flowers (E) and fruits (F) of *Cerasus sargentii*, by JEOL JMS-700. Polyamine peaks were identified by MS. Abbreviations for polyamines are shown in Table 1.**

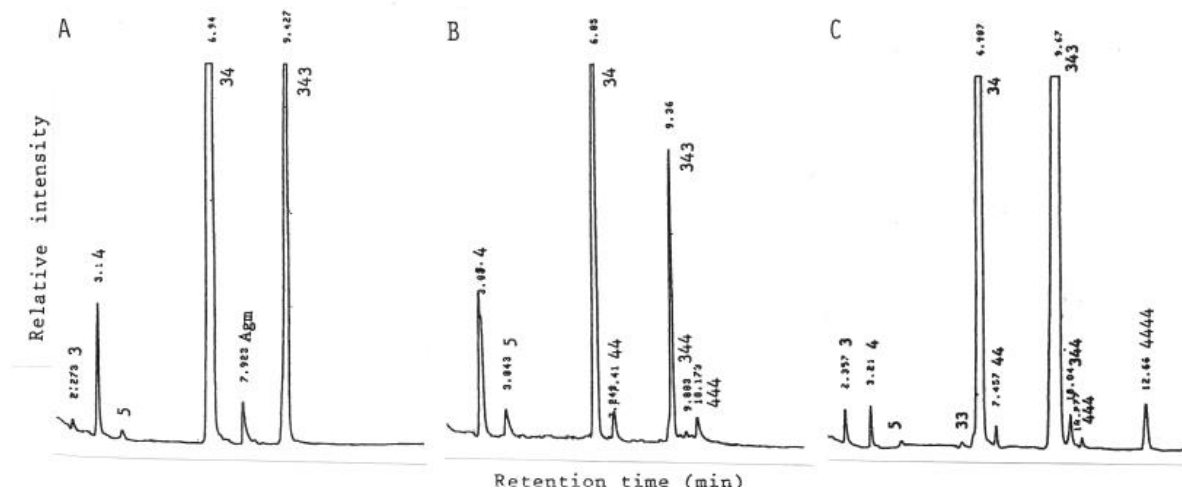
### 3.2 Brassicales plant organs (Table 1)

*Brassicales* plants are important vegetables, furthermore *Arabidopsis thaliana* as the type species of seed plants, belongs in the order *Brassicales*. Polyamine analysis of *Moringa oleifera* of the family *Moringaceae* and some *Brassicaceae* species were added in the present study. *Moringa* (horseradish tree) is a short-lived, fast-growing, drought-resistant tree and is widely cultivated for its young seed pods and leaves, which are used as vegetables and for traditional herbal medicine. Put, Spd and Spm were the major polyamines found in the leaves and seeds of moringa. The stem of *Brassica oleracea* var. *gongylodes* contained Dap, NSpd, HSpd and Agm in addition to Put, Spd and Spm, detected as common polyamines in other *Brassicales* leaves (Hamana et al., 2015). *Raphanus sativus* and *Nasturium officinales*, newly analyzed in the present study, contained

common polyamines. HSpd and TSpM were distributed as a minor polyamine in *Brassicales* plants (Hamana et al., 2015). The large root of *Raphanus sativus* have lower Spm concentrations. The morphology of the large stem of turnip (*B. rapa*) and kohlrabi (German turnip or turnip cabbage) (*B. oleracea*) and the large root of Japanese radish (*R. sativus*) is different. The flower buds of broccoli and cauliflower have a specific morphology and were rich in agmatine, however its level was higher in the green flower buds of broccoli rather than the white flower bud of cauliflower (Hamana et al., 2015). The polyamine distribution profile of their organs may be influenced by their species-specific organ morphology within the order *Brassicales*.

### 3.3 Leguminous plant organs (Table 1)

Leguminous plants consist of 650-745 genera (12,000-19,500 species) belonging to a large taxon, family *Fabaceae* (formerly *Leguminosae*) of the order *Fabales* in angiosperms and are important for agriculture products and food usage (Kondo et al., 1989). Unusual tetra-amines such as TSpM, AHSpd, Can and HSpM had been detected in the mature seeds but not in the immature seeds (Fig. 4) (Otsuka et al., 2005). An unusual long aliphatic diamine, 1,6-diaminohexane (Dah) (6), had been found in the roots of ten species and the seeds of two species (Hamana et al., 2019). In the sprout (seedling), the root region increased in the levels of Put and Cad levels, and the stem and seed parts increased in cadaverine level. Dap, NSpd, NSpm and/or CPen were distributed in some roots and leaves (Hamana et al., 2019).



**Fig. 4: GC retention charts of leguminous polyamines extracted from immature seeds (A), mature seeds (B) and mature seeds stored for 5 years after harvest (C) of *Vicia sativa* by SHIMADZU GC-9A (Otsuka et al., 2005). Abbreviations for polyamines are shown in Table 1.**

We have reported the occurrence of HSpd, NSpm, TSpm, CPen and HCPen polyamines in addition to common polyamines in the leaves of rooibos, *Aspalathus linearis* (Hamana et al., 2019). HSpd and NSpm were detected also in two different leaf products [Rooibos tea], reanalyzed in the present study. It is suggested that the occurrence of NSpm is universal within Rooibos tea products.

