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THERMAL DEGRADATION OF 2-DEOXY-D-*arabino*-HEXONIC ACID AND 3-DEOXY-D-*ribo*-HEXONO-1,4-LACTONE

FRED SHAFIZADEH AND YUAN-ZONG LAI
Wood Chemistry Laboratory, Department of Chemistry and School of Forestry, University of Montana, Missoula, Montana 59801 (U. S. A.)

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ABSTRACT

Heating of 2-deoxy-D-*arabino*-hexonic acid results in substantial lactonization on melting. Decomposition of the lactone involves dehydration, decarboxylation, and fission to provide mainly water, 5-(2-hydroxyethylidene)-2(5*H*)-furanone, carbon dioxide, carbon monoxide, acrylaldehyde, and acetic acid. 3-Deoxy-D-*ribo*-hexono-1,4-lactone, which could not readily undergo β-elimination, is thermally more stable and gives a mixture of fission and dehydration products.

INTRODUCTION

Pyrolysis of cellulosic materials and carbohydrates, in general, forms considerable amounts of carbon dioxide, even on moderate heating[1–4]. Experiments with ^{14}C-labelled 1,6-anhydro-β-D-glucopyranose (levoglucosan) have shown that 30, 35, or 50% of the carbon dioxide originates from C-1 of the sugar moiety, depending on whether the pyrolysis is catalyzed by alkali, uncatalyzed, or catalyzed by a Lewis acid, respectively[5]. Theoretically, formation of carbon dioxide from C-1 may involve rearrangement of the sugar moiety to intermediate 2-deoxy- or 3-deoxy-hexonic acid derivatives and subsequent decarboxylation of the products. Formation of saccharinic acids on alkaline treatment of carbohydrates at normal temperatures is well-known[6], and 2-deoxy-D-*arabino*-hexonic acid and its lactone have been found among the radiolysis products of D-glucose in aqueous solutions[7,8]. The latter transformation has been attributed to the abstraction of a hydrogen atom from the sugar, and subsequent dehydration and rearrangement of the molecule[8]. A somewhat similar mechanism of dehydration and rearrangement has been postulated for the formation of 2-deoxy-D-aldonic acid as an intermediate in the production of carbon dioxide from the pyrolysis of carbohydrates[5].

We now report on the thermal properties of 2-deoxy-D-*arabino*-hexonic acid, the corresponding 1,4-lactone, and 3-deoxy-D-*ribo*-hexono-1,4-lactone.

RESULTS AND DISCUSSION

The physical and chemical transformations which take place on heating 2-deoxy-D-*arabino*-hexonic acid, the corresponding 1,4-lactone, and 3-deoxy-D-*ribo*-hexono-1,4-lactone ("α"-D-glucometasaccharinolactone) were investigated by coordinated dynamic thermal analysis and chemical methods through the entire range of the thermal events, and finally by isothermal pyrolysis at 550°.

Thermal analysis. — Thermal analysis of 2-deoxy-D-*arabino*-hexonic acid produced the curves shown in Fig. 1. In this Figure, the d.t.a. (differential thermal) curve shows a major, endothermic peak (negative ΔT) at 146°, corresponding to the melting point of the compound. This peak, however, is broader than the sharp endotherms associated with simple physical transformations[9] (*cf.* the melting endotherm of the lactone discussed later), and indicates a concurrent chemical transformation. The initial endotherm is followed by a characteristic, broad decomposition peak centered at 260°. These observations are confirmed by the t.g. (thermogravimetric) curve, which shows a minor weight-loss of $\sim$10% associated with the melting endotherm and a major weight-loss of $\sim$50% associated with the decomposition peak, leaving 35% of the residue at 400°. The d.t.g. (derivative thermogravimetric) curve, which shows two peaks centered at 157 and 252° corresponding to the major thermal events, indicates the rates of weight loss at different temperatures.

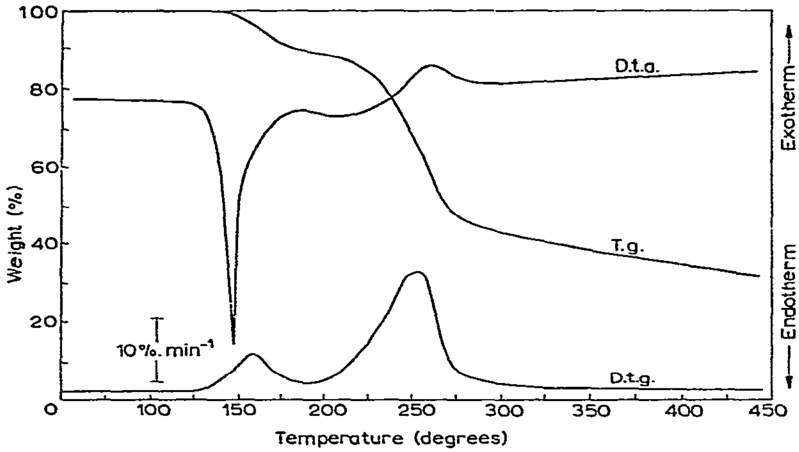


Fig. 1. Thermal-analysis curves of 2-deoxy-D-*arabino*-hexonic acid.

