TABLE X

AMPLIFIED SEPARATION OF METHYL OLEATE FROM STEARIC ACID WITH METHYL CAPROATE AS THIRD SOLUTE ADDED TO DEVELOPING SOLVENT

Expt. No.	Lot No.	Vol. of eluate, ml.	Wt. of methyl oleate, mg.	Contamination, % stearic acid
1[a]	1	500	55.8	<0.1
	2	500	40.6	
	3	500	0.3	
2[b]	1	500	73.0	< .1
	2	500	25.3	
	3	500	0.0	
3[c]	1	500	96.1	< .1
	2	500	4.2	
	3	500	0.0	
4[d]	1	1000	100.6	< .07
	2	500	0.0	
	3	500	0.0	

[a] 102.8 mg. of methyl oleate plus 104.2 mg. of stearic acid were dissolved in 100 ml. of petroleum ether and adsorbed on 12.0 g. of silica gel, 4.7 cm. high by 2.3 cm. wide. Predevelopment with 200 ml. of 0.5% methyl caproate in petroleum ether and development with petroleum ether at 25° at 350 ml./hr. [b] Same solute and adsorbent as in (a). Predevelopment with 300 ml. of 0.5% methyl caproate in petroleum ether and development with petroleum ether at 28° at 350 ml./hr. [c] Same solute and adsorbent as in (a). Predevelopment with 500 ml. of 0.5% methyl caproate in petroleum ether and development with petroleum ether at 25° at 400 ml./hr. [d] 102.2 mg. of methyl oleate plus 100.9 mg. of stearic acid. The other details of solution and adsorbent the same as in (a). Predevelopment with 1000 ml. of 0.25% methyl caproate in petroleum ether and development with petroleum ether at 25° at 400 ml./hr.

roate, $n^{20}\text{D}$ 1.4048, by its correct value of $n^{20}\text{D}$ 1.4522. The best recovery, 98.4% in 2.5 hours, does not appear to be the limit obtainable by this method.

In comparing amplified chromatographic separations with those obtained by carrier displacement chromatography it can be said that in each type the separation of the tail of C from the head of A is initiated by the presence of B which permits the movement of both B relative to A and of C relative to B to proceed according to the relationships found for *K* values. Thereafter, the situation is different. In carrier displacement chromatography the beneficial effect of B on the separation is restricted to its maintenance of *K* value conditions. In amplified chromatographic separations the greater concentration of B at the B/C than at the B/A interface produces an amplified movement of C relative to A, hence the use of this work in describing the process. The data recorded in Table IX indicate the amplifying effect of B may be large and, therefore, of potential value in effecting otherwise difficult separations. Pending a fuller investigation of the relationships, it appears from the data of Tables IX and X that it is desirable to employ a uniform concentration of solute B in the preliminary stages of a separation. This can be accomplished, either as in carrier displacement chromatography, through the use of a displacing agent in the development of a solution of the three solutes or, as in Table X, by a predevelopment of A and C with a solution of B. Presumably when, in a separation, A and C had reached positions in the column corresponding to those in Fig. 3a it would be safe to utilize the amplifying effect of B to speed the further separation of C from A.

WASHINGTON 25, D. C. RECEIVED APRIL 14, 1951

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

Optically Active 1-Cyclohexenyl- and 1-Cyclopentenylmethylcarbinols[1]

BY JAMES ENGLISH, JR., AND VINCENT LAMBERTI

1-Cyclohexenylmethylcarbinol and 1-cyclopentenylmethylcarbinol have been prepared in optically active form through the brucine salts of their hydrogen phthalates. The mutarotation of these compounds in the liquid state has been found due to ether formation.

Substituted allyl alcohols have been the subject of considerable study by a number of workers,[2] particularly from the point of view of their rearrangements. Kenyon[3] and coworkers reported the preparation and resolution of several alkyl-substituted allyl alcohols and observed the anomalous mutarotations of these substances. Kenyon, Partridge and Phillips[4] reported the retention of optical activity of α-phenyl-γ-methylallyl alcohol during its rearrangement. Prior to the recent publications of Braude, *et al.*,[5] no examples of allylic alcohols in which the allylic system is part of a ring are reported. These workers studied the rearrangement in acid solution of some cyclohexenyl- and cyclopentenyl-substituted carbinols in optically inactive form. All of these rearrangements seem, in the light of recent work,[2] to have been acid catalyzed, whether or not acid was deliberately added.

