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SYNTHESIS OF SOME ESTERS AND LACTONES OF ALDONIC ACIDS

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INTRODUCTION

Characterization of the methyl esters of a few aldonic acids, namely, D[1]- and L-arabinonic[2], D- and L-galactonic[3], and D-erythronic acids[4], has been reported in the literature. Among the limiting factors encountered in the synthesis of esters of aldonic acids is the nature of the reactants. Variation occurs among aldonic acids in the ease with which they form methyl or ethyl esters. Little has been reported concerning the preparation of their higher alkyl esters. When higher alcohols are employed, lactone formation is often favored over esterification. Alkyl esters of fully acetylated or benzoylated aldonic acids are readily formed, without dependence upon the reactant aldonic acid or alcohol.

RESULTS AND DISCUSSION

Addition of hydrogen chloride in methanol to potassium D-arabinonate afforded methyl D-arabinonate almost quantitatively[1]; however, ethanolic hydrogen chloride gave mostly D-arabinono-1,4-lactone. Gas–liquid chromatography of the trimethylsilylated[5] reaction product indicated yields of the ethyl ester and lactone of 11 and 65%, respectively.

Addition of hydrogen chloride to potassium D-arabinonate and benzyl, butyl, isobutyl, isopropyl, or propyl alcohol resulted in isolation of the lactone only. This use of isopropyl alcohol furnishes an effective route to D-arabinono-1,4-lactone (89% yield). By an earlier procedure[1], the lactone has been prepared by conversion of potassium D-arabinonate into the calcium salt, followed by treatment with oxalic acid in water[1]. The lactone has also been prepared by the reaction of D-arabinonic acid and ethanolic hydrogen chloride under pressure[6].

Addition of hydrogen chloride to isopropyl tetra-*O*-acetyl-D-arabinonate in isopropyl alcohol yielded the deacetylated lactone (60%), instead of the isopropyl ester. However, addition of hydrogen chloride to the lactone or its triacetate in methanol produced the methyl ester (70–79%). Treatment of the lactone in ethanol by a reported[7] method gave the ethyl ester in a yield of only 16%. Higher conversion into the ethyl ester (57%, as determined by g.l.c.) occurred when a solution of D-arabinonic acid in ethanol containing 0.5% of hydrogen chloride was refluxed for 24 h; the lactone was formed also (18%).

The solubility of the equilibrium products appears to be a limiting factor. In the corresponding alcohol at 23°, D-arabinono-1,4-lactone is 38, 27, 7, 5, and 2 times as soluble as methyl, ethyl, propyl, isopropyl, and butyl D-arabinonate, respectively. The methyl ester has been isolated after dissolving the lactone in methanol without a catalyst[7]. Agitation of the lactone and ethanol without a catalyst yielded ethyl D-arabinonate (51%). The isopropyl ester could not be similarly obtained. However, a solution of the lactone and sulfuric acid, in a volume of the respective alcohol favoring separation of the ester, afforded butyl, isopropyl, and propyl D-arabinonate. L-Arabinose was oxidized with bromine[2], and the resulting crude lactone was treated with the corresponding alcohols containing sulfuric acid, to provide enantiomorphs of the above esters.

Methyl D-mannonate was obtained from D-mannono-1,4-lactone by a similar procedure. By treatment of the lactone with hydrogen chloride and the appropriate alcohol, ethyl[8] (but not butyl, isopropyl, and methyl) D-mannonate could be obtained as reported, the latter having been described without analyses[9]. Ethyl L-mannonate has been isolated on recrystallization of the lactone from ethanol[10].