The thermal analysis curves (Fig. 2) for 2-deoxy-D-*arabino*-hexono-1,4-lactone also indicate the temperature for the corresponding thermal events. However, in this case, the melting endotherm is very sharp and is preceded by another endothermic transition. As discussed previously[10], different types of pre-melting transitions are often noted on thermal analysis of carbohydrates and some of them are corroborated by other physical methods. Furthermore, the decomposition takes place at a higher temperature range (~300°) and leaves a smaller residue (~20%) at 400°.

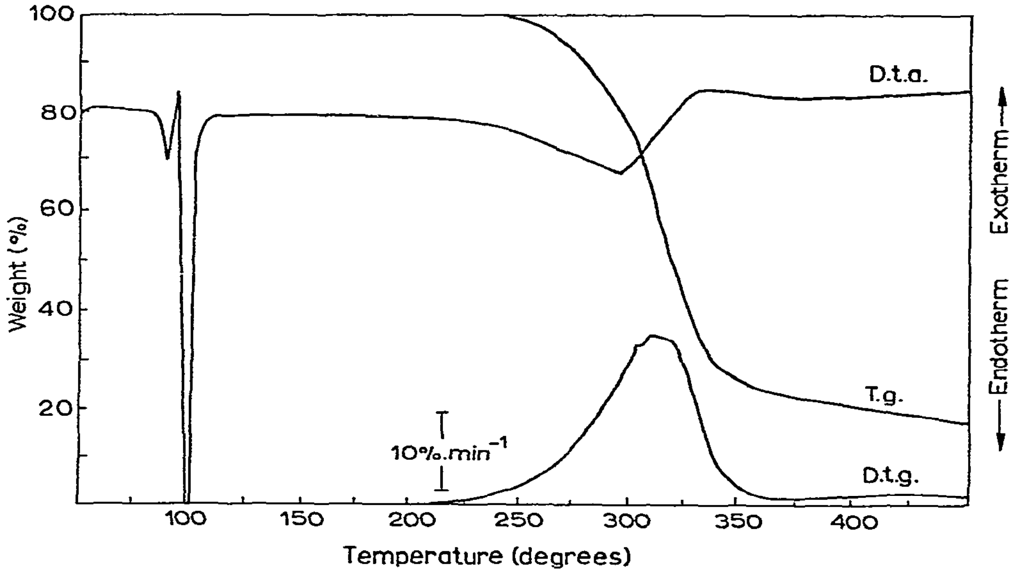


Fig. 2. Thermal analysis curves of 2-deoxy-D-*arabino*-hexono-1,4-lactone.

Closely similar data were obtained for 3-deoxy-D-*ribo*-hexono-1,4-lactone, which melted sharply at 107° without prior transition and decomposed at a still higher temperature range centered at 347° (Fig. 3).

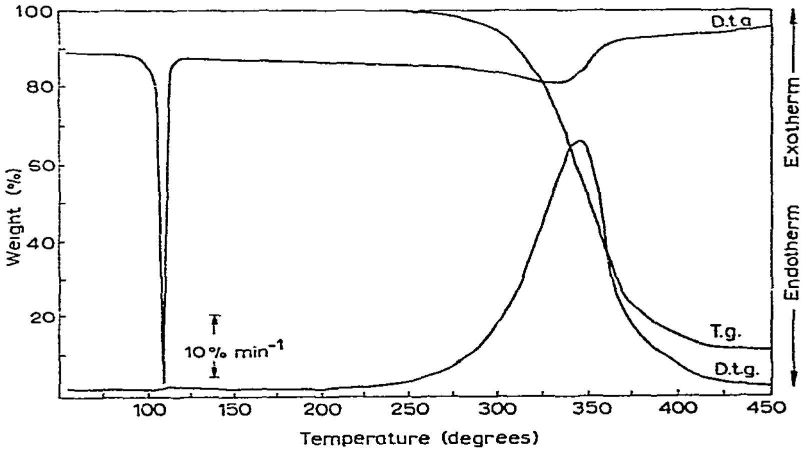


Fig. 3. Thermal analysis curves of 3-deoxy-D-*ribo*-hexono-1,4-lactone.

*Pyrolysis of 2-deoxy-*D-arabino-*hexonic acid.* — To determine the nature of the chemical transformations which were signalled by the thermal analysis, samples of 2-deoxyhexonic acid were heated in a controlled system, at the same rate as in the thermal-analysis experiments, and the reaction mixtures produced at different temperatures were analyzed by spectroscopic methods and gas–liquid chromatography (g.l.c.) of the trimethylsilyl ether derivatives. The results (Table I) indicate that melting of the acid is accompanied by the formation of the corresponding lactones. The 1,4- and 1,5-lactones gave overlapping peaks on g.l.c., but their infrared (i.r.) spectra showed distinct carbonyl bands at 1770 and 1730 cm^{-1}, respectively. The i.r. analysis showed that a sample heated just through the melting point (146°) contained mainly the 1,5-lactone, but continued heating (to 190°) resulted in predominant formation of the more stable 1,4-lactone. Apparently, the two forms are interconvertible, and the 1,4-lactone, which is known to be more stable under aqueous conditions[11], is also the main species at elevated temperatures. Heating of the mixture to the decomposition temperatures (200 and 250°) also produced small proportions of 1-deoxy-D-arabinitol, indicating the occurrence of decarboxylation.