Since a similar spontaneous change in rotation was observed by Kögl[6] in the crystalline auxins **a** and **b**, it seemed of interest to prepare some simple models in which the allylic system is located on a ring as in the structures proposed for the auxins. The structures first chosen were 1-cyclohexenylmethylcarbinol and 1-cyclopentenylmethylcarbinol. The method of synthesis used is indicated below.

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[1] Taken from the dissertation of Vincent Lamberti presented to the Graduate School of Yale University in partial fulfilment of the requirement for the Ph.D. degree.

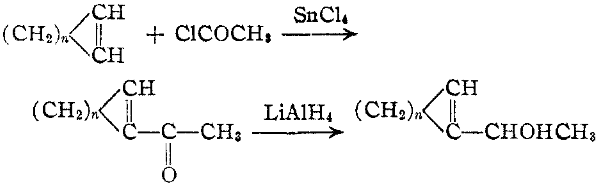
[2] E. A. Braude, *Ann. Repts. on Progress. Chem.* (*Chem. Soc. London*), **46**, 126 (1950).

[3] H. W. J. Hills, J. Kenyon and H. Phillips, *J. Chem. Soc.*, 576 (1936); B. C. Platt, *ibid.*, 316 (1941); R. S. Airs, M. P. Balfe and J. Kenyon, *ibid.*, 20 (1942); C. L. Arcus and J. Kenyon, *ibid.*, 312 (1938).

[4] J. Kenyon, S. M. Partridge and H. Phillips, *ibid.*, 207 (1937).

[5] E. A. Braude and W. F. Forbes, *ibid.*, 1755 (1951).

[6] F. Kögl, C. Konigsberger and H. Erxleben, *Z. physiol. Chem.*, **244**, 266 (1936).



n = 3 or 4

Of the several methods of preparation of cyclohexenyl methyl ketones available[7] the most convenient was found to be a modification of that of Cologne and Mostafavi[8] which has been used for the preparation of other unsaturated ketones in this Laboratory.[9] The use of small amounts of stannic chloride and prompt working up of the reaction mixtures were found essential to satisfactory yields. In the case of cyclopentenyl methyl ketone the method of Rapson and Robinson[10] was found satisfactory. Lithium aluminum hydride and aluminum isopropylate were both used in the reduction of the ketones. The extensive isopropyl ether formation observed with the latter reagent was of course absent in the lithium aluminum hydride reactions but in both cases the cycloalkenylmethylcarbinols were contaminated with up to 20% of unchanged ketones.

The presence of unchanged ketone in spite of the use of an excess of reducing agent was interpreted as due to enolization and reaction of the enol with the basic reagents; it was found that a second treatment of the crude carbinols with lithium aluminum hydride reduced the ketone content to the point where a careful fractional distillation sufficed to give pure carbinol samples.

The carbinols were resolved through the brucine salts of their hydrogen phthalates by recrystallization from acetone. Since the alkaline hydrolysis of phthalates of allyl alcohols is known to produce racemization[11] they were decomposed by lithium aluminum hydride reduction.[12] In this way, (−)-cyclohexenylmethylcarbinol, $[\alpha]^{25}\text{D}$ −1.48° (liquid), was obtained. Catalytic reduction gave the known (+)-cyclohexylmethylcarbinol, $[\alpha]^{25}\text{D}$ +5.36°; Domleo and Kenyon[13] reported $[\alpha]^{25}\text{D}$ +5.58° for this substance obtained by direct resolution. (−)-Cyclopentenylmethylcarbinol obtained in an identical manner showed a much higher specific rotation, $[\alpha]^{25}\text{D}$ −10.21° (liquid).

Both alcohols showed the rather marked dependence of rotation on temperature previously observed with substituted allyl alcohols[14] and both underwent slow spontaneous mutarotation. This change was shown in the case of cyclohexenylmethylcarbinol to be due to ether formation and to be catalyzed by traces of acid. Redistillation of a sample one month old, $[\alpha]^{25}\text{D}$ −1.58°, gave the original material $[\alpha]^{25}\text{D}$ −1.46° and a higher boiling ether fraction.

