Carbohydrate Research, 57 (1977) 205–214

STRUCTURAL IDENTIFICATION OF ISOMERIC *O*-TRIMETHYLSILYL DERIVATIVES OF SOME HEXURONIC ACIDS*

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(Received December 30th, 1976; accepted for publication, February 10th, 1977)

ABSTRACT

The structures of the isomeric products obtained on trimethylsilylation of naturally occurring hexuronic acids and their sodium salts and lactones have been established by the application of n.m.r. (for anomeric configuration) and mass spectrometry (for ring size). The equilibria of some of the hexuronic acids in methyl sulphoxide involved a larger proportion of furanoid forms than those in water or pyridine. The proportion of furanoses was also increased by the addition of hexamethyldisilazane. Kinetic evidence indicated that two molecules of each hexuronic acid interacted autocatalytically during mutarotation.

INTRODUCTION

G.l.c. of monosaccharides as their *O*-trimethylsilyl derivatives[1] is now a well-established procedure, and extension of the method to hexuronic acids required careful modifications to a non-conventional system[2]. Analyses are based on a prior knowledge of the isomer ratios for each monosaccharide at equilibrium in a particular solvent. The concentration of a monosaccharide and the method of silylation can affect this equilibrium[2], so that a knowledge of the structures of the components thereof will permit a greater understanding of the processes involved.

N.m.r. and mass spectrometry have become increasingly used for structural analysis in carbohydrate systems[3,4]. We now report on the application of n.m.r. and mass spectrometry to the isomeric products formed on trimethylsilylation of hexuronic acids, and separated by g.l.c., together with preliminary results of kinetic studies on the anomerisation process in methyl sulphoxide.

RESULTS AND DISCUSSION

Several workers[5,6] have noted a difference in the relative intensities of the ions at *m/e* 204 ($[Me_3SiO.CH=CH.OSiMe_3]^{+\cdot}$) and 217 ($[Me_3SiO.CH=CH.$

*Dedicated to the memory of Sir Edmund Hirst, C.B.E., F.R.S.

$CHOSiMe_3]^{+\cdot}$) in the mass spectra of trimethylsilylated furanose and pyranose derivatives. These fragments are common in the breakdown of the *O*-trimethylsilyl derivatives of carbohydrates. For trimethylsilylated aldoses, DeJongh *et al.*[7] obtained a major peak at *m/e* 204 and a smaller peak at *m/e* 217 for pyranoses, whereas furanoses produced little of the ion *m/e* 204 but a major peak at *m/e* 217. Karady and Pines[5] observed similar differences for the trimethylsilyl ethers of 2-hexuloses. Studies[6,8] on permethylated pentoses and hexoses showed similar differences in the abundance of the corresponding peaks at *m/e* 88 and 101, for furanose and pyranose isomers.

The hexuronic acids, lactones, and salts in Table I were trimethylsilylated, and the products were subjected to g.l.c.–m.s. The fragment *m/e* 217 occurs widely in *O*-trimethylsilyl derivatives of carbohydrates of differing structures, both furanoid and pyranoid. Its origin seems to be non-specific. The fragment *m/e* 204, however, is readily produced by pyranoid structures, but is structurally more difficult to produce from furanoid isomers. Thus, it is proposed that a comparison of the intensities of

TABLE I

STRUCTURAL ASSIGNMENTS FOR *O*-TRIMETHYLSILYL DERIVATIVES OF HEXURONIC ACIDS AND THEIR LACTONES

Hexuronic acid	*Structure*[a]	*Retention time*	*Abundance of* m/e *204* (m/e *217* = *100*)
D-Galacturonic acid	α-f	1.48	4.2
	β-f	1.89	7.2
	α-p	2.01	108
	β-p	2.60	120
D-Glucurono-6,3-lactone	α-f	1.20	21.0
	β-f	1.27	14.5
D-Glucuronic acid	α-f β-f	1.73	3.8
	α-p	2.10	67
	β-p	2.54	63
L-Gulurono-6,3-lactone	α-f	0.86	—
	β-f	1.15	—
L-Idurono-6,3-lactone	α-f β-f	1.00	11.1
Sodium L-iduronate	α-f	1.48	3.2
	β-f	1.80	15.4
	α-p β-p	2.00	167
D-Mannurono-6,3-lactone	α-f	1.22	24
	β-f	1.58	20.7
Sodium D-mannuronate	α-f	2.11	12.5
	β-f	2.54	2.8
	α-p	1.52	70
	β-p	2.21	—