Although methyl D-galactonate has been obtained by treatment of the lactone in methanol with catalysts of hydrogen chloride or methyl sulfate[3], no ester was isolated when ethanol was used. Treatment of potassium D-galactonate with ethanolic hydrogen chloride gave the lactone. Potassium D-ribonate, D-*glycero*-D-*gulo*-heptonate, D-lyxonate, and D-erythronate in methanolic hydrogen chloride followed a similar course. Earlier work also failed to yield the corresponding methyl ester from the reaction of L-ribono-1,4-lactone in this medium[7]. Similar use of isopropyl alcohol provides a recommended route to D-lyxono- and D-erythrono-1,4-lactone (72–78%). D-Lyxono-1,4-lactone and D-*glycero*-D-*gulo*-heptono-1,4-lactone have been prepared previously by treatment of the aldonic acid hydrazide with nitrous anhydride[11]. Methyl[4] and butyl D-erythronate[12] and syrupy methyl[13] and crystalline ethyl D-gluconate[14] have been reported earlier.

Most of the known esters of fully acetylated aldonic acids have been methyl esters, prepared by using diazomethane[15]. Among others reported have been the ethyl esters of acetylated D-galactonic[16], D-gluconic, and DL-xylonic acids[17]. In the present study, esters were prepared without complication in 80–90% yields from a variety of alcohols and acetylated D-arabinoyl[16], L-arabinoyl[18], D-lyxonyl, D-ribonyl[18], D-gluconyl[19], D-galactonyl[16], D-*glycero*-D-*gulo*-heptonyl[20], and tri-*O*-benzoyl-L-erythronyl chloride. Certain esters, which were obtained as liquids, were distilled under diminished pressure without decomposition. Tetra-*O*-acetyl-D-lyxonyl chloride and hexa-*O*-acetyl-D-*glycero*-D-*gulo*-heptonyl chloride, which resisted crystallization, were similarly purified. Intermediate amides distilled were L-erythronamide and tetra-*O*-acetyl-D-lyxonamide[21].

The data for the new compounds obtained appear in Table I.

Preferred synthetic methods developed in this study are described in the experimental section.

EXPERIMENTAL

General. — Melting points, determined in capillary tubes, are corrected; boiling points are uncorrected. Vacuum distillation was conducted with a stirred, oil-jacketed, 100-ml Hickman still and an oil pump connected to a two-stage diffusion, glass ejector pump. Known substances were identified by mixed melting points and by infrared spectra.

Infrared spectra. — I. r. spectra were recorded for potassium bromide disks in a Baird Atomic Spectrophotometer, Model NK-1, having sodium chloride optics. The esters showed λ_{max} 3.0–3.5 μ (s, OH), indicating hydrogen bonding. Ethyl, propyl, and butyl D-arabinonate and methyl and ethyl D-mannonate had, in addition, sharp λ_{max} 2.9 μ (OH), indicating weaker hydrogen-bonding. Carbonyl absorption (strong) appeared at 5.8 μ for methyl D-galactonate; at 5.78 μ for ethyl and propyl, and at 5.75 μ for butyl D-arabinonate; and at 5.7 μ for ethyl and 5.67 μ for butyl tetra-*O*-acetyl-D-arabinonate. Esters showed variable strong bands for the -O- group, but consistent peaks at 8.0–8.2 μ (vs, -O-) when acetylated. Methyl esters absorbed at 7.3 μ (s, *sym*-CH_3); when acetylated, they showed maxima at 7.0 μ (w) and 7.3 μ (s). Lactones had λ_{max} 5.63–5.68 μ (s, C=O). When acetylated, they showed λ_{max} 5.58 μ (strained lactone C=O) and 5.7 μ (C=O).

Preparation of potassium aldonates. — A modified method[1,20] of oxidation of D-glucose provided potassium D-arabinonate. Precipitation of the salt from aqueous methanol prevented further degradation.

Oxygen was added through two dispersion tubes to a rapidly stirred solution of potassium hydroxide (672 g) in water (1.44 l) and methanol (6 l). Simultaneous addition of D-glucose (720 g, 4 moles) in water (1.44 l) was made over 7.75 h. The temperature was maintained at 30–35°. Crystallization began after 3 h. When the addition of D-glucose was complete, introduction of oxygen was continued for 0.5 h. [The rate of addition of oxygen caused a decrease of pressure from an initial cylinder pressure of 1700 to a final pressure of 1500 $lb.in^{-2}$ (224-ft^3 cylinder).] Air was then introduced for 48 h. Methanol was added periodically to replace that lost by evaporation. Filtration afforded potassium D-arabinonate (620 g, 76%). Recrystallization, from 4 volumes of water by adding 8 volumes of methanol, furnished pure product (92% recovery), m.p. 219° (dec.).