Natural occurrence of the two guanidinoamines,  $\gamma$ -guanidinooxypropylamine decarboxylated product of L-canavanine and homoagmatine (HAgm) decarboxylated product of L-homoarginine in the wisteria *Wisteria floribunda* and the sword bean *Canavalia gladiata* was reported (Hamana and Matsuzaki, 1985b). L-Canavanine and L-homoarginine are non-proteinogenic amino acids found in certain leguminous plant seeds. Leguminous seeds are rich in various polyamines and a treasure trove of biogenic amino acids and polyamines.

### **3.4 Organs of Asterids (Table 1)**

Asterids are a large clade (monophyletic group) of seed (flowering) plants, composed of 17 orders and more than 80,000 species, about a third of the total seed plant species. The asterids are divided into two unranked clades lamiids (8 orders) and campanulids (7 orders) and the single orders *Cornales* and *Ericales*. The evergreen leaf of the tea plant is used as green tea. Olive oil and camellia oil as a food are extracted from their fruits. The fruits of kaki and kiwifruit (*Actinidia deliciosa*) are used as an edible fruit. *Eucommia ulmoides* is a species of small tree native to China and is highly valued in herbology such as traditional Chinese medicine. Olive is self-incompatible plant whereas the fragrant orange-colored olive is a dioecious plant.

A major occurrence of Spm was found in the evergreen leaves of *Camellia sinensis* (tea plant), *Camellia japonica* (camellia) and *Olea europaea* (olive), and in the leaves of *Diospyros kaki* (kaki), and *Helianthus tuberosus* (Jerusalem artichoke). A little amount of Spm was detected in the leaves of *Pyrola japonica*, *Rhododendron molle* (Japanese azalea), *Eucommia ulmoides* and *Osmanthus fragrans* (fragrant orange-colored olive). HSpd was detected in the roots. A chemotaxonomically specific polyamine profile was not found in Asterids.

### **3.5 Edible root, tuberous root, tuber and corm (bulbotuber) (Table 1 and 2)**

Polyamine components of the stem of kohlrabi, the stem (root in Hamana et al., 2015) of turnip and the root of Japanese radish in *Brassicales*, and the tuber of potato and the tuberous root of sweet potato in *Solanales* and the root of lotus in *Proteales*, and the tuber of Jerusalem artichoke in *Asterales*, and the corm (bulbotuber) of konjac, the tuber of taro, and the root of ginger in Monocots, resemble those of the normal stem or root within the same orders of each other.

### **3.6 Aquatic plants under low osmotic pressure (Table 1 and 2)**



Although aquatic plants are sporadically distributed in seed plants, new polyamine analysis was not contained in the present study. The leaf of *Nelumbo nucifera* (lotus) of the order *Proteales* of Rosids contained HSpd and AHSpd, the leaf of *Spirodela polyrhiza* (duckweed) of the order *Alismatales* of Monocots contained HSpd, NSpm and CPen, and the leaf of *Eichhornia crassipes* (water hyacinth) of the order *Commelinales* of Monocots contained NSpd, HSpd, NSpm, TSpM and HSpM, as reported in Hamana et al., 1994. The occurrence of these unusual triamines, tetraamines and pentaamines is possible to be aquatic plant-specific polyamines for osmotic stress.

### **3.7 Salt-tolerant plants of the order *Caryophyllales* (Table 1)**

*Salicornia europaea* and *Mesembryanthemum crystallinum* belonging to the order *Caryophyllales* of Rosids are salt-tolerant seed plants. The two contained Put and Spd as the major polyamines and Cad, HSpd, Spm and Agm as minor polyamines. The occurrence of Cad and the low concentration of Spm is possibly related to their salt tolerance.

### **3.8 Saprophytic plants of *Ericales* and parasitic plants of *Santalales* (Table 1)**

*Monotropa* and *Monotropastrum* are small genera of non-photosynthetic, myco-heterotrophic (saprophytic) plants, with monotropoid mycorrhizae, belonging to the order *Ericales* of Asterids of Eudicots in Angiosperms. They have a short underground stem (rhizome), roots and chloroplast-deficient scale leaves. Although *Pyrola japonica*, a close relative to them, contained HSpd and Agm in addition to Put, Spd and Spm, the simple polyamine profile of the saprophytic species *Monotropa hypopitys* and *Monotropastrum humile* was Put, Spd, and Spm.

*Viscum album*, belonging to the order *Santalales* of Rosids of Eudicots in Angiosperms, is an evergreen semi-parasitic plant on deciduous trees. The leaf of *V. album* was rich in Put, Spd and Spm. The Spm level was poor in the roots. Within the present analyses, HSpd was not detected in a semi-parasitic plant nor in the two myco-heterotrophic plants.

### **3.9 Mangrove plants (Table 1)**

Mangrove plants belonging to the order *Malpighiales* of Rosids of Eudicots in Angiosperms are salt-tolerant and are adapted to live in harsh coastal conditions and have evergreen leaves. The three red mangrove species (*Bruguiera gymnorhiza*, *Kandelia obovata*, *Rhizophora mucronata*) survives in the most inundated areas, props itself above the water level with stilt or prop roots and then absorbs air through lenticels in its bark. In the three species, evergreen leaves contained high levels of Put and Spd and low levels of Spm. Agm was detected in the leaves. The roots of three species contained AHSpd in addition to high concentration of HSpd. These polyamine-characteristics seems to adapt to coastal conditions and are salt-tolerant.