It is felt that the remarkable mutarotation described by Kenyon[3] in which (+)-α,γ-dimethylallyl alcohol, for example, showed a complete reversal of sign, must have been due to a similar "spontaneous" etherification (catalyzed presumably by traces of acid). In this case the ether is known to have a strong levo-rotation[15] and there is no evidence in Kenyon's papers that the alcohol samples in his mutarotation studies were carefully fractionated before determining the rotations.

Attempts to obtain pure samples of the rearrangement products, 2-ethylidenecyclopentanol and 2-ethylidenecyclohexanol, by independent synthesis were only partially successful. The poor yields obtained in the condensation of acetaldehyde with cyclohexanone and cyclopentanone made it impractical to accumulate enough material to undertake a resolution. *dl*-Ethylidenecyclohexanol and *dl*-ethylidenecyclopentanol on standing showed negligible change in refractive index and on distillation were recovered unchanged except for the formation of considerable non-volatile polymer, presumably derived from the corresponding dienes. No appreciable ether formation or rearrangement was observed.

Experimental[16]

1-Acetylcyclohexene.—A solution of 34 g. of anhydrous stannic chloride in 121 g. of carbon disulfide was added with stirring to 178 g. of cyclohexene and 78.5 g. of acetyl chloride in 190 g. of carbon disulfide at −4 to −6°. After 3 hours stirring at −5° the mixture was poured into 250 g. of ice and 250 cc. of 6 *N* hydrochloric acid. Ether was added and the mixture extracted with this solvent; the combined extracts were washed with cold water and sodium bicarbonate and mixed with 149 g. of diethylaniline. After brief drying over sodium sulfate the solvents and excess cyclohexene were removed and the residue heated at 180° (bath temperature) for 2 hours. The cooled mixture was filtered, the filtrate taken up in ether, washed with water and sodium bicarbonate and dried over sodium sulfate. 1-Acetylcyclohexene was obtained by distillation in 79% yield. The pure ketone boiled at 88–89° (19.5 mm.), had $n^{20}\text{D}$ 1.4914 and gave a semicarbazone, m.p. 218–220° (dec.).[17]

2-Ethylidenecyclohexanone.—Of a number of different experimental conditions those proposed by Knorr and Weissenborn[18] were found most satisfactory, but even here the yield of fractionated ketone, b.p. 87–89° (18 mm.), $n^{25}\text{D}$ 1.4893, was only about 10%. 2-Ethylidenecyclohexanone was found to darken rapidly in air and gave a stable semicarbazone, m.p. 189–190° (dec.).

2-Ethylidenecyclopentanone.—To a stirred mixture of 144 g. of cyclopentanone and 2.3 g. of powdered potassium hydroxide (dried by distilling benzene from the powder) was added dropwise at 5°, 50 g. of freshly distilled acetaldehyde. The addition required 5 hours, after which carbon dioxide was passed in, the mixture diluted with ether and filtered. On removal of solvent and excess cyclopentanone *in vacuo*, the residue (non-volatile) was treated with a crystal of iodine and distilled at 80–100° (17 mm.). Refractionation of the organic phase gave 9 g. (7%) of 2-ethylidenecyclopentanone; b.p. 72–24° (18 mm.), $n^{20}\text{D}$ 1.4870, d^{20}_{4} 0.9834; *MR* calculated 31.87, found 32.21. This ketone darkened rapidly and absorbed oxygen from the air so that no satisfactory analysis could be obtained. The semicarbazone, m.p. 219–220° (from dioxane), was prepared and found to be stable.

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[8] J. Cologne and K. Mostafavi, *Bull. soc. chim.*, [5] **6**, 335 (1939).

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[10] W. S. Rapson and R. Robinson, *J. Chem. Soc.*, 1287 (1935).

[11] M. P. Balfe and J. Kenyon, *Nature*, **148**, 196 (1941).

[12] W. E. Doering and H. H. Zeiss, THIS JOURNAL, **72**, 149 (1950).

