

Synthesis and Characterization of 1,6- and 1,7-Dihydroxy Alkanes and Their Acrylic Esters. I

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Synopsis

The 1,6- and 1,7-dihydroxy alkanes having chain lengths C_{13} – C_{24} were synthesized in high purity by lithium aluminum hydride reduction of corresponding 6-oxo and 7-oxoalkanoic acids. These were then converted to 6-hydroxy and 7-hydroxy acrylic esters, respectively, and were characterized by infrared, 1H nuclear magnetic resonance, and mass spectroscopic methods.

INTRODUCTION

Hydroxy acrylic esters have special important applications in anaerobic adhesive formulations.^{1,2} Also they can be used as structural adhesives in the form of urethane acrylics.³⁻⁸ No work has been reported on the synthesis of 6-hydroxy and 7-hydroxy long-chain acrylic esters and their applications in adhesive technology.

In this communication, we are therefore reporting only the synthesis and spectroscopic characterization of 1,6- and 1,7-dihydroxy long-chain (C_{13} – C_{24}) alkanes and their mono acrylic esters. The anaerobic adhesive formulations based on these monomers will be the subject of a subsequent article.

EXPERIMENTAL

Synthesis of 1,6- and 1,7-Dihydroxy Long-Chain (C_{13} – C_{24}) Alkanes

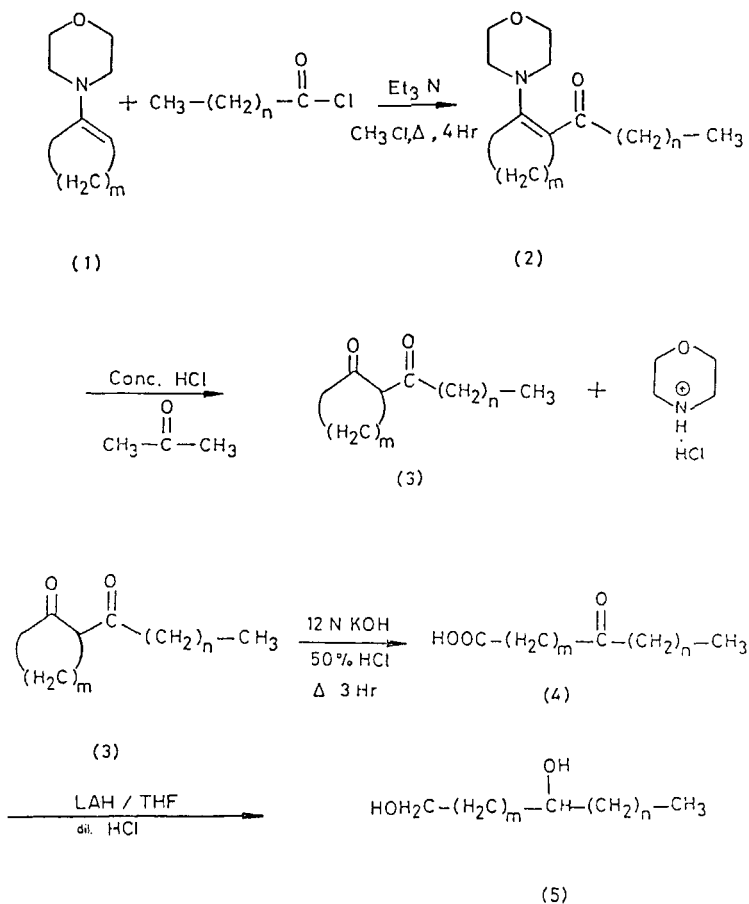
6-Oxo and 7-oxo alkanolic acids were prepared by the acylation of 1-morpholino cyclopentene and 1-morpholino cyclohexene, respectively, as per the standard procedure⁹ (Scheme 1). 6-Oxo and 7-oxo alkanolic acids of C_{13} – C_{24} alkyl chain length were synthesized by us¹⁰ with purity more than 99%. They were also characterized by 1H -NMR and mass spectroscopic methods.

