Carbohydrate Research, 204 (1990) 37–49
Elsevier Science Publishers B.V., Amsterdam

Conversion of xylan, starch, and chitin into carboxylic acids by treatment with alkali*

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(Received September 13th, 1989; accepted for publication, November 7th, 1989)

ABSTRACT

Treatment of xylan, starch, and chitin with M and 3M sodium hydroxide at 175° and 190° gave mixtures of non-volatile carboxylic acids in yields of 50–70%, 40–60%, and 5–13%, respectively, in which >60 hydroxy monocarboxylic acids and dicarboxylic acids were identified. The main compounds were glycolic, lactic, 2-hydroxybutanoic, 3-deoxypentonic, xyloisosaccharinic, and 3,4,5-trideoxyheptaric acids from xylan; glycolic, lactic, 3,4-dideoxypentonic, glucoisosaccharinic, and 3,4-dideoxyhexaric acids from starch; and glycolic, lactic, 2-hydroxybutanoic, and 3,4-dideoxyhexaric acids from chitin.

INTRODUCTION

Degradation[1-3] of cellulose with hot aqueous alkali yields >60 hydroxy monocarboxylic acids and dicarboxylic acids. Even though there are preponderant products of potential value, such as glycolic, lactic, and 2-hydroxybutanoic acids, their isolation from such complex mixtures is not practicable at present.

Therefore, in preliminary studies now reported, xylan, starch, and chitin have been subjected to similar treatments in order to ascertain whether mixtures of carboxylic acids, more suitable for exploitation, could be obtained.

EXPERIMENTAL

Materials. — Xylan and chitin were obtained from Fluka, and starch from Merck. The chitin was ground (20 mesh) before use but not purified further (ash 5%).

Samples (1.5 g) of polysaccharides were each treated under nitrogen with M or 3M sodium hydroxide (50 mL) at 175° or 190° for 1 h (xylan and starch) or 2 h (chitin) in a rotating autoclave.

G.l.c. — A sample (1 mL) of each reaction mixture was analysed for non-volatile carboxylic acids, after converting[4] them into their ammonium salts and trimethylsilyl derivatives. Xylitol (0.125 mg) was added as the internal standard. Analyses were performed with a Hewlett–Packard 5880 A gas chromatograph equipped with a flame-

* Presented at EUROCARB V, the Vth European Symposium on Carbohydrates, Prague, Czechoslovakia, August 21–25, 1989.

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ionisation detector and NB-30 or NB-54 fused-silica capillary columns (0.32 mm i.d. × 25 m), of which the latter was used mainly to separate[5] 2-hydroxy-2-methylpropanoic acid from lactic and glycolic acids. The temperature program was 2 min at 95°, 15°.min^{-1} to 245°, and 5 min at 245°. 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 combined with a Hewlett–Packard 5790 A gas chromatograph and the above NB-30 column. The temperature program was similar to that used in g.l.c. The scanning range was 60–600 m.u. with a cycle time of 1 s.

Identification of hydroxy monocarboxylic acids and dicarboxylic acids was based on the results of previous studies[1,2,5,6]. Identification of glycine (from chitin) as the *N,N,O*-tris(trimethylsilyl)[7] derivative and phosphoric acid as tris(trimethylsilyl)phos-

