dium borohydride, a solution of N H_2SO_4 was added at such a rate that a pH of 3–4 (test paper) was maintained. An evolution of hydrogen gas occurred throughout a reaction period of 45–60 minutes. Ten minutes after the last addition of the reducing agent, 5 ml. of N H_2SO_4 was added to destroy any remaining hydride. The solution was diluted immediately with 2 volumes of water and passed slowly through columns containing 300 g. each of Amberlite IR-100-H[10] and IR-4-B,[10] respectively. The effluent was concentrated under reduced pressure to *ca.* 50 ml., and 100 ml. of ethanol was added. The solution was again evaporated to 50 ml. and placed in an ice-box overnight. The crystalline mass was filtered and washed with ethanol and with ether; yield 5.94 g., m.p. 191.5–192°, $[\alpha]^{27}\text{D}$ −20° (c 3, water, final). Upon ethanol addition and evaporation a second crop was obtained; yield 3.40 g., m.p. 191–192°, $[\alpha]^{24}\text{D}$ −19° (c 3, water, final); likewise a third crop; yield 0.677 g., m.p. 180–182°, $[\alpha]^{25}\text{D}$ −16° (c 3, water, final); total yield 10.02 g. (66.5%). Recrystallization from methanol afforded pure material; m.p. 191–192°, $[\alpha]^{23}\text{D}$ −20° (c, 3.5, water, final, upward mutarotation) in agreement with those recorded by Fischer[11] for β-D-gluco-D-*gulo*-heptose.

Anal. Calcd. for $C_7H_{14}O_7$: C, 40.00; H, 6.72. Found: C, 40.01; H, 7.08.

Reductions carried out in 95% aqueous methanol solution gave much lower yields than in water while in absolute methanol the reaction was extremely slow or absent.

Reduction of D-Gluco-D-*gulo*-heptono-γ-lactone to *meso*-Gluco-*gulo*-heptitol.—A solution of D-gluco-D-*gulo*-heptono-γ-lactone (15.00 g.) in 30 ml. of water was added dropwise to a mechanically stirred solution of sodium borohydride (3 g.) in 50 ml. of water at room temperature. This was the reverse addition to that for reduction of the lactone to the aldose. The reaction time was 10 minutes. The temperature was not allowed to exceed 50°. A pH of 8 was observed on complete addition of the lactone. After standing for an additional 10 minutes, a few drops of 6 N H_2SO_4 were added until no further evolution of hydrogen gas occurred. The solution was then diluted to 300 ml. with water and passed through columns containing 300 g. each of Amberlite IR-100-H[10] and IR-4-B.[10] The effluent was treated with decolorizing charcoal, filtered and the filtrate was evaporated to a thin sirup under reduced pressure. Ethanol (100 ml.) was added and the volume was again reduced to *ca.* 40 ml., whereupon crystallization occurred. After standing at ice-box temperature overnight, the crystalline mass was filtered and washed with ethanol and ether; yield 9.2 g., m.p. 123–127°. A second crop was obtained on further concentration of the filtrate; yield 1.01 g., m.p. 115–125°; total yield 10.21 g. (67.2%). Recrystallization from methanol gave pure material; m.p. 126.5–128° (accepted value[11] 127–128°).

Anal. Calcd. for $C_7H_{16}O_7$: C, 39.60; H, 7.60. Found: C, 39.61; H, 7.72.

Qualitative Experiments with Other Lactones.—Under the above described conditions for reducing the lactone to the aldose, D-galactono-γ-lactone, D-ribono-γ-lactone and D-manno-D-*gala*-heptono-γ-lactone all gave final reaction mixtures strongly reducing to Benedict solution. From the first there was isolated some dulcitol; yield *ca.* 35%, m.p. 185° (accepted 188.5–189°).

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[10] Resinous Products and Chemical Co., Philadelphia, Pennsylvania.

[11] E. Fischer, *Ann.*, **270**, 64 (1892).