[13] A. Domleo and J. Kenyon, *J. Chem. Soc.*, 1841 (1926).

[14] J. Kenyon, H. W. J. Hills and H. Phillips, *J. Soc. Chem. Ind.*, **52**, 660 (1933).

[15] M. P. Balfe, H. W. J. Hills, J. Kenyon, H. Phillips and B. C. Platt, *J. Chem. Soc.*, 556 (1942).

[16] All m.ps. and b.ps. are corrected.

[17] G. A. Kon, *J. Chem. Soc.*, 1801 (1926).

[18] A. Knorr and A. Weissenborn, U. S. Patent 1,714,378 (1929); *C. A.*, **23**, 3477 (1929).

Anal. Calcd. for $C_8H_{13}ON_3$: C, 57.40; H, 7.84. Found: C, 57.10; H, 7.95.

Lithium Aluminum Hydride Reduction. The unsaturated ketones were all reduced by lithium aluminum hydride in dry ether. An ether solution of the ketone was gradually added to a solution of a slight excess of lithium aluminum hydride at such a rate as to maintain gentle reflux. Fifteen minutes after the addition was complete the mixture was treated with water and then cold 10% sulfuric acid. The ether layer was separated, combined with ether extracts of the acid layer, washed with sodium bicarbonate, dried and distilled. Since the crude product contained up to 20% of unchanged ketone it was "re-reduced" in the same manner (using lithium aluminum hydride in excess) before final purification by fractionation through a 2-ft. Podbielniak type column.

Unless the unchanged ketone was removed in this way to the point where the ultraviolet absorption at 239 mμ was negligible it was found impossible to obtain correct analytical values. The carbon content was apparently lowered by the absorption of oxygen and color developed rapidly in such samples.

1-Cyclohexenylmethylcarbinol was obtained as above in 88% yield, b.p. 87–88° (14 mm.), n^{25}D 1.4827, d^{25}_4 0.9486. The characteristic ultraviolet absorption of 1-acetylcyclohexene (233 mμ) was absent.

Anal. Calcd. for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.08; H, 11.18.

The 3,5-dinitrobenzoate was prepared in pyridine–benzene at room temperature (2 to 7 days) and recrystallized from absolute ethanol, m.p. 58–59°.

Anal. Calcd. for $C_{15}H_{16}O_6N_2$: C, 56.24; H, 5.04; N, 8.75. Found: C, 56.45; H, 5.26; N, 8.58.

From a year-old sample of pure cyclohexenylmethylcarbinol there was obtained by fractionation an ether, presumed to be di-(1-cyclohexenylmethylcarbinyl) ether, b.p. 125° (6 mm.), n^{25}D 1.4900.

Anal. Calcd. for $C_{16}H_{26}O$: C, 82.0; H, 11.2. Found: C, 81.8; H, 11.4.

1-Cyclopentenylmethylcarbinol was obtained as above in 60–80% yields: b.p. 79° (30 mm.), n^{25}D 1.4715, d^{25}_4 0.9418; *MR* calculated 33.38, found 33.32. The characteristic ultraviolet absorption of the starting ketone (239 mμ) was absent.

Anal. Calcd. for $C_7H_{12}O$: C, 74.88; H, 10.79. Found: C, 74.63; H, 10.90.

The 3,5-dinitrobenzoate was prepared at room temperature, m.p. 79–79.5° (from absolute ethanol).

Anal. Calcd. for $C_{14}H_{14}O_6N_2$: C, 54.90; H, 4.60; N, 9.15. Found: C, 55.09; H, 4.55; N, 9.09.

This ester gave no depression in m.p. with that prepared from a sample of 1-cyclopentenylmethylcarbinol from the reaction of 1-cyclopentenealdehyde with methylmagnesium iodide.

From a year-old sample of the pure carbinol which had become somewhat colored there was isolated by distillation about 30% of an ether, b.p. 120° (11 mm.), n^{25}D 1.4820, presumed to be di-(1-cyclopentenylmethylcarbinyl) ether.

Anal. Calcd. for $C_{14}H_{22}O$: C, 81.49; H, 10.75. Found: C, 81.50; H, 10.83.