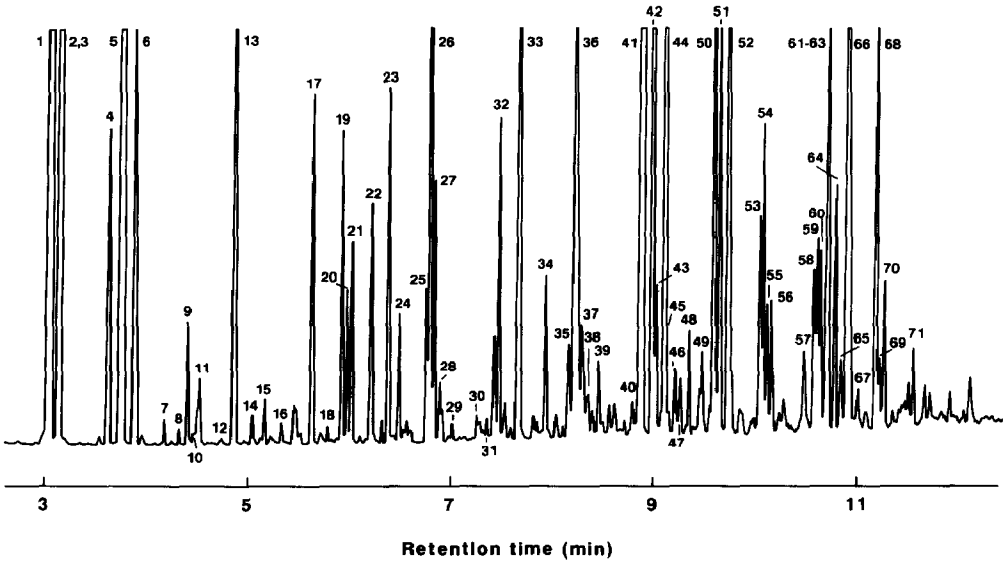

Fig. 1. Gas chromatogram on NB-30 of the trimethylsilylated carboxylic acids obtained after treatment of xylan with M NaOH at 175°; 1, lactic; 2, 2-hydroxy-2-methylpropanoic; 3, glycolic; 4, oxalic; 5, 2-hydroxybutanoic; 6, 2-hydroxy-2-methylbutanoic; 7, 2-hydroxy-3-methylbutanoic; 8, 2-hydroxy-3-methyl-2-cyclopenten-1-one; 9, a 2-hydroxypentenoic; 10, malonic; 11, 2-hydroxypentanoic; 12, benzoic; 13, 4-hydroxybutanoic; 14, methylmalonic; 15, 5-hydroxypentanoic; 16, phosphoric; 17, succinic; 18, methylsuccinic; 19, 2-*C*-methylglyceric; 20, glyceric; 21, fumaric; 22, *C*-methyltartronic; 23, 2-hydroxy-2-hydroxymethyl-3-butenoic; 24, tartronic; 25, 2,2′-oxydiacetic (diglycolic); 26, 3-deoxytetronic; 27, *C*-ethyltartronic; 28, 3-deoxy-2-*C*-methyltetronic; 29, 3,5-dideoxy-*threo*-pentonic; 30, 3,4-dihydroxybenzaldehyde; 31, 2-deoxy-3-*C*-methyltetraric (citramalic); 32, malic; 33, 3,4-dideoxypentonic; 34, artifact; 35, a branched hydroxyhexanedioic; 36, 2,3-dideoxypentaric; 37, 2,3-dideoxy-4-*C*-methylpentaric; 38, a branched hydroxyhexanedioic; 39, a hydroxypentenedioic; 40, β-anhydroisosaccharinic; 41, xyloisosaccharinic; 42, 3-deoxy-*erythro*-pentonic; 43, 2,3,4-trideoxyhexaric; 44, 3-deoxy-*threo*-pentonic; 45, *C*-(2-hydroxyethyl)tartronic; 46, 2,3,4-trideoxy-5-*C*-methylhexaric; 47, 3-deoxy-*erythro*-pentaric; 48, 3-deoxy-*threo*-pentaric; 49, *C*-(3-hydroxypropyl)tartronic; 50, xylitol (internal standard); 51, unknown I; 52, unknown II, 53, a branched trideoxyheptaric; 54, a branched trideoxyheptaric; 55, 3,4-dideoxy-*threo*-hexaric; 56, 3,4-dideoxy-*erythro*-hexaric; 57, a trideoxyheptaric; 58, a trideoxyheptaric; 59, a trideoxyheptaric + 3-deoxy-*lyxo*-hexonic; 60, 3-deoxy-*xylo*-hexonic; 61, β-glucoisosaccharinic; 62, 3-deoxy-*ribo*-hexonic; 63, 3-deoxy-*arabino*-hexonic; 64, α-glucoisosaccharinic; 65, a 3-deoxyhexaric; 66, 3,4,5-trideoxyheptaric; 67, a dihydroxyoctanedioic; 68, unknown III; 69, a dihydroxyoctanedioic; 70, a dihydroxyoctanedioic; and 71, dihydroxynonanedioic acids.

phate[8] was based on the published mass spectra. Identification of 2,2'-oxydiacetic acid (from xylan) was confirmed (retention time, mass spectrum) by comparison with a reference sample. Mass spectrum of its bis(trimethylsilyl) ester: *m/z* 263 (10%) ($M^+ - 15$), 219 (3), 204 (16), 189 (3), 177 (18), 147 (58), 132 (7), 117 (17), 103 (10), and 73 (100).

Final identification of the diastereomeric 3-deoxyhexonic[9] and 4-deoxy-2-*C*-methyltetronic[10] acids was based on their known orders of elution.

RESULTS AND DISCUSSION

Degradation of xylan. — More than 80 peaks appeared in the chromatograms obtained from xylan-derived samples (Fig. 1), and few products remained unidentified.

TABLE I

Yields[a] of hydroxy monocarboxylic acids obtained on treatment of xylan with sodium hydroxide

Monocarboxylic acid	*175°*		*190°*	
	M	3M	M	3M
Glycolic	30	24	19	26
Lactic	118	130	117	149
3-Hydroxypropanoic	–[b]	+	1	1
2-Hydroxy-2-methylpropanoic	14	19	18	20
2-Hydroxybutanoic	122	83	123	98
4-Hydroxybutanoic	6	4	5	7
2-Hydroxy-2-methylbutanoic	5	3	8	4
2-Hydroxy-3-methylbutanoic	+	+	+	+
2-Hydroxypentenoic	1	1	1	1
2-Hydroxypentanoic	1	3	2	2
5-Hydroxypentanoic	+	+	+	+
3-Hydroxytetrahydrofuran-3-carboxylic	–	+	1	1
Glyceric	1	+	1	+
2-*C*-Methylglyceric	2	3	3	3
3-Deoxytetronic	6	5	8	13
3-Deoxy-2-*C*-methyltetronic	+	1	+	+
3,5-Dideoxy-*threo*-pentonic	+	+	+	–
3,4-Dideoxypentonic	8	14	10	11
2-Hydroxy-2-hydroxymethyl-3-butenoic	2	1	–	–
3-Deoxy-*erythro*-pentonic	11	14	13	10
3-Deoxy-*threo*-pentonic	23	24	26	19
Xyloisosaccharinic	61	92	74	83
β-Anhydroisosaccharinic	+	–	+	–
3-Deoxy-*lyxo*-hexonic	1	1	1	1
3-Deoxy-*xylo*-hexonic	1	1	1	2
3-Deoxy-*ribo*- and -*arabino*-hexonic	2	2	2	2
β-Glucoisosaccharinic	3	2	3	3
α-Glucoisosaccharinic	2	1	2	2
Total amount (mg.g^{-1} of xylan)	420	428	439	459

[a] Weights (mg) are from 1 g of xylan. [b] Key: +, traces; –, not detected.

