When treated with sodium metaperiodate (sodium bicarbonate buffer),[14] this product (IX) did not consume any oxidant.

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(14) Procedure A described by M. J. Weiss and co-workers, *J. Am. Chem. Soc.*, **81**, 4050 (1959).

2,3-Dideoxy-DL-pentose

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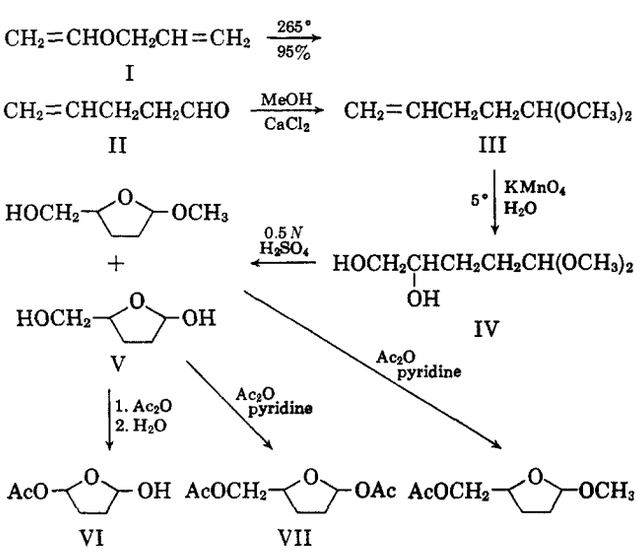
In view of the importance of ribose and 2-deoxyribose in biological systems, we wished to develop a more convenient and practical synthesis of 2,3-dideoxyribose (V) than that described from arabinose[2a] or of the phenylhydrazone from 2-deoxy-D-ribose.[2b] The racemic form is obtained by the Claisen rearrangement of allyl vinyl ether to 4-pentenal,[3,4] conversion to the methyl acetal, and permanganate oxidation.



The furanose ring system for the 5-acetate (VI) as well as the 1,5-diacetate (VII) is indicated by the chemical shifts for the 4 and 5 hydrogens in the nmr spectra.

Experimental Section

Allyl vinyl ether (I) was prepared by mercuric acetate catalyzed reaction of butyl vinyl ether with allyl alcohol, distilling the crude product directly from the reaction mixture held at 87°. After fractional distillation, material containing 70% I was obtained. This was washed with water to remove allyl alcohol and dried over sodium sulfate. Refractionation gave a 51% yield of 95% pure I (by vpc) and one more distillation produced 30% of 99.5% pure I, bp 66–67.2°, n^{20}D 1.4111.[5]

Allyl butyl acetal was isolated by careful fractionation of the initial residue in the above preparation, bp 70–71° (22 mm), n^{20}D 1.4144.

Anal. Calcd for $C_9H_{18}O_2$: C, 68.32; H, 11.47. Found: C, 68.26; H, 11.52.

4-Pentenal (II).—Conditions for optimum pyrolytic conversion of I to II were carefully explored. The best results (>97% conversion, >98% yield) were obtained by passing I through a 24 × 0.5 in. o.d. glass tube packed with 30–60 mesh, nonacid-washed Chromosorb W and maintained at 265°. A flow rate of 15 cc/min of dry nitrogen was maintained while 12 g/hr of I was passed through the column. The product which liquefied in a water-cooled condenser amounted to 97% of charged I and the purity (by vpc) ranged from 95 to 99% in twelve conversions. The column required cleaning about every four runs owing to accumulation of polymer. The redistilled II had bp 102–104°, n^{20}D 1.4165, d^{20} 0.851.[3]

The infrared spectrum showed bands at 3.27 (sh), 3.46 (31), 3.55 (34), 3.69 (29), 5.84 (90), 6.11 (26), 7.00 (sh), 7.12 (33), 7.22 (sh), 7.45 (sh), 9.5 (18), 10.06 (25), and 10.93 (33) μ (per cent absorbance). The nmr spectrum (neat) showed absorption for one hydrogen each at τ 0.8, at 4.2–5, at 5.3 (doublet, J = 5.5 cps), and at 5.42 (doublet J = 2.7 cps) and for four hydrogens at 7.7–7.9.

1,1-Dimethoxy-4-pentene (III) was prepared by adding 320 g of II (in 10-ml portions) to 300 g of anhydrous calcium chloride in 2 l. of absolute methanol at 0°. After standing for 36 hr at 25°, the product was extracted with petroleum ether (bp 30–60°) and distilled to provide 400 g (81%) of 99% pure III, bp 60.5–61.2° (49 mm), n^{20}D 1.4120, d^{20} 0.868.

