Carbohydrate Research, 194 (1989) 37–47
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

IDENTIFICATION OF *O*-α-D-GALACTOPYRANOSYLSACCHARINIC ACIDS AS THEIR TRIMETHYLSILYL DERIVATIVES BY MASS SPECTROMETRY*

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(Received February 23rd, 1989; accepted for publication, May 5th, 1989)

ABSTRACT

Kraft pulping of pine wood and treatment of guaran with alkali gave several *O*-α-D-galactopyranosylsaccharinic acids or related compounds, which were analysed by capillary g.l.c.–m.s. Of these compounds, twelve were identified and eight were new. The degradation of galactomannans by alkali is discussed.

INTRODUCTION

In certain galactomannans and galactoglucomannans, the α-D-galactopyranosyl groups are (1→6)-linked[1–3] to the β-D-mannopyranosyl or β-D-glucopyranosyl[4] residues. When this kind of polysaccharide is treated with alkali, as during the pulping of softwood, the (1→6) linkages are more stable[5] than the (1→4) linkages between the mannosyl and glucosyl residues. Accordingly, *O*-α-D-galactopyranosylsaccharinic acids should be formed, but only one example is known[6].

In order to facilitate the identification of this type of saccharinic acid, the mass spectra are now reported for the trimethylsilyl derivatives of several *O*-α-D-galactopyranosylsaccharinic acids, which were identified[7] in a spent liquor ("black liquor") from kraft pulping of pine wood. These acids have now been prepared also by treatment of guaran with alkali under various conditions.

EXPERIMENTAL

Kraft pulping of pine wood. — Two samples of black liquor from kraft pulping of industrial pine wood chips were investigated. Conventional black liquor was obtained as described[8]. The charge of active alkali (as NaOH) was 22%, the sulfidity [100 × Na_2S/(NaOH + Na_2S)] was 30%, and the liquor:wood ratio was 4 L kg^{-1}. The time to maximum temperature (20→170°) was 95 min and the time at 170° was 70 min. The yield of pulp was 47.5%.

*G.l.c.–m.s. Studies on Pine Kraft Black Liquors, Part VII. For Part VI, see *Holzforschung*, 43 (1989) 169–171.

0008-6215/89/$ 03.50

The second cook was carried out as above, but anthraquinone was added (0.2% of the wood) and the time at 170° was reduced to 55 min. The yield of pulp was 49.2%.

Treatment of guaran. — Guaran (300 mg), isolated[9] from commercial guar flour (Sigma), was treated with 0.5M sodium hydroxide (50 mL) under nitrogen for 30 min at 170° in a rotating autoclave. Since the presence of anthraquinone[10] or oxygen[11,12] during the treatment of mannan is known to affect the composition of the final (monomeric) products, one treatment was carried out after adding 70 mg of anthraquinone, and another treatment was carried out under oxygen (200 kPa).

G.l.c. — Non-volatile carboxylic acids in 1 mL of the black liquors or guaran-derived samples were trimethylsilylated[13]. Separations were performed with a Hewlett–Packard 5890 A gas chromatograph equipped with a flame-ionisation detector and an SE-54 fused-silica capillary column (25 m × 0.32 mm i.d.). The temperature programme was 2 min at 100°, 15° min^{-1} to 265°, and 15 min at 265°. The temperature of both the injection port and the detector was 275°. The carrier gas was hydrogen at 2 mL min^{-1}.