[CONTRIBUTION FROM THE CRYOGENIC LABORATORY AND THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

Structure of Barium Titanate at Elevated Temperatures

BY JAMES W. EDWARDS, RUDOLPH SPEISER AND HERRICK L. JOHNSTON

The crystal structure of barium titanate has been investigated over the temperature range 200 to 1372°. The structure remains cubic perovskite throughout this range. Unit cell dimensions were observed as a function of temperature, and are listed in Table I. The 200° value of a_0 is in close agreement with that obtained by Megaw.[1]

Introduction

$BaTiO_3$ has been shown by Megaw[1] to exist in a tetragonal structure up to 120° and to have the cubic perovskite structure between 120 and 200°. Megaw[2] and other workers[3] have also reported hexagonal modifications.

The object of the present work was to study the structure of $BaTiO_3$ from 200° to near its melting point. A series of X-ray diffraction powder patterns made in the temperature range 200 to 1372° show the perovskite modification to exist over this entire range.

Experimental

The specimen was prepared from a sample of $BaTiO_3$ obtained from Linde Air Products Co., Buffalo, New York. At room temperature, patterns obtained agreed with Megaw's[2] tetragonal polymorph. The material was ground to a fine powder in a mullite mortar then moistened with distilled water to make a thick paste. This paste was forced through 0.020 inch i.d. glass capillary to form a small rod which was subsequently dried in air and fired at 1100° for 3 hours. The rod was then cemented into a platinum specimen holder with a paste made of finely ground $BaTiO_3$ and distilled H_2O. This was finally placed in the high temperature camera.[4] The camera was fitted with platinum furnace elements and was not evacuated during heating and exposure. Copper Kα radiation was used with the value[5] λ 1.537395 Kx.

The temperature of the interior of the furnace was measured with a platinum–platinum–10% rhodium thermocouple, which was calibrated (before mounting) at the freezing points of tin, zinc, aluminum and copper. The metal samples used were standard samples from the National Bureau of Standards. The thermal gradient between specimen and thermocouple hot junction was determined to be less than 10° at the gold point (1063°) by melting a pure gold wire at the specimen position.

Results

TABLE I

Temperature, °C.	Unit cell edge, a_0, Kx.
201	4.0037
401	4.0136
601	4.0239
901	4.0415
1114	4.0539
1301	4.0658
1372	4.0701

Visual examination and intercomparison of

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[1] Helen D. Megaw, *Proc. Roy. Soc. (London)*, **A189**, 261 (1947).

[2] Helen D. Megaw, *ibid.*, **58**, 133 (1946).

[3] H. Blattner, B. Matthias and W. Merz, *Helv. Phys. Acta*, **20**, 225 (1947); R. D. Burbank and H. T. Evans, Jr., *Acta Cryst.*, **1**, 330 (1948).

[4] J. W. Edwards, R. Speiser and H. L. Johnston, *Rev. Sci. Instr.*, **20**, 343 (1949).

[5] See Table I, p. 586 "Internationale Tabellen zur Bestimmung von Kristallstrukturen."

relative line intensities of the diffraction patterns shows that $BaTiO_3$ retains the cubic perovskite structure throughout the temperature range 200 to 1372°. The patterns could be indexed in the cubic system, all lines being accounted for. The unit cell dimensions listed in Table I were determined from the back-reflections using the Bradley–Jay[6] extrapolation method. The value of a_0 at 201° is in close agreement with the value a_0 = 4.0040 ± 0.0005 Kx. at 200° obtained by Megaw.[1] We estimate that the probable error in our values of a_0 amounts to about 0.0003 Kx. unit.

Acknowledgment.—We wish to acknowledge the assistance of the Linde Air Products Co. in support of this investigation.

COLUMBUS, OHIO RECEIVED DECEMBER 22, 1950

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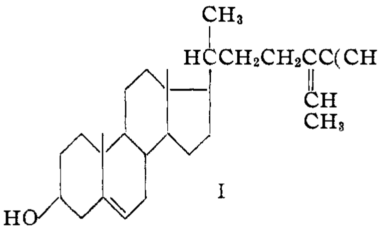
[6] A. J. Bradley and A. H. Jay, *Proc. Phys. Soc.*, **44**, 564 (1932).

