

Complexation between Monosaccharide and Potassium Ion in Gas Phase.  
 A Correlation between Relative FABMS Peak-Intensities and Gas Phase  
 Stabilities of the Cluster Ions

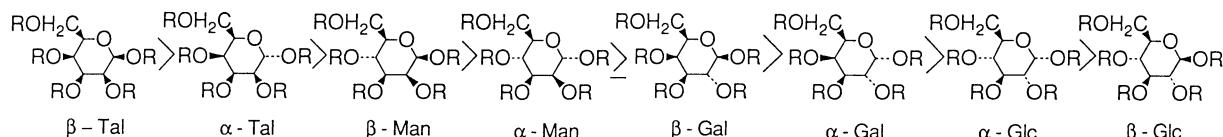
Masami SAWADA,\* Li OUYANG, Yoshio TAKAI, Hitoshi YAMADA, Terukiyo HANAFUSA  
 Takeshi KINOSHITA,<sup>†</sup> and Tomoko MOCHIZUKI<sup>†</sup>

Material Analysis Center, The Institute of Scientific and Industrial  
 Research, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567

<sup>†</sup>Analytical and Metabolic Research Laboratories, Sankyo Co., Ltd.,  
 Hiromachi, Shinagawa-ku, Tokyo 140

Relative FABMS peak-intensities of the cluster ions between a set of permethylated aldopyranoses and potassium ion provide a close relation with relative FABMS/MS area-intensities of the corresponding cluster ions between a set of methyl aldopyranosides and potassium ion.

In a previous paper of this series, we reported that relative FABMS peak-intensities of the cluster ions between a set of permethylated monosaccharides and alkylammonium ion or potassium ion reflect configuration effect of the  $\text{OCH}_3$  groups.<sup>1)</sup> The intensity-order is as follows (see Table 1, FABMS (glycerin matrix);  $\text{R}=\text{CH}_3$ ).<sup>2)</sup>



However, in the similar quantitative FABMS measurements for another set of monosaccharide derivatives such as anomeric oxygen-monomethylated saccharides,<sup>3)</sup> ( $\text{M}$ ), the above intensity-order of the corresponding cluster ions,  $(\text{M}+\text{A})^+$ , with an additive ion,  $(\text{A})^+$ , (for example,  $\beta$ -phenylethylammonium ion or potassium ion), disappeared (see Table 1, FABMS (glycerin matrix);  $\text{R}=\text{H}$ ). Especially, the behavior of methyl  $\alpha$ - or  $\beta$ -taloside seemed to be strange. One possible reason is ascribed to specific intermolecular saccharide-glycerin interaction<sup>4)</sup> which reduces the ejection of the saccharide from the glycerin solution by fast atom bombardment.

FAB mass spectrometry/mass spectrometry (MS/MS or tandem MS) must provide gas phase ion phenomena without interference of such a liquid-matrix. Because, MS/MS operating principle is (1) selected ion species can be sent into the second mass spectrometer, and (2) the ion species (precursor ion) can be decomposed by Ar collision, and (3) the resulted fragment ions can be analysed.<sup>5</sup>

For our FABMS/MS measurements, the Puzo's three-component ion being composed of (i) methyl aldopyranoside, (compounds, No. 1-8, FABMS/MS; R=H in Table 1), (ii) potassium ion, and (iii) diethanol amine, (DEA as FAB matrix) was utilized as the selected precursor ion,  $(M+K+DEA)^+$ , ( $m/z=338$ ).<sup>6,7</sup> Here, we communicate a set of relative gas phase stabilities of the cluster ions,  $(M+K)^+$ , obtained from FABMS/MS area-intensities, and compare it with a set of the previous relative FABMS peak-intensities.<sup>1)</sup> The FABMS/MS area-intensity data will provide a measure of relative stabilities (relative binding-energies) of the  $(M+K)^+$  cluster ions ( $m/z=233$ ) to the reference  $(DEA+K)^+$  ion ( $m/z=144$ ) in gas phase.<sup>8)</sup>