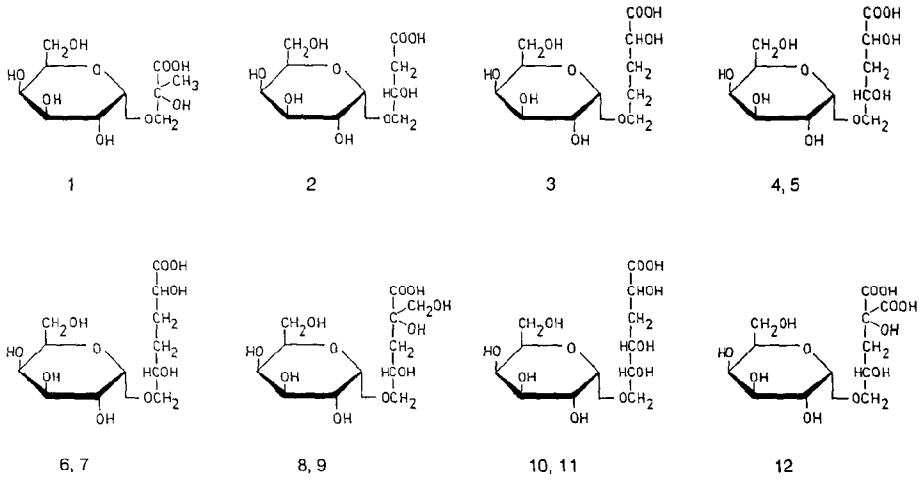
Mass spectrometry. — E.i.-mass spectra were recorded at 70 eV with a JEOL JMS-DX303 instrument in combination with a Hewlett–Packard 5790 A gas chromatograph and the above column. The temperature programme was similar to that used in g.l.c. The accelerating voltage was 2 kV and the scanning range was 50–930 with a cycle time of 1 s. The temperature of the ion source was 280°. The resolution was 500.

RESULTS AND DISCUSSION

At least 18 galactopyranosylsaccharinic acids or related compounds were detected after kraft pulping of pine wood or after the treatments of guaran, and the structures of 12 were determined (Table I). Of these compounds, only four were known hitherto (**8** and **9** from melibiose[14] and from guaran[6], and **10** + **11** from melibiose[14–16]). Compounds related to **10** + **11**, namely, 3-deoxy-6-*O*-β-D-glucopyranosyl-D-hexonic[17,18] (*ribo* and *arabino*), 3-deoxy-6-*O*-α-D-glucopyranosyl-D-hexonic[16] (*ribo* and *arabino*), and 3-deoxy-6-*O*-β-D-galactopyranosyl-D-hexonic[19] (*xylo* and *lyxo*) acids have been obtained from other carbohydrates, but none has been characterized as the trimethylsilyl derivative.

The orders of elution of the trimethylsilyl derivatives of the diastereomeric pairs **4** + **5**, **6** + **7**, and **10** + **11** were assumed to be similar to those[8,20] of their monomeric counterparts. The components of the mixture of **8** + **9** could be separated only after converting them into the corresponding 1,4-lactones[7]. Yields of **1–11** from kraft and kraft–anthraquinone pulping are given in ref. 7.

Determination of the molecular weights. — No molecular ions were present in the mass spectra of the trimethylsilyl derivatives of **1–12**. The molecular weights could be determined readily, however, from weak $(M - 15)^+$ and $(M - 15 - 90)^+$ $[M - Me - Me_3SiOH]^+$ ions, and from more abundant $(M - 349)^+$ ions (Table



II), in accordance with various related compounds, such as the trimethylsilyl derivatives of disaccharides[21–27] and disaccharide-alditols[28–34]. Here the $(M - 349)^+$ ions result from the fragmentation of $[Me_3SiO–CH=O^+–Acid]$. Similar fragmentation has also been found useful in the characterization of other aldosylaldonic acids or related compounds, such as β-D-glucopyranosylglycolic acid[35], and D-glucopyranosylaldonic acids[36] and their lactones[37], as their trimethylsilyl derivatives.