Their corresponding dihydroxy compounds were prepared by reducing these oxo alkanolic acids with lithium aluminum hydride. In a three-necked flask fitted with a mechanical stirrer, a dropping funnel, and a double-walled con-

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$m = 4$ for 1,6-Dihydroxy alkanes
 $m = 5$ for 1,7-Dihydroxy alkanes

Scheme I. Synthesis of dihydroxy alkanes.

denser, 0.120 mol (20% excess) of lithium aluminum hydride (LAH) was taken in 600 mL of dry tetrahydrofuran (THF). To this slurry of LAH, a solution of 0.1 mol of oxo alcanoic acid in dry THF was added at a rate sufficient to cause gentle reflux. The stirring was continued for one hour after the addition was completed. The contents of the flask were then cooled to 0–5°C and hydrolyzed with cold 10% aqueous sulfuric acid. The reaction product was filtered and the filtrate was extracted with ether. The ether extract was then washed with 10% potassium carbonate aqueous solution to remove the unconverted oxo alcanoic acid.

The crude product was purified by crystallizing it from alcohol two times. The purity of dihydroxy alkanes was checked by chemical analysis and thin-layer chromatography (TLC) using *n*-hexane : ethyl ether : acetic acid (25 : 75 : 1, v/v/v) as eluting solvent. The chromatographic plates were sprayed with chromic acid solution and charred to identify the spots. The $R_f \times 100$

values of dihydroxy alkanes were in the range of 25–30 depending on the length of the alkyl chain, and the corresponding oxo alkanic acids appeared at $R_f \times 100$ values of 80–90. The physicochemical characteristics of 1,6- and 1,7-dihydroxy alkanes are given along with their yields and purity in Table I.

Synthesis of 6-Hydroxy and 7-Hydroxy Acrylic Esters

1,6-Dihydroxy and 1,7-dihydroxy long-chain alkanes were esterified with acrylic acid in the presence of an acidic catalyst to yield 6-hydroxy and 7-hydroxy mono acrylic esters, respectively. A typical experiment is given here as an example.

In a 500-mL flask, 0.1 mol of 1,6-dihydroxy alkane was taken in benzene (200 mL), and to this 0.11 mol of acrylic acid, 0.5 g hydroquinone and 0.5 g *p*-toluene sulfonic acid were added and heated to reflux. The course of reaction was followed by the amount of water collected azeotropically in Dean and Stark trap. After the completion of the reaction, which takes not more than 4 h, the catalyst was neutralized by the addition of sodium acetate and the benzene was stripped off using water suction. The crude hydroxy acrylic ester was extracted with ether and washed free of acrylic acid. It was then bleached with active carbon and filtered. The ether was then stripped off. The hydroxy acrylate thus obtained was pale yellow in color and was about 90–95% pure as determined by TLC and chemical analysis.^{11,12} This technical grade hydroxy acrylate was sufficient for adhesive formulations. The physicochemical characteristics of 6-hydroxy and 7-hydroxy long-chain acrylic esters are given in Table II.

Characterization of Dihydroxy Long-Chain Alkanes and Their Mono Acrylic Esters by Spectroscopy

Infrared Spectroscopy (IR)

The IR spectra were recorded using a Perkin-Elmer (Model 221) spectrophotometer. The IR spectra of 1,6-dihydroxy and 1,7-dihydroxy alkanes are

TABLE I
Physicochemical Characteristics of 1,6- and 1,7-Dihydroxyl Alkanes

Dihydroxy alkanes	Yield (%)	Melting point (°C)	Hydroxyl value		Purity (%)	TLC ($R_f \times 100$) value
			Found	Theory		
(1, 6)						
C ₁₅	90	65.0	459.0	459.8	99+	25.5
C ₁₇	85	72.2	412.6	412.5	99+	26.5
C ₁₉	87	78.3	373.1	374.0	99+	27.8
C ₂₁	83	83.1	341.0	342.1	98+	29.1
C ₂₃	85	88.5	313.6	315.2	99+	30.0
(1, 7)						
C ₁₃	90	52.3	518.0	519.4	99+	25.1
C ₁₆	82	71.0	432.7	434.8	98+	26.0
C ₁₈	80	76.2	391.2	392.3	99+	27.0
C ₂₀	82	81.5	356.8	357.3	99+	28.2
C ₂₂	80	85.3	327.6	328.1	99+	29.4
C ₂₄	80	91.4	302.8	303.3	99+	30.0