### **3.10 Succulents in seed plants (Table 2)**

The succulent plant *Aloe arborescens* belonging to the order *Asparagales* of Monocots in Angiosperms was analyzed in the present study. Put, Spd, HSpd, Spm and Agm were detected in the leaf of the succulent plant. Low Put level of the leaf was lower than other seed plant leaves.

### **3.11 Evergreen leaves and fallen leaves in broadleaf trees (Table 1)**

Three types of carbon assimilation cycle are known in plant leaves. The C3 plant in which the first photosynthetic product is 3 carbon compounds, is the majority in seed plants. The C4 plant in which the first photosynthetic product is 4 carbon compounds is found in some seed plants and adapt to dry, strong light and hot environments. The CAM (Computer Aided Manufacturing) plant in which CO<sub>2</sub> is absorbed at night and photosynthesis occurs during the day enabling them to adapt to arid areas and deserts. A relation between the three types and polyamine distribution profiles was not found in our studies and polyamine data from plants grown in different climatic zones were not found in others.

In evergreen leaves of evergreen broadleaf trees of Eudicots of Angiosperms, Spm was detected in mistletoe, tea plant, camellia and olive as a major polyamine, whereas in three mangrove plants and in fragrant orange-colored olive it was present as a minor polyamine. When polyamines of leaves (green leaves) and fallen leaves in the deciduous broadleaf trees, cherry, mulberry and pin oak, in Eudicots were analyzed, a decreased Spm level was found in the three fallen leaves. In addition to Spm, other polyamines were present at high levels in photosynthetically active green leaves in the deciduous broadleaf trees. On the other hand, Spm level increased in the fallen leaves of two species of gymnosperms, as described in 13. Organs of Gymnosperms.

### **3.12 Organs of Monocots (Table 2)**

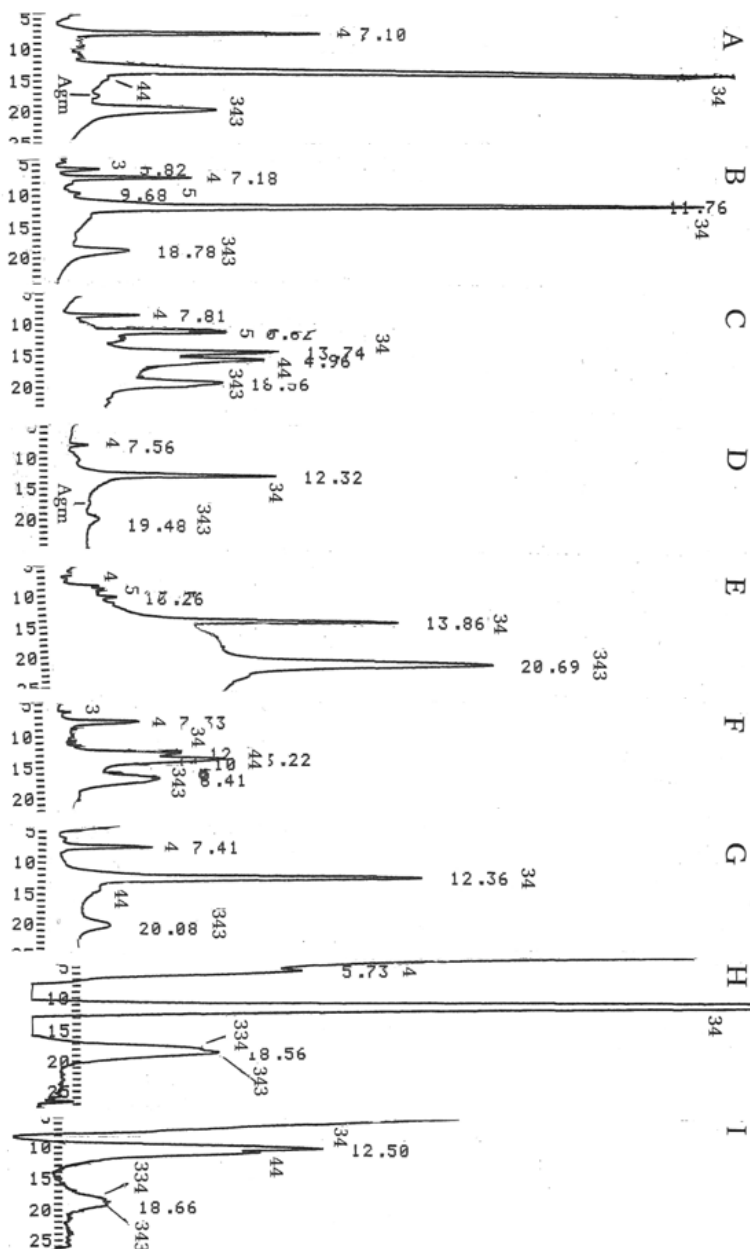
Polyamines of the organs of *Amorphophallus konjac* (konjac), *Colocasia esculenta* (taro), *Musa acuminata* (banana), *Zingiber officinale* (ginger) and *Tradescantia ohiensis* (spiderwort) were analyzed in the present study. The leaf and flower of konjac were rich in HSpd and Spm whereas its corm (bulbotuber) was poor in the two polyamines. A high concentration of Cad was found in the flower. A low Spm level was found in the fruit of banana and the ginger organs. Dap was found in the ginger leaf and flower, furthermore the flower was rich in Agm. Dap, Put, Cad and Agm were widely distributed within Monocots and the distribution profiles seems to be organ specific (Hamana et al., 1994). As described in INTRODUCTION of this report, the identification of polyamines in the silica bodies of rice and analysis of their function in silica formation is interesting (Ozaki, 2018). Polyamines of brown rice, rice bran and fermented rice bran are described in CONCLUSION 3.