Anal. Calc. for $C_5H_9KO_6$: C, 29.4; H, 4.4. Found: C, 29.6; H, 4.6.

In similar preparations of potassium D-lyxonate (68%) from D-galactose, and of potassium L-erythronate (64%) from L-arabinose, an equal volume of methanol was added after the addition of air. Stirring for 24 h then resulted in crystallization of product suitable for synthetic use.

Other potassium aldonates were obtained by combining methanolic solutions of potassium hydroxide and the appropriate lactones.

Preparation of aldono-1,4-lactones. — The preparation of L-erythrono-1,4-lactone illustrates the general procedure. Into a stirred suspension of potassium L-erythronate (173 g, 1.05 mole) in isopropyl alcohol (700 ml) was passed hydrogen

TABLE I

PROPERTIES AND ANALYSES OF ESTERS AND LACTONES OF ALDONIC ACIDS

Compound	*Recrystallization solvent*	*M.p., degrees*[a]	*B.p., degrees/microns Hg*	n_D^{25} [b]	*Formula*	$[\alpha]_D^{25}$ *degrees*[c]	*Calc., %* C	H	*Found, %* C	H
Benzyl tri-*O*-benzoyl-L-erythronate			205/2	1.5716	$C_{32}H_{26}O_8$	−14.8	71.4	4.9	71.3	5.1
Bis-*O*-(penta-*O*-acetyl-D-gluconyl)ethylene glycol	EtOH	83–84			$C_{34}H_{46}O_{24}$	+16.2	48.7	5.5	48.6	5.8
Bis-*O*-(tetra-*O*-acetyl-D-arabinoyl)ethylene glycol	MeOH	106			$C_{28}H_{38}O_{20}$	+33.2	48.4	5.5	48.2	5.6
Butyl D-arabinonate	BuOH	104–105			$C_9H_{18}O_6$	−3.0	48.6	8.2	48.5	8.5
Butyl DL-arabinonate	BuOH	99–100				0			48.8	8.1
Butyl L-arabinonate	BuOH	104–105				+3.5			48.7	8.2
Butyl tetra-*O*-acetyl-D-arabinonate			111/4	1.4410	$C_{17}H_{26}O_{10}$	+29.3	52.3	6.7	52.4	7.0
Ethyl D-arabinonate	EtOH	132–133			$C_7H_{14}O_6$	0	43.3	7.3	43.5	7.4
Ethyl DL-arabinonate	EtOH	112				0			43.1	7.3
Ethyl hexa-*O*-acetyl-D-*glycero*-D-*gulo*-heptonate	EtOH–pentane	91			$C_{21}H_{30}O_{14}$	+16.0	49.8	6.0	49.7	5.7
Ethyl tetra-*O*-acetyl-D-arabinonate	EtOH	111			$C_{15}H_{22}O_{10}$	+34.0	49.7	6.1	49.5	6.2
Ethyl tetra-*O*-acetyl-DL-arabinonate	EtOH	93–94				0			49.5	6.3
Ethyl tetra-*O*-acetyl-L-arabinonate	EtOH	111				−33.7			49.8	6.3
Ethyl tetra-*O*-acetyl-D-lyxonate			97/1	1.4418		+14.0			49.6	6.1
Ethyl tetra-*O*-acetyl-D-ribonate	iso-PrOH	58				−13.5			49.9	6.4
Ethyl tri-*O*-benzoyl-L-erythronate			182/5	1.5528	$C_{27}H_{24}O_8$	−16.3	68.3	5.1	68.5	5.4
Hexa-*O*-acetyl-D-*glycero*-D-*gulo*-heptonyl chloride			126/8[d]	1.4585	$C_{19}H_{25}ClO_{13}$[e]	+23.5	46.0	5.1	45.8	5.1
Isobutyl penta-*O*-acetyl-D-galactonate	EtOH	111			$C_{20}H_{30}O_{12}$	+22.0	51.9	6.5	51.8	6.4
Isobutyl tetra-*O*-acetyl-D-arabinonate	Et_2O–pentane	40			$C_{17}H_{26}O_{10}$	+27.7	52.3	6.7	52.3	6.7
Isopropyl D-arabinonate	iso-PrOH	142–143			$C_8H_{16}O_6$	−3.8	46.2	7.8	46.3	7.5
Isopropyl DL-arabinonate	iso-PrOH	121				0			46.0	7.7
Isopropyl L-arabinonate	iso-PrOH	142–143				+4.2			46.4	7.9
Isopropyl hexa-*O*-acetyl-D-*glycero*-D-*gulo*-heptonate			133/3[f]	1.4480	$C_{22}H_{32}O_{14}$	+16.7	50.8	6.2	50.7	6.5
Isopropyl penta-*O*-acetyl-D-galactonate	EtOH	99–100			$C_{20}H_{28}O_{12}$	+24.2	50.9	6.3	50.7	6.0
Isopropyl penta-*O*-acetyl-D-gluconate	EtOH	95				+11.5			51.0	6.5
Isopropyl tetra-*O*-acetyl-D-arabinonate	EtOH–pentane	73			$C_{16}H_{24}O_{10}$	+28.5	51.1	6.4	51.2	6.6