[a]Key: f, furanoid; p, pyranoid.

these two fragments in the mass spectra of isomers of the hexuronic acid as their *O*-trimethylsilyl derivatives provides a means of determining the ring size (Table I). For this purpose, the intensity of *m/e* 217 is set at 100. Thus, for example, for D-glucuronic acid, the relative intensities of *m/e* 204 for *T* 2.10 and 2.54 are 67 and 63, respectively. These values are high (pyranose) compared with that (3.8) of *m/e* 204 for *T* 1.73, which is low (furanose). In our data, no relative intensities for *m/e* 204 fall in the range 25–62. Fuller mass-spectral details are given in the Experimental.

Analysis of the n.m.r. spectra of each of the isomers separated by g.l.c. allowed configurational assignments to be made. For D-glucuronic acid[2], the pyranoid forms with retention times (*T*) at 2.54 and 2.10 gave doublets for H-1 at τ 5.50 (*J* 6.86 Hz) and 5.00 (*J* 3.14 Hz) indicative[9] of β and α configurations, respectively; *cf.* 3.5 and 7.0 Hz for methyl α- and β-D-glucopyranoside[10]. There were also signals in the regions τ 9.8–9.9 (corresponding to the 45 protons of the trimethylsilyl groups) and 5.9–6.7 (corresponding to the other 4 ring protons). These signals were present in the spectrum of each compound in Table I. No n.m.r. spectrum was obtained for the furanoid isomer having *T* 1.73, which was possibly an $\alpha\beta$ mixture.

Likewise, the α and β configurations for the pyranoid derivatives of D-galacturonic acid (*T* 2.01 and 2.60) followed from the splittings (1.71 and 6.6 Hz) of the doublets for H-1 at τ 4.93 and 5.57, respectively; *cf.* 3.5 and 8.0 Hz for methyl α- and β-D-galactopyranoside[10], respectively. The doublet for H-1 in the furanoid isomer *T* 1.48 occurred at τ 4.93, and the splitting of 4.3 Hz was indicative of the α configuration; *cf.* 4.5 Hz for methyl α-D-galactofuranoside[10].

The two products (Table I) from D-glucurono-6,3-lactone had furanoid structures, and the n.m.r. data (τ 4.85, *J* $\sim$0 Hz) for H-1 in the major component (*T* 1.27) indicated it to be the β anomer. The minor component (α anomer) had a signal for H-1 at τ 4.67 (*J* 3.71 Hz). Capon and Thacker[10] observed similar results for the α- and β-D-glucofuranosides.

D-Mannurono-6,3-lactone also gave two furanoid derivatives (Table I). The signal for H-1 for the major component (*T* 1.58) occurred at τ 4.89, and the splitting of 4.3 Hz indicated the β configuration. The corresponding signal for the minor component (α anomer) occurred at τ 4.82 and had zero spitting.

For the above compounds, with the exception of D-mannuronic acid, the isomers with the greater retention times were the β-pyranose forms. For those products in Table I for which no n.m.r. data were obtained, structures were assigned on the basis of cumulative evidence obtained from analyses of other isomers.

The determination of the structure of the derivatives in Table I allows investigation of the kinetic behaviour of the anomers in solution. The mutarotation of an isomer can be followed by g.l.c. of its *O*-trimethylsilyl derivative; trimethylsilylation of monosaccharides in solution does not affect the isomer distribution[1,2]. Peak areas reflect the proportions of isomers, as pyranoid and furanoid isomers produce the same detector response.

The crystalline hexuronic acids studied were mainly in the pyranoid form. Comparative data for the equilibria established in methyl sulphoxide and pyridine are

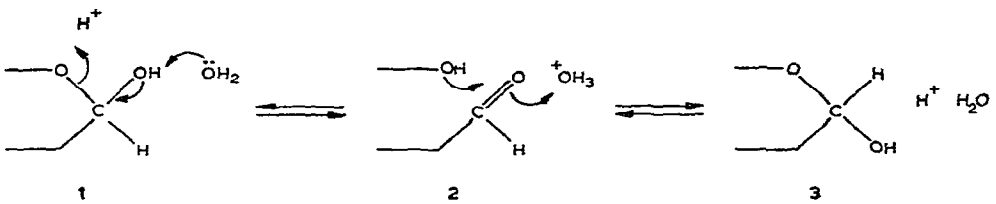
shown in Table II. The formation of pyranoid derivatives is favoured in pyridine, whereas the proportion of furanoid forms is substantially increased in methyl sulphoxide. The sodium salts of the hexuronic acids consistently produced a greater proportion of furanoid isomers at equilibrium in methyl sulphoxide than did the free acids.