The separation of 2,3,4-trideoxyhexaric acid (peak 43) from 3-deoxy-*erythro*-pentonic acid (peak 42) is noteworthy, because previous attempts at resolution on OV-101[1,2,4,11] and SE-54[5] capillary columns failed. The good separation of *C*-ethyltartronic acid (peak 27) from 3-deoxytetronic acid (peak 26) is also noteworthy, but, unfortunately, *C*-(2-hydroxyethyl)tartronic acid could not be separated from 3-deoxy-*threo*-pentonic acid (peak 44).

Nearly 30 hydroxy monocarboxylic acids were formed from xylan (Table I), and the main compounds were lactic, 2-hydroxybutanoic, and xyloisosaccharinic (3-deoxy-2-*C*-hydroxymethyltetronic) acids, each of which is well known as a product of the peeling reaction of xylan[12]. Substantial amounts of 3-deoxypentonic acids most probably arose from the L-arabinofuranoses present[13] in the xylan samples, whereas the routes of formation of glycolic and 2-hydroxy-2-methylpropanoic acids are not so clear. These 7 major compounds represented ~90% of the hydroxy monocarboxylic acids and corresponded to ~40% of the xylan charge.

Among the C_4- and C_5-compounds were several new products, such as 4-hydroxybutanoic, 2-hydroxy-2-methylbutanoic, 2-hydroxypentanoic, and 3-deoxy-2-*C*-methyltetronic acids. Each of these acids has been detected[5,14] in spent liquors from the alkaline pulping of wood, and tracing the origins has been difficult. The present data show that, in addition to cellulose[6] and glucomannan[11], xylan may contribute to their formation.

The origins of small amounts of several C_6-saccharinic acids are obscure, even though the formation of glucoisosaccharinic, 3-deoxy-*ribo*-hexonic, and 3-deoxy-*arabino*-hexonic acids from the mild treatment of D-xylose with alkali has been reported[15]. 3-Deoxy-*xylo*- and -*lyxo*-hexonic (galactometasaccharinic) acids may have originated from galactose impurities. Another possible source is the glycolaldehyde intermediate, which yields[16], amongst others, 3-deoxyhexonic acids during treatment with alkali.

The yields of hydroxy monocarboxylic acids, under the present conditions (*cf.* ref. 17), were lower than expected. To some extent, this may be due to the stabilization effect of the L-arabinofuranose substituents. The different conditions had little effect on the yield of these acids.

A wide variety of dicarboxylic acids was identified (Table II), and their formation was increased when the higher concentration of sodium hydroxide was used. Of the present compounds, succinic, 2,3-dideoxypentaric, 3,4-dideoxyhexaric, and 3,4,5-trideoxyheptaric acids have long been known as products of the treatment of xylan[18] and beech wood[19] with alkali. Other compounds appear to be new products of the non-oxidative degradation of xylan with alkali. Higher proportions of oxalic and succinic acids have been obtained[20] from xylan by the alkali fusion method.

A remarkable proportion of the dicarboxylic acids contained >5 carbon atoms, strongly suggesting the occurrence of condensation reactions. The main compound of this type, 3,4,5-trideoxyheptaric acid, was also the most abundant dicarboxylic acid. Unfortunately, it has not been possible to determine the complete structures of many of the C_7–C_9 hydroxydicarboxylic acids, many of which have been found after treatment of cellulose with alkali under various conditions[1–3].

TABLE II

Yields[a] of dicarboxylic acids obtained on treatment of xylan with sodium hydroxide

Dicarboxylic acid	*175°*		*190°*	
	M	3M	M	3M
Oxalic	4	8	3	3
Malonic	+[b]	1	1	1
Methylmalonic	+	+	+	+
Fumaric	1	1	1	2
Succinic	2	2	3	4
Methylsuccinic	+	+	+	1
2,2'-Oxydiacetic	1	1	+	−
Tartronic	1	+	−	−
C-Methyltartronic	2	3	4	3
C-Ethyltartronic	2	5	4	6
Malic	2	2	3	3
2-Deoxy-3-*C*-methyltetraric	+	+	−	−
2,3-Dideoxypentaric	14	31	18	22
2,3-Dideoxy-4-*C*-methylpentaric	1	+	1	2
2,3,4-Trideoxyhexaric	1	1	1	2
2,3,4-Trideoxy-5-*C*-methylhexaric	+	+	+	1
C-(2-Hydroxyethyl)tartronic	4	3	2	+
C-(3-Hydroxypropyl)tartronic	+	+	−	−
3-Deoxy-*erythro*-pentaric	+	+	+	−
3-Deoxy-*threo*-pentaric	1	+	+	−
3,4-Dideoxy-*erythro*-hexaric	1	3	2	3
3,4-Dideoxy-*threo*-hexaric	1	3	2	3
3,4,5-Trideoxyheptaric	15	27	26	43
Hydroxyhexanedioic (3 branched isomers)	2	1	1	1
Trideoxyheptaric (5 isomers)	5	6	4	6
Dihydroxyoctanedioic (4 isomers)	2	3	3	3
Dihydroxynonanedioic (2 isomers)	+	+	1	+
Unknown I	4	7	4	6
Unknown II	11	21	16	27
Unknown III	7	4	2	+
Total amount ($mg.g^{-1}$ of xylan)	86	133	102	145