TABLE I *(contd.)*

Compound	*Recrystallization solvent*	*M.p., degrees*[a]	*B.p., degrees/microns Hg*	n_D^{25} [b]	*Formula*	$[\alpha]_D^{25}$, *degrees*[c]	*Calc.,* % *C*	*H*	*Found* % *C*	*H*
Isopropyl tetra-*O*-acetyl-D-ribonate			102/1	1.4369		−10.0			50.8	6.5
Isopropyl tri-*O*-benzoyl-L-erythronate			180/3	1.5458	$C_{28}H_{26}O_8$	−21.0	68.6	5.3	68.8	5.1
Methyl DL-arabinonate	MeOH	141			$C_6H_{12}O_6$	0	40.0	6.7	40.0	6.8
Methyl D-mannonate	MeOH	134–135[d]			$C_7H_{14}O_7$	+5.0	40.0	6.7	40.1	6.6
Methyl *O*-(penta-*O*-acetyl-D-gluconyl)-glycolate	EtOH	62–63			$C_{19}H_{26}O_4$	+15.3	47.7	5.5	47.9	5.7
Methyl *O*-(tetra-*O*-acetyl-D-arabinoyl)-glycolate	MeOH	66–67			$C_{16}H_{22}O_{12}$	+31.2	47.3	5.5	47.5	5.5
Methyl tetra-*O*-acetyl-DL-arabinonate	EtOH	116			$C_{14}H_{20}O_{10}$	0	48.3	5.8	48.2	5.9
Methyl tetra-*O*-acetyl-D-lyxonate			92/1	1.4431		+15.3			48.3	6.0
Methyl tri-*O*-benzoyl-L-erythronate			189/1	1.5583	$C_{26}H_{22}O_8$	−18.0	67.6	4.8	67.8	5.0
Propyl D-arabinonate	PrOH	123–124			$C_8H_{16}O_6$	−3.3	46.2	7.8	46.5	8.1
Propyl DL-arabinonate	PrOH	105–106				0			45.9	8.0
Propyl L-arabinonate	PrOH	123–124				+3.3	46.2	7.8	46.1	7.9
Propyl hexa-*O*-acetyl-D-*glycero*-D-*gulo*-heptonate			132/3	1.4500	$C_{22}H_{32}O_{14}$	+13.7	50.8	6.2	50.9	6.3
Propyl penta-*O*-acetyl-D-galactonate	EtOH	114			$C_{19}H_{28}O_{12}$	+14.8	50.9	6.3	50.7	6.1
Propyl penta-*O*-acetyl-D-gluconate	EtOH	82				+12.5			50.8	6.2
Propyl tetra-*O*-acetyl-D-arabinonate	Et_2O-pentane	44			$C_{16}H_{24}O_{10}$	+29.2	51.1	6.4	51.0	6.6
Propyl tetra-*O*-acetyl-D-ribonate			100/1[h]	1.4395		−17.3			51.3	6.5
Tetra-*O*-acetyl-D-lyxonamide			141/1[i]	1.4643	$C_{13}H_{19}NO_9$[j]	+18.7	46.9	5.8	46.8	5.9
Tetra-*O*-acetyl-D-lyxonyl chloride			99/2	1.4511	$C_{13}H_{17}ClO_9$	+16.5	44.3	4.9	43.9	5.2
2,3,5-Tri-*O*-acetyl-D-arabinono-1,4-lactone	EtOH	81[k]			$C_{11}H_{14}O_8$	+53.2	48.2	5.2	48.4	5.0
2,3,5-Tri-*O*-acetyl-DL-arabinono-1,4-lactone	EtOH	60				0			48.0	5.1
2,3,5-Tri-*O*-acetyl-L-arabinono-1,4-lactone	EtOH	81[l]				−53.0			48.0	5.3
Tri-*O*-benzoyl-L-erythronyl chloride	Et_2O-pentane	94			$C_{25}H_{21}ClO_4$[m]	+1.5	64.3	4.1	64.3	4.3