2-Ethylidenecyclohexanol was obtained as described above in 55% yield; b.p. 85° (16 mm.), n^{20}D 1.4902, d^{20}_4 0.9594; *MR* calculated 38.00, found 38.04. Due to the small sample it was all converted to the 3,5-dinitrobenzoate, m.p. 75–76°, for analysis.

Anal. Calcd. for $C_{15}H_6O_6N$: C, 56.24; H, 5.04; N, 8.75. Found: C, 56.35; H, 5.48; N, 8.85.

2-Ethylidenecyclopentanol was obtained as described above in 50% yield; b.p. 79° (25 mm.), n^{20}D 1.4807, d^{20}_4 0.9514; *MR* calculated 33.50, found 33.52.

Anal. Calcd. for $C_7H_{12}O$: C, 74.88; H, 10.79. Found: C, 74.33; H, 10.64.

The 3,5-dinitrobenzoate was obtained as needles from absolute ethanol, m.p. 59.5–60.5°, to a cloudy liquid which clears at 64°.

Anal. Calcd. for $C_{14}H_{14}O_6N_2$: C, 54.90; H, 4.61; N, 9.15. Found: C, 55.13; H, 5.15; N, 8.70.

Resolution Procedure.—Both cyclopentenylmethylcarbinol and cyclohexenylmethylcarbinol were resolved by conversion to their acid phthalates in pyridine at room temperature. Under these conditions reaction was rather slow and the reaction mixtures were allowed to stand for 2–4 weeks. The reaction mixtures were decompposed with ice and hydrochloric acid and the phthalates removed by benzene extraction. The sirupy esters obtained on removal of solvent *in vacuo* were ground under cold water until crystallization set in (10–20 minutes).

The *dl*-hydrogen phthalate of cyclohexenylmethylcarbinol, recrystallized from ether–pentane, melted at 90–91°, neutralization equivalent 277 (calculated 274), yield 80%.

The *dl*-hydrogen phthalate of cyclopentenylmethylcarbinol was recrystallized from a mixture of dry ether and pentane, m.p. 78–80°, neutralization equivalent 263 (calculated 260).

(−)-1-Cyclohexenylmethylcarbinol.—Equivalent amounts of the crystalline *dl*-hydrogen phthalate and brucine were mixed with about five times the amount of refluxing dry acetone and brought into solution by gradual addition of chloroform. On cooling, crystals of the brucine salt separated and were recrystallized to a constant rotation, $[\alpha]^{25}$D −29.6°, *c* 3.3 (chloroform), from a mixture of chloroform and acetone. It was found that after one crystallization from chloroform–acetone two or three digestions with refluxing dry acetone sufficed to bring 85% of the levorotatory salt to constant rotation. The salt was decomposed by shaking with 0.3 *N* hydrochloric acid and ether at 0°, washing the ether free of acid, and evaporating the dried solution *in vacuo*. A sirupy phthalate, $[\alpha]^{25}$D +28.7°, *c* 3.0 (chloroform), was obtained which resisted attempts at crystallization. Accordingly, the crude sirup was dissolved in dry ether and added slowly to a 70% excess of lithium aluminum hydride in dry ether. After stirring for 30 minutes ethyl acetate was added to decompose the excess lithium aluminum hydride. Water was then added and stirring continued until all of the alcoholate complex was converted to snow-white precipitate of lithium and aluminum hydroxides. After washing the ether solution first with sodium hydroxide, then with water, and drying over sodium carbonate, the (−)-1-cyclohexenylmethylcarbinol was fractionated. There was obtained 72% (based on the brucine salt) of carbinol: b.p. 87.6° (15.5 mm.), n^{25}D 1.4818, d^{25}_4 0.9498, $[\alpha]^{25}$D −1.48° (homogeneous). The observed rotations α_D, at different temperatures, are given in Table I.