TABLE II
Physicochemical Characteristics of 6-Hydroxy and 7-Hydroxy Long-Chain Acrylic Esters

	Yield (%)	Iodine value ^a		Purity (%)	TLC ^b ($R_f \times 100$)
		Found	Theory		
6-Hydroxy acrylic ester of 1,6-dihydroxy alkane					
C ₁₅	75	78.41	85.23	92	50
C ₁₇	77	70.90	77.91	91	52
C ₁₉	78	68.16	71.75	95	54
C ₂₁	75	61.17	66.49	92	55
C ₂₃	73	56.57	61.95	91	55
7-Hydroxy acrylic ester of 1,7-dihydroxy alkane					
C ₁₃	80	86.54	94.07	92	50
C ₁₆	78	75.71	81.41	93	54
C ₁₈	75	71.00	74.70	95	54
C ₂₀	75	65.57	69.02	95	55
C ₂₂	73	57.73	64.14	90	55
C ₂₄	72	53.90	59.90	90	56

^a Determined by pyridine sulfate dibromide method.¹¹

^b Solvent system: *n*-hexane : ethyl ether; 50 : 50 v : v.

quite similar and hence are not discussed in detail for each compound. The C—H stretching vibration bands of the saturated aliphatic side chain appeared as two strong bands at 2930 and 2860 cm⁻¹. The asymmetric C—CH₃ deformation appeared at 1370 cm⁻¹. The O—H stretching vibration appeared at 3430 cm⁻¹.

The IR spectra of 6-hydroxy and 7-hydroxy acrylic esters are similar. Two characteristic C—H out-of-plane deformation vibrations of acrylic ester appeared at 900 cm⁻¹ and as doublet at 950–980 cm⁻¹; C=C stretching and C—H in plane vibrations of acrylic esters appeared at 1630 cm⁻¹ and as doublet at 1240 and 1260 cm⁻¹, respectively. C=O stretching vibration of ester appeared as strong band at 1720 cm⁻¹ and C—O stretching vibrations of ester are shown at 1110–1160 cm⁻¹ and at 1050 cm⁻¹.

¹H Nuclear Magnetic Resonance Spectroscopy (¹H-NMR)

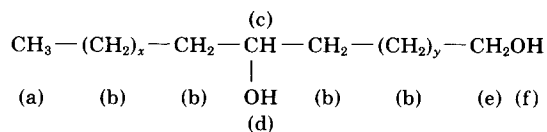
¹H-NMR spectra of the monomer in deuterated chloroform were recorded using FT-NMR-JEOL-FX-90-Q-MHZ NMR spectrophotometer and chemical

TABLE III
Comparative Integral Values of Protons of a Typical 1,7-Dihydroxy Tridecane

1,7-Dihydroxy tridecane	Integral values of protons (no. of protons)		
	a	b, c, d, f	e
Neat	9.0 (3)	69 (23)	6.0 (2)
Deuterated	7.5 (3)	52 (21)	5.0 (2)

shifts are recorded in δ values (ppm) with tetramethylsilane (TMS) as internal standard. For all compounds, the spectra are consistent with the structures and only essential features are described here.

The general structural formula of 1,6- and 1,7-dihydroxy alkanes may be represented as follows:



$$y = \begin{cases} 3 & \text{for 1,6-dihydroxy alkane} \\ 4 & \text{for 1,7-dihydroxy alkane} \end{cases}$$

The protons corresponding to methyl group (a) appeared as triplet at 0.93. The methylene protons (b) together with methine proton (c) and hydroxyl protons (d) and (f) appeared at 1.2–1.6. On D_2O exchange, the protons corresponding to both the hydroxyls disappeared, as noted from the comparative integral values shown in Table III and Fig. 1. The protons corresponding to (e) appeared at 4.2 as triplet. The very low resolution is due to low solubility and low concentration of the diols in the deuterated chloroform.