Evolution of the volatile products at different temperatures was monitored by evolved-gas detection (e.g.d.) and mass spectrometry. The e.g.d. instrument, which is

TABLE I

G.L.C. ANALYSIS OF THE PYROLYSIS RESIDUE

Sample temperature (degrees)	*Acid* (%)[a]	*Lactone* (%)	*1-Deoxy-*D-*arabinitol* (%)	*2-Deoxy-*D-erythro-*pentose* (%)	*2-Deoxy-*D-erythro-*pentitol* (%)
2-Deoxy-D-*arabino*-hexonic acid					
20	100.0	—	—		
135	95.5	4.5	—		
140	62.3	37.2	—		
147	42.7	56.0	—		
175	15.5	66.0	T[b]		
200	9.1	50.3	5.2		
250	T	29.8	6.5		
2-Deoxy-D-*arabino*-hexono-1,4-lactone					
20	—	100.0	—		
250	—	95.2	—		
275	T	51.5	1.2		
300	—	20.2	1.8		
3-Deoxy-D-*ribo*-hexono-1,4-lactone					
20	—	100.0		—	—
290	T	82.5		—	—
315	T	75.6		—	—
325	T	55.2		T	T
335	—	14.6		4.5	1.8

[a] The percentages are based on the original weight. [b] T = trace amounts.

equipped with a flame-ionization detector, gave only one peak corresponding to the decomposition of the 2-deoxyhexonic acid, indirectly confirming the process of lactonization and formation of water at the first thermal event.

More direct evidence was obtained by mass spectrometry, which showed that evolution of water forms two distinct peaks at 150 and 250°, corresponding to the melting and decomposition events, respectively, and the evolution of carbon dioxide gives a sharp peak at 250° (see Fig. 4).

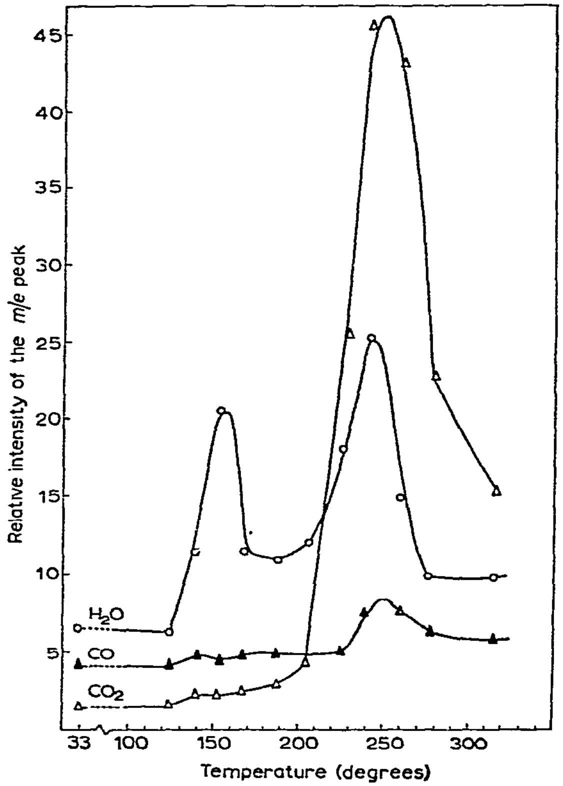


Fig. 4. Evolution of CO_2, CO, and H_2O on heating of 2-deoxy-D-*arabino*-hexonic acid.

Fig. 5 shows the formation of other major ions, at *m/e* 126, 84, 82, 55, 54, and 43, which can be detected as the decomposition proceeds. The ion at *m/e* 126 is of special interest because it corresponds to the loss of 3 molecules of water from the acid. The dehydration product discussed later gives stronger peaks at *m/e* 82 and 54 (see Fig. 6).

Further information about the sequence of the pyrolytic reactions was obtained by isothermal heating of the acid at 550°. As shown in Table II, the products consisted of water, carbonaceous char, tar, carbon dioxide, carbon monoxide, and a variety of volatile organic compounds. Direct g.l.c. analysis of the volatile compounds showed