TABLE II

EQUILIBRIUM COMPOSITIONS OF HEXURONIC ACIDS AND THEIR LACTONES

	Solvent[a]	*Anomers* (%)[b]			
		α-f	*β-f*	*α-p*	*β-p*
D-Galacturonic acid	Pyr	15	5	31	49
	Me_2SO	57	12	16	15
Sodium D-galacturonate	Pyr	—	—	—	—
	Me_2SO	82	18	0	0
D-Glucurono-6,3-lactone	Pyr	27	73	0	0
	Me_2SO	8	92	0	0
D-Glucuronic acid	Pyr	45		20	35
	Me_2SO	4		44	52
Sodium D-glucuronate	Pyr	10		40	50
	Me_2SO	31		24	35
L-Gulurono-6,3-lactone	Pyr	—	—	—	—
	Me_2SO	87	13	0	0
Sodium L-guluronate	Pyr	—	—	—	—
	Me_2SO	—	—	—	—
L-Idurono-6,3-lactone	Pyr	—	—	—	—
	Me_2SO	93	7	0	0
Sodium L-iduronate	Pyr	—	—	—	—
	Me_2SO	36	54	10	
D-Mannurono-6,3-lactone	Pyr	19	81	0	0
	Me_2SO	75	25	0	0
Sodium D-mannuronate	Pyr	44	0	56	—
	Me_2SO	27	0	60	13

[a]Pyr, pyridine. [b]Key: f, furanoid; p, pyranoid.



Several mechanisms have been proposed for the mutarotation of monosaccharides in solution. That proposed by Pedersen[11], in which the ring oxygen is

protonated (1⇌3), is widely accepted, and is satisfactory for aqueous solution where water can act both as proton donor and acceptor. However, methyl sulphoxide is aprotic, and cannot act as a proton donor, so that little mutarotation would be expected. This situation was exemplified with D-glucose, for which no change occurred after several days[12]. The hexuronic acids were found to undergo slow mutarotation. The equilibration of α-D-galactopyranuronic acid in methyl sulphoxide was studied over the concentration range 0–1 mg/ml, and the initial rate of loss of the starting anomer was measured. The initial rate of reaction showed a bimolecular dependence on the total concentration (Fig. 1), which is consistent with catalysis by one molecule of α-D-galactopyranuronic acid of the anomerization of another. However, D-galacturonic acid did not catalyse the mutarotation of D-glucose.

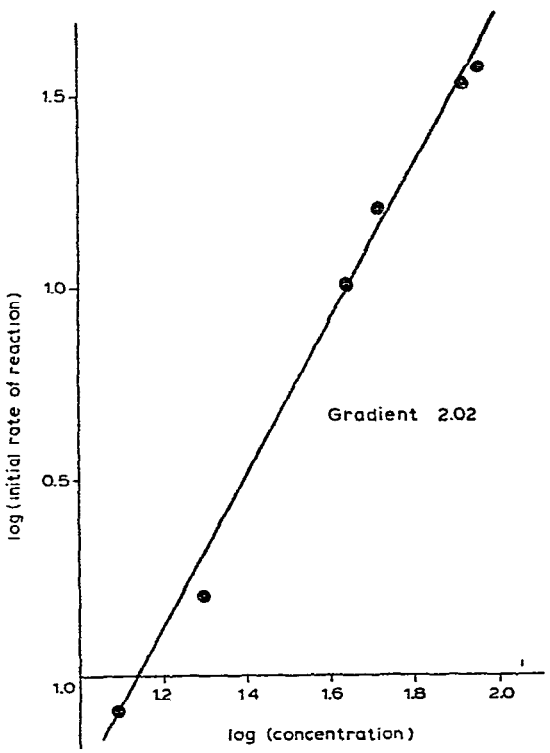


Fig. 1. Plot of log (initial rate of reaction) against log (concentration) for the mutarotation of D-galacturonic acid in methyl sulphoxide.

The equilibrium of isomers in methyl sulphoxide was displaced towards the furanoid forms on adding hexamethyldisilazane. The cause of this effect remains to be identified.