[a]After recrystallization from the solvent indicated. [b]After redistillation at the boiling point and pressure indicated. [c]For acetylated and benzoylated derivatives, $c = 2$, in chloroform; all others were determined in water. [d]Ref. 20 reports a syrup suitable for use. [e]Calc.: Cl, 7.1. Found: Cl, 6.9. [f]Crystallized, m.p. 64°. [g]Ref. 9 gives m.p. 155°. [h]Crystallized, m.p. 37°. [i]Ref. 21 reports a syrup suitable for use. [j]Calc.: N, 4.2. Found: N, 4.3. [k]G. B. ROBINS AND F. W. UPSON [*J. Am. Chem Soc.*, 62 (1940) 1074] gave m.p. 68–69°. [l]C. PAAL AND M. KINSCHER [*Ber.*, 44 (1911) 3548] reported m.p. 52–54°. [m]Calc.: Cl, 7.6. Found: Cl, 7.4.

chloride during 20 min. The mixture was cooled, and hydrogen chloride was again passed in. The mixture was heated to boiling, and the precipitated potassium chloride was collected, and rinsed with isopropyl alcohol. Crystallization of the product occurred when the filtrate was concentrated *in vacuo* to 200 ml. The mixture was kept overnight at 5°, and the crystals (90 g) were collected; the filtrate yielded a second crop (6.4 g). Recrystallized from isopropyl alcohol, the lactone (89 g, 72%) had m.p. 100–101° (lit.[22] m.p. 103–104°).

*2,3,5-Tri-*O*-acetyl-*D-, L-, *and* DL*-arabinono-1,4-lactone.* — The enantiomorphs, obtained as described, showed properties at variance with those reported (Table I). Anhydrous zinc chloride (8.8 g) was dissolved in acetic anhydride (100 ml) by stirring for 2 h at 0°. The respective lactone (14.8 g, 0.1 mole) was added, and the colorless mixture was stirred for 2 h at 5° and overnight at room temperature. Acetic anhydride was evaporated off *in vacuo* with warming, and 200 g of ice was added to the resulting syrup. Crystallization occurred during several h. After recrystallization, the yields were 76–79%.