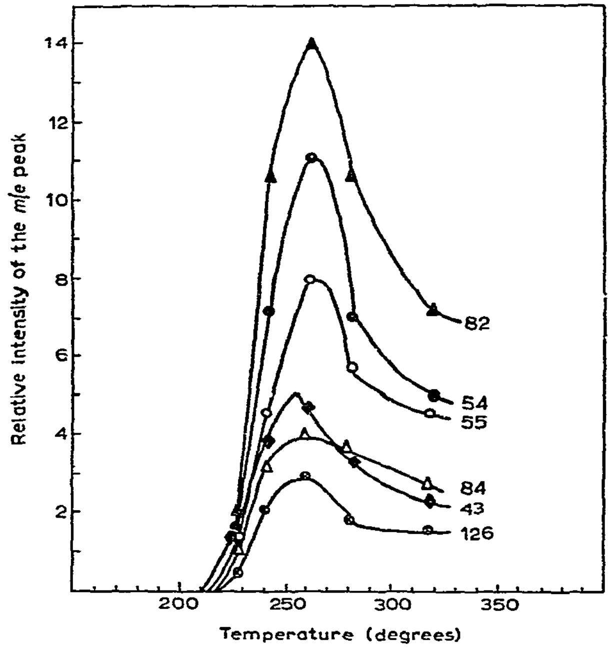


Fig. 5. Mass spectrometry of the pyrolysis products of 2-deoxy-D-*arabino*-hexonic acid.

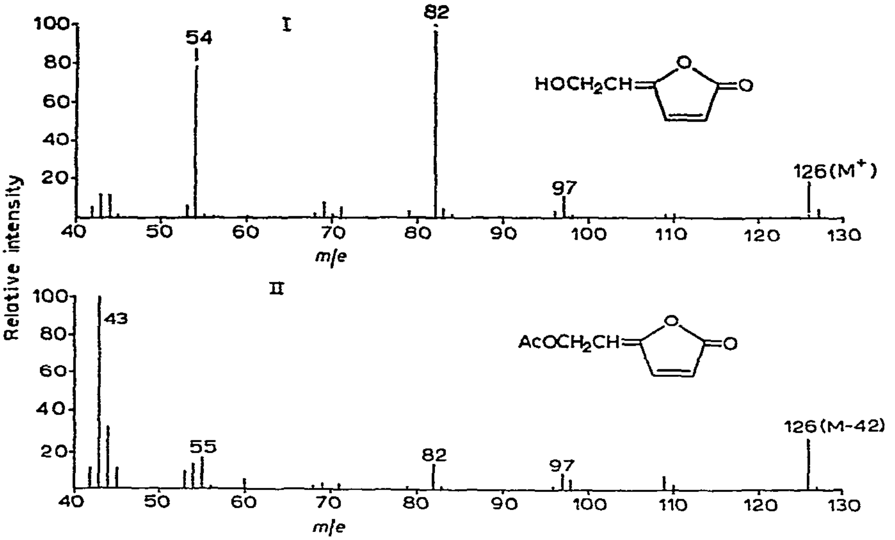


Fig. 6. Mass spectra of 5-(2-hydroxyethylidene)-2(5*H*)furanone (I) and its acetate (II).

significant amounts of an unknown compound, acrylaldehyde, acetic acid, glyoxal, and 1-hydroxy-2-propanone. The last two compounds could not be resolved by g.l.c. for quantitative analysis, and were determined as a mixture. The volatile fraction also contained some furan derivatives, 2-butenal, 2,3-butanedione, and acetaldehyde which, although present in small quantities, indicated the nature of the transitional or secondary reactions.

As discussed previously[3–5], these compounds are derived from the dehydration and fission reactions of the original molecule. The structure of the initial dehydration product was determined by investigation of the unknown compound. The mass spectrum (Fig. 6) of this compound contained a peak at *m/e* 126 for the molecular ion, corresponding to the loss of two molecules of water from the lactone, and major peaks at *m/e* 82 and 54 derived from the resulting furanone ring structure, shown in Scheme 1. The ultraviolet (u.v.) data showed an absorption band at 272 nm which diminished on gradual addition of alkali, suggesting the presence of two double bonds conjugated with the carbonyl group[12]. These data pointed to the structure of 5-(2-hydroxyethylidene)-2(5*H*)furanone for the unknown compound formed as a major volatile product on isothermal and dynamic pyrolysis. This structure was confirmed by comparing the mass spectra of the acetylated unknown (see Fig. 6) and an authentic sample of 5-(2-acetoxyethylidene)-2(5*H*)furanone[13], which were identical.

The tar fraction contained some 1-deoxypentitol and undecomposed lactone detected by g.l.c. The rest consisted of heterogeneous condensation-products of higher molecular weight, showing characteristic streaks on thin-layer chromatography (t.l.c.). The yields of various pyrolysis products that could be isolated as a single chemical entity are shown in Table II.