[a] Weights (mg) are from 1 g of xylan. [b] Key: +, traces; −, not detected.

All of the C_6 hydroxydicarboxylic acids have been obtained by treatment of other polysaccharides with alkali, including 2,3-dideoxy-4-*C*-methylpentaric acid from cellulose[1-3] and pectic acid[14], 2,3,4-trideoxyhexaric acid from cellulose[1-3,21,22] and mannan[11], *C*-(3-hydroxypropyl)tartronic acid from cellulose[1-3,21] and alginates[23], and 3,4-dideoxyhexaric acid from cellulose[1-3,18,21,22], mannan[11,18], and alginates[23]. All of these acids were obtained also from chitin (see below).

The formation of small amounts of 2,2'-oxydiacetic acid, not reported hitherto as a product of degradation of carbohydrates, was unexpected, and its origin is unknown.

Only small amounts of *C*-(2-hydroxyethyl)tartronic acid were detected, but it is known[24] that its formation is accelerated in the presence of oxygen.

The structures of three compounds (I–III, Table II) formed in moderate amounts remain unclear, but they are probably dicarboxylic acids. The mass spectra of the trimethylsilyl derivatives of I and II were identical [*m/z* 393 (0.2%), 349 (0.3), 275 (8), 246 (57), 235 (7), 203 (7), 191 (28), 190 (15), 157 (10), 147 (68), 117 (19), and 73 (100)], indicating them to be diastereomers, but the molecular weights could not be determined. For the trimethylsilyl derivative of III, the molecular weight was 570 but the mass spectrum [*m/z* 555 ($M^+ - 15$, 3%), 527 (8), 467 (3), 453 ($M^+ - 117$, 17), 369 (4), 281 (12), 267 (3), 231 (4), 207 (12), 147 (31), 103 (25), and 73 (100)] could not be interpreted fully, although a hydroxymethyl branch clearly was present.