$^1\text{H-NMR}$ spectra of 6-hydroxy and 7-hydroxy long-chain acrylic esters were similar to each other. In these cases the spectra were recorded on a 300 MHz NMR unit for better resolution in the region 4.0–6.2 δ . Their general structural formula may be represented as follows:

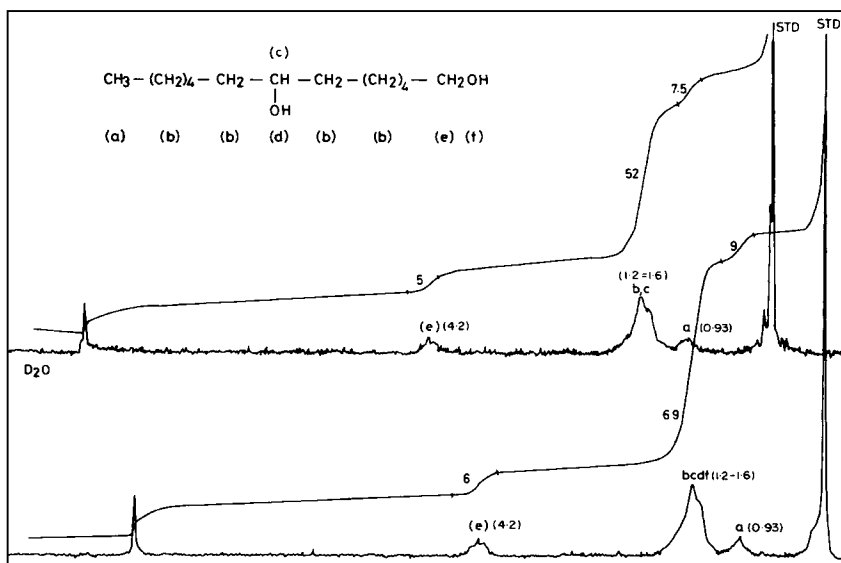
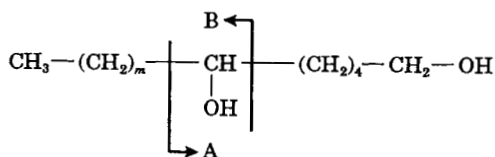


Fig. 1. $^1\text{H-NMR}$ of a typical 1,7-dihydroxytridecane.

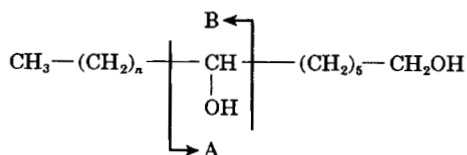
TABLE IV
 Fragmentation Pattern of 1,6- and 1,7-Dihydroxy Alkanes

Dihydroxy alkanes	Fragmentation peaks m/z and their intensities (%)							
	(M-18)-1	M-36	B	(B-18)-1	A	A-18	A-36	A-62
(1, 6)								
C ₁₅	227 (6)	208 (1)	157 (20)	138 (1)	117 (55)	99 (85)	81 (100)	55 (95)
C ₁₇	255 (1)	226 (1)	185 (12)	166 (1)	117 (62)	99 (92)	81 (100)	55 (95)
C ₁₉	283 (1)	264 (1)	213 (10)	194 (2)	117 (72)	99 (90)	81 (100)	55 (95)
C ₂₁	311 (1)	292 (1)	241 (8)	222 (1)	117 (80)	99 (95)	81 (100)	55 (95)
C ₂₃	339 (1)	320 (3)	269 (8)	250 (3)	117 (90)	99 (93)	81 (100)	55 (92)
(1, 7)								
C ₁₃	199 (1)	180 (0)	115 (18)	96 (12)	131 (21)	113 (23)	95 (100)	69 (52)
C ₁₆	241 (1)	222 (0)	157 (12)	138 (1)	131 (32)	113 (28)	95 (100)	69 (62)
C ₁₈	269 (1)	250 (2)	185 (10)	166 (4)	131 (50)	113 (35)	95 (100)	69 (58)
C ₂₀	297 (5)	278 (1)	213 (8)	194 (2)	131 (58)	113 (32)	95 (100)	69 (60)
C ₂₂	325 (1)	306 (1)	241 (4)	222 (2)	131 (62)	113 (22)	95 (100)	69 (63)
C ₂₄	353 (1)	334 (3)	269 (4)	250 (5)	131 (68)	113 (35)	95 (100)	69 (64)

