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Note

The mass spectra of trimethylsilylated D-glucopyranosylaldonic acid lactones

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Mass-spectral data on glucosylaldonic acids or higher oligosaccharides carrying an aldonic acid end-group are very limited[1]. Because of our need to identify substances of this type in studies of the oxidative, alkaline degradation of oligosaccharides[2,3], we have studied the mass spectra of the trimethylsilyl (Me_3Si) derivatives of 2-*O*-β-D-glucopyranosyl-D-erythronic (glucosylerythronic), 3-*O*-β-D-glucopyranosyl-D-arabinonic (glucosylarabinonic), and 4-*O*-β-D-glucopyranosyl-D-gluconic (cellobionic) acids. In addition, attempts were made to characterize cellobiosylaldonic acids, which are formed after oxidation of cellotriose[3].

Table I shows the relative retention times in g.l.c. of glucosylaldono- and cellobiosylaldono-lactones. Only the 1,4-lactone for glucosylerythronic acid and the 1,5-lactone for cellobionic acid exist. Glucosylarabinonic acid can occur both as 1,4- and 1,5-lactones, although only one peak was obtained in this work, probably originating from the 1,4-lactone which is the preferred form for a monomeric arabinonic acid. The resolution of the glucosylerythrono- and glucosylarabinono-

TABLE I

RELATIVE RETENTION TIMES OF THE Me_3Si DERIVATIVES OF GLUCOSYLALDONO- AND CELLOBIOSYLALDONO-LACTONES. COLUMN PACKING: 3% QF-1 ON CHROMOSORB W-HMDS (80-100 MESH), TEMPERATURE: ISOTHERMAL 220° (R_{GA}) OR PROGRAMMED 55–230° AT 2.5°/min (R'_{GA})

Lactone	R_{GA}	R'_{GA}
2-*O*-β-D-Glucopyranosyl-D-threono	0.88	0.97
3-*O*-β-D-Glucopyranosyl-D-arabinono (GA)	1.00	1.00
2-*O*-β-D-Glucopyranosyl-D-erythrono	1.09	1.01
4-*O*-β-D-Glucopyranosyl-D-glucono	1.39	1.05
4-*O*-β-D-Glucopyranosyl-D-mannono	1.56	1.06
3-*O*-β-D-Cellobiosyl-D-arabinono	9.27	1.42
2-*O*-β-D-Cellobiosyl-D-erythrono	9.68	1.43
4-*O*-β-D-Cellobiosyl-D-mannono	13.90	1.56

lactones was incomplete, and, surprisingly, the former had the longer retention time. The retention time of the cellobiosylerythronolactone is probably also longer than that of the cellobiosylarabinonolactone. The peaks for these compounds overlapped, and only in some cases could a partial separation be achieved.

Table II presents the partial mass spectra of the glucosylaldonolactones. The *m/e* values with the highest intensity were found in the low-mass range, especially at 70 eV. The peaks at *m/e* 73, 75, 89, 103, 117, 129, 147, 169, 191, 204, 217, 305, and 361 were of high intensity and characteristic. At 15 eV, *m/e* 204 was the base peak,

TABLE II

PARTIAL MASS SPECTRA OF Me_3Si DERIVATIVES OF SOME GLUCOSYLALDONOLACTONES

m/e	*Lactone 1*[a]		*Lactone 2*[b]		*Cellobionolactone*	
	15 eV	*70 eV*	*15 eV*	*70 eV*	*15 eV*	*70 eV*
173	3.7 (ald$^+$)	10.7	0.5	2.9	2.0	2.5
217	100.0	100.0	100.0	100.0	100.0	100.0
243	7.7	9.2	4.2	5.4	11.3	15.0
244	2.4	3.4	15.8	20.5	4.2	4.2
247	24.2	26.3	2.8	3.2	5.3	3.3
263	4.5	4.3	—	0.2	2.4	1.6
271	6.0	5.8	3.2	4.4	35.0	47.3
275	—	—	4.7 (ald$^+$)	3.0	1.4	1.5
286	—	—	—	—	5.7	5.5
291	56.4	41.4	1.2	2.0	1.7	4.2
292	18.0	10.4	0.3	0.8	10.1	4.1
304	11.0	11.3	0.5	2.1	0.5	0.9
315	6.3	3.0	—	0.2	1.0	1.1
317	5.1	4.6	1.1	1.9	3.8	2.6
319	4.6	6.3	4.3	4.7	22.8	9.1
347	1.1	—	3.3	2.5	3.1	2.3
349	0.8	—	2.2	1.9	7.2	3.0
357	1.0 (M−283)	—	—	—	0.4	0.4
359	—	—	0.7	0.8	18.0	8.9
361	17.8	14.2	12.7	11.0	75.6	38.8
371	2.2 (M−269)	1.7	—	—	—	0.3
377	7.0 (M−263)	7.1	1.1	0.7	14.5 (ald$^+$)	4.8
379	4.0 (M−261)	2.9	0.5	0.2	3.2	1.8
393	1.1	0.7	28.0	12.3	2.0	1.3
405	5.5	4.8	—	—	1.0	0.9
406	1.8	1.5	2.5	1.9	0.6	0.5
407	1.5	1.0	1.5	1.6	2.1	1.0
419	1.0 (M−221)	0.7	—	—	—	—
423	—	—	0.3	—	1.3	0.5
427	—	—	—	—	1.1	0.3
433	—	—	0.6	0.4	0.7	0.5
435	0.8	0.9	2.0	1.4	2.1	1.5
445	1.5 (M−105−90)	1.3	0.3	—	—	0.2
447	1.6 (M−103−90)	0.8	0.4	—	0.2	0.2
450	1.5	0.8	0.7	0.2	1.1	0.6

(Continued next page).