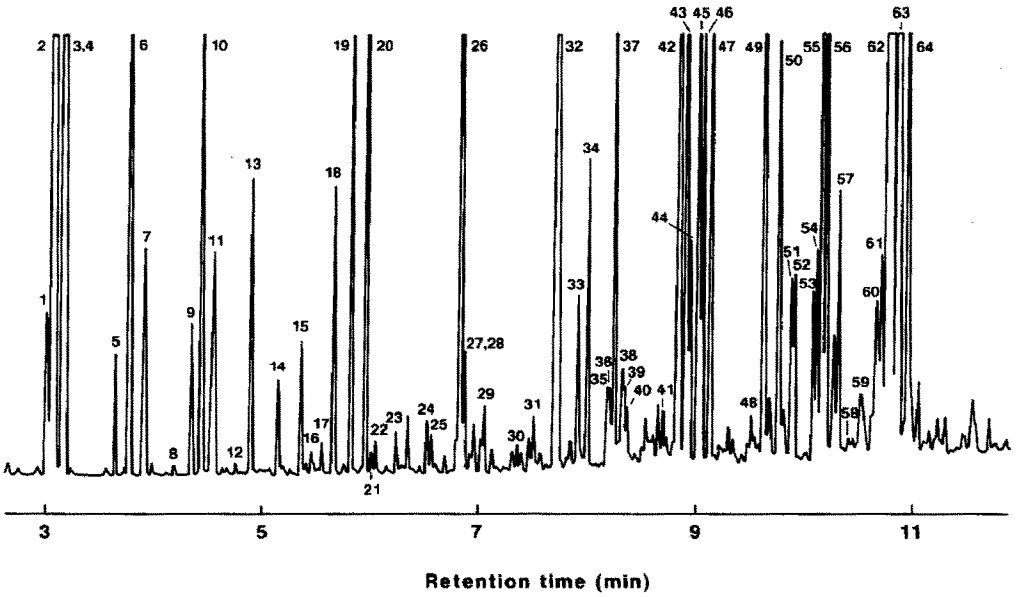

Fig. 2. Separation on NB-30 of the trimethylsilylated carboxylic acids obtained after treatment of starch with M NaOH at 190°: 1, artifact; 2, lactic; 3, 2-hydroxy-2-methylpropanoic; 4, glycolic; 5, oxalic; 6, 2-hydroxybutanoic; 7, 2-hydroxy-2-methylbutanoic; 8, 2-hydroxy-3-methylbutanoic; 9, 2-hydroxy-3-methyl-2-cyclopenten-1-one; 10, a 2-hydroxypentenoic; 11, 2-hydroxypentanoic; 12, benzoic; 13, 4-hydroxybutanoic; 14, 3-ethyl-2-hydroxy-2-cyclopenten-1-one; 15, phosphoric; 16, a C_3-substituted 2-hydroxy-2-cyclopenten-1-one; 17, a 2-hydroxyhexenoic; 18, succinic; 19, methylsuccinic; 20, 2-*C*-methylglyceric; 21, glyceric; 22, fumaric; 23, *C*-methyltartronic; 24, 4-deoxy-2-*C*-methylthreonic; 25, 4-deoxy-2-*C*-methylerythronic; 26, 3-deoxytetronic; 27, *C*-ethyltartronic; 28, 3,5-dideoxy-*erythro*-pentonic; 29, 3,5-dideoxy-*threo*-pentonic; 30, 2-deoxy-3-*C*-methyltetraric; 31, malic; 32, 3,4-dideoxypentonic; 33 and 34, unknown amino acids (mol. wt., 375); 35, a branched hydroxyhexanedioic; 36, a branched hydroxyhexanedioic; 37, 2,3-dideoxypentaric; 38, 2,3-dideoxy-4-*C*-methylpentaric; 39, a branched hydroxyhexanedioic; 40, a branched hydroxyhexanedioic; 41, a hydroxyheptanedioic; 42, *β*-anhydroisosaccharinic; 43, xyloisosaccharinic; 44, *α*-anhydroisosaccharinic; 45, 3-deoxy-*erythro*-pentonic; 46, 2,3,4-trideoxyhexaric; 47, 3-deoxy-*threo*-pentonic; 48, *C*-(3-hydroxypropyl)tartronic; 49, xylitol (internal standard); 50, unknown II; 51, 3,4-dideoxy-*erythro*-hexonic; 52, 3,4-dideoxy-*threo*-hexonic; 53, a branched trideoxyheptaric; 54, a branched trideoxyheptaric; 55, 3,4-dideoxy-*threo*-hexaric; 56, 3,4-dideoxy-*erythro*-hexaric; 57, unknown IV; 58, a 2-*C*-methylpentonic; 59, a dihydroxyoctanedioic; 60, 3-deoxy-*lyxo*-hexonic; 61, 3-deoxy-*xylo*-hexonic; 62, *β*-glucoisosaccharinic; 63, *α*-glucoisosaccharinic; and 64, 3,4,5-trideoxyheptaric acids.

Degradation of starch. — Fig. 2 shows a gas chromatogram of carboxylic acids derived from starch. The separation of xyloisosaccharinic acid (peak 43) from two isomeric anhydroisosaccharnic acids (peaks 42 and 44) is noteworthy, since this was not possible on OV-101[11] or SE-54[5] fused-silica columns.

Approximately 35 hydroxy monocarboxylic acids were detected (Table III), of

TABLE III

Yields[a] of hydroxy monocarboxylic acids obtained on treatment of starch with sodium hydroxide

Monocarboxylic acid	*175°*		*190°*	
	M	3M	M	3M
Glycolic	23	24	23	28
Lactic	59	68	70	83
2-Hydroxy-2-methylpropanoic	6	9	6	7
2-Hydroxybutanoic	5	9	13	12
3-Hydroxybutanoic	−[b]	−	−	1
4-Hydroxybutanoic	1	2	2	3
2-Hydroxy-2-methylbutanoic	1	2	2	3
2-Hydroxy-3-methylbutanoic	+	+	+	1
2-Hydroxypentenoic	3	3	4	6
2-Hydroxypentanoic	2	3	2	2
5-Hydroxypentanoic	+	+	−	1
2-Hydroxyhexenoic	+	+	+	+
Glyceric	1	+	+	1
2-*C*-Methylglyceric	5	7	5	7
3-Deoxytetronic	9	13	12	11
2-Deoxytetronic	+	+	−	−
4-Deoxy-2-*C*-methylthreonic	+	+	+	+
4-Deoxy-2-*C*-methylerythronic	+	+	+	+
3,5-Dideoxy-*erythro*-pentonic	+	−	+	+
3,5-Dideoxy-*threo*-pentonic	1	+	+	+
3,4-Dideoxypentonic	31	28	42	37
3-Deoxy-*erythro*-pentonic	2	2	3	2
3-Deoxy-*threo*-pentonic	2	3	4	2
Xyloisosaccharinic	4	6	8	6
β-Anhydroisosaccharinic[c]	7	9	13	12
α-Anhydroisosaccharinic[c]	1	2	2	2
erythro-2,5,6-Trihydroxy-3-hexenoic	1	+	−	−
threo-2,5,6-Trihydroxy-3-hexenoic	1	+	−	−
3,4-Dideoxy-*erythro*-hexonic	1	1	1	1
3,4-Dideoxy-*threo*-hexonic	1	1	1	1
2-*C*-Methylpentonic	+	+	+	−
3-Deoxy-*lyxo*-hexonic	1	1	1	1
3-Deoxy-*xylo*-hexonic	1	2	2	2
3-Deoxy-*ribo*- and -*arabino*-hexonic	not determined			
β-Glucoisosaccharinic	124	142	146	160
α-Glucoisosaccharinic	53	49	65	79
Total amount (mg.g^{-1} of starch)	345	385	431	480

[a] Weights (mg) are from 1 g of starch. [b] Key: +, traces; −, not detected. [c] 4-Hydroxy-2-(hydroxymethyl)-tetrahydrofuran-4-carboxylic acids.

which only glycolic, lactic, 2-*C*-methylglyceric, and glucoisosaccharinic acids were identified[25,26] after the degradation of amylose at $<200°$. More recent studies[27–29] of the degradation of starch at $>200°$ resulted in the identification of glycolic, lactic, 2-hydroxy-2-methylpropanoic, 2-hydroxybutanoic, and 2-hydroxypentanoic acids.

