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NON-OXIDATIVE AND OXIDATIVE ALKALINE DEGRADATION OF PECTIC ACID

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ABSTRACT

As alkaline degradation products of pectic acid, 6 hydroxymonocarboxylic, 16 dicarboxylic, and 2 tricarboxylic acids were identified by g.l.c.–m.s. as their trimethylsilyl derivatives. In the absence of oxygen, the most abundant degradation products are 3-deoxy-2-*C*-(hydroxymethyl)pentaric, 2,3-dideoxypentaric, 2-deoxy-3-*C*-methyltetraric, malic, and 2^1,4-anhydro-3-deoxy-2-*C*-(hydroxymethyl)pentaric acids, whereas, in the presence of oxygen, glycolic, oxalic, malic, 3-deoxypentaric, and 2-*C*-carboxy-3-deoxypentaric acids preponderate. The routes of formation of these acids show many similarities with those encountered in the alkaline degradation of cellulose.

INTRODUCTION

The xylem both of softwood and hardwood species contains only small proportions of pectic substances (generally, <1%), whereas their content in inner bark is much higher[1]. During kraft pulping[2], these substances are completely degraded by routes for which only very little information is available. From sodium hydroxide treatment of a pectic substance, malic and 3-deoxy-2-*C*-(hydroxymethyl)pentaric acids have been identified[3]. Moreover, a reaction scheme for the formation of 3-deoxy-2-*C*-(hydroxymethyl)pentaric, 2,3-dideoxypentaric, and 3-deoxypentaric acids has been presented[4]. The formation of formylpyrotartaric acid from pectic substances of sugar beet has also been reported[5]. Degradation products from the treatment of pectic acid with sodium hydroxide have now been studied by applying analytical methods recently developed[6]. The effect of oxygen on the degradation has also been investigated.

EXPERIMENTAL

Materials. — Pectic acid was purchased from Nutritional Biochemicals Corp., Cleveland, Ohio. A sample of 2-*C*-carboxy-3,4-dideoxypentaric acid was prepared from 2-oxoglutaric acid (Fluka AG, Switzerland) by a cyanohydrin synthesis, followed by hydrolysis with sulfuric acid. G.l.c.–m.s. indicated the formation of the desired compound in ~10% yield.

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Treatment of pectic acid, and analysis of the degradation products. — Pectic acid (500 mg) was treated with 0.5M NaOH (100 mL) for 2 h at 120° under a nitrogen or an oxygen atmosphere (0.4 MPa). The degradation of pectic acid was 86% and 62%, respectively. Nonvolatile carboxylic acids were analyzed as their trimethylsilyl derivatives by g.l.c.–m.s., using the apparatus and technique described earlier[6].

RESULTS AND DISCUSSION

Identification of the degradation products. — G.l.c.–m.s. of the trimethylsilyl derivatives of the nonvolatile products of the alkali treatment of pectic acid revealed the presence of 6 novel degradation products, of which 4 could be identified. Two almost identical mass spectra (I in Fig. 1) were recorded for "α"- and "β"-2^1,4-anhydro-3-deoxy-2-*C*-(hydroxymethyl)pentaric acids, (*erythro* and *threo* forms). Because the *threo* forms usually preponderate, the major diastereomer was probably this form.

The molecular mass of the trimethylsilyl derivative of an unknown acid was identical to that of citric and isocitric acids (480) and its mass spectrum (II in Fig. 1) had many features in common with their mass spectra[7,8]. Prominent peaks at m/z 436 (M − 44) and 305 indicated that the acid is a *C*-substituted tartronic acid[9]. The spectra of the sample and reference substance were identical, and confirmed the