A FABMS/MS sample solution was prepared by a mixture of the two solutions. The one ( $0.5 \mu L$ ) is 1 M aq. solution of methyl aldopyranoside. The other ( $1.0 \mu L$ ) is 0.1M aq. DEA solution (1:1 V/V) of KCl. Throughout the work, standard FABMS/MS technics<sup>9)</sup> were employed under constant conditions. A typical FABMS/MS spectrum is shown in Fig. 1. Relative abundance at the required  $m/z$  values, (area-intensity at  $m/z=233$ )/(area-intensity at  $m/z=144$ ), was measured and summarized in Table 1 (FABMS/MS (DEA matrix); R=H).<sup>10)</sup>

A selectivity of talose derivatives has appeared in the FABMS/MS case, as seen in Table 1. Figure 2 shows a log-log plot of the relative FABMS peak-intensity data against the relative FABMS/MS area-intensity data of the corresponding  $(M+K)^+$  ions.<sup>11)</sup> Here, the former compounds are a set of

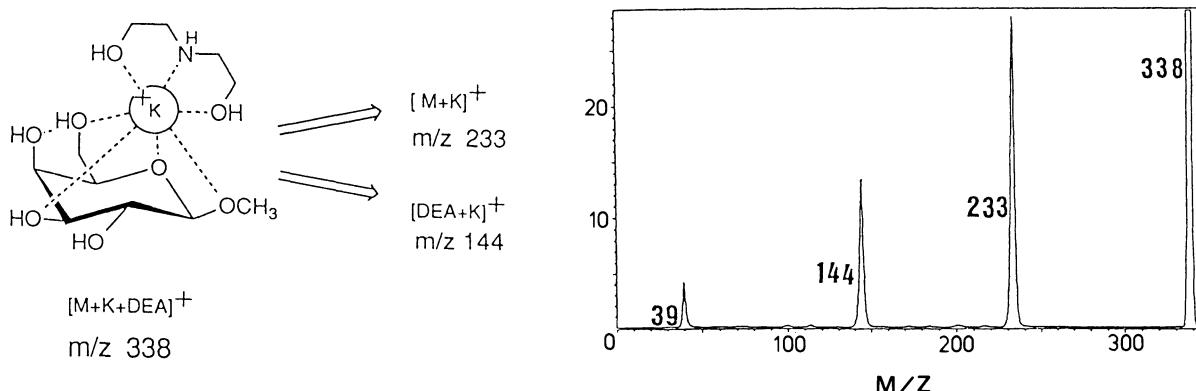


Fig. 1. Typical FABMS/MS spectrum of  $[M+K+DEA]^+$  ion ( $m/z338$ ). M = methyl  $\beta$ -D-galactoside.

permethylated monosaccharides ( $R=CH_3$ ) and the latter ones are a set of monomethylated monosaccharides ( $R=H$ ).

There exists a correlation between the above two sets (Fig. 2). The correlation suggests that relative FABMS peak-intensities of the cluster ions, ( $\text{permethylated monosaccharide} + K$ ) $^+$ , reflect their relative thermodynamic stabilities in gas phase.<sup>12)</sup> The finding implies that if free OH groups are permethylated in saccharides, the relative peak-intensities of the corresponding cluster ion, ( $M + A$ ) $^+$ , in conventional FABMS spectrometry (glycerin matrix) give information of their relative gas phase stabilities. Accordingly, the present correlation will provide new methodology to study gas phase host-guest complexations of saccharides by using FAB mass spectrometry.<sup>13)</sup>

Table 1. Relative Peak Intensities ( $I[M+K]^+/I[R+K]^+$ ) values

No.	M	FABMS		FABMS/MS $R=H$ <sup>c)</sup>
		$R=CH_3$ <sup>a)</sup>	$R=H$ <sup>b)</sup>	
1	$\beta$ -Glc		0.2	(0.4)
2	$\alpha$ -Glc		0.5	(0.4)
3	$\alpha$ -Gal		0.7	-
4	$\beta$ -Gal		1.0	-
5	$\alpha$ -Man		1.0	(= 1.0)
6	$\beta$ -Man		3.7	-
7	$\alpha$ -Tal		12	(0.7)
8	$\beta$ -Tal		18	(0.9)

Reference compound (R); a)  $\alpha$ -Man-5(OMe)-d<sub>12</sub>=Methyl 2,3,4,6-tetra-O-CD<sub>3</sub>- $\alpha$ -D-mannopyranoside, b)  $\alpha$ -Glc-(OMe)-d<sub>3</sub>=Methyl-d<sub>3</sub>  $\alpha$ -D-glucopyranoside, c) DEA.