Two other series of fragmentations also produced ions, with surprisingly high

TABLE I

GALACTOPYRANOSYLSACCHARINIC ACIDS OBTAINED BY TREATMENT OF GUARAN WITH ALKALI OR BY KRAFT PULPING OF PINE WOOD, AND THE MOLECULAR WEIGHTS (MOL. WT.) AND RETENTION TIMES (T) OF THEIR TRIMETHYLSILYL DERIVATIVES

Compound[a]	*Mol. wt.*	T
1 3-*O*-R-2-*C*-Methylglyceric	714	0.736
2 2-Deoxy-4-*O*-R-D-*glycero*-tetronic[b]	714	0.779
3 3,4-Dideoxy-5-*O*-R-pentonic	728	0.818
4 3-Deoxy-5-*O*-R-D-*erythro*-pentonic[b,c]	816	0.863
5 3-Deoxy-5-*O*-R-D-*threo*-pentonic[b,c]	816	0.869
6 3,4-Dideoxy-6-*O*-R-D-*erythro*-hexonic[c]	830	0.942
7 3,4-Dideoxy-6-*O*-R-D-*threo*-hexonic[c]	830	0.945
8 3-Deoxy-5-*O*-R-2-*C*-hydroxymethyl-D-*erythro*-pentonic[d]	918	1.000
9 3-Deoxy-5-*O*-R-2-*C*-hydroxymethyl-D-*threo*-pentonic[d]	918	1.000
10 3-Deoxy-6-*O*-R-D-*ribo*-hexonic	918	1.019
11 3-Deoxy-6-*O*-R-D-*arabino*-hexonic	918	1.026
12 2-*C*-Carboxy-3-deoxy-5-*O*-R-D-pentonic[e]	932	1.023

[a]R = α-D-galactopyranosyl. [b]Increased formation from guaran in the presence of oxygen. [c]Increased formation from guaran and pine wood in the presence of anthraquinone. [d]Absolute retention time, 17.6 min. Compounds **8** and **9** could be separated after converting them into 1,4-lactones. [e]Detected after oxygen–alkali treatment of guaran only.

intensities, which permitted confirmation of the molecular weights of the deoxyaldonic acid moieties (Table II). The formation of the $(M - 393)^+$ ions probably arises from the loss of the methyl group from an intermediate corresponding to the trimethylsilylated deoxyaldonic acids, analogous with the formation[24] of the weak *m/z* 525 ions from hexose disaccharides. The formation of analogous ions, also with high intensities, from the trimethylsilylated glucopyranosylaldonolactones, has been reported[37], but their origins were not discussed. It appears from Table II that the intensities of the $(M - 393)^+$ ions usually decrease with the increasing molecular weights of the acid moieties.

The loss of 2,3,4,6-tetrakis(trimethylsilyl)galactopyranosyloxy structures gave rise to abundant $(M - 467)^+$ ions, although the intensity decreased with the increasing molecular weight of the acid unit. Analogous, relatively abundant ions have been reported[37] to arise from the trimethylsilylated glucopyranosylaldonolactones.

In addition to these general fragmentations, there are some more structure-specific fragmentations, which also assist with the determination of the molecular weights and are discussed below.

Deoxytetronic acids. — The formation of three different *O*-α-D-galactopyranosyldeoxytetronic acids from guaran or pine galactoglucomannans is mechanistically possible. Of these, **2** was detected, as expected (*cf.* refs. 11 and 12), as the main dimeric product of the treatment of guaran with oxygen–alkali. The branched structure of **1** was shown, for example, by its remarkably shorter retention time (Table I).

Partial e.i.-mass spectra of the trimethylsilyl derivatives of **1** and **2** are shown in Fig. 1. In the upper mass range, weak ions can be detected at *m/z* 407, 435, 451, 467, and 479. The ion with *m/z* 479 $[(M - 235)^+]$ most probably has the structure of $[Me_3SiO–CH=C(OSiMe_3)–CH=O^+–Acid]$, analogous to that of the ion *m/z* 683, formed[21,24] from certain hexose disaccharides. The ion *m/z* 467 $[2,3,4,6\text{-tetrakis}(Me_3Si)Gal–O]^+$ was of low abundance because of the more favoured formation of the $(M - 467)^+$ ions, as noted above.