TABLE I

OBSERVED ROTATIONS AT VARIOUS TEMPERATURES

T, °C.	1-Cyclohexenylmethylcarbinol α_D (l = 1)	1-Cyclopentenylmethylcarbinol α_D (l = 1)
11.0	+0.74	
13.4	+ .39	
15.5	+ .01	
16.6	− .15	
20.0	− .66	
25.0	−1.41	− 9.64
30.0	−2.10	− 9.90
40.0	−3.41	−10.40
50.0	−4.65	−10.87
60.0	−5.78	
70.0	−6.82	

On standing for 29 days at room temperature a sample of initial rotation, $[\alpha]^{25.0}$D −1.41° (l = 1), had increased to 1.57°; on redistillation a small higher boiling fraction, b.p. 125° (6 mm.), n^{25}D 1.4868 was obtained and the remainder had properties identical with the original sample.

Bis-ether of *dl*-1-Cyclohexenylmethylcarbinol.—This substance was prepared by treatment of the *dl*-carbinol with a trace of aqueous hydrochloric acid, standing at room temperature for 3–4 days and fractional distillation. The pure ether boils at 125° (6 mm.), n^{25}D 1.4897. A similar experiment with (−)-1-cyclohexenylmethylcarbinol showed a shift in α_D from −1.46° (l = 1) to −6.46° in 73 hours; again on redistillation a higher fraction of ether (n^{25}D 1.4894) was obtained.

Anal. Calcd. for $C_{16}H_{26}O$: C, 82.0; H, 11.2. Found: C, 81.7; H, 11.4.

(+)-Cyclohexylmethylcarbinol.[13]—A solution of 1.073 g. of (−)-1-cyclohexenylmethylcarbinol in 40 cc. of ethanol was reduced with platinum oxide catalyst at room temperature and atmospheric pressure. The hydrogen uptake was 191 cc. (S.T.P.) or 1.01 molar equivalents. Filtration, removal of solvent, and distillation yielded (+)-cyclohexylmethylcarbinol, n^{25}D 1.4631, $[\alpha]^{25}$D +5.36° (homogeneous).

The (−)-1-Cyclopentenylmethylcarbinol.—Equivalent amounts of the *dl*-hydrogen phthalate of 1-cyclopentenylmethylcarbinol and brucine were dissolved in refluxing dry acetone and the hot solutions mixed, filtered and allowed to cool. The resulting crystals of brucine salt together with those obtained by evaporation of the acetone to one-half volume, were recrystallized from acetone to constant rotation. The pure brucine salt melts at 154–155° with decomposition, $[\alpha]^{29.8}$D −31.9°, (*c* 4.3, $CHCl_3$). The salt was decomposed and reduced exactly as described for the cyclohexenyl analog to yield (−)-1-cyclopentenylmethylcarbinol: b.p. 89.2–90.4° (36 mm.), n^{25}D 1.4707, d^{25}_4 0.9438, $[\alpha]^{25}$D −10.21° (homogeneous). The observed rotations at different temperatures are given in Table I.

NEW HAVEN, CONNECTICUT RECEIVED OCTOBER 29, 1951

[CONTRIBUTION FROM THE DIVISION OF AGRICULTURAL BIOCHEMISTRY, UNIVERSITY OF MINNESOTA]

A Reinvestigation of the Preparation of β-Methyl Lactoside[1,2]

BY F. SMITH AND J. W. VAN CLEVE

Pure crystalline β-methyl lactoside has been prepared. Its structure has been proved by oxidation with periodic acid and by methylation followed by hydrolysis and identification of the methylated monosaccharides.

In 1902, Ditmar[3] reported the preparation of crystalline β-methyl lactoside and the corresponding crystalline heptaacetyl β-methyl lactoside but since then there seems to have been no further mention of the preparation of either of these compounds in the crystalline form. It is perhaps of some interest to note that Hudson[4] deduced from the Isorotation Rules and the specific rotation quoted by Ditmar for his acetate that the latter was probably impure.

