TABLE I

PROPERTIES OF β-ALKYL GLUCOSIDES AND THEIR TETRAACETATES

	d-Glucoside							*d*-Glucoside tetraacetate				
				Analyses, %								
				Carbon		Hydrogen			Acetyl no.[a]			
Name	M. p., °C. (cor.)	$[\alpha]_D$ in H_2O	$[M]_D$ in H_2O	Calcd.	Found	Calcd.	Found	M. p., °C. (cor.)	Calcd.	Found	$[\alpha]_D$ in $CHCl_3$	$[M]_D$ in $CHCl_3$
n-Propyl[b,c]	102.5–3.5	−39.5	−8,780	48.64	48.4	8.16	8.3	103	10.26	10.21	−21.3	−8,300
n-Butyl[b,d]	66–67	−37.4	−8,830	50.83	50.7	8.53	8.6	65–66	9.90	9.83	−21.2	−8,560
n-Amyl	89.5–90.0	−35.7	−8,930	52.78	52.5	8.86	9.1	46–47	9.57	9.62	−21.5	−8,990
n-Heptyl	76–78	−33.1	−9,200	56.09	55.9	9.42	9.5	68.0–8.5	8.97	9.03	−19.7	−8,800
i-Propyl[b,c,e]	128.5–9.5	−37.6	−8,350	48.64	48.5	8.16	8.3	136–137	10.26	10.15	−22.9	−8,930
i-Butyl[b,d]	113–114	−38.2	−9,010	50.83	50.7	8.53	8.5	122.5–3.0	9.90	9.91	−20.2	−8,160
t-Butyl[d,f]								148	9.90	9.90	−12.8	−5,130

[a] A. Kunz and C. S. Hudson, THIS JOURNAL, **48**, 1978 (1926). [b] E. Bourquelot and M. Bridel, *Ann. chim. phys.*, [8] **29**, 145 (1913). [c] S. Veibel and F. Eriksen, *Bull. soc. chim.*, [5] **3**, 277 (1936). [d] S. Veibel and H. Lillelund, *Bull. soc. chim.*, [5] **5**, 494 (1938). [e] W. J. Hickenbottom, *J. Chem. Soc.*, 3140 (1928). [f] S. Veibel and E. Nielsen, *Compt. rend.*, **203**, 126 (1936).

purpose, they having originally reported the rotations of these compounds in methanol.

TABLE II

MOLECULAR ROTATION IN CHLOROFORM OF ALKYL-*d*-GLUCOSIDE TETRAACETATES

	β-*n*-Hexyl-[a]	β-*n*-Nonyl-	β-*n*-Decyl-	β-*n*-Dodecyl-
$[\alpha]_D$	−20.0	−19.3	−18.6	−16.6
$[M]_D$	−8,640	−9,150	−9,070	−8,110

[a] E. Pacsu, THIS JOURNAL, **52**, 2563 (1930).

These data and similar data in the literature agree with the findings of Pigman and Isbell[8] that the molecular rotations of the N-alkyl-β-*d*-glucosides having more than three carbon atoms in the aglucone lie between 8700 and 9200 in water, while those of the corresponding tetraacetates lie between 8300 and 9200 in chloroform. It can also be seen that while the molecular rotations of the secondary and/or iso series of alkyl β-*d*-glucosides, both free and acetylated, are about the same, those of the corresponding tertiary series are considerably lower, measured under the same conditions.

(8) W. W. Pigman and H. S. Isbell, *Bur. Standards J. Research*, **27**, 9 (1941).

DEPARTMENT OF CHEMISTRY
BETHEL COLLEGE
NORTH NEWTON, KANSAS

RECEIVED FEBRUARY 4, 1942

D-Mannosan<1,5>β<1,6> from β-Phenyl-D-mannoside

BY EDNA M. MONTGOMERY, NELSON K. RICHTMYER AND C. S. HUDSON

The syntheses of epi-cellobiose and cellobiose which have been described recently by Haskins, Hann and Hudson[1] involve the use of D-mannosan<1,5>β<1,6>; the total synthesis of this anhydride of D-mannose is thus a necessary step for attaining totality in the syntheses of the disaccharides. The total synthesis of D-mannose was accomplished by Emil Fischer[2]; the problem therefore reduces to the conversion of D-mannose to D-mannosan<1,5>β<1,6>. This transformation has been effected during the course of our study of the action of alkali upon certain glycosides,[3] and it may well be described separately at this time.