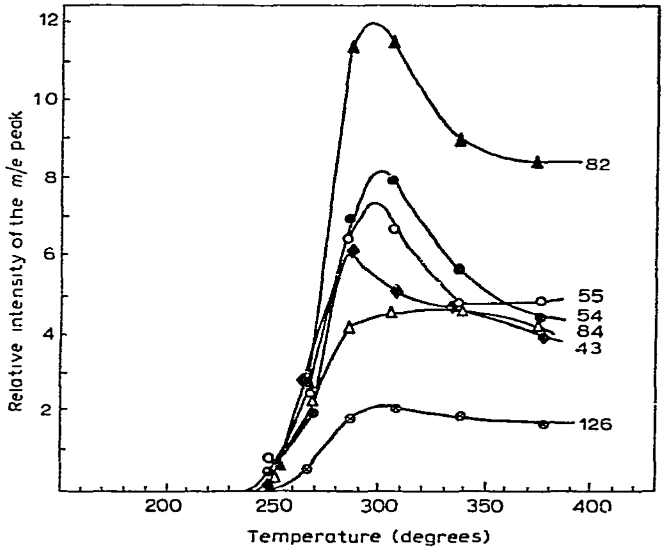


Fig. 7. Mass spectrometry of the pyrolysis products of 2-deoxy-D-*arabino*-hexono-1,4-lactone.

TABLE II

PRODUCTS OF PYROLYSIS OF 2-DEOXY-D-*arabino*-HEXONIC ACID AND THE 1,4-LACTONE AND 3-DEOXY-D-*ribo*-HEXONO-1,4-LACTONE AT 550°

Product	*2-Deoxy (%)*				*3-Deoxy-lactone (%)*			
	Acid	*Lactone*			*Neat*	*+Acid*	*+ZnCl$_2$*	*+Na$_3$CO$_2$*
		Neat	*+ZnCl$_2$*	*+Na$_2$CO$_3$*				
Acetaldehyde	0.5	1.8	0.9	1.1	3.4	1.6	1.2	2.6
Furan	T	0.2	T	T	1.4	0.5	1.0	0.2
Acetone	T	T	T	T	T	3.3	T	1.9
Acrylaldehyde	4.1	8.3	4.5	1.8	1.0	T	1.9	0.1
2-Methylfuran	T[a]	T	1.2	0.2	0.7	1.0	0.2	0.1
2,3-Butanedione	1.3	1.8	1.2	0.6	1.8	1.5	1.8	1.4
2-Butenal	1.0	0.6	0.4	0.8	1.7	1.2	1.0	0.8
1-Hydroxy-2-propanone } Glyoxal }	2.7	9.1	1.0	3.0	1.9	0.6	T	3.1
Acetic Acid	4.1	3.6	1.8	2.0	2.5	1.9	3.7	3.2
α-Angelicalactone	T	T	T	T	1.8	0.1	0.2	0.7
2-Furaldehyde	0.6	0.9	T	0.2	T	0.2	0.3	0.3
2-Furfuryl alcohol	0.2	0.3	0.1	T	1.6	1.0	1.3	0.5
β-Angelicalactone	T	T	T	T	3.6	0.3	0.4	1.4
5-(2-Hydroxyethylidene)-2(5*H*)furanone	10	14	4	3	1	<1.0	<1.0	<1.0
Carbon monoxide	5.3	3.3	2.8	3.8	3.8	8.8	7.0	6.2
Carbon dioxide	12.6	8.4	12.5	19.0	7.8	22.8	19.3	16.5
Water	26.1	17.5	19.5	16.0	8.7	10.8	17.1	16.0
Char	18.2	9.4	29.3	32.8	1.9	15.0	38.2	31.2
Tar	16.5	25.1	17.1	10.0	62.3	22.8	4.2	8.8
2-Deoxy-lactone	(11.8)[b]	(34.5)	(1.0)	(0.7)				
1-Deoxy-D-arabinitol	(2.0)	(1.1)	(0.4)	(0.5)				
3-Deoxy-lactone					(72.2)	(7.2)	(28.5)	(29.5)
2-Deoxy-D-*erythro*-pentose					(1.5)	(1.3)	(1.2)	(1.7)
2-Deoxy-D-*erythro*-pentitol					(0.5)	(0.3)	(1.1)	(1.2)

[a] T = trace amounts. [b] Numbers in parentheses are percentages of the tar fraction.

*Pyrolysis of 2-deoxy-*D-arabino*-hexono-1,4-lactone.* — The data obtained on dynamic and isothermal pyrolyses of the lactone were similar to those obtained for the acid, with some notable exceptions. The lactone, as shown by the thermal analysis data, was more stable and decomposed at ~300° instead of 250°. The comparative thermal stability was confirmed by the g.l.c. analysis of the reaction mixture within the temperature range of 250–300° (see Table I). Monitoring the evolution of water and carbon dioxide by mass spectrometry showed that there was only one peak for water, and the maximal rates of evolution occurred at the decomposition temperature of ~300°. The volatile products formed on gradual heating were also maximal at 300°, and showed the same mass ions noted for the free acid (*cf.* Figs. 5 and 7). The remarkable corroboration, by conventional chemical methods, of the conclusions reached through thermal analysis indicates the usefulness of the new techniques as powerful tools for organic chemists.

Analysis of the isothermal pyrolysis products formed at 550° (see Table II) showed only quantitative differences. There was increased formation of volatile products, including acetaldehyde, acrylaldehyde, 1-hydroxy-2-propanone (and/or glyoxal), the furanone derivative, and tar. This enhancement was at the expense of water, char, and carbon dioxide.