TABLE II (*continued*)

m/e	*Lactone 1*[a]		*Lactone 2*[b]		*Cellobionolactone*	
	15 eV	*70 eV*	*15 eV*	*70 eV*	*15 eV*	*70 eV*
451	1.5 (Gl^+)	0.9	0.6 (Gl^+)	0.6	9.9 (Gl^+)	4.2
459	—	—	0.6 (M−283)	0.4	—	—
461	1.1 (M−90−89)	1.5	—	—	—	0.2
467	4.7 ($Gl\text{-}O^+$)	2.6	0.9 ($Gl\text{-}O^+$)	0.6	3.9 ($Gl\text{-}O^+$)	1.8
473	—	—	0.6 (M−269)	0.8	—	—
479	1.1	0.8	2.0 (M−263)	1.7	0.6	—
481	0.4	—	1.4 (M−261)	1.1	—	—
493	0.3 (M−147)	0.6	0.3	0.2	0.4	0.2
494	0.6	—	0.3	0.2	—	0.4
495	—	—	0.2	0.2	65.6	20.3
507	0.3 (M−43−90)	—	3.7	2.0	—	—
508	—	—	1.8	0.9	1.5	0.8
517	—	—	—	—	0.7	0.2
521	—	—	0.6 (M−221)	0.7	—	0.2
525	—	—	0.1	—	0.2	0.2
535	1.6 (M−105)	1.0	—	—	0.3	0.3
537	0.4 (M−103)	0.8	—	—	3.6	1.2
539	—	—	0.4	0.2	3.8	1.0
540	—	—	0.3	—	1.8	0.7
547	—	—	1.2 (M−105−90)	0.9	—	—
549	—	—	0.8 (M−103−90)	—	—	—
550	0.4 (M−90)	0.2	0.5	0.6	—	—
561	—	—	—	—	0.4 (M−283)	—
563	—	—	0.3 (M−90−89)	0.2	—	—
575	—	—	0.1	—	0.6 (M−269)	0.3
581	—	—	0.2	—	1.8 (M−263)	1.1
583	—	—	—	—	1.2 (M−261)	0.6
595	—	—	0.4 (M−147)	—	—	—
597	0.3 (M−43)	—	0.3	—	—	—
598	—	—	3.7 (M−144)	1.7	—	—
609	—	—	0.2 (M−43−90)	—	4.3	1.8
623	—	—	—	—	0.6 (M−221)	0.4
625	0.3 (M−15)	0.1	0.1	—	—	0.3
637	—	—	1.0 (M−105)	1.2	—	—
640	0.3 (M)	0.1	0.3	—	—	—
649	—	—	—	—	0.7 (M−105−90)	0.3
651	—	—	—	—	0.6 (M−103−90)	0.4
652	—	—	0.1 (M−90)	—	0.5	0.3
665	—	—	—	—	0.5 (M−90−89)	0.2
697	—	—	—	—	0.8 (M−147)	0.3
699	—	—	0.1 (M−43)	—	0.5	0.3
700	—	—	0.2	—	0.8 (M−144)	0.4
727	—	—	0.3 (M−15)	0.3	0.2	—
739	—	—	—	—	1.0 (M−105)	0.5
741	—	—	—	—	0.7 (M−103)	0.3
754	—	—	—	—	0.1 (M−90)	—
829	—	—	—	—	0.5 (M−15)	0.2
844	—	—	—	—	0.7 (M)	0.4

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[a] 2-*O*-β-D-Glucopyranosyl-D-erythronolactone (**1**). [b] 3-*O*-β-D-Glucopyranosyl-D-arabinonolactone (**2**).

whereas m/e 73 was the base peak at 70 eV; m/e values below 200 were generally much stronger at 70 eV, whereas, at 15 eV, the more distinct fragments were found in the higher mass range. The fragments of low molecular weight are somewhat unspecific for glucosylaldonic acids; they are common for the Me_3Si derivatives of various hydroxyl compounds, *e.g.*, for D-glucose, which is formed after cleavage of the glycosidic bond[4].