As expected from similar studies[1] with cellulose, the main monocarboxylic acids from starch were glycolic, lactic, 3-deoxytetronic, 3,4-dideoxypentonic, anhydroisosaccharinic, and glucoisosaccharinic acids, but several minor compounds were formed as well. Their origins have been discussed in detail[1–3,6,11,16,22] elsewhere. Small amounts of xyloisosaccharinic and 3-deoxy-*xylo*- and -*lyxo*-hexonic acids were formed, probably from xylan and galactose impurities.

The total yields of hydroxy monocarboxylic acids were ~35–50%, which is somewhat less than expected. Studies[30] with glycogen have shown that this type of stability may be due to the liberation of shorter chains terminated with glucoisosaccharinic acid units that are resistant to further degradation. Periodate oxidation should remove this effect and should contribute to more pronounced[31] formation of glycolic and 3-deoxytetronic acids during a subsequent treatment with alkali.

TABLE IV

Yields[a] of dicarboxylic acids obtained on treatment of starch with sodium hydroxide

Dicarboxylic acid	*175°*		*190°*	
	M	3M	M	3M
Oxalic	2	1	2	2
Fumaric	−[b]	−	+	1
Succinic	1	1	2	4
Methylsuccinic	1	2	3	5
Tartronic	+	+	−	−
C-Methyltartronic	1	+	+	1
C-Ethyltartronic	+	3	1	3
Malic	+	1	+	2
2-Deoxy-3-*C*-methyltetraric	+	−	+	+
2,3-Dideoxypentaric	4	3	5	6
2,3-Dideoxy-4-*C*-methylpentaric	+	+	1	1
2,3,4-Trideoxyhexaric	3	3	4	6
C-(3-Hydroxypropyl)tartronic	+	+	+	+
C-(2,3-Dihydroxypropyl)tartronic	+	1	−	−
3,4-Dideoxy-*erythro*-hexaric	8	17	8	31
3,4-Dideoxy-*threo*-hexaric	8	17	8	32
3,4,5-Trideoxyheptaric	6	8	8	10
Hydroxyhexanedioic (4 branched isomers)	+	+	2	4
Trideoxyheptaric (3 isomers)	+	+	3	4
Dihydroxyoctanedioic (2 isomers)	−	−	+	+
Unknown II	−	+	4	6
Unknown IV	3	4	2	3
Total amount ($mg.g^{-1}$ of starch)	37	61	53	121

[a] Weights (mg) are from 1 g of starch. [b] Key: +, traces; −, not detected.

Several dicarboxylic acids were also identified (Table IV), which agrees well with the studies of cellulose[1]. Unidentified compounds included one (II) formed also from xylan, and a further compound (IV) for which the molecular weight could not be determined: *m/z* 453 (0.5%), 365 (3), 347 (12), 303 (5), 275 (5), 245 (6), 205 (9), 171 (10), 147 (18), 129 (15), 103 (11), and 73 (100).

Degradation of chitin. — The degradation of chitin produced the most simple mixtures of carboxylic acids (Fig. 3), of which only some minor compounds remained unidentified. Nearly all of these compounds were hydroxy monocarboxylic acids or dicarboxylic acids, with the exception of one amino acid (glycine, peak 17) and one tricarboxylic acid (2-*C*-carboxy-3-deoxytetraric acid, peak 40).

Although the conditions of treatment with alkali were slightly stronger than those usually applied[32-34] for the deacetylation of chitin, the yields of non-volatile carboxylic acids were lower than expected (Tables V and VI). Obviously, this relative stability of