The pyrolysis process and products were affected by the presence of catalysts. As seen in Table III, addition of zinc chloride or sodium carbonate lowered the decomposition temperature recorded by thermal analysis to ~200°, produced more residue (52% at 400°), and also lowered the peak temperature observed for evolution of water and carbon dioxide. Chemical analysis of the pyrolysis products indicated that the catalysts inhibit or reduce the formation of the volatile organic compounds, and enhance the production of carbon dioxide and char. The results listed in Table II show not only that smaller proportions of the volatile products are formed in the presence of the catalysts, but also that only traces of the lactone (0.17–0.07%, compared to 8.5% for the uncatalyzed pyrolysis) have escaped in the tar fraction. From these data and the fact that, when catalysts are added, decomposition takes place at lower temperatures with evolution of water and carbon dioxide, it is concluded that the catalysts promote decarboxylation, dehydration, and condensation of the products to non-volatile molecules of higher molecular weight, which are charred on further heating. The charring process involves further elimination of the substituent groups, free-radical formation, and, eventually, development of new C–C bonds. Further discussion of this process, which has been covered in other articles[1,14,15], is beyond the scope of this presentation.

Since both the free acid and the lactone provide the same types of compounds, including the decarboxylation products, it is quite clear that the two forms are interconvertible. In the absence of external water, the free acid readily lactonizes when the rigid, crystalline lattice is fused and the molecule gains the necessary freedom of movement for the rearrangement. However, before complete lactonization and loss of the resulting water, thermal decomposition begins. Consequently, the decomposition temperature and the quantitative mixture of the pyrolysis products formed

TABLE III

THERMAL ANALYSIS AND MASS-SPECTROMETRIC SCANNING OF ALDONO-1,4-LACTONES

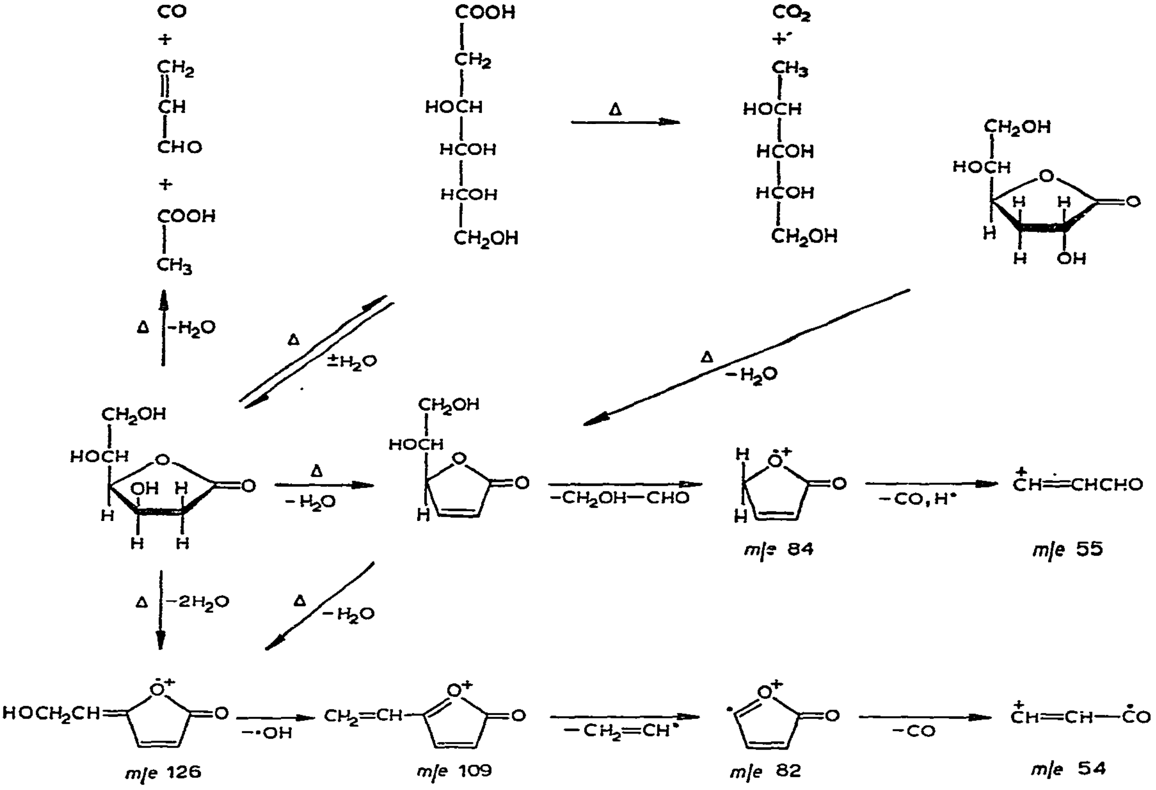
	Thermal analysis				*Mass spectrometry Maximum rate of evolution of*		
	D.t.a. peaks		*D.t.g. peaks*	*T.g. data*			
	M.p. (degrees)	*Dec. (degrees)*	*Dec. (degrees)*	*Residue at 400° (%)*	*Water (degrees)*	*Carbon Monoxide (degrees)*	*Carbon Dioxide (degrees)*
2-Deoxy-D-*arabino*-hexono-1,4-lactone							
Neat	97	295	310	21	285		295
$+ZnCl_2$	85	205,237[a]	225	52	220	240	235
$+Na_2CO_3$	86	200[a]	195	52	187		205
3-Deoxy-D-*ribo*-hexono-1,4-lactone							
Neat	107	330	347	16	300		350
+Free acid	—	310	320	27	320	320	325
$+ZnCl_2$	101	260,310[a]	255,300	50	250	307	307
$+Na_2CO_3$	102	300[a],325,370[a]	290	38	275	277	280
D-Glucono-1,4-lactone							
Neat	137	300[a]	290	33			