### **3.13 Organs of Gymnosperms (Table 3)**

The gymnosperms include conifers, cycads, ginkgo, and gnetophytes, forming the clade Gymnospermae. Some genera have ectomycorrhiza fungal associations with roots (*Pinus*), while in some others (*Cycas*) small specialized roots called coralloid roots are associated with nitrogen-fixing cyanobacteria. A long time ago, the presence of mobile sperms of cycad and ginkgo was found in Japan. We had analyzed polyamines of the three groups (a cycad, ginkgo (a single living species) and some conifers) (Hamana and Matsuzaki, 1985). Unfortunately, HPGC-MS analysis of the polyamines of the three groups encountered issues in the present study. TSpm was estimated to be detected in the leaves and seeds of ginkgo based on our ion-exchange/post-labeled HPLC analysis (Fig. 7), therefore 0.01 (μmol/g wet weight) is tentatively filled in Table 3. The occurrence of TSpm in some seed plants including ginkgo had been reported by reversed-phase (RP) HPLC after benzylation (Takahashi et al., 2018; Takano et al. (2012). The leaves of *Ginkgo biloba*, a deciduous conifer, and the deciduous conifer *Larix kaempferi*, as well as evergreen leaves of *Cycas revoluta* and other conifers analyzed contained a low level of Spm. Its level increased in the fallen yellow leaves of the former two. HSpd was found in the roots of three conifers as a major polyamine in the present study. The polyamine distribution profiles were slightly different among the three gymnosperm groups and their polyamine profiles are distinguished slightly from the profiles of another seed plant clade, Angiosperms.

**Table 3: Polyamine concentrations in plant organs of Gymnosperms**

Plant species	Organs	References	Polyamines (μmol/g wet weight)													
			Dap	Put	Cad	NSpd	Spd	HSpd	NSpm	TSpm	Spm	AHSpd	Can	HSpm	CPen	HCPen
			3	4	5	33	34	44	333	334	343	344	434	444	3333	3334
<b>Gymnosperms</b>																
<b>Class Cycadoopsida</b>																
<i>Cycas revoluta</i> (Sago palm) "Sotetsu"	evergreen leaf	Hamana and Matsuzaki, 1985	-	0.41	-	-	0.36	-	-	-	0.01	-	-	-	-	-
	root	Hamana and Matsuzaki, 1985	-	0.62	0.02	-	0.05	-	-	-	0.01	-	-	-	-	0.07
	coralloid root	Hamana and Matsuzaki, 1985	-	1.30	0.68	-	0.68	0.02	-	-	0.13	-	-	-	-	0.39
<b>Class Ginkgoopsida</b>																
<i>Ginkgo biloba</i> (Ginkgo) "Icho"	leaf	Hamana and Matsuzaki, 1985	-	0.16	-	-	0.64	-	-	-	0.14	-	-	-	-	-
	root	Hamana and Matsuzaki, 1985	0.01	0.10	-	-	0.10	0.08	-	-	0.01	-	-	-	-	-
	seed	Hamana and Matsuzaki, 1985	0.01	0.14	-	-	0.16	-	-	-	0.03	-	-	-	-	-
	fallen yellow leaf		-	0.30	-	-	0.85	-	-	0.01	0.40	-	-	-	-	-
	seed		-	1.10	-	-	0.50	0.08	-	0.01	0.10	-	-	-	-	-
<b>Class Pinopsida [conifer]</b>																
<i>Cedrus deodara</i> (Deodar cedar) "Himaraya-sugi"	evergreen leaf	Hamana and Matsuzaki, 1985	-	0.85	-	-	0.71	-	-	-	0.16	-	-	-	-	-
<i>Torreya nucifera</i> (Japanese totteya) "Kaya"	evergreen leaf	Hamana and Matsuzaki, 1985	-	0.14	-	-	0.14	-	-	-	0.01	-	-	-	-	-
	female inflorescence	Hamana and Matsuzaki, 1985	-	0.10	-	-	0.01	-	-	-	0.01	-	-	-	-	-
<i>Pinus thunbergii</i> (Japanese black pine) "Kuro-mat"	evergreen leaf	Hamana and Matsuzaki, 1985	-	0.25	-	-	0.26	-	-	-	0.08	-	-	-	-	-
	female inflorescence	Hamana and Matsuzaki, 1985	-	2.40	-	-	0.11	-	-	-	0.09	-	-	-	-	-
	male inflorescence	Hamana and Matsuzaki, 1985	-	0.38	-	-	0.25	-	-	-	0.03	-	-	-	-	-
	fruit	Hamana and Matsuzaki, 1985	-	1.59	-	-	0.28	-	-	-	0.16	-	-	-	-	-
<i>Metasequoia glyptostroboides</i> (Dawn redwood)	leaf	Hamana and Matsuzaki, 1985	-	0.16	0.01	-	0.21	0.01	-	-	0.01	-	-	-	-	-
<i>Abies firma</i> (Momi fir)	evergreen leaf		-	0.47	-	-	0.75	0.01	-	-	0.25	-	-	-	-	0.02
	acupuncture leaf		0.09	0.30	0.02	-	1.35	-	-	-	0.13	-	-	-	-	-
	root (young)		-	0.47	-	-	0.45	0.35	-	-	0.26	-	-	-	-	0.03
<i>Larix kaempferi</i> (Japanese larch) "Kara-matsu"	leaf		-	0.10	-	-	0.78	-	-	-	0.10	-	-	-	-	0.01
	fallen yellow leaf		-	0.01	0.01	-	0.20	-	-	-	0.26	-	-	-	-	-
	root (young)		-	0.20	0.02	-	0.37	0.15	-	-	0.22	-	-	-	-	-
<b>Class Taxopsida [conifer]</b>																
<i>Taxus cuspidata</i> (Japanese yew) "Ichii"	evergreen leaf		0.02	0.20	-	-	0.73	0.02	-	-	0.06	-	-	-	-	-
	root (young)		-	0.15	0.02	-	0.22	0.15	-	-	0.18	-	-	-	-	-