Pure β-methyl lactoside, prepared as described herein by the interaction of α-acetobromolactose[5] with methanol to give heptaacetyl β-methyl lactoside followed by deacetylation with sodium methoxide according to the method of Zemplén,[6] crystallizes as a monohydrate, m.p. 206°, $[\alpha]^{20}$D +5.6° in water. The specific rotation is in close agreement with that calculated by Hudson[4] from the Isorotation Rules. The m.p., however, is more than thirty degrees higher than that quoted by Ditmar.[3] The structure of the β-methyl lactoside was proved by methylation studies and by periodate oxidation. The crystalline heptamethyl-β-methyl lactoside was hydrolyzed and the resulting methylated cleavage fragments, 2,3,4,6-tetramethyl-D-galactose and 2,3,6-trimethyl-D-glucose, were separated by column chromatography[7,8] using methyl ethyl ketone–water azeotrope as the solvent and identified in the usual way. The heptaacetyl derivative of β-methyl lactoside could not be induced to crystallize either when prepared directly from the α-acetobromolactose or by acetylation of crystalline β-methyl lactoside.

Experimental

Preparation of β-Methyl Lactoside.—Lactose octaacetate (18.0 g.) was converted to acetobromolactose (yield 15.2 g.) by the method of Fischer.[9] To a solution of the acetobromolactose (not recrystallized) in absolute methanol (200 ml.) was added an excess of dry silver carbonate and the mixture was shaken for 16 hours. The solution was treated with a little charcoal, filtered and evaporated under reduced pressure giving heptaacetyl β-methyl lactoside as a sirupy residue which failed to crystallize. It was redissolved in absolute methanol (*ca.* 100 ml.) and a small piece of sodium was added to effect deacetylation.[6] The solution was refluxed for 30 minutes and then allowed to cool. The crude β-methyl lactoside which separated while the reaction mixture was being heated was filtered off and recrystallized from hot 95% ethanol (yield 5.1 g.); $[\alpha]^{26}$D +5.6° in water (*c* 3); m.p. 206°. Ditmar[3] has recorded a melting point of 172° for this substance. His preparation, for which he failed to give a specific rotation, was evidently impure.

Anal. Calcd. for $C_{12}H_{24}O_{11}\cdot H_2O$: C, 41.7; H, 7.0; $-OCH_3$, 8.3. Found: C, 41.9; H, 6.8; $-OCH_3$, 8.6.

When the monohydrate was heated at 150° *in vacuo* for one hour, 1 molecule of water was lost (tested by weighing) and the product showed $[\alpha]^{23}$D +6.3° in water (*c* 3.5). Hudson[4] has calculated a value of $[\alpha]^{20}$D +6.0° (in water) for β-methyl lactoside.

Oxidation of β-Methyl Lactoside with Periodic Acid.—To a solution of β-methyl lactoside monohydrate (0.0522 g.) in water (150 ml.) was added 20 ml. of 0.1 *N* periodic acid and the mixture was diluted with water to 200 ml. and kept at 5°. After 95 hours titration of an aliquot of the reaction mixture with standard sodium arsenite solution in the usual way[10] showed that 3.1 moles of periodic acid had been consumed per mole of β-methyl lactoside.

Methylation of β-Methyl Lactoside.—β-Methyl lactoside monohydrate (5.0 g.) was methylated with 30% sodium hydroxide and methyl sulfate.[11] After one methylation the crude sirupy product (6.0 g.) was methylated to completion by dissolving it in anhydrous toluene, digesting with metallic sodium and treating the sodio derivative so formed with methyl iodide.[12] After filtering off the sodium iodide from the reaction mixture, concentration of the filtrate gave a sirup which crystallized spontaneously in the flask. Two recrystallizations from boiling petroleum ether gave heptamethyl-β-methyl lactoside in the form of long, colorless needles, m.p. 86–86.5°; $[\alpha]^{19}$D −22.2° in ethanol (*c* = 2.1). Haworth and Leitch[11] who obtained heptamethyl-β-methyl lactoside by direct methylation of lactose followed by fractional distillation of the product, reported a melting point of 77–82° and a specific rotation of $[\alpha]^{20}$D −16.9° in ethanol for this substance.

Anal. Calcd. for $C_{20}H_{38}O_{11}$:. C, 52.9; H, 8.4; $-OCH_3$, 54.6. Found: C, 52.9; H, 8.6; $-OCH_3$, 54.8.

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(1) From a thesis submitted to the graduate faculty of the University of Minnesota in partial fulfilment of the requirements for the degree of Doctor of Philosophy by John W. Van Cleve.

(2) Paper No. 2710, Scientific Journal Series, Minnesota Agricultural Experiment Station.

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