EXPERIMENTAL

Materials. — D-Glucurono-6,3-lactone, sodium D-glucuronate, D-galacturonic acid, and D-mannurono-6,3-lactone were commercial samples. An aqueous solution of L-guluronic acid was kindly supplied by the late Dr. A. Haug (Institute of Seaweed Research, Trondheim, Norway), and 1,2-*O*-isopropylidene-L-idurono-6,3-lactone by Professor D. Horton (Ohio State University, U.S.A.). L-Idurono-6,3-lactone was prepared from the foregoing derivative (1 mg) by hydrolysis with M hydrochloric acid (1 ml) at 100° for 3 h followed by removal of hydrogen chloride by vacuum evaporation over aqueous sodium hydroxide and concentration to dryness. Sodium D-galacturonate, D-mannuronate, and L-iduronate were prepared by careful addition of equivalent amounts of M sodium carbonate to aqueous solutions of D-galacturonic acid, D-mannurono-6,3-lactone, and L-idurono-6,3-lactone (1 mg/ml).

Hexamethyldisilazane and chlorotrimethylsilane were obtained from Pierce Chemical Co. All solvents were dried and redistilled before use.

O-Trimethylsilyl derivatives of the hexuronic acids. — The *O*-trimethylsilyl derivatives of the hexuronic acids and their lactones were prepared by the method described previously[2]. G.l.c. was carried out under the same conditions[2], with the *O*-trimethylsilyl derivative of ribitol as the internal standard.

N.m.r. spectrometry. — A solution of the hexuronic acid or lactone (1 mg/ml) was incubated for various times in order to obtain preponderance of a particular isomer, and silylated by the standard method, and the products were subjected to g.l.c. The mixture was then maintained at 4°, and the upper layer of hexamethyldisiloxane was removed from the solidified methyl sulphoxide layer and concentrated at 50–60° *in vacuo*. The n.m.r. spectrum of a solution of the residual *O*-trimethylsilyl derivatives in carbon tetrachloride was recorded at 100 MHz (Perkin–Elmer instrument) with tetramethylsilane as the internal standard.

Mass spectrometry. — Mixtures of the *O*-trimethylsilyl derivatives of a particular hexuronic acid or lactone were prepared as described above for n.m.r. spectrometry. The oily products were dissolved in hexane and subjected to g.l.c.–m.s. using a Perkin–Elmer Model 881 gas-chromatograph fitted with a coiled column (10 ft × 5 mm) of OV-1 on Chromosorb, operating at 175° with a helium flow-rate of 40 ml/min, and coupled to an AEI MS 902 mass spectrometer (kind assistance from PCMU, Harwell) operating at 70 eV with a source temperature of 220°. An enhanced metastable spectrum was obtained from the same instrument by using a special detector.

Kinetic measurements. — The mutarotation of the hexuronic acids in methyl sulphoxide was followed by trimethylsilylation and g.l.c. as previously described[2]. Initial rate of reaction measurements were made by drawing a tangent to the reaction curve at zero time at a point at which 100% of one isomer was known to exist.

Mass spectra of per-O-trimethylsilylated derivatives. — The mass spectrum of the trimethylsilylated hexuronic acids and lactones showed, *inter alia*, peaks as follows.

Sample *T* 1.48: α-D-galactofuranuronic acid, *m/e* 73 (59%), 75 (7), 77 (3), 93 (6), 103 (3), 129 (2), 131 (1), 133 (2), 147 (17), 189 (3), 191 (12), 204 (4), 217 (100),

230 (1), 245 (4), 291 (1), 292 (25), 305 (7), 319 (6), 335 (3), 346 (2), 359 (3), 421 (1), 449 (1), and 539 (2, $M^+ - 15$).

Sample *T* 1.89: β-D-galactofuranuronic acid, *m/e* 73 (66%), 75 (30), 77 (12), 93 (20), 95 (8), 103 (3), 129 (3), 131 (2), 133 (3), 147 (20), 189 (3), 191 (12), 204 (7), 217 (100), 230 (1), 231 (2), 245 (7), 285 (2), 291 (1), 292 (25), 305 (8), 319 (8), 335 (4), 346 (2), 359 (3), 449 (1), and 539 (2, $M^+ - 15$).

Sample *T* 2.01: α-D-galactopyranuronic acid, *m/e* 73 (92%), 75 (23), 77 (11), 93 (15), 95 (6), 103 (2), 117 (2), 129 (3), 131 (3), 133 (5), 143 (4), 147 (33), 189 (4), 191 (19), 204 (100), 217 (92), 232 (2), 233 (6), 237 (4), 245 (4), 265 (3), 291 (2), 292 (27), 305 (24), 319 (3), 331 (2), 333 (2), 335 (3), 359 (2), 375 (2), 421 (2), 449 (3), and 539 (3, $M^+ - 15$).