TABLE II

THE MOST IMPORTANT IONS (*m/z* AND % OF THE BASE PEAK) USED IN THE DETERMINATION OF THE MOLECULAR WEIGHTS OF **1–12** AS THEIR TRIMETHYLSILYL DERIVATIVES

Compound	$(M - 15)^+$		$(M - 15 - 90)^+$		$(M - 349)^+$		$(M - 393)^+$		$(M - 467)^+$	
1	699	0.1	609	0.2	365	2	321	6	247	16
2	699	0.1	609	0.3	365	8	321	12	247	90
3	713	0.1	623	0.2	379	4	335	5	261	39
4, 5	801	0.1	711	0.2	467	2	423	1	349	17
6, 7	815	0.1	725	0.2	481	4	437	5	363	13
8, 9	903	0.1	813	0.1	569	1	525	1	451	17
10, 11	903	0.1	813	0.2	569	1	525	1	451	16
12	917	0.1	827	0.1	583	2	539	1	465	13

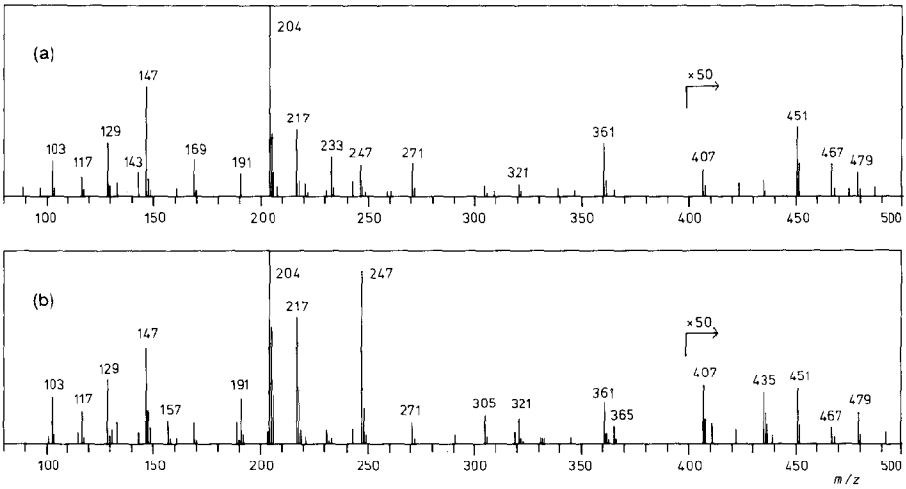


Fig. 1. Partial e.i.-mass spectra at 70 eV of the trimethylsilylated derivatives of (a) 3-*O*-α-D-galactopyranosyl-2-*C*-methylglyceric (**1**) and (b) 2-deoxy-4-*O*-α-D-galactopyranosyl-D-*glycero*-tetronic acid (**2**).

The intensities of the ion *m/z* 451 [2,3,4,6-tetrakis(Me_3Si)Gal]$^+$ were low probably due to the ready loss of one or two Me_3SiOH moieties, giving the ions *m/z* 361 and 271. In addition to disaccharides and their derivatives, the ions *m/z* 451 and 361 are also characteristic[38–40] of the trimethylsilyl derivatives of many other types of hexose glycosides of natural origin. The structures of the ions *m/z* 435 and 407 remain obscure, even though the latter may possess a structure similar to that of the ions *m/z* 435 and 537, found[37] in the mass spectra of the trimethylsilyl derivatives of 3-*O*-β-D-glucopyranosylarabinonolactone and cellobionolactone, respectively.

In addition to the ions $(M - 15)^+$ and $(M - 15 - 90)^+$, only one weak ion (*m/z* 519, 0.2%) was recorded for the trimethylsilyl derivatives of **1** and **2** in the mass range >500, corresponding to the loss of two Me_3SiOH moieties from the ion $(M - 15)^+$.

Most of the intense ions in the lower mass ranges, such as those with *m/z* 103, 117, 129, 147, 169, 191, 204 (the base peak), 217, and 305, were common to each spectrum and arose from the sugar moiety[41]. The intensity of the ion *m/z* 73, not shown in the Figs., was 75–85% in each spectrum.