[a] Exothermic.

from the acid and the lactone are different. The remaining free acid could decarboxylate directly. It could also exert a catalytic effect, similar to those discussed before[3,5,9,15]. Both of these phenomena could account for the lower decomposition temperature of the acid. Carbon dioxide and 1-deoxypentitol are also formed on pyrolysis of the lactone, but in smaller quantities and at higher temperatures, because hydrolysis of the lactone ring requires water which is produced by dehydration. Production of substantial amounts of 5-(2-hydroxyethylidene)-2(5*H*)furanone from the pyrolysis of lactone indicates that the dehydration reaction starts within the lactone ring and proceeds to the side chain to provide a conjugated system. This type of β-elimination, providing mono- and di-unsaturated compounds, takes place even at normal temperatures due to the acidic natuie of the hydrogen which is α to the carbonyl group[12,16].

The primary thermal reactions of the 2-deoxy-lactone and the source of the mass ions discussed before are summarized in Scheme 1.

*Pyrolysis of 3-deoxy-*D-ribo-*hexono-1,4-lactone.* — In accordance with the thermal analysis data, the 3-deoxy lactone was consideiably more stable than the



Scheme 1. Thermal reactions of 2-deoxy-D-*arabino*-hexono-1,4-lactone and mass ions of the principal dehydration product.

2-deoxy-lactone (*cf.* Figs. 2 and 3) and, on gradual heating within the decomposition range (see Table I), produced 2-deoxy-*erythro*-pentitol, the expected decarboxylation product, as well as 2-deoxy-*erythro*-pentose. There was substantial decomposition of the lactone before the appearance of these products. Scanning mass spectrometry also showed that evolution of both water and carbon dioxide starts at ~250°, but maximal rates are recorded at 300° for water and 350° for carbon dioxide. Scanning of the volatile products of higher molecular weight showed the same mass ions that were detected for the 2-deoxy compounds (Fig. 7), but the intensity was much lower.

The peaks at *m/e* 54 and 82 derived from the dehydration product, 5-(2-hydroxyethylidene)-2(5*H*)furanone, were particularly weak as compared to those at *m/e* 43, 55, and 84, which are apparently derived from the initial cleavage of the side-chain (see Scheme 1). Both groups disappeared when zinc chloride or sodium carbonate was added to the substrate. These additives also lowered the decomposition temperature. It is interesting to note that a similar effect (see Table III) was observed when the lactone contained some free acid.

The products obtained from isothermal pyrolysis of the 3-deoxy-lactone at 550°, neat or mixed with the above additives, are shown in Table II. Because of the relatively high thermal stability, the lactone was extensively evaporated to form a large tar-fraction (62%), containing 72% of intact material. This fraction also contained some 2-deoxypentose and 2-deoxypentitol, and streaked on t.l.c., indicating the presence of heterogeneous condensation products. The volatile pyrolysis products contained 4-hydroxy-3-pentenoic acid and 4-hydroxy-2-pentenoic acid γ-lactones (α- and β-angelicalactones, respectively), acetaldehyde, acetic acid, and small proportions of other dehydration and fission products, including 5-(2-hydroxyethylidene)-2(5*H*)furanone. Pyrolysis of the lactone mixed with the free acid, zinc chloride, or sodium carbonate, however, as before, provided large proportions of water, carbon dioxide, carbon monoxide, and char, but much less tar and organic volatile products.

It is interesting to compare the thermal degradations of the 3-deoxy- and 2-deoxy-lactones. Both of these compounds show initial dehydration. However, the 2-deoxy-lactone, having a hydroxyl group at C-3, decomposes more readily by β-elimination and forms large quantities of 5-(2-hydroxyethylidene)-2(5*H*)furanone. D-Glucono-1,4 lactone also degrades at a lower temperature than the 3-deoxy compound (see Table III). Decomposition of the 3-deoxy-lactone, which proceeds at higher temperatures, gives a mixture of the dehydration and fission products, including the α- and β-angelicalactones. Another common feature is decarboxylation of free acids formed by hydrolysis of lactone rings. In addition to the 2-deoxypentitol, the 3-deoxy compound also gives some 2-deoxypentose, which could derive from decarbonylation of the lactone, or from a combination of decarboxylation and dehydration of the free acid. This observation is in line with known decarboxylation and decarbonylation reactions of the α-hydroxy carboxylic acids in aqueous acid[17,18].