1,6-Dihydroxy alkanes:



1,7-Dihydroxy alkanes:



The base peaks of these diols correspond to the A-36 fragment. Thus the base peaks of 1,6-dihydroxy and 1,7-dihydroxy alkanes are at m/z 81 and 95, respectively. In these series of 1,6- and 1,7-dihydroxy alkanes, some interesting mass spectral fragmentation pattern was observed. It was found that the intensity of fragment A, m/z 117 in the case of 1,6-dihydroxy alkanes and m/z 131 in the case of 1,7-dihydroxy alkanes having both the hydroxyl groups, increased with the increase in the alkyl chain. On the other hand the intensity of fragments A-18 and A-62 remained almost unchanged with the increase in the alkyl chain length. The mass spectra of 1,6-dihydroxy alkanes (C₁₇ and C₂₃) and 1,7-dihydroxy alkanes (C₁₈ and C₂₄) are given in Figs. 3-6 to show the facts claimed here.

The mono acrylic esters of the diols, i.e., 6-hydroxy and 7-hydroxy alkanes showed fragmented peaks at m/z 27 (CH₂=CH⁺), 55 (CH₂=CH-CO⁺), 71 (CH₂=CH-CO-O⁺), and 85 (CH₂=CH-CO-O-CH₂⁺) (Fig. 7). The main

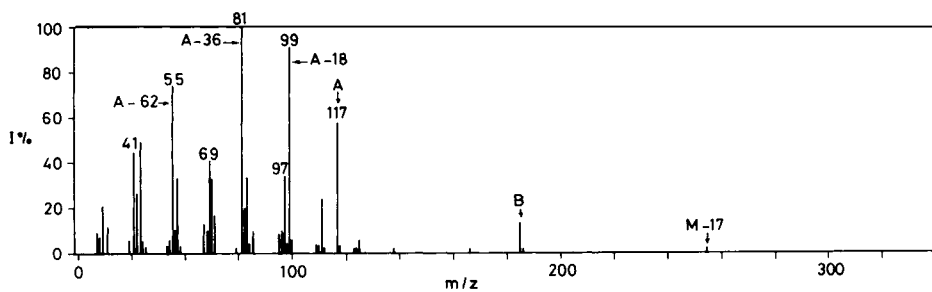


Fig. 3. Mass spectrum of 1,6-dihydroxy heptadecane.

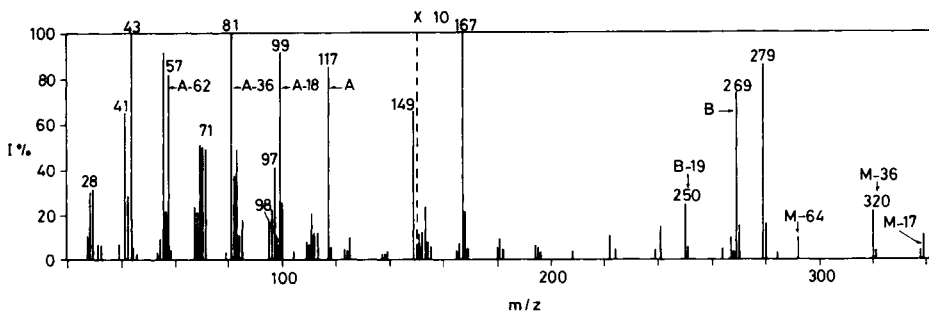


Fig. 4. Mass spectrum of 1,6-dihydroxy tricosane.

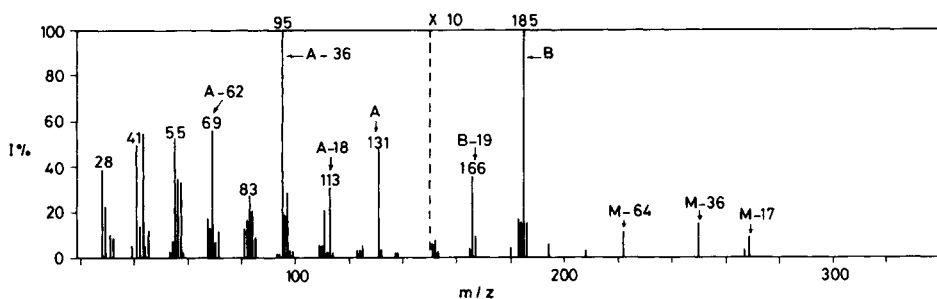


Fig. 5. Mass spectrum of 1,7-dihydroxy octadecane.