The solubility of lactones. — On agitation of an excess of the lactone in 100 ml of the alcohol for 24 h at 23°, methyl, ethyl, benzyl, isopropyl, propyl, and butyl alcohol dissolved 66.0, 16.6, 5.4, 5.0, 4.7, and 3.1 g, respectively, of D-arabinono-1,4-lactone. Methyl, ethyl, and isopropyl alcohol dissolved 1.8, 0.3, and 0.1 g, respectively, of D-mannono-1,4-lactone. Methyl alcohol dissolved 23.2, 5.6, and 1.0 g of D-lyxono-, D-galactono, and D-*glycero*-D-*gulo*-heptono-1,4-lactone, respectively, and 1.4 g of D-glucono-1,5-lactone. Ethyl alcohol dissolved 1.1 g of D-galactono-1,4-lactone.

Preparation of esters of aldonic acids. — *(a) From potassium* D*-arabinonate.* Treatment of this salt and methanol with hydrogen chloride as described[1] afforded methyl D-arabinonate (98%); it was recrystallized from methanol, with concentration *in vacuo* (92% recovery), m.p. 143° (*lit.*[1] m.p. 140°). Concentration by boiling (600 g sample in methanol) gave only 53% recovery and syrup.

For the preparation of the ethyl ester, the method was inferior, and it failed for the higher esters.

(b) From aldono-1,4-lactones. Ethyl D-arabinonate was obtained by shaking a suspension of D-arabinono-1,4-lactone (5 g, 0.034 mole) in ethanol (25 ml) for 24 h, yielding 3.3 g (51%) of the ester, m.p. 131–132° (lit.[7] m.p. 126.5°).

Propyl D-arabinonate was prepared by a general procedure. A solution of D-arabinono-1,4-lactone (60.5 g, 0.41 mole) in propyl alcohol (750 ml) containing sulfuric acid (2 ml) was concentrated to 585 ml by boiling, and the mixture was kept overnight at 5°. The flaky mass was collected (70 g), and a second crop (7.4 g) was obtained. The product was recrystallized from propyl alcohol; yield, 56.5 g (75%). Similar treatment of the lactone with the corresponding alcohol afforded isopropyl (9%), butyl (39%), and ethyl (56%) D-arabinonate. Unreacted lactone could be further treated; *e.g.*, repeated concentration of the acidic filtrates, followed by crystallization, gave a 69% yield of isopropyl D-arabinonate. Methyl D-mannonate was similarly prepared (46%, in two crops).

(c) From fully acetylated or benzoylated aldonyl chlorides. The aldonyl chlorides

required were prepared by the thionyl chloride method[18]. The synthesis of isopropyl tetra-*O*-acetyl-D-gluconate provides an example. To a solution of tetra-*O*-acetyl-D-gluconyl chloride[19] (12.4 g, 0.029 mole) and 5 ml of isopropyl alcohol in dichloromethane (125 ml) was added pyridine (8 ml). The ensuing reaction was exothermic. After 2 h, the solution was extracted with an excess of 10% hydrochloric acid, and the combined, aqueous phases were extracted with dichloromethane. The organic phases were combined, extracted with water, and dried over anhydrous sodium sulfate. Filtration, and concentration *in vacuo*, provided a solid (12.3 g). Recrystallization gave the pure ester (11.6 g, 89%).

Equivalent amounts of ethylene glycol were used for preparing its esters.

Liquid esters were purified by distillation

(*d*) *Racemic esters.* Recrystallization together of equal amounts of the enantiomorphs furnished optically inactive isomers.

The solubility of esters. — The corresponding alcohol (100 ml) at 23° dissolved 1.7, 0.7, 0.7, 0.9, and 1.5 g of methyl, ethyl, propyl, isopropyl, and butyl D-arabinonate, and 1.1 and 0.3 g of methyl and ethyl D-mannonate, respectively.

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SUMMARY

The formation of esters of aldonic acids by treatment with an alcohol in the presence of an acid depends on the nature of the reagents and on the solubility of the products. The formation of aldonolactones is often a favored, competing reaction. Fully acetylated or benzoylated aldonic esters are formed without these restrictions. Among the products, liquid esters and certain of their acid chloride and amide intermediates are distillable. Some effective methods of synthesis of esters and lactones are described, based on the results of this investigation.

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