Sample *T* 2.60: β-D-galactopyranuronic acid, *m/e* 73 (90%), 75 (22), 77 (9), 93 (13), 95 (5), 103 (2), 129 (3), 131 (3), 133 (4), 143 (4), 147 (29), 189 (4), 191 (19), 204 (100), 217 (82), 232 (2), 233 (7), 237 (4), 245 (2), 265 (2), 291 (2), 292 (27), 305 (22), 319 (1), 331 (2), 333 (3), 335 (2), 359 (1), 375 (2), 421 (1), 449 (4), and 539 (3, $M^+ - 15$).

Sample *T* 2.54: β-D-glucopyranuronic acid, *m/e* 73 (84%), 75 (9), 103 (2), 117 (2), 129 (3), 131 (2), 133 (4), 143 (5), 147 (29), 189 (4), 191 (24), 204 (63), 217 (100), 231 (1), 232 (2), 233 (9), 245 (2), 257 (2), 291 (2), 292 (26), 305 (26), 319 (1), 331 (2), 333 (4), 335 (2), 359 (2), 375 (2), 408 (1), 421 (1), 449 (6), 464 (0.2, $M^+ - 90$), and 539 (0.6, $M^+ - 15$).

Sample *T* 2.10: α-D-glucopyranuronic acid, *m/e* 73 (80%), 75 (7), 103 (2), 129 (3), 131 (2), 133 (4), 143 (4), 147 (30), 169 (2), 189 (3), 191 (28), 204 (67), 217 (100), 232 (2), 233 (10), 245 (3), 257 (2), 291 (2), 292 (27), 305 (27), 319 (1), 331 (2), 333 (2), 335 (2), 359 (2), 375 (2), 421 (1), 449 (6), 464 (0.4, $M^+ - 90$), and 539 (1, $M^+ - 15$).

Sample *T* 1.73: αβ-D-glucofuranuronic acid, *m/e* 73 (56%), 75 (8), 103 (3), 129 (3), 131 (1), 133 (2), 143 (2), 147 (20), 157 (2), 189 (4), 191 (13), 204 (4), 217 (100), 230 (4), 231 (2), 245 (2), 285 (2), 291 (1), 292 (25), 305 (6), 319 (6), 331 (1), 333 (1), 335 (3), 346 (2), 347 (2), 359 (5), 449 (1), and 539 (1.6, $M^+ - 15$).

Sample *T* 1.20: α-D-glucurono-6,3-lactone, *m/e* 73 (100%), 75 (19), 103 (5), 113 (2), 117 (4), 129 (6), 131 (4), 133 (6), 143 (3), 145 (2), 147 (25), 157 (2), 169 (3), 189 (4), 191 (2), 197 (5), 204 (2), 213 (4), 217 (11), 230 (73), 243 (6), 245 (6), 259 (6), 287 (9), 319 (2), 349 (1), 377 (4, $M^+ - 15$), and 392 (0.5, M^+).

Sample *T* 1.27: β-D-glucurono-6,3-lactone, *m/e* 73 (100%), 75 (13), 103 (6), 113 (2), 117 (2), 129 (6), 131 (2), 133 (5), 145 (3), 147 (17), 169 (2), 189 (4), 191 (2), 204 (2), 217 (14), 230 (86), 243 (5), 245 (8), 259 (4), 287 (6), 319 (2), 349 (2), 377 (9, $M^+ - 15$), and 392 (0.5, M^+).

Sample *T* 1.00: αβ-L-idofuranurono-6,3-lactone, *m/e* 73 (47%), 75 (7), 103 (3), 113 (1), 117 (1), 129 (4), 131 (2), 133 (3), 143 (2), 145 (2), 147 (7), 157 (1), 169 (1), 189 (3), 191 (2), 204 (2), 217 (16), 230 (100), 243 (2), 245 (5), 259 (2), 287 (1), 319 (1), 349 (2), 377 (1, $M^+ - 15$), and 392 (0.5, M^+).