A weak peak for the molecular ion was found only for the glucosylerythrono- and cellobiono-lactones. Peaks at *m/e* $M-Me$, $M-Me_3SiOH$, $M-(Me+Me_3SiOH)$, $M-147$, $M-(CH_2OSiMe_3+Me_3SiOH)$, and $M-(Me+2Me_3SiOH)$ were present in each spectrum, and the molecular weight can be deduced therefrom. Peaks at *m/e* $M-43$ and $M-(43+90)$, which are characteristic of the Me_3Si derivatives of aldonolactones[5], were found in the spectra of the glucosylerythrono- and glucosylarabinonolactones. The fragment ion *m/e* $M-144$, which was found only in the spectra of the glucosylarabinono- and cellobiono-lactones, is probably formed after fragmentation of the aldonic acid moiety (elimination of $-CH_2OSiMe_3-CH+CO$).

The weak fragments at *m/e* $M-221$ $(M-132-89)$ and at *m/e* $M-283$ $(M-103-2\times 90)$ are characteristic of all these spectra, and their formation may be analogous to that suggested for methylated monosaccharides[6]. Weak fragments could also be found at *m/e* $M-261$, $M-263$, and $M-269$ in each spectrum.

The peaks at *m/e* 451 and 467 (Gl^+ and $Gl-O^+$), which are formed after scission of the bond between D-glucose and aldonolactone residues, were comparatively strong in each spectrum. The prominent peak at *m/e* 361 is formed from the fragment ion *m/e* 451 *via* elimination of trimethylsilanol. The D-glucose residue can also be fragmented by many other routes to give abundant ions. Similarly, the aldonolactone end-residue (erythrono, arabinono, and mannono) can be found in the appropriate spectra (*m/e* 173, 275, and 377, respectively), and these ions can also be degraded to lower fragments. The peaks at *m/e* 539 and 540 can be formed after cleavage of the glycosidic bond, as described earlier[7]. A further elimination of trimethylsilanol, alone or together with a methyl group, results in the fragments at *m/e* 450 and 435.

The very distinct peaks at *m/e* 291, 393, and 495, with a spacing of 102 mass units, suggest the formation of the fragment $Me_3Si{-}O^+{=}CH{-}O{-}$aldonolactone. It has been shown[7–9] with disaccharides that the peak $Me_3Si{-}O^+{=}CH{-}O{-}Gl$ is abundant. The peaks at *m/e* 304, 406, and 508, respectively, suggest the fragment $Me_3Si{-}O{-}CH{=}CH{-}O{-}$aldonolactone, which can be formed analogously to the fragmentation of monosaccharides[6]. The prominent fragments at *m/e* 405, 507, and 609 can be formed analogously[7] by the fragmentation of cellobiose to $Me_3Si{-}O{-}CH{=}C(OSiMe_3){-}CH{=}O^+{-}Gl$. These three fragments permit an accurate assignment of the molecular weight of the aldonolactone end-residue.

Although the mass spectra of aldobionic acids with various molecular weights can easily be interpreted, the epimeric aldobionic acids possess very similar mass spectra with only small variations in intensity (*cf.* ref. 5). 2-*O*-β-D-Glucopyranosyl-D-threonic (glucosylthreonic) and 4-*O*-β-D-glucopyranosyl-D-mannonic (glucosylmannonic) acids are formed on oxidation of cellobiose with oxygen. They gave mass spectra very similar to those of glucosylerythronic and cellobionic acids.

On oxidation with oxygen, cellotriose and higher oligosaccharides give cellobiosylaldonic acids, the lactones of which have been analysed, as the Me_3Si derivatives[3], by g.l.c. The identification of these compounds by g.l.c.–m.s., however, is difficult because of the high molecular weights (>1000).

The signals in the low-mass range were very similar to those of the corresponding glucosylaldonolactones. All the main fragments originating from D-glucose and glucosylaldonolactones could be found, and the typical fragmentation products from cellobiose were also present[7]. Cellobiosylaldonic acids with various molecular weights can easily be identified by means of these fragments. For example, the fragments glucosylaldonolactone and *O*-glucosylaldonolactone are indicated by the peaks at *m/e* 653 and 669 for cellobiosylarabinonic acid. The intense peak at *m/e* 771 corresponds to the fragment $Me_3Si{-}O^+{=}CH{-}O{-}Gl$–aldonolactone.

EXPERIMENTAL

The glucosylarabinonic and glucosylerythronic acids were obtained[10] as Ca salts. Cellobionic acid was a commercial product[10]. Before analysis, the cations were removed by using Dowex-50W(H^+) resin, and the acids (lactones) were silylated as described earlier[2]. Trisil-reagent (1 ml, Pierce Chemical Co., Rockford, Ill., U.S.A.) was added to the sample (~10 mg), and the mixture was kept at 70° with occasional shaking. After 1 h, the sample (2 μl) was injected into a Perkin–Elmer 270B gas chromatograph–mass spectrometer. Stainless steel columns (0.125 in. × 2 m) of 3% QF-1 on 80–100 mesh Chromosorb W were used. The column temperature was programmed from 190–230° at 2.5°/min. Helium was used as a carrier gas.

The mass-spectrometric measurements were made at 15 and 70 eV, using an accelerating voltage of 2000 V. The temperature of the manifold was 280° and that of the ionic chamber 110–120°. The scanning time over the mass range *m/e* 15–850 was ~20 sec (10 sec/decade).

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