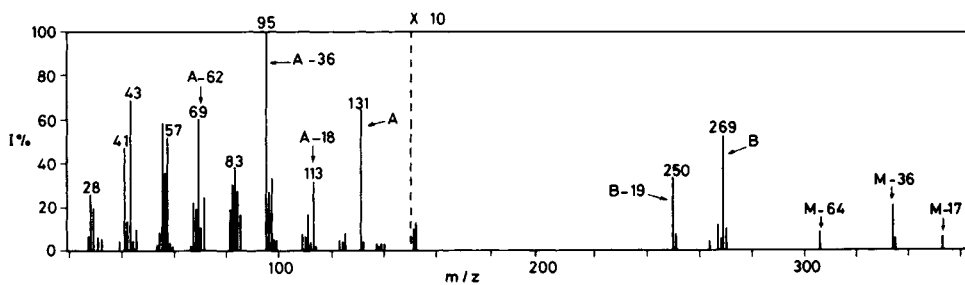


Fig. 6. Mass spectrum of 1,7-dihydroxy tetracosane.

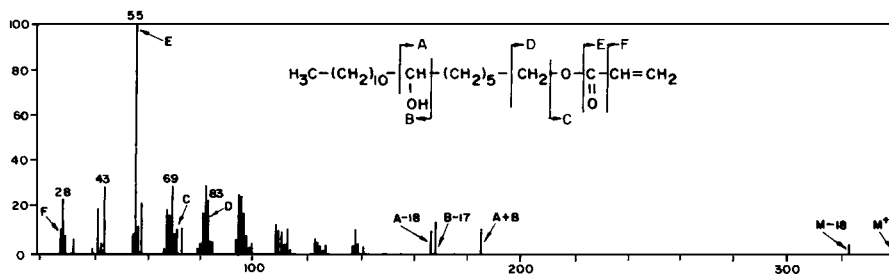
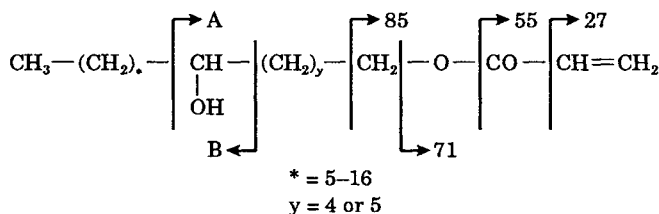


Fig. 7. Mass spectrum of 7-hydroxy octadecyl acrylate.

fragments A and B, as shown here, were also observed and were used as diagnostic peaks (Table V).



CONCLUSIONS

1,6-Dihydroxy and 1,7-dihydroxy alkanes could be prepared in high purity (99+) by LAH reduction of 6-oxo and 7-oxo alkanic acids. Their mass spectra have revealed an interesting fragmentation pattern. The intensity of fragment A having both the hydroxyls increased with the chain length of the dihydroxy alkanes.

6-Hydroxy and 7-hydroxy acrylic esters were prepared from the dihydroxy alkanes and their characterization by $^1\text{H-NMR}$ and mass spectroscopic methods were reported for the first time.

TABLE V
Fragmentation Pattern of 6-Hydroxy and 7-Hydroxy Acrylic Esters

	Diagnostic fragmented peaks m/z				
	M	A	A-18	B	B-17
6-Hydroxy acrylic ester					
C ₁₅	298	171	153	157	140
C ₁₇	326	171	153	185	168
C ₁₉	354	171	153	213	196
C ₂₁	382	171	153	241	224
C ₂₃	410	171	153	269	252
7-Hydroxy acrylic ester					
C ₁₃	270	185	167	115	98
C ₁₆	312	185	167	157	140
C ₁₈	340	185	167	185	168
C ₂₀	368	185	167	213	196
C ₂₂	396	185	167	241	224
C ₂₄	424	185	167	269	252

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