**Fig. 7:** HPLC elution charts of the conifer polyamines extracted from evergreen leaves (A) and acupuncture leaves (witches' broom disease) (B) of *Abies firma*, the roots (C), leaves (D) and fallen yellow leaves (E) of *Larix kaempferi*, and the roots (F) and evergreen leaves (G) of *Taxus cuspidate*, and the gymnosperm polyamines extracted from fallen yellow leaves (H) and seeds (I) of *Ginkgo biloba* by Hitachi L6000. In the low attenuation peaks in H and I, a shoulder peak corresponding to 334 in the broad peak of 343 was estimated. Abbreviations for polyamines are shown in Table 1.

### **3.14 Polyamines in green algae, mosses and ferns in plant evolution and classification**

The Archaeplastida (or kingdom Plantae) comprise the photoautotrophic glaucophytes (Glaucophyta), red algae (Rhodophyta), green algae and land plants (known as Embryophyta). Viridiplantae (green plants) include green algae of Chlorophyta and Streptophyta including Charophyta, as a higher evolved part of green algae, and land plants. Embryophytes have a common ancestor with green algae, having emerged within the Phragmoplastophyta clade of fresh water charophyte green algae as a sister taxon of Charophyceae, Coleochaetophyceae and Zygnematophyceae. Living embryophytes include hornworts, liverworts, mosses, lycophytes, ferns, gymnosperms and angiosperms.

We have analyzed polyamines in green algae (Hamana et al., 2018, 2023), mosses (Bryophyta) (Hamana and Matsuzaki, 1985a) and ferns (Polypodiophyta) (synonym Pteridophyta, Pteridopsida) (Hamana and Matsuzaki, 1985a; Hamana et al., 1988). Dap, Put, NSpd, Spd, HSpd, NSpm, Spm and TSpm were widely distributed in unicellular chlorophyte green algae. However, the tetra-amines, NSpm, Spm and TSpm were major polyamines in multicellular species. CPen and HCPen were detected in the multicellular green algal species. All polyamines detected in Chlorophyta green algae were distributed within unicellular and multicellular species of streptophyte green algae. Although major polyamines of species of mosses (14 species) and ferns (15 species) were analyzed by HPLC analysis, similar distributions of polyamines were observed in them. All polyamines distributed within seed plants as described in the present study had been distributed already through green algae, mosses and ferns in plant evolution.

## **4. CONCLUSIONS**

### **4.1 Novel polyamines and polyamine derivatives in seed plants**

Although novel polyamines and polyamine derivatives were not detected in the additional 95 plant organs analyzed in the present study, various unusual polyamines and polyamine derivatives had been found in our course of plant polyamine analyses.  $N^1$ -Aminopropylagmatine (3Agm) and  $N^1$ -aminobutylagmatine (4Agm) found in bacteria (Oshima, 2023; Ohnuma et al. 2005) have never been found in plants and algae.

#### **4.1.1 Linear and branched polyamines in seed plants**

Legume crops of seed plants are rich sources of long polyamines, especially in their mature seeds (Fig. 4). When we analyzed the mature seeds of 73 leguminous plant species, the tetra-amines aminopropylhomospermidine (AHSpd) (344), canavamine (Can) (434) and homospermine (HSpm) (444), and the penta-amines caldopentamine (CPen) (3333), aminopropylcanavamine (APCan) (3434), aminobutylcanavamine (ABCan) (4434) and homopentamine (HPen) (4444), were sporadically distributed in leguminous seeds (Hamana et al., 1991, 1992a, 1996; Matsuzaki

et al., 1990b; Otsuka et al., 2005). Tertiary branched  $N^5$ -aminobutylhomospermine (AB5HSp<sub>m</sub>) (4(4)44) was detected in the seeds of *Vicia villosa*, *Vicia sativa* and *Phaseolus coccineus* (Hamana et al., 1991, 1992a, 1996). Quaternary branched  $N^4$ -bis(aminopropyl)spermidine (BAPSp<sub>d</sub>) (3(3)(3)4) was detected in the seeds of *Crotalaria spectabilis* (Hamana et al., 1996). Penta-amines were not detected in immature seeds (Fig. 4). The occurrence of unusual long polyamines may be significant in protecting the seed against water deficiency and heat. Leguminous seeds are important for agriculture and foods are good sources for plant polyamines.