The Alkaline Degradation of β-Phenyl-D-mannoside to D-Mannosan<1,5>β<1,6>.—Tetraacetyl-β-phenyl-D-mannoside, of m. p. 169° and rotation[4] −62.9° in chloroform (*c*, 2), was obtained in small yield as a by-product in the preparation of tetraacetyl-α-phenyl-D-mannoside from α-pentaacetylmannose, phenol and zinc chloride by a modification[5] of the method used by Helferich and Winkler.[6] Deacetylation produced β-phenyl-D-mannoside of m. p. 175° and rotation −71.7° in water (*c*, 1). All these data are in agreement with those of Helferich and Winkler.

A solution of 5.000 g. of pure β-phenylmannoside in 250 cc. of 2.6 *N* aqueous potassium hydroxide in a metallic vessel (a clean beer can) was boiled gently under a reflux condenser; the rotation changed in the course of five days from −70.6°, calculated as mannoside, to a constant value of −114°, calculated as mannosan. The yellow solution was cooled, neutralized to methyl orange with 3 *N* sulfuric acid, and concentrated *in vacuo* to dryness. The product was extracted from the potassium sulfate with hot absolute alcohol, and the extract concentrated *in vacuo* to a sirup. Acetylation of this sirup with acetic anhydride and pyridine produced 4.4 g. of pure 2,3,4-triacetyl-D-mannosan<1,5>β<1,6>, of m. p. 89–90° and rotation −123.8° in chloroform (*c*, 2) in agreement with the published data.[7]

By deacetylation of the triacetate catalytically with

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(1) Haskins, Hann and Hudson, THIS JOURNAL, **63**, 1724 (1941); **64**, 1289 (1942).

(2) Fischer, *Ber.*, **23**, 370 (1890).

(3) Montgomery, Richtmyer and Hudson, unpublished results from this Laboratory; see *Science*, **93**, 438 (1941).

(4) Throughout the article the rotations are specific rotations at 20° for sodium light; *c* designates concentration in grams per 100 cc. of solution.

(5) Montgomery, Richtmyer and Hudson, THIS JOURNAL, **64**, 690 (1942).

(6) Helferich and Winkler, *Ber.*, **66**, 1556 (1933).

(7) Zemplén, Gerecs and Valatin, *ibid.*, **73**, 575 (1940); Knauf, Hann and Hudson, THIS JOURNAL, **63**, 1447 (1941).

barium methylate 1.8 g. of the D-mannosan was isolated as prisms upon crystallization from a 3:1 mixture of ethyl alcohol and ethyl acetate. The yield, phenylmannoside to mannosan, was 57%. The product was identified as D-mannosan<1,5>β<1,6> by its rotation of −127.4° in water (*c*, 1.0), and its m. p. of 210°, in agreement with the data of Knauf, Hann and Hudson.[7] The melting point was not depressed when the substance was mixed with an authentic sample of D-mannosan<1,5>β<1,6>.

DIVISION OF CHEMISTRY
NATIONAL INSTITUTE OF HEALTH
BETHESDA, MARYLAND

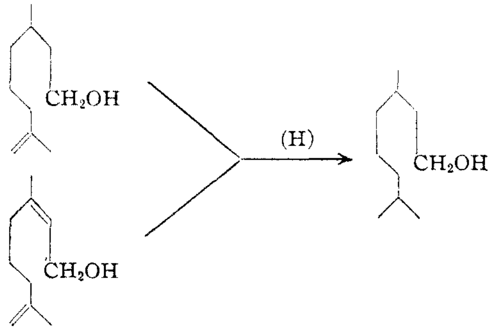
RECEIVED MAY 11, 1942

3,7-Dimethyloctene-2

BY SAMUEL NATELSON, SIDNEY P. GOTTFRIED AND SEYMOUR KORNBLAU

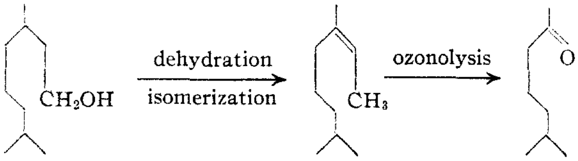
The diterpenes of the citronellol and geraniol family are of interest in the possible synthesis of cholesterol and related products such as the antirachitic vitamin. They possess the side chain of cholesterol and two extra carbon atoms.