#### References

- 1) M. Sawada, L. Ouyang, Y. Takai, H. Yamada, and T. Hanafusa, Chem. Lett., 1989, 1743.
- 2) All monosaccharides utilized are substantially C1 conformation. For example, S. J. Angyal and K. Dawes, Aust. J. Chem., 21, 2747 (1968).

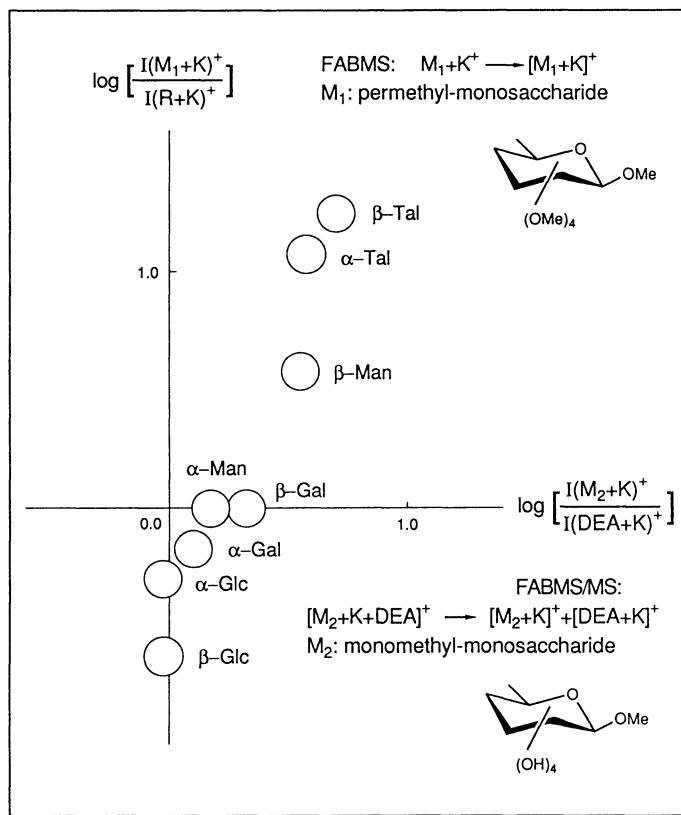


Fig. 2. Comparison between FABMS and FABMS/MS data

- 3) Anomeric oxygen-methylation is necessary to fix stereochemistry of  $C_1-OCH_3$ .
- 4) For example, see Y. Aoyama, Y. Tanaka, and S. Sugahara, J. Am. Chem. Soc., 111, 5397 (1989).
- 5) F. W. McLafferty, Acc. Chem. Res., 1980, 33.
- 6) G. Puzo, J. -J. Fournie, and J. -C. Prome, Anal. Chem. 57, 892 (1985).
- 7) G. Puzo, J. -C. Prome, and J. -J. Fournie, Carbohydr. Res., 140, 131 (1985).
- 8) For example, R. G. Cooks and T. L. Kruger, J. Am. Chem. Soc., 99, 1279 (1977); G. Bojesen, ibid., 100, 5557 (1987).
- 9) T. Kinoshita, T. Nakamura, and H. Nagaki, Nippon Kagaku Kaishi, 1986, 1665.
- 10) Data in parentheses are normalized as 1.0 for the  $\alpha$ -Man case. Appearance of  $K^+$  peak in our conditions does not influence any serious problems to the present purpose.
- 11) See Eq. 2 in Ref. 1.
- 12) J. A. Sunner, R. Kulatunga, and P. Kebarle, Anal. Chem., 58, 1312, 2009 (1986).
- 13) K. Laali and R. P. Lattimer, J. Org. Chem., 54, 496 (1989).

(Received May 7, 1990)