In the roots of ten leguminous species and the seeds of two leguminous species, a novel long aliphatic diamine, 1,6-diaminohexane (Dah) (6), has been detected (Hamana et al., 2019). Biological decarboxylation of L-homolysine (L-2,7-diaminoheptanoic acid), a non-natural amino acid, to produce 1,6-diaminohexane is unknown.

A novel tetra-amine,  $N,N'$ -bis(3-aminopropyl)-1,2-ethanediamine (323) was detected in the aquatic plant *Nuphar japonicum* (Hamana et al., 1998). Two tertiary branched polyamines,  $N^4$ -aminopropylhomospermidine (AP4NSp<sub>d</sub>) (3(3)3) and  $N^4$ -aminopropylspermidine (AP4Sp<sub>d</sub>) (3(3)4) were found in aquatic plants (Hamana et al., 2000). NSp<sub>d</sub> (333) and AHSp<sub>d</sub> (344) were widely distributed in aquatic seed plants (Hamana et al., 1994, 1998, 2000). The presence of unusual tetra-amines in aquatic plants suggested that active polyamine metabolism may be essential for the control of osmotic stress in land seed plants submerged in water.

#### 4.1.2 Methylpolyamines ( $N$ -methylated polyamines) in seed plants

$N^4$ -methylthermospermine (3(M)34) and  $N^6$ -methylagmatine (MAg<sub>m</sub>) were first found in several leguminous mature seeds (Hamana et al., 1992a, 1993, 1996; Matsuzaki et al., 1990a). MAg<sub>m</sub> has been found in several gramineous plant seed and seedlings (Hamana et al., 1994).  $N^4$ -methylspermidine (3(M)4) was discovered in an aquatic plant (Hamana et al., 1998). The occurrences of  $N^1$ -methylputrescine (M4),  $N^1,N^4$ -dimethylputrescine (M4M),  $N^1$ -methylhomospermidine (M44) and  $N^1,N^9$ -dimethylhomospermidine (M44M) were identified in *Solanales* plant roots (Hamana et al., 2017; Niitsu et al., 2014). The occurrence of  $N^1$ -methylcadaverine (M5) was found in the root of *Canavalia gladiata* which is rich in cadaverine (5) (Hamana et al., 2019).  $N^1$ -Methylputrescine (M4),  $N^1,N^4$ -dimethylputrescine (M4M),  $N^8$ -methylspermidine (34M),  $N^4$ -methylspermidine (3(M)4),  $N^1$ -methylhomospermidine (M44) and/or  $N^5$ -methylhomospermidine (4(M)4) were detected in the roots, roots containing nodules or root nodules of *Glycine max*, *G. soja*, *Phaseolus vulgaris*, *Pueraria montana*, *Vigna angularis*, *V. umbellata* and *V. unguiculata* (Hamana et al., 2019). 3(M)4 was found in the seedling of *Vigna mungo* (Hamana et al., 2019). The endogenous distribution of  $N$ -methylated polyamine derivatives in plants is attractive for considering polyamine metabolism in relation to the route to some alkaloids and its function in plants.

*N*-Acetylpolyamines have never been reported in plant samples. Ac-Put, *N*<sup>1</sup>-Ac-Spd, *N*<sup>8</sup>-Ac-Spd and Ac-Spm, have been found in bacteria and mammals in our studies and others, but were not detected in seed plant organs in our studies.

#### **4.1.3 Hydroxypolyamines in seed plants**

The hydroxy derivatives of polyamines, 2-hydroxyputrescine (1,4-diamino-2-butanol, 1,4-diaminobutan-2-ol) (abbreviated as H-4 or H-Put) and  $\gamma$ (3)-hydroxyagmatine (H-Agm) were found in some leguminous seeds and seedlings (Hamana and Matsuzaki, 1993). H-Put and 2-hydroxyspermidine (H-Spd) produced from H-Put, were found in some bacteria as a major polyamine.

#### **4.1.4 Alkanolpolyamines (Polyaminoalkylalcohols) in seed plants**

In the 95 plant organs analyzed in the present study, no alkanolpolyamines or polyaminoalkylalcohol were found. The two aminopropylaminoalcohols *N*-(3-aminopropyl) aminoethanol (32OH) and *N*-(3-aminopropyl) aminopropanol (33OH) were first found in the seeds of a leguminous plant, *Dolichos lablab* (Hamana et al., 1992b). 33OH was also detected in the seeds of leguminous *Cassia obtusefolia*, *Sesbania rostrata* and *Gleditschia japonica* (Hamana et al., 1996). *N*-(7-amino-4-azaheptyl)aminopropanol (333OH) had been found in the seeds of leguminous *Vigna mungo* (*Rudua mungo*) (Otsuka et al., 2005). 33OH have been found in gramineous sorghum (*Sorghum bicolor*) and timothy (*Phleum pratense*) seeds (Hamana et al., 1994). *N*-(4-aminobutyl)aminoethanol (42OH) and *N*-(4-aminobutyl)aminopropanol (43OH), were found in the root (containing nodules) of *Glycine soja* (Hamana et al., 2019). 42OH was detected in the root nodule of *Phaseolus vulgaris*, *Vigna angularis*, *Vigna umbellata* and *Vigna unguiculata* (Hamana et al., 2019). Although biological function of polyaminoalkylalcohols (alkanolpolyamines) is not clear, the occurrence of alcohol-derivatives of polyamines in leguminous roots, leguminous seeds and gramineous seeds is interesting.