Other, more structure-specific ions were few in the lower mass range. The ion at *m/z* 233 in the spectrum of **1** most probably arose from the cleavage of the C-2–C-3 bond of the glyceric acid structure, and subsequent loss of Me_3SiOH gives the ion *m/z* 143. These ions, with varying intensities, have been recorded for the trimethylsilyl derivatives of many other 2-*C*-methyl substituted aldonic acids[42,43] or related compounds[44]. This fragmentation further supports the branched structure of **1**.

Dideoxyaldonic acids. — Fig. 2 shows partial e.i.-mass spectra of the tri-

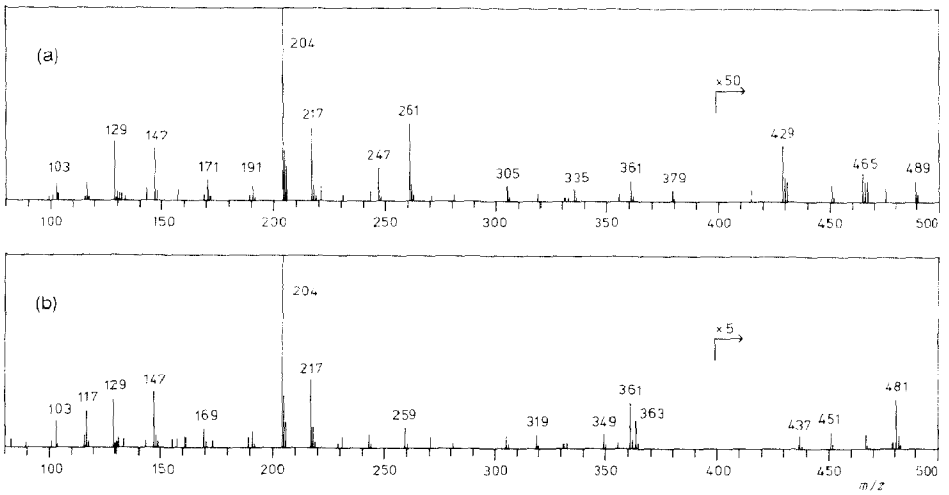


Fig. 2. Partial e.i.-mass spectra at 70 eV of the trimethylsilylated derivatives of (a) 3,4-dideoxy-5-*O*-α-D-galactopyranosylpentonic (**3**) and (b) 3,4-dideoxy-6-*O*-α-D-galactopyranosyl-D-*erythro*-hexonic acid (**6**).

methylsilyl derivatives of **3** and **6**. A related "dideoxyaldonic" acid derivative, 4-α-D-galactopyranosyloxybutanoic acid, was not found, although its formation should be possible[10].

Among the most characteristic ions in the spectrum of **3** were those at *m/z* 261 (further loss of Me_3SiOH gives the ion *m/z* 171) and 247. The latter ion has most probably arisen from cleavage of the C-4–C-5 of the acid, even though this fragmentation was unexpected. The more expected cleavage of the C-5–C-6 bond of **6** is responsible for the formation of the ions *m/z* 349 and 259, which are abundant also in the mass spectra of the trimethylsilylated 3,4-dideoxyhexonic[10,45] and 3,4-dideoxy-6-*O*-methylhexonic[45] acids.

In the upper mass range of the spectrum of **3**, weak ions with *m/z* 429, 465, 489, 503 (0.4%), and 533 (0.1%) were found. The formation of the ion *m/z* 465 follows a path analogous with that responsible for the formation[37] of the $(M - 263)^+$ ions from the trimethylsilylated glucopyranosylaldonolactones, but the structures of the ions *m/z* 429, 489, and 503 remain unexplained. The ion *m/z* 533 appears to arise from the fragmentation of $(M^+ - 15 - 2 \times 90)$.

Only two ions were recorded for the trimethylsilyl derivative of **6** in the mass range of 500–600; the peaks at *m/z* 567 (0.2%) and 595 (0.1%) correspond to the ions $(M - 263)^+$ and $(M - 235)^+$, respectively.