The pyrolytic properties of the deoxyaldonic acid and lactones generally support the data and theories on production of carbon dioxide presented in the Introduction.

EXPERIMENTAL

Preparation of samples. — Bromine oxidation of 2-deoxy-D-*arabino*-hexose[19,20] gave 2-deoxy-D-*arabino*-hexonic acid, m.p. 144–147° (lit.[20] m.p. 145°), ν_{max} 1740 cm^{-1}; and 1,4-lactone, m.p. 95–96° (lit.[7,20] m.p. 94–96, 97°), ν_{max} 1770 cm^{-1}. A reference sample of 1-deoxy-D-arabinitol was prepared by reductive desulfuration[21] of D-arabinose diethyl dithioacetal tetra-acetate followed by deacetylation[22]. The product, after crystallization from methanol–ether, had m.p. 128–130°; lit.[23,24] m.p. 129–131°, 131–132°.

3-Deoxy-D-*ribo*-hexono-1,4-lactone was prepared from 2-deoxy-D-*erythro*-pentose by the Kiliani synthesis[25] and had m.p. 107–108°; lit.[25] m.p. 108–109°. A sample of this lactone containing 20% of the free acid was obtained as a syrup by stirring an aqueous solution of the corresponding calcium salt with Amberlite IR-120(H^+) resin, filtering, and freeze-drying. A reference sample of 2-deoxy-D-*erythyro*-pentitol was prepared by reduction of 2-deoxy-D-*erythro*-pentose with sodium borohydride.

Samples of the 2-deoxy- and 3-deoxy-lactones containing 5% of sodium carbonate were obtained by grinding the calculated proportions of the two compounds to a fine powder in a mortar. Samples of these lactones containing 5% of zinc chloride were prepared by adding the calculated proportion of zinc chloride in methanol and evaporating the solvent under vacuum.

Analytical methods. — The thermal analysis, measurement of u.v., i.r., and mass spectra, g.l.c., and t.l.c. were conducted as previously described[9,15,26,27]. Volatilization of organic compounds (e.g.d.) was measured with a DuPont Model 916 thermal evolution analyzer programmed at the rate of 16°.min^{-1} in a 29.4 ml.min^{-1} flow of nitrogen.

Thermal reaction. — Samples (~2 mg) of 2-deoxy-D-*arabino*-hexonic acid, the corresponding 1,4-lactone, and 3-deoxy-D-*ribo*-hexono-1,4-lactone were heated in a d.t.a. instrument at the rate of 15°.min^{-1} to temperatures corresponding to various thermal events. The heated samples were then trimethylsilylated and anlyzed by g.l.c., using D-glucitol as an internal standard and the known compounds for reference. The results obtained are listed in Table I.

Mass spectrometry of volatile products. — Water, carbon dioxide, carbon monoxide, and other volatile products evolved on gradual heating of the samples were monitored by mass spectrometry. A sample (2 mg) of each of the free acid and lactones, with or without the additive, was placed in a small pan and heated at a rate of 15°.min^{-1} in a current of helium directly connected to the mass spectrometer. The rates of release of the volatile compounds were followed by changes in the ratio of the corresponding peaks (*m/e* 17, 28, 44, and others) to the peak for background oxygen (*m/e* 32). These ratios were found to be constant in blank experiments. The results obtained are presented in Figs. 4, 5, and 7, and Table III.

Thermal degradation. — Samples (100 mg) of each of the 2-deoxy and 3-deoxy compounds, with and without the catalysts, were heated under nitrogen for 8 min at

550° in a modified Sargent micro-combustion unit, and the products were separated and analyzed by the methods described previously[15]. For direct analysis of the volatile products and water, small samples (5 mg) of the 2-deoxy or 3-deoxy compounds were pyrolyzed at 550° in a unit directly connected to a gas chromatograph. The products were resolved by g.l.c., and identified by established methods[3,4]. Identification of α- and β-angelicalactones was based on the retention time on g.l.c., and the mass spectra, which were identical to those of the authentic samples. The results are given in Table II.

Identification of 5-(2-hydroxyethylidene)-2(5H)furanone. — Splitting of the gas-chromatograph effluent, in a ratio of 20 to 1, gave a small sample of the unknown compound. A solution of this compound in methanol showed a u.v. absorption at 272 nm (conjugated system) which diminished on gradual addition of alkali. The mass spectrum (Fig. 6), obtained by combined g.l.c.–m.s. analysis, showed peaks at *m/e* 126 and 127 for M^+ and $M+1^+$, and major fragmentation peaks at *m/e* 82 and 54, consistent with the structure of 5-(2-hydroxyethylidene)-2(5*H*)furanone (see Scheme 1). Furthermore, the acetate derivative of this compound gave a mass spectrum identical to that of an authentic sample of 5-(2-acetoxyethylidene)-2(5*H*)-furanone[13].

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