#### **4.2 Polyamine change in microbial symbiosis and infection in seed plants**

In the present study, polyamines of acupuncture (witches' broom disease) leaves caused by the infection of the fungus *Melampsorella caryophyllacearum* in the leaf of a conifer, *Abies firma*, were analyzed (Table 3). In comparison with normal green leaves of *Abies firma*, Spd and Spm increased, whereas Dap and Cad appeared in the acupuncture leaves, suggesting an activation of polyamine synthesis and/or degradation in the infected leaves.

It has been suggested that polyamines are able to play a defensive role against microbial infections in seed plants, and may also contribute to cooperative interactions between host and symbiont in the microbial symbiosis of seed plants. The coralloid root of a fern palm, *Cycas revoluta*, containing a symbiotic cyanobacterium, *Anabaena cycadeae*, have HSpd (Hamana and Mastuzaki,

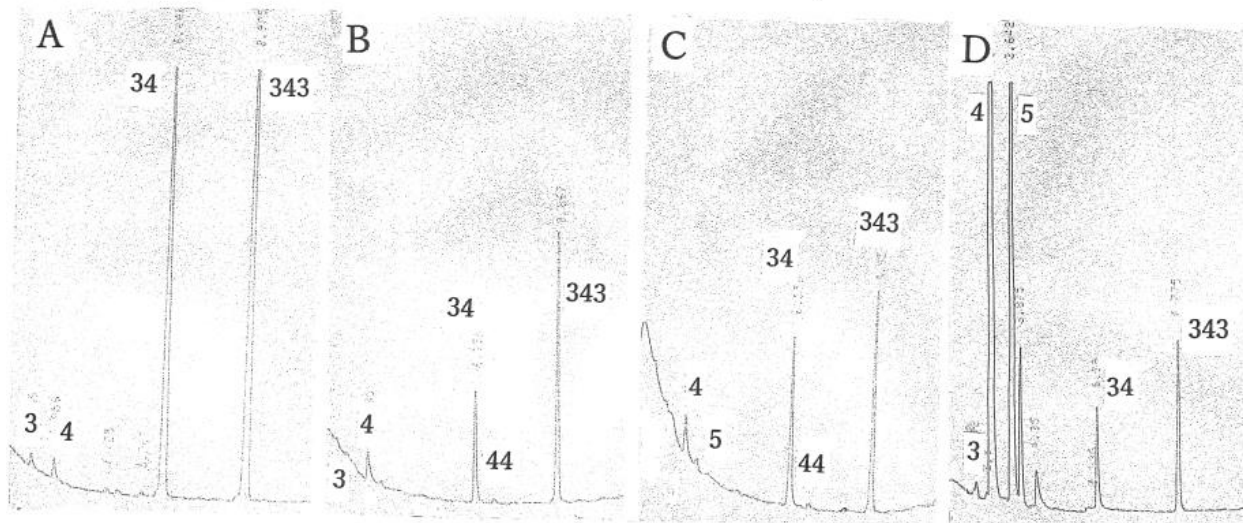
1985; Hamana et al., 1988). Legumes belonging to the family *Fabaceae* are notable in that most of them have symbiotic relation with the nitrogen-fixing rhizobia *Azorhizobium*, *Bradyrhizobium*, *Mesorhizobium*, *Rhizobium* and *Sinorhizobium*. We found Cad, HSpd and new aminobutylcadaverine (ABCad) (45) in leguminous root nodules (Hamana et al., 2019). We showed a change in polyamine distributions in several plant disease conditions: *Brassica* clubroots caused by the infection of a cercozoan *Plasmodiophora brassicae*, in root-knot galls of tomato and eggplant by a root-knot nematode *Meloidogyne incognita*, and in powdery scab of potato tuber caused by the cercozoa *Spongospora subterranean* (Hamana et al, 2015, 2017). Though phytopathogenic tumor inducing (Ti) strains of *Rhizobium radiobacter* (formerly *Agrobacterium tumefaciens*), *R. rhizogenes*, *R. vitis*, *R. rubi* and *R. larrymoorei* are the causal agents of crown gall disease in higher land plants, we have shown the increase of HSpd in the crown galls of *Roseales* and *Fagales* plants (Hamana et al., 2025).

On the other hand, the closed leaf pockets of the ferns *Azolla imbricata* and *Azolla japonica* belonging to the phylum Polypodiophyta (Pteridophyta) contains a symbiotic cyanobacterium, *Anabaena azollae*. A significant amount of HSpd has been detected in the  $N_2$ -fixing *Anabaena*-symbiotic organs (Hamana et al., 1988).