As a preliminary study citronellol and geraniol were reduced catalytically to 3,7-dimethyloctanol-1.



Methods for dehydrating large amounts of this material were studied. After some experimentation it was found that the 3,7-dimethyloctanol-1 could be dehydrated readily in a catalytic chamber with a small amount of phosphorus pentoxide at a temperature above 180°. The distillate was found to be different from that reported by Braun and Teffert for 3,7-dimethyloctene-1.[1] Elementary analysis showed it to be isomeric with 3,7-dimethyloctene-1. That the product had one double bond was shown by its iodine number and titration with benzoyl hydrogen peroxide. The oxide derivative was isolated.

The main product of the reaction after ozonolysis was found to be methyl isohexyl ketone. This was identified by the preparation of the semicarbazone and elementary analysis of the ketone and semicarbazone. This product could only have been formed if the double bond had shifted, during the process, from the terminal position to the tertiary position.



The fore-runnings of the fractionation of the unsaturated hydrocarbon, b. p. 159–162°, were ozonized to get an idea of its composition. The product of ozonolysis was found to consist mainly of methyl isohexyl ketone. In addition, an appreciable amount of product after ozonolysis was found to boil at a higher temperature than the methyl isohexyl ketone and a residue was observed. This higher boiling fraction was not obtained on ozonizing the main fraction; b. p. 162–163°. This higher boiling fraction was not identified.

Experimental

Dimethyloctanol-1.—The dimethyloctanol was prepared by reduction of geraniol with a platinum oxide catalyst in the standard reducing machine at three atmospheres. It was also prepared by reduction with Raney nickel at 100° at twenty atmospheres,[2] b. p. 113–114° (7 mm.); d^{20} 0.8362; $n^{20}\text{D}$ 1.4433.

3,7-Dimethyloctene-2.—Twenty grams of phosphorus pentoxide was placed in a Claisen distilling flask, fitted with a dropping funnel leading to the bottom and a thermometer. The flask was placed in an oil-bath so that the bulb of the flask was completely immersed. The side arm was attached to an air condenser. The temperature of the oil-bath was raised to 200–210° and 20 cc. of the dimethyloctanol was added slowly; 1000 g. of dimethyloctanol was then added drop by drop at the same rate that the decylene and water distilled over. The distillate came over between 160–180° and was transferred to a separatory funnel and the lower water layer removed. The oily layer was washed with dilute bicarbonate, then water and finally dried over anhydrous sodium sulfate. On distillation 810 g. of a product boiling from 159–163° was obtained. On fractionation with a Vigreux column (2 ft.) 600 g. of a product boiling from 162–163° (761 mm.) was obtained; b. p. 162–163°; d^{24} 0.7501; $n^{22}\text{D}$ 1.4258. *Anal.* Calcd.: C, 85.63; H, 14.37; iodine no., 181.3. Found: C, 85.77; H, 14.42; iodine number, 191.

Methyl Isohexyl Ketone.—3–5% ozone was passed through a mixture of 20 g. of 3,7-dimethyloctene-2 with 30 cc. glacial acetic acid until a test sample did not decolorize bromine in carbon tetrachloride. The mixture was then dissolved in 150 cc. of ether, and 20 g. of zinc dust was added. The mixture was cooled in an ice and salt bath, 20 cc. of water was added slowly with vigorous stirring. Stirring was continued until a test with potassium iodide

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(1) Braun and Teffert, *Ber.*, **62**, 235–241 (1929).

(2) Dimethyloctanol is commercially available. The authors are grateful to Dr. Arthur Wendt of Seeley and Co., New York, N. Y., for large samples of this material.