Anal. Calcd for $C_7H_{14}O_2$: C, 64.57; H, 10.84. Found: C, 64.73; H, 10.63.

The infrared spectrum showed bands at 3.24 (69), 3.31 (50), 6.13 (18), 6.97 (37), 7.08 (15), 7.29 (31), 7.38 (30), 8.44 (51), 8.92 (94), 9.41 (90), 10.10 (39), 10.35 (35), and 11.00 (67) μ (per cent absorbance). The nmr spectrum (neat) showed absorption for one hydrogen each at τ 4.7–4.9, at 5.3 (doublet, J = 4.9 cps), at 5.5 (doublet, J = 2 cps), and at 6.0 (triplet, J = 4.9 cps), for six hydrogens at 7.1, and for four hydrogens at 8–8.6.

1,1-Dimethoxy-4,5-pentanediol (IV) was prepared from III essentially by the procedure described for the permanganate oxidation of acrolein diethyl acetal.[6] A solution of 79 g (0.5 mole) of potassium permanganate in 1800 ml of water was added dropwise over 4 hr to 65.1 g (0.5 mole) of III in 300 ml of water maintained at 5 ± 0.5°. The reaction mixture, which gelled, was allowed to stand overnight then heated at 95° for 1 hr. After filtration, the product was salted out with potassium carbonate. The orange oil was treated with activated charcoal and anhydrous magnesium sulfate and distilled to give 45% of IV, bp 103.8–103.9° (0.25 mm), n^{20}D 1.4518, d^{25} 1.079.

Anal. Calcd for $C_7H_{16}O_4$: C, 51.20; H, 9.82. Found: C, 50.73; H, 9.75.

The infrared spectrum showed bands at 2.94 (90), 3.44 (72), 6.95 (72), 7.25 (46), 7.35 (47), 8.41 (54), 8.52 (52), 8.86 (91), 9.45 (97), 10.34 (52), 10.91 (31), and 11.34 (35) μ (per cent absorbance). The nmr spectrum in deuteriochloroform showed an apparent quartet at τ 5.7–6.0 (3 H), broad absorption at 6.5–6.8 (3 H), a singlet at 6.95 (6 H), and broad absorption at 8.3–8.8 (4 H).

2,3-Dideoxypentose (V).—Hydrolysis of IV by 0.5 N sulfuric acid in a steam bath for 3 hr followed by neutralization, evaporation, and methanol extraction gave an amber syrup (~100% yield), n^{20}D 1.4704, giving a positive Benedict's test, undoubtedly a mixture of ring and stereo isomers.

The infrared spectrum showed bands at 2.94 (88), 3.40 (53), 6.92 (41), 7.38 (36), 7.81 (30), 7.99 (26), 8.25 (37), 8.81 (52), 9.10 (70), 9.5 (8.4), 10.12 (70), 11.19 (41), 11.6 (27), and 12.4 (21) μ (per cent absorbance).

The **dinitrophenylhydrazone** was prepared by the procedure of Richards,[7] as yellow needles from ethyl acetate: mp 134–135°.

Anal. Calcd for $C_{11}H_{14}N_4O_6$: C, 44.29; H, 4.73; N, 18.78. Found: C, 44.55; H, 4.85; N, 18.55.

(1) From a Ph.D. Dissertation by R. B. Balsley, University of Pennsylvania, 1964.

(2) (a) R. Allerton, W. G. Overend, and M. Stacey, *J. Chem. Soc.*, 255 (1952); (b) M. G. Blair, D. Lipkin, J. C. Sowden, and D. R. Strobach, *J. Org. Chem.*, **25**, 1679 (1960).

(3) C. D. Hurd and M. A. Pollack, *J. Am. Chem. Soc.*, **60**, 1905 (1938).

(4) R. F. Webb, A. J. Duke, and J. A. Parsons, *J. Chem. Soc.*, 4192 (1961).

(5) W. H. Watanabe and L. E. Conlon, *J. Am. Chem. Soc.*, **79**, 2828 (1957).

(6) E. J. Witzemann, W. L. Evans, H. Hass, and E. F. Schroeder, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p 307.

(7) G. N. Richards, *J. Chem. Soc.*, 3638 (1954).

The **5-acetate** of V was prepared from 11.8 g of V and 6 g of anhydrous sodium acetate in 60 ml of acetic anhydride by heating for 2 hr at 95°. After standing at 25° with 400 ml of water, salt was added and the product was extracted with four 100-ml portions of ether. Distillation gave 2.3 g of 97% pure (by vpc) **5-*O*-acetyl-2,3-dideoxypentofuranose (VI)**, bp 102–103° (1 mm), $n^{20}D$ 1.4573.