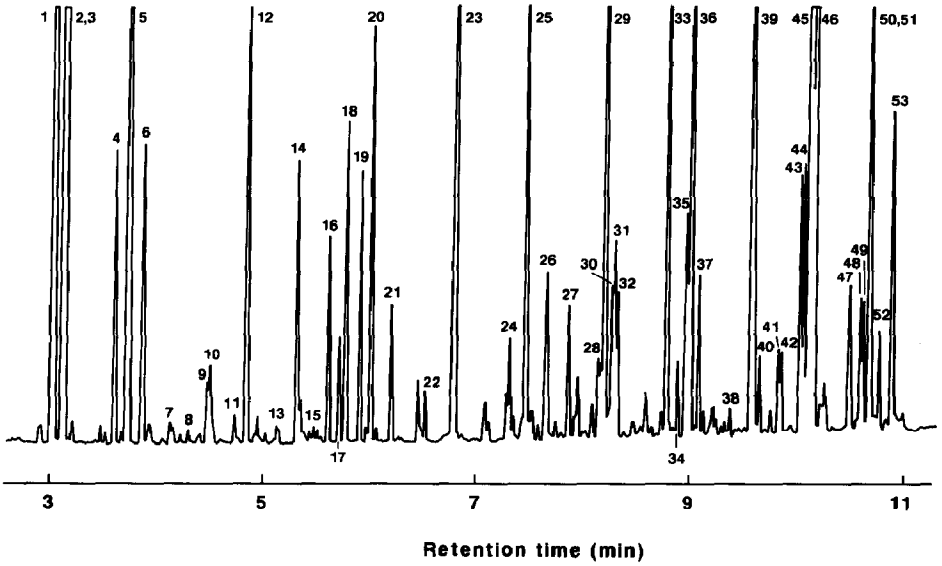

Fig. 3. Separation on NB-30 of the trimethylsilylated carboxylic acids obtained after treatment of chitin with 3M NaOH at 190°: 1, lactic; 2, 2-hydroxy-2-methylpropanoic; 3, glycolic; 4, oxalic; 5, 2-hydroxybutanoic; 6, 2-hydroxy-2-methylbutanoic; 7, 2-hydroxy-3-methylbutanoic; 8, 2-hydroxy-3-methyl-2-cyclopenten-1-one; 9, artifact; 10, 2-hydroxypentanoic; 11, benzoic; 12, 4-hydroxybutanoic; 13, 4-hydroxypentanoic; 14, phosphoric; 15, maleic; 16, succinic; 17, glycine; 18, methylsuccinic; 19, 2-*C*-methylglyceric; 20, fumaric; 21, *C*-methyltartronic; 22, methylfumaric (mesaconic); 23, 3-deoxytetronic; 24, a *C*-propenyltartronic; 25, malic; 26, 3,4-dideoxypentonic; 27, 2,3-dideoxypentonic; 28, a branched hydroxyhexanedioic; 29, 2,3-dideoxypentaric; 30, 2,3-dideoxy-4-*C*-methylpentaric; 31, a branched hydroxyhexanedioic; 32, a branched hydroxyhexanedioic; 33, *β*-anhydroisosaccharinic; 34, *α*-anhydroisosaccharinic; 35, 3-deoxy-*erythro*-pentonic (+ unknown); 36, 2,3,4-trideoxyhexaric; 37, 3-deoxy-*threo*-pentonic; 38, 3-deoxy-*threo*-pentaric; 39, xylitol (internal standard); 40, 2-*C*-carboxy-3-deoxytetraric; 41, 3,4-dideoxy-*erythro*-hexonic; 42, 3,4-dideoxy-*threo*-hexonic; 43, a branched trideoxyheptaric; 44, a branched trideoxyheptaric; 45, 3,4-dideoxy-*threo*-hexaric; 46, 3,4-dideoxy-*erythro*-hexaric; 47, a dihydroxyoctanedioic; 48, 3-deoxy-*lyxo*-hexonic; 49, 3-deoxy-*xylo*-hexonic; 50, 3-deoxy-*ribo*-hexonic; 51, 3-deoxy-*arabino*-hexonic; 52, a dihydroxyoctanedioic; and 53, 3,4,5-trideoxyheptaric acids.

chitin is due to its crystalline structure and the fact that it cannot be degraded by a peeling mechanism. Apparently, the products of the degradation of chitin with aqueous alkali have not been reported hitherto.

The best known reaction of chitin in aqueous alkali, at elevated temperatures, is partial *N*-deacetylation, but some acetamide may also be cleaved off, as suggested by its formation during saponification[35] of di-*N*-acetyl-hexa-*O*-acetylchitobiose and during pyrolysis[36,37] of chitin. The degradation of chitin with alkali is expected to give 2-amino-2-deoxyglucose, 2-acetamido-2-deoxyglucose, or their anhydro derivatives[38] (and oligomeric products), which are then rapidly degraded further. More than 20 hydroxy monocarboxylic acids were identified as such conversion products (Table V).

At 190°, the main hydroxy monocarboxylic acid was lactic acid, which was found[39] as early as 1880 after the treatment of 2-amino-2-deoxyglucose hydrochloride with sodium hydroxide. The formation of glyceraldehyde[40] and pyruvaldehyde[41] (the precursors of lactic acid) from 2-amino-2-deoxyglucose has also been reported.

Also formed from chitin in moderate amounts were glycolic, 2-hydroxy-2-meth-

TABLE V

Yields[a] of hydroxy monocarboxylic acids obtained on treatment of chitin with sodium hydroxide