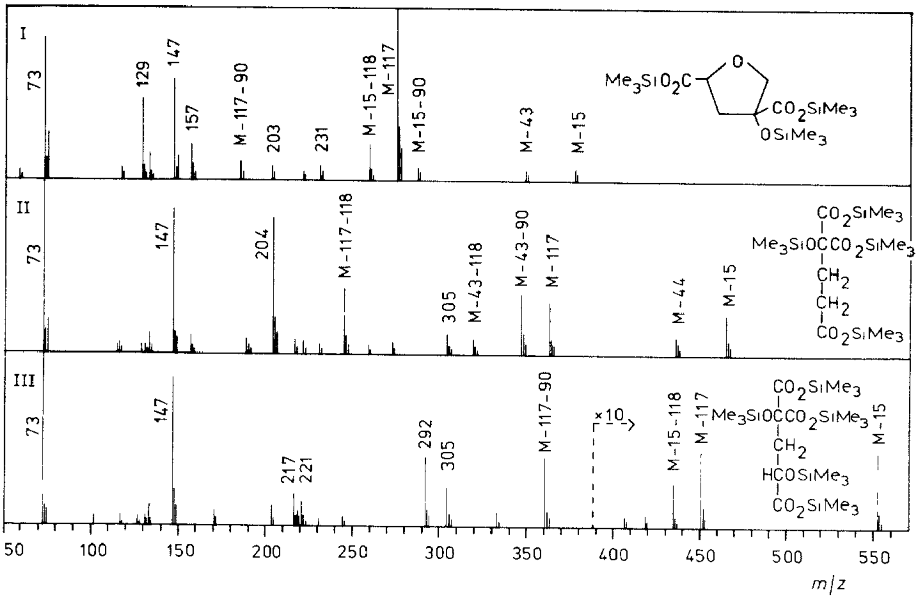


Fig. 1. Mass spectra at 70 eV of the Me_3Si derivatives of 2^1,4-anhydro-3-deoxy-2-*C*-(hydroxymethyl)pentaric (I), 2-*C*-carboxy-3,4-dideoxypentaric (II), and 2-*C*-carboxy-3-deoxypentaric (III) acids.

TABLE I

THE DEGRADATION PRODUCTS OF PECTIC ACID[a] UNDER REACTION CONDITIONS OF 500 mg OF PECTIC ACID/ 100 mL OF 0.5M NaOH, FOR 2 h AT 120° UNDER A PRESSURE OF 0.4 MPa

Product	N_2	O_2	*Retention time*[b]
Monocarboxylic acids			
Lactic	3.2	3.3	0.305
Glycolic	1.3	23.0	0.315
2-Hydroxybutanoic	0.2	—	0.373
2-*C*-Methylglyceric	2.0	0.4	0.607
Glyceric	+	1.3	0.612
3-Deoxytetronic	0.3	—	0.700
Dicarboxylic acids			
Oxalic	0.8	7.8	0.360
Succinic	0.8	2.7	0.572
C-Methyltartronic	1.5	2.3	0.637
Tartronic	0.6	3.1	0.667
2-Deoxy-3-*C*-methyltetraric	7.0	—	0.759
Malic (deoxytetraric)	5.9	12.3	0.773
2,3-Dideoxypentaric	7.6	2.3	0.850
"β"-2^1,4-Anhydro-3-deoxy-2-*C*-(hydroxymethyl)pentaric[c]	2.8	—	0.904
"α"-2^1,4-Anhydro-3-deoxy-2-*C*-(hydroxymethyl)pentaric	1.8	—	0.939
3-Deoxy-*erythro*-pentaric	0.6	4.4	0.961
3-Deoxy-*threo*-pentaric	0.8	7.8	0.971
2,5-Dihydroxy-3-hexenedioic	0.6	0.2	1.083
3-Deoxy-2-*C*-(hydroxymethyl)-*threo*-pentaric	42.1	7.0	1.181
3-Deoxy-2-*C*-(hydroxymethyl)-*erythro*-pentaric	12.9	2.3	1.208
3-Deoxy-*xylo*-hexaric	0.8	0.5	1.190
3-Deoxy-*lyxo*-hexaric	1.3	0.7	1.197
Tricarboxylic acids			
2-*C*-Carboxy-3,4-dideoxypentaric	0.6	0.3	1.069
2-*C*-Carboxy-3-deoxypentaric	—	14.7	1.239
Unidentified	4.5	3.6	

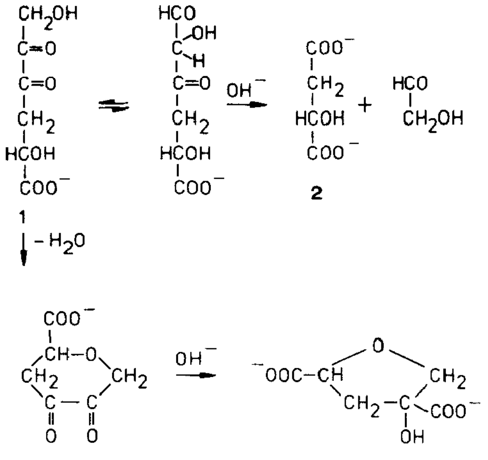
[a] The figures given are % of total nonvolatile acids. [b] Retention of Me_3Si derivatives relative to the xylitol derivative. [c] For comparison, the retention time of anhydroisosaccharinic acid is 0.911.

structure as that of a 2-*C*-carboxy-3,4-dideoxypentaric acid. An acid occurring in large proportion after oxygen–alkali treatment was identified as a 2-*C*-carboxy-3-deoxypentaric acid (III in Fig. 1). The molecular masses of the trimethylsilyl derivatives of the unidentified acids were 538 and 582. All of the other compounds had been identified during previous studies[6].

Degradation routes. — As expected, most of the acids identified were dicarboxylic acids (see Table I). In the absence of oxygen, 3-deoxy-2-*C*-(hydroxymethyl)pentaric acids were the most abundant degradation products. Markedly less of these acids was formed in the presence of oxygen. Their formation can be explained by the isomerization of the reducing galacturonic acid end group, followed by a β-elimination and benzilic acid rearrangement of the 3-deoxy-4,5-

hexodiulosonic acid liberated[4]. These acids have previously been prepared by alkaline treatment of alginates[10], 4-*O*-methylglucuronic acid[3], and 2-*O*-(4-*O*-methylglucosyluronic acid)-xylose[11].