#### **4.3 Polyamines of seed plant organs as a food nutrient for human health**

In the present study, the polyamine profile of fermented rice bran for the pickled rice bran “Nucazuke” in Japan was compared to those of brown rice and original rice bran obtained from brown rice (Fig. 6) (Table 2). Polyamine profiles of bran and brown rice were closely similar, and polyamine concentration was much higher in bran, suggesting that polyamines of brown rice are localized in bran. After fermentation, Dap, Put, Cad levels were increased in bran, indicating that the three diamines were derived from plant lactic acid bacteria, plant propionic acid bacteria and film yeasts grown in the fermented bran. The levels of polyamine components, especially agmatine, in soybean seeds increased during fermentation using *Bacillus subtilis* to produce the fermented soybean known as “Natto” in Japan (Otsuka and Hamana, 2006), as cited in Table 1. Ordinarily it is expected that fermented seed plant organs as a food result in increased polyamine levels. On the other hand, comparison of soybean cultivars for enhancement of the polyamine content in soybean “Natto” has been reported (Kobayashi et al., 2017). Phyto-polyamine supplements extracted from rice germs, soybeans (soya beans) and yeasts derived from Sake are commercially available in Japan.





**Fig. 6: GC retention charts of polyamines extracted from rolled barleys (A) of *Hordeum vulgare*, and grains of brown rice (seeds) (B), rice bran (C) and pickled rice bran (D) of *Oryza sativa*, by SHIMADZU GC-9A. Unknown tow peaks between the peaks of 5 and 34 were detected. Abbreviations for polyamines are shown in Table 1.**

Polyamines are considered to play a role in the longevity of living animals and in prolonging mammalian lifespan as well as in the growth of plants (Handa et al., 2018; Madeo et al., 2018), so that ingestion of polyamines from foods have been proposed to combat the decrease in mammalian cellular polyamine levels caused by aging (Nishimura et al., 2006; Soda, 2015). It has been reported that oral supplementation of Spd and Spm increased blood levels of Spd and Spm and enhanced their possible biochemical and physiological functions in mammals (Soda, 2015, 2021).

Dietary spermidine for lowering high blood pressure was reported (Eisenberg et al., 2017). Al-Habsi, et al. (2022) reported that spermidine activates mitochondrial trifunctional protein and improves antitumor immunity in mice.

Polyamine analyses of leaves, fruits, seeds, and tubers of seed plants reported in our previous and present studies contribute provide valuable nutritional information on polyamine ingestion. In addition to a phylogenetic polyamine distribution catalogue in seed plants, the polyamine distribution profile in various differentiated plant organs as a plant-based food is significant, as suggested by Tiburcio and Alcazar, 2018. In humans, the common major polyamines of plants, Put, Spd and Spm, included in plant-derived foods are released by food digestion in the stomach under strong acidic conditions and in the small intestine under weak acidic conditions, and then absorbed in the intestinal tract (Soda, 2015, 2021). Green leaf powder of seed plants as well as bacterial and algal powders is a good polyamine source. Though polyamines derived from

intestinal bacteria in human intestines are also absorbed, the enhancement of the growth of intestinal bacteria is needed for total polyamine intake (Matsumoto, 2021).

#### **4.4 Polyamines in CO<sub>2</sub> assimilation of photosynthetic plant cells**

Carbon dioxide assimilation is the process by which organisms convert carbon dioxide (CO<sub>2</sub>) into organic compounds. This process is also known as biological carbon fixation or the Calvin-Benson cycle. CO<sub>2</sub> can be adsorbed chemically into biogenic amines, polyamines and alkanolamines (aminoalcohols) (Yasumoto and Hirose, 2018). It has been known that polyamines stimulate the incorporation of carbonic acid (CO<sub>2</sub>+H<sub>2</sub>O = HCO<sub>3</sub><sup>-</sup> + H<sup>+</sup>) in bacteria and eukaryotic cells (Yasumoto et al., 2014, 2018; Kubota et al., 2024). Biogenic polyamines capture CO<sub>2</sub> and accelerate extracellular bacterial CaCO<sub>3</sub> formation (Yasumoto et al., 2014). Furthermore, atmospheric CO<sub>2</sub> captured by biogenic polyamines is transferred as a possible substrate to Rubisco for the carboxylation reaction (Yasumoto et al., 2018). Since polyamines can adsorb and hold CO<sub>2</sub>, plant polyamines are essential for CO<sub>2</sub> assimilation in photosynthesizing plant cells. However, high concentration (level) of Put, Spd and Spm were found in photosynthetically active leaves of seed plants, as shown in the present study. Furthermore, alkanolpolyamines (polyaminoalkylalcohols) were found in seed plants and algae. Non-photosynthetic, saprophytic seed plants have low polyamine levels, as shown in the present study.

For separating/collecting CO<sub>2</sub> from the atmosphere in DAC (Direct Air Capture) technology, membranes of amines (aminoethanol NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH, etc.) are used. The absorbed CO<sub>2</sub> is released from amines by hot water vapor. CO<sub>2</sub> in the exhaust gas from thermal power stations is absorbed in an aminoalcohol solution. This process is similar to the biological CO<sub>2</sub>-separating/collecting mechanism in the CO<sub>2</sub> assimilation during the photosynthesis of plants and algae. For the fixation of CO<sub>2</sub> in exhaust gas through microalgal liquid culture, CO<sub>2</sub> can be absorbed by endogenous algal polyamines and is used for carbon assimilation in algae.

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