Monocarboxylic acid	*175°*		*190°*	
	M	3M	M	3M
Glycolic	13	18	5	6
Lactic	8	16	14	31
2-Hydroxy-2-methylpropanoic	6	9	6	7
2-Hydroxybutanoic	4	5	4	10
4-Hydroxybutanoic	+[b]	+	2	3
2-Hydroxy-2-methylbutanoic	1	1	1	2
2-Hydroxy-3-methylbutanoic	−	−	−	+
2-Hydroxypentanoic	+	+	+	+
4-Hydroxypentanoic	−	−	+	+
2-*C*-Methylglyceric	−	+	+	2
3-Deoxytetronic	1	1	1	4
3,4-Dideoxypentonic	−	1	+	1
2,3-Dideoxypentonic	−	+	+	1
3-Deoxy-*erythro*-pentonic	+	1	+	1
3-Deoxy-*threo*-pentonic	+	1	+	1
β-Anhydroisosaccharinic[c]	1	2	1	3
α-Anhydroisosaccharinic[c]	−	+	+	+
3,4-Dideoxy-*erythro*-hexonic	+	+	+	+
3,4-Dideoxy-*threo*-hexonic	+	+	+	+
3-Deoxy-*lyxo*-hexonic	+	+	+	1
3-Deoxy-*xylo*-hexonic	+	+	+	1
3-Deoxy-*ribo*- and -*arabino*-hexonic	1	1	2	3
Total amount (mg.g^{-1} of chitin)	34	58	36	77

[a] Weights (mg) are from 1 g of chitin. [b] Key: +, traces; −, not detected. [c] 4-Hydroxy-2-(hydroxymethyl)-tetrahydrofuran-4-carboxylic acids.

TABLE VI

Yields[a] of dicarboxylic acids obtained on treatment of chitin with sodium hydroxide

Dicarboxylic acid	*175°*		*190°*	
	M	3M	M	3M
Oxalic	1	3	2	3
Maleic	–[b]	–	–	+
Fumaric	1	1	2	3
Methylfumaric	–	1	+	+
Succinic	+	1	1	1
Methylsuccinic	+	1	1	2
Tartronic	+	+	–	–
C-Methyltartronic	+	+	1	1
C-Propenyltartronic	–	–	+	+
Malic	1	3	2	4
2,3-Dideoxypentaric	+	2	1	4
2,3-Dideoxy-4-*C*-methylpentaric	+	+	+	1
2,3,4-Trideoxyhexaric	1	1	2	4
3-Deoxy-*threo*-pentaric	–	–	+	+
3,4-Dideoxy-*erythro*-hexaric	5	9	5	13
3,4-Dideoxy-*threo*-hexaric	5	9	4	13
3,4,5-Trideoxyheptaric	+	1	1	2
Hydroxyhexanedioic (3 branched isomers)	+	+	1	2
Trideoxyheptaric (2 branched isomers)	+	–	1	3
Dihydroxyoctanedioic (2 isomers)	–	–	+	1
Total amount ($mg.g^{-1}$ of chitin)	14	32	23	53

[a] Weights (mg) are from 1 g of chitin. [b] Key: +, traces; –, not detected.

ylpropanoic, 2-hydroxybutanoic, 3-deoxytetronic, and 3-deoxyhexonic acids. Of these, 3-deoxytetronic, 3-deoxy-*ribo*-hexonic, and 3-deoxy-*arabino*-hexonic acids were found[42] after treatment of 2-amino-2-deoxyglucose with alkali and reflected similarities in the degradation of glucose and its 2-amino-2-deoxy derivative. Such similarities are also shown by the formation[43] of arabinonic acid during the treatment of 2-amino-2-deoxyglucose with alkali in the presence of oxygen.

The glucoisosaccharinic acids were not formed from chitin even though their formation from chitotriose and tri-*N*-acetylchitotriose has been confirmed[44]. Small amounts of anhydroisosaccharinic acids were identified that were identical with those derived from starch. The routes of formation of the small amounts of 2,3-dideoxypentonic and 3,4-dideoxyhexonic acids remain obscure (*cf.* ref. 11).

The liberation[39,44,45] of ammonia during the degradation of chitin with alkali probably restricts[46] the formation of hydroxy carboxylic acids, for example by contributing to the formation of pyrazines[47,48]. No attempts were made to analyse such compounds.

Higher temperatures and concentrations of alkali increased the formation of dicarboxylic acids (Table VI), even though their yields remained relatively low. With the

exceptions of fumaric and methylfumaric (mesaconic) acids, all of these acids are formed on similar treatments of cellulose[1].

Formation of cyclic compounds. — Qualitative g.l.c. and g.l.c.–m.s. of the products extracted with chloroform, after acidification to pH 2, revealed the presence of alkyl-substituted 2-cyclopenten-1-ones[3], 2-hydroxy-2-cyclopenten-1-ones[49], and other compounds in each reaction mixture. No furans[50] were formed from chitin. A more detailed analysis of these cyclic compounds, which appear to be responsible for the brown colour of the reaction mixtures, was outside the scope of this study.

Concluding remarks. — The present results show that the mixtures of carboxylic acids derived from xylan, starch, and chitin are as complex as those[1] from cellulose. Several main products are formed simultaneously in addition to formic and acetic acids[1–3,27–29], which were not analysed here. Little is known about many of these main compounds, such as 3,4-dideoxypentonic acid, isosaccharinic acids, and certain hydroxydicarboxylic acids, and thence there is a need to identify conditions[29] that favour the formation of certain desired compounds or to pay more attention to the use of these acids as mixtures. Some potential applications of mixtures of these acids have been summarised[1].

The degradation of chitin with alkali, under more drastic conditions, is being studied further.

ACKNOWLEDGMENTS

Professor E. Sjöström is thanked for his interest, and Professor D. Horton for helpful discussions on amino sugars.

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