Sample *T* 1.48: α-L-idofuranuronic acid, *m/e* 73 (80%), 75 (13), 77 (2), 93 (3),

95 (1), 103 (3), 129 (4), 131 (2), 133 (4), 143 (3), 147 (30), 157 (3), 189 (4), 191 (13), 204 (3), 217 (100), 230 (3), 245 (2), 285 (1), 291 (1), 292 (17), 305 (8), 319 (5), 331 (2), 333 (1), 335 (3), 346 (2), 347 (1), 359 (5), 421 (1), 449 (1), and 539 (1, M^+-15).

Sample *T* 1.80: β-L-idofuranuronic acid, *m/e* 73 (97%), 75 (18), 77 (3), 93 (4), 95 (2), 103 (4), 117 (2), 129 (5), 131 (3), 133 (4), 143 (3), 147 (33), 157 (3), 189 (5), 191 (13), 204 (15), 217 (100), 230 (4), 245 (2), 257 (1), 285 (2), 291 (1), 292 (15), 305 (9), 319 (5), 331 (1), 333 (2), 335 (3), 346 (2), 347 (1), 359 (3), 421 (1), 449 (2), and 539 (0.5, M^+-15).

Sample *T* 2.00: αβ-L-idopyranuronic acid, *m/e* 73 (100%), 75 (26), 77 (5), 93 (5), 103 (3), 117 (2), 129 (4), 131 (3), 133 (5), 143 (6), 147 (41), 189 (6), 191 (9), 204 (76), 217 (44), 230 (2), 233 (2), 245 (2), 257 (2), 291 (1), 292 (7), 305 (10), 319 (1), 331 (1), 333 (2), 335 (2), 347 (1), 359 (3), 449 (3), 464 (1, M^+-90), and 539 (0.6, M^+-15).

Sample *T* 1.22: α-D-mannurono-6,3-lactone, *m/e* 73 (100%), 75 (69), 77 (5), 93 (11), 95 (5), 103 (6), 117 (5), 129 (10), 131 (4), 133 (6), 143 (3), 147 (75), 189 (7), 191 (4), 204 (5), 217 (21), 230 (91), 243 (8), 245 (9), 257 (8), 259 (7), 287 (6), 319 (3), 349 (3), 377 (4, M^+-15), and 392 (1, M^+).

Sample *T* 1.58: β-D-mannurono-6,3-lactone, *m/e* 73 (100%), 75 (66), 77 (8), 93 (10), 95 (4), 103 (4), 117 (3), 129 (6), 131 (5), 133 (6), 143 (2), 147 (57), 189 (3), 191 (2), 204 (2), 217 (9), 230 (55), 243 (3), 245 (2), 259 (3), 287 (1.5), 319 (1), 349 (1.5), 377 (1, M^+-15), and 392 (0.5, M^+).

Sample *T* 2.11: α-D-mannofuranuronic acid, *m/e* 73 (60%), 75 (8), 103 (2), 117 (1), 129 (2), 131 (1), 133 (3), 143 (2), 147 (22), 189 (3), 191 (16), 204 (13), 217 (100), 230 (2), 232 (2), 233 (2), 245 (4), 257 (1), 285 (1), 291 (1), 292 (32), 305 (14), 319 (5), 331 (1), 333 (2), 335 (4), 346 (2), 347 (2), 359 (3), 421 (1), 449 (2), and 539 (2, M^+-15).

Sample *T* 2.54: β-D-mannofuranuronic acid, *m/e* 73 (47%), 75 (4), 103 (2), 117 (1), 129 (2), 131 (1), 133 (2), 143 (1), 147 (12), 169 (1), 189 (3), 191 (14), 204 (3), 217 (100), 230 (1), 233 (1), 245 (1), 285 (2), 291 (2), 292 (26), 305 (6), 319 (7), 331 (1), 333 (2), 335 (2), 346 (2), 347 (2), 359 (3), 421 (1), 449 (1), and 539 (2, M^+-15).

Sample *T* 1.52: α-D-mannopyranuronic acid, *m/e* 73 (75%), 75 (6), 103 (2), 117 (1), 129 (2), 131 (2), 133 (4), 143 (4), 147 (24), 169 (2), 189 (4), 191 (23), 204 (70), 217 (100), 232 (2), 233 (10), 245 (2), 257 (2), 285 (1), 291 (2), 292 (25), 305 (26), 319 (1), 331 (2), 333 (5), 335 (3), 347 (1), 359 (2), 375 (2), 421 (1), 449 (4), 464 (1, M^+-90), and 539 (3, M^+-15).

ACKNOWLEDGMENT

The authors thank the S.R.C. for a research scholarship (to S.M.R.).

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