Anal. Calcd for $C_7H_{12}O_4$: C, 52.54; H, 7.56. Found: C, 52.32; H, 7.60.

The infrared spectrum showed bands at 2.92 (74), 3.41 (65), 5.80 (89), 6.98 (61), 7.33 (81), 8.05 (91), 8.40 (65), 8.93 (62), 9.35 (83), 9.60 (88), 9.80 (84), 10.26 (84), 10.74 (57), 11.13 (57), 11.74 (42), and 12.20 (37) μ (per cent absorbance). The nmr spectrum (neat) showed a poorly defined peak at τ 4.7 (HOC*H*OR), a singlet at τ 5.4 (O*H*), a doublet at 6.0 (2 H, J = 4.5 cps, CH_2OAc), an irregular quintet at 6.5 (J = 4.5 cps), and a singlet at 8.0 (3 H) overlapping a multiplet at 7.9–8.3 (4 H).

The position of the acetyl group is established by a positive Benedict's test and the chemical shift of the proton in the 1 position, which would be expected to be much greater if adjacent to an acetyl group.[8] A furanose ring structure is suggested by the chemical shifts of the peaks corresponding to the protons in the 4 and 5 positions when these are compared to approximate theoretical values calculated using reference compounds of similar structure.[8] The calculated values for a pyranose structure are τ 4.8 for the 4 position and 6.5 for the 5 position, whereas a furanose structure was predicted to have values of 6.2 for the 4 position and 5.9 for the 5 position. The observed values were τ 6.5 for the 4 position and 6.0 for the 5 position. The complexity of the peaks for the 1 and 5 hydrogens is no doubt due to the presence of α and β isomers in the product.

(5-*O*-Acetyl-2,3-dideoxypentofuranosyl) 5-*O*-Acetyl-2,3-dideoxypentofuranoside.—This compound was isolated by continued fractional distillation of the residue from the distillation of 5-*O*-acetyl-2,3-dideoxypentofuranose above. A total of 2.4 g of crude material was obtained, bp 160–166° (0.8 mm), $n^{20}D$ 1.4637, undoubtedly a mixture of isomers.

Anal. Calcd for $C_{14}H_{22}O_7$: C, 55.62; H, 7.34. Found: C, 55.96; H, 7.59.

The infrared spectrum showed bands at 3.41 (42), 5.78 (76), 6.97 (35), 7.32 (59), 8.09 (77), 8.90 (43), 9.10 (50), 9.57 (70), 10.23 (69), 11.13 (35), 11.70 (30), and 12.15 (20) μ (per cent absorbance).

Methyl 5-*O*-Acetyl-2,3-dideoxypentofuranoside.—This compound was isolated from the forerun of the distillation of crude VII. It was probably formed by acetylation of methyl 2,3-dideoxypentoside present in the crude 2,3-dideoxypentose used for the preparation of the diacetate. This suggests that methyl 2,3-dideoxypentoside is an intermediate in the hydrolysis of 1,1-dimethoxy-4,5-pentanediol to 2,3-dideoxypentose. This view is supported by the presence of sharp bands at τ 6.8 and 6.9 in the crude V, which might be due to the presence of some α- and β-methyl 2,3-dideoxypentosides. A pure sample of methyl 5-*O*-acetyl-2,3-dideoxypentofuranoside ($n^{20}D$ 1.4387) was obtained by vpc collection over the appropriate retention time range.

Anal. Calcd for $C_8H_{14}O_4$: C, 55.16; H, 8.10. Found: C, 54.78; H, 7.80.

The infrared spectrum showed bands at 3.51 (66), 5.81 (95), 6.99 (62), 7.37 (84), 8.14 (100), 8.89 (79), 9.22 (86), 9.61 (100), 10.40 (71), 11.01 (60), 11.40 (54), and 12.26 (26) μ (per cent absorbance).