3-Deoxyaldonic acids. — Fig. 3 shows partial e.i.-mass spectra of the trimethylsilyl derivatives of **4** and **11**. A lower homologue in this deoxyaldonic (metasaccharinic) acid series, 3-deoxy-4-*O*-α-D-galactopyranosyltetronic acid, was not detected (its relative retention time was predicted[20] to be ~0.77).

The most characteristic fragmentation of the trimethylsilyl derivatives of **4** and **11**, as well as those of simple 3-deoxyaldonic[42] and 3-deoxyaldaric[46] acids, is

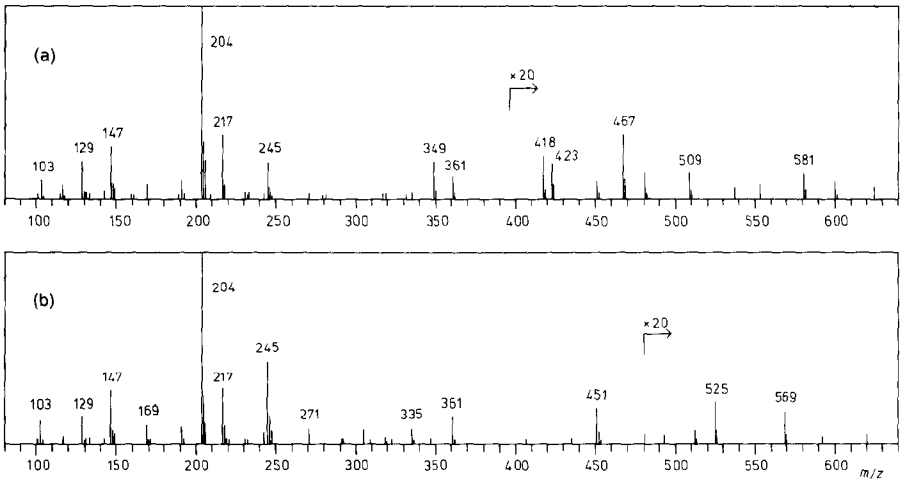


Fig. 3. Partial e.i.-mass spectra at 70 eV of the trimethylsilylated derivatives of (a) 3-deoxy-5-*O*-α-D-galactopyranosyl-D-*erythro*-pentonic (**4**) and (b) 3-deoxy-6-*O*-α-D-galactopyranosyl-D-*arabino*-hexonic acid (**11**).

cleavage of the C-4–C-5 bond of the acid, giving a weak ion with *m/z* 335, which is further fragmented to a more intense ion at *m/z* 245. This ion showed a much higher intensity for **11** than for **4**.

The mass spectrum of **4** exhibited weak ions with *m/z* 533 and 581 (0.1%), corresponding to the ions $(M - 263)^+$ and $(M - 235)^+$, respectively. The ion $(M - 263)^+$ was recorded also for the trimethylsilyl derivative of **11**, at *m/z* 655 (0.1%).

2-C-Substituted 3-deoxypentonic acids. — Fig. 4 shows partial e.i.-mass spectra of the trimethylsilyl derivatives of **8/9**, and **12**. Of these, **8/9** was unique among the hydroxy acids **1–12**, by giving an ion with *m/z* 540 (in addition to the ion *m/z* 525), corresponding to the trimethylsilyl derivative of the deoxyaldonic acid moiety. An analogous ion has been found[24] only for the trimethylsilyl derivatives of some (1→1)-linked hexose disaccharides.

In the mass ranges of >600, the peaks corresponding to the ions $(M - 235)^+$, with intensities of 0.1%, were recorded for both of **8/9**, and **12**. Small peaks at *m/z* 611 and 625 appear to be analogous with the ion *m/z* 611 derived[24] from certain hexose disaccharides.