Small proportions of 3-deoxypentaric and 2,3-dideoxypentaric acids were also formed, as postulated by Löwendahl *et al.*[4]. In good agreement with previous results on 4-*O*-methylglucuronic acid[3], the proportions of 3-deoxypentaric acids were much larger after oxygen–alkali treatment. Other competitive reactions resulting in the formation of malic acid (**2**) and 2^1,4-anhydro-3-deoxy-2-*C*-(hydroxymethyl)pentaric acids (**3**) from pectic acid are, respectively, a hydrolytic cleavage of 3-deoxy-4,5-hexodiulosonic acid (**1**), and benzilic acid rearrangement of its



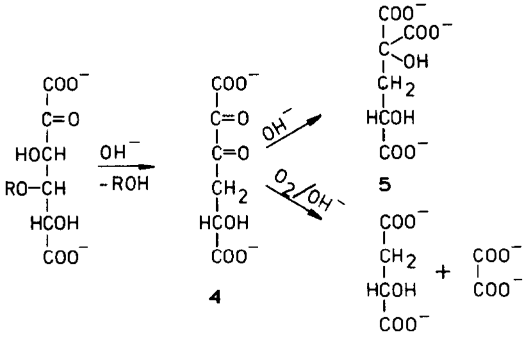
Scheme 1

anhydro derivative (see Scheme 1), in analogy with the alkaline degradation of cellulose [which gives rise to 2-deoxytetronic acid[12] and an anhydroisosaccharinic acid (2^1,4-anhydro-3-deoxypentonic acid)[13]]. In addition, appreciable proportions of a 2-deoxy-3-*C*-methyltetraric acid were formed, but only in the absence of oxygen. A possible reaction path involves benzilic acid rearrangement of 3,4-dioxopentanoic acid, formed as an intermediate.

2,5-Dihydroxy-3-hexenedioic acid is probably derived from the end group formed by β-hydroxy elimination. Further β-elimination yields an unstable intermediate, from which 2,5-dihydroxy-3-hexenedioic acid is formed by benzilic acid rearrangement, in similarity with the reaction route for the formation of 2,5,6-trihydroxy-3-hexenoic acid from cellulose[14]. The presence of 3-deoxy-*lyxo*-hexaric and 3-deoxy-*xylo*-hexaric acids indicates that a complete peeling of the pectic acid chains is possible.

Only a small proportion of monocarboxylic acids was formed in the absence of oxygen. Of these, 2-hydroxybutanoic acid is known to be derived from xylan, *via* 3-deoxytetrulose[15], but its formation from pectic acid most probably requires another (unknown) intermediate. After oxygen–alkali treatment, glycolic acid was the main degradation product.

The formation of 2-*C*-carboxy-3-deoxypentaric acid during oxygen–alkali treatment most likely follows a reaction path analogous to that responsible for the formation of *C*-(2-hydroxyethyl)tartronic acid from xylan[16] and *C*-(2,3-dihydroxypropyl)tartronic acid from cellulose[14] and cellobiose[17]. The first step is oxidation of the reducing end-group, followed by a β-elimination. The liberated dicarbonyl compound is subjected either to benzilic acid rearrangement, which gives 2-*C*-carboxy-3-deoxypentaric acid (**5**), or to a fragmentation resulting in the formation of malic acid (**6**) and oxalic acid (**7**) (see Scheme 2). 2-*C*-Carboxy-3-deoxypentaric acid has previously been prepared by nitric acid oxidation of glucoisosaccharinic and 3-deoxy-2-*C*-(hydroxymethyl)pentaric acids[10,18]. Another tricarboxylic acid, 2-*C*-carboxy-3,4-dideoxypentaric acid, was formed in small proportion in both the presence and absence of oxygen. The corresponding dicarboxylic acid, *C*-(3-hydroxypropyl)tartronic acid has been reported to be formed from cellobiose during oxygen–alkali treatment[17], and from cellulose during hot-alkali treatment[19].



Scheme 2 **6** **7**

Concluding remarks. — Of the dicarboxylic acids identified, all but 3-deoxyhexaric, 2¹,4-anhydro-3-deoxy-2-*C*-(hydroxymethyl)pentaric, and 2,5-dihydroxy-3-hexenedioic acids have been reported to be present in the "black" liquors of softwood[4,20] and hardwood[21]. In addition, small proportions of 3-deoxyhexaric acids have been found in pine and alder kraft black liquors[22]. It is obvious that the most important sources for the production of dicarboxylic acids from wood during alkaline pulping are the pectic substances, in addition to the 4-*O*-methylglucuronic acid groups in xylan.

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