1,5-*O*,*O*-Diacetyl-2,3-dideoxypentofuranose (VII).—A mixture of 10 ml of acetic anhydride and 20 ml of pyridine was cooled to 0° in an ice bath. To this was added gradually with swirling 6.7 g of crude 2,3-dideoxypentose. The resulting yellow solution was allowed to stand at room temperature for 36 hr. The pyridine, acetic acid, and excess acetic anhydride were removed by fractional distillation at 17 mm. The residual amber oil (9.3 g) was treated with 100 ml of anhydrous ether and a small amount of activated charcoal. The charcoal and a small amount of insoluble material were removed by filtration and the filtrate was warmed on a steam bath to evaporate the ether. The residual yellow oil (9.0 g) was distilled, and the three center cuts, bp 78–84° (0.17 mm), were found by vpc analysis to consist largely of 1,5-*O*,*O*-diacetyl-2,3-dideoxypentofuranose plus small amounts of 5-*O*-acetyl-2,3-dideoxypentofuranose. Attempts to obtain a pure sample of the former by vpc collection were unsuccessful owing to decomposition. The center cuts (5.8 g, 50%) were all colorless and had a strong, but not unpleasant odor, bp 79–80° (0.17 mm), $n^{21}D$ 1.4452.

Anal. Calcd for $C_9H_{14}O_5$: C, 53.46; H, 6.98. Found: C, 53.15; H, 6.83.

The infrared spectrum showed bands at 3.46 (28), 5.82 (95), 7.00 (40), 7.35 (73), 8.13 (100), 8.85 (48), 9.11 (64), 9.57 (77), 9.93 (80), 10.42 (67), 10.72 (51), and 11.55 (46) μ (per cent absorbance). The nmr spectrum showed a poorly defined peak at τ 4.0, a doublet at 5.8 (J = 2.9 cps), a poorly defined multiplet at 6.3, and a singlet at 8.0 overlapping a multiplet at 8.2. The peak areas were in the approximate ratio 1:2:1:6:4. The values of the chemical shifts for the protons in the 4 position (τ 6.3) and the 5 position (τ 5.8) were in good agreement with the calculated values of 6.2 for the 4 position and 5.9 for the 5 position of a furanose structure.

Treatment of the diacetate VII with dry HBr in glacial acetic acid produced an amber syrup from which we did not succeed in obtaining the pure acetobromo sugar. The syrup gave a voluminous precipitate with methanolic silver nitrate and formed triethylamine hydrobromide when treated with triethylamine in toluene. Reaction with 2,4-diethoxy-5-methylpyrimidine cleaved one ethyl ether and dithyminyl mercury gave thymine as the only identified product.[9]

(8) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Inc., New York, N. Y., 1959, p 55 ff.

(9) M. J. Robins and R. K. Robins [*J. Am. Chem. Soc.*, **86**, 3585 (1964)] have reported a useful synthesis of 2′,3′-dideoxyadenosine directly from deoxyadenosine.

12-Chloro-*cis*-9-octadecenyl Chloride

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In developing syntheses of hindered amides of ricinoleic (12-hydroxy-*cis*-9-octadecenoic) acid, we noted claims[2–4] regarding the preparation of ricinoleoyl chloride (presumably 12-hydroxy-*cis*-9-octadecenyl chloride) from this acid and thionyl chloride. We found, as expected from the known reactions of alcohols and thionyl chloride,[5] that the principal monomeric product in this case is a chloro acid chloride. If this reaction proceeded as expected, the product would be 12-chloro-*cis*-9-octadecenyl chloride (I). This chloro acid chloride, incompletely characterized, was described by Ulrich[6] who obtained it by reaction of ricinoleic acid with phosphorus pentachloride. The alcohol function also was converted to the related bromide with hydrogen bromide[7] or phosphorus pentabromide,[8] and Grigor, *et al.*,[9] reported that unstable 12-chloro esters

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(2) A. A. L. Challis and G. R. Clemo, *J. Chem. Soc.*, 613 (1947).

(3) C. F. H. Allen, J. R. Byers, Jr., W. J. Humphlett, and D. D. Reynolds, *J. Chem. Educ.*, **32**, 394 (1955).

(4) C. F. H. Allen, J. R. Byers, Jr., and W. J. Humphlett, *Org. Syn.*, **37**, 66 (1957).

(5) For discussions see E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, New York, N. Y., 1959, pp 294–296; J. D. Roberts and M. C. Caserio, "Basic Principles of Organic Chemistry," W. A. Benjamin, Inc., New York, N. Y., 1964, pp 392–394.

(6) K. Ulrich, *Z. Chem.*, **10**, 545 (1867).

(7) A. Kasansky, *J. Prakt. Chem.*, [2] **62**, 363 (1900).

(8) A. Grün, *Chem. Ber.*, **39**, 4400 (1906).

(9) J. Grigor, D. D. MacInnes, J. McLean, and A. J. P. Hogg, *J. Chem. Soc.*, 1069 (1955).