The most characteristic ions in the upper mass ranges of **8/9**, and **12** were, however, those with *m/z* 888 (0.1%), resulting[47] from a McLafferty type rearrangement to give the ions $(M - 30)^+$ and $(M - 44)^+$, respectively. These fragmentations show that **8/9** is a 2-*C*-alkyl-substituted glyceric acid and that **12** is a 2-*C*-alkyl-substituted tartronic acid (*cf.* ref. 43). On the other hand, because **8/9** is a 2-*C*-hydroxymethyl derivative of **4**, the ions with *m/z* 437 (335 + 102) and 347 (245 + 102) were formed, resulting from the cleavage of the C-4–C-5 bond of the acid. Surprisingly, the spectrum of **8/9** also showed a distinct ion with *m/z* 243, typical[42] of the trimethylsilyl derivative of glucoisosaccharinic acid.

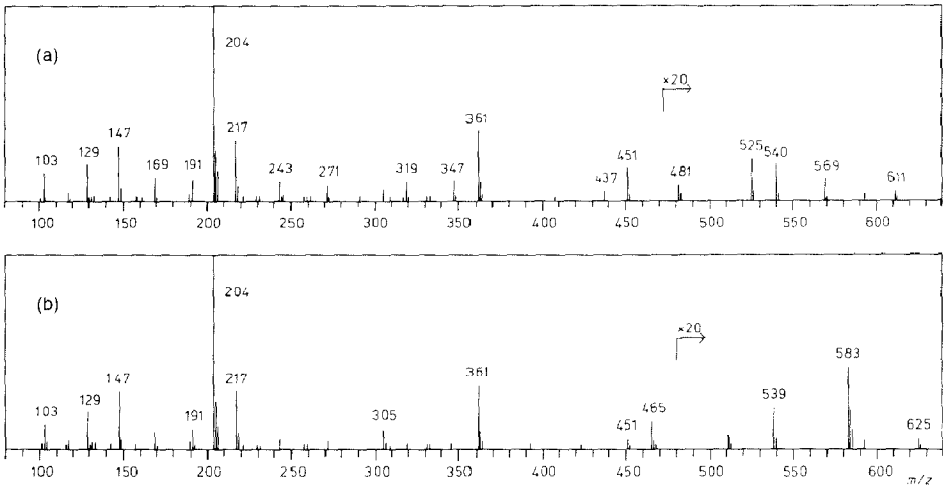


Fig. 4. Partial e.i.-mass spectra at 70 eV of the trimethylsilylated derivatives of (a) 3-deoxy-5-*O*-α-D-galactopyranosyl-2-*C*-hydroxymethyl-D-pentonic (**8/9**) and (b) 2-*C*-carboxy-3-deoxy-5-*O*-α-D-galactopyranosyl-D-pentonic acid (**12**).

Because the two diastereomers **8** and **9** co-eluted in g.l.c., attempts were made to analyse them as the lactones. Samples of the black liquor from kraft pulping of pine wood were cation-exchanged [Dowex 50W-X8 (H^+) resin], dissolved in 2M hydrochloric acid solution, and concentrated, and the residues were trimethylsilylated. G.l.c. then gave two peaks, corresponding to the derivatives of (3*S*,5*S*)- (**13**) and (3*R*,5*S*)-3-hydroxy-3-hydroxymethyl-5-α-D-galactopyranosyloxymethyldihydro-2(3*H*)-furanones (**14**). The (3*S*,5*S*) *(erythro)* isomer was assumed[20] to be eluted first.

The partial e.i.-mass spectrum of the trimethylsilyl derivative of **14** is shown in Fig. 5. In addition to peaks for M^+, $(M - 15)^+$, and $(M - 15 - 90)^+$ at *m/z* 756 (0.1%), 741 (0.1%), and 651 (0.3%), respectively, a distinct, typical rearrangement[48,49] ion at *m/z* 726 (0.8%) was recorded in the upper mass range.

The ions with *m/z* 609, 561, 521, 493, and 407 correspond to the expected[37] fragmentations of $(M - 147)^+$, $(M - 15 - 2 \times 90)^+$, $(M - 235)^+$, $(M - 263)^+$, and $(M - 349)^+$, respectively. The ion *m/z* 420 is analogous with the ion (M −

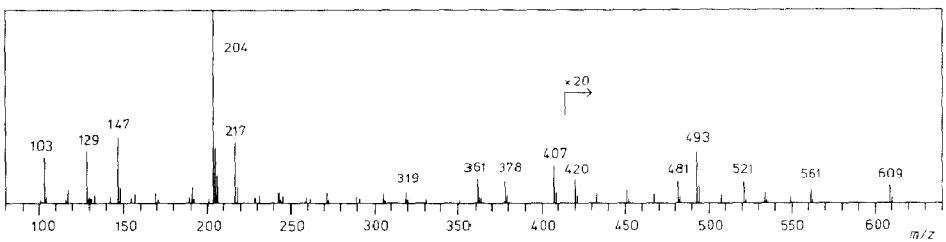
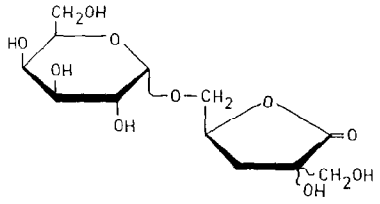


Fig. 5. Partial e.i.-mass spectrum at 70 eV of the trimethylsilylated derivative of 3-deoxy-5-*O*-α-D-galactopyranosyl-D-*threo*-pentono-1,4-lactone (**14**).



13, 14

336)$^+$ found in the mass spectra[37] of the trimethylsilyl derivatives of gluco-pyranosylaldonolactones; these ions were not recorded for the trimethylsilyl derivatives of **1–12**. Surprisingly, the spectrum of **14** did not contain the ion $(M - 467)^+$.

An unusually abundant ion with *m/z* 378 refers to the trimethylsilyl derivative of the lactone part of **14** (*cf.* the ion *m/z* 540; in the spectrum of **8/9**), but no ions with *m/z* 363 or 348 were recorded.

Degradation of galactomannans. — Various reactions occur simultaneously during the non-oxidative, alkaline degradation of mannan[10–12] and other polysaccharides composed of (1→4)-linked hexopyranoses, such as cellulose[43,50,51] and alginates[52], resulting in the formation of complex mixtures of saccharinic acids and related compounds. The present identification of **2–9** after treatment of galactomannans with alkali, usually in ratios[7] related to those of the corresponding monomeric acids from other polysaccharides, indicates that the 6-substituents have only a limited influence on the degradation. However, the slight formation of **3** and the complete absence of the anhydroisosaccharinic acids, 3-hydroxy-5-α-D-galacto-pyranosyloxymethyltetrahydrofuran-3-carboxylic acids, are noteworthy. Compounds **1** and **10** + **11**, found in small amounts only, appear to be products of the "stopping-reaction" of the (finally) liberated 6-*O*-α-D-galactopyranosyl-D-mannoses.

Although the galactosidic linkages are relatively stable, some release and further degradation of galactose is evident, as shown by the detection of small amounts of 3-deoxy-*xylo*-hexonic and 3-deoxy-*lyxo*-hexonic acids after treatment of mannan[10,12] and guaran with alkali. It is difficult, however, to estimate the amount of the galactopyranose residues liberated on the basis of these meta-saccharinic acids, because most of the galactose is converted rapidly into other products[53], mainly lactic acid.

Increased formation of **2** and **4** + **5** during the oxidative treatment, as well as identification of **12** (*cf.* ref. 54), accord with the formation of similar monomeric compounds from mannan and cellulose under identical conditions.

Thus, trimethylsilylation and g.l.c.–m.s. provide a useful technique for characterising and determining the structure of ω-*O*-hexopyranosylsaccharinic acids. It remains to be established whether this method can be used to characterise other types of deoxyaldobionic acids, such as those arising from alkaline degradation[55] or radiolysis[56,57] of 4-*O*-D-hexopyranosyl-D-hexoses.

ACKNOWLEDGMENTS

Professor E. Sjöström is thanked for his interest, and Mr. A. Mäkelä for assistance with the experimental work.

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