NOTES

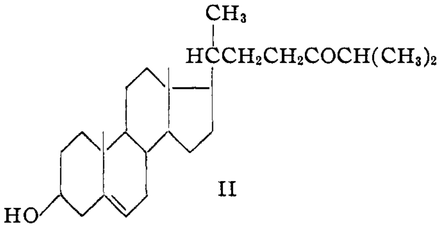
Sterols of Algae. II. The Structure of Fucosterol[1]

BY WERNER BERGMANN AND MARYLIN KLOSTY

During the past years a systematic study of the sterols of algae has been carried out in this Laboratory.[2] In the course of these investigations the structure for fucosterol (I) which has been proposed by MacPhillamy[3] has been substantiated by converting this sterol in a variety of procedures to the known 24-ketocholesterol (II).[4] The report on these observations was anticipated in all its significant features by a recent British publication.[5] The present communication is therefore restricted to those experiments which have not already been described by the British authors.



I



II

It has been found that the conversion of I to II may readily be carried out by way of *i*-fucosteryl methyl ether. The latter was ozonized in a carbon tetrachloride solution, and the ozonide was converted by reduction with zinc in acetic acid followed by a treatment with zinc acetate into the acetate of (II).

Experimental

***i*-Fucosteryl Methyl Ether.**—A solution of 1.1 g. of fucosteryl *p*-toluenesulfonate in 75 ml. of anhydrous methanol and 1.3 g. of freshly fused potassium acetate was refluxed for four hours. The solvent was then removed under reduced pressure, and the residue triturated with water and extracted with ether. The ether extract was washed with a 4% solution of sodium hydroxide and then water until neutral to litmus, dried over anhydrous potassium carbonate and evaporated to dryness under reduced pressure. The residual sirup, 0.8 g. ($[\alpha]_D$ +33°) was dissolved in 10 ml. of hexane and shaken with 2 g. of activated alumina. After filtration and removal of the solvent there remained 0.6 g. of a sirup, $[\alpha]^{23}_D$ +36.1° (*c* 1.0, in chloroform) which failed to yield crystalline material.

24-Ketocholesteryl Acetate.—A stream of oxygen containing 4.5% of ozone was passed at room temperature through a solution of 1 g. of *i*-fucosteryl methyl ether in 30 ml. of carbon tetrachloride for 20 minutes. The solvent was then removed under reduced pressure at room temperature, and the residue was dissolved in 20 ml. of glacial acetic acid. The solution was then stirred vigorously with 1 g. of zinc dust and one drop of a 1% silver nitrate solution for 15 minutes. The zinc dust was removed by centrifugation, and the solution was refluxed for two hours with 1 g. of anhydrous zinc acetate. The mixture was then diluted with water and extracted with ether, and the ether extract was washed free of acetic acid, concentrated and diluted with methanol. A crystalline material appeared which was recrystallized several times from methanol (0.4 g.), m.p. 127–128°; $[\alpha]^{22}_D$ −41.1 (*c* 0.97, in chloroform). The m.p.'s reported for ketocholesteryl acetate are 127–128°; $[\alpha]_D$ −41°,[5] and 124–131°; $[\alpha]_D$ −41°.[4]

Anal. Calcd. for $C_{29}H_{46}O_3$: C, 78.75; H, 10.40. Found: C, 78.53; H, 10.50.

The 2,4-dinitrophenylhydrazone melted at 168–169°; reported[5] m.p. 169–170°.

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[1] Contributions to the Study of Marine Products. XXVII.

[2] Bergmann and Feeney, *J. Org. Chem.*, **15**, 812 (1950).

[3] MacPhillamy, THIS JOURNAL, **64**, 1732 (1942).

[4] Riegel and Kaye, *ibid.*, **66**, 723 (1944).

[5] Hey, Honeyman and Peal, *J. Chem. Soc.*, 2883 (1950).

The Synthesis of 4-Chloromethylthiazole Hydrochloride and β-(4-Thiazolyl)-alanine Hydrochloride[1]

BY WILLIAM T. CALDWELL AND SIDNEY M. FOX[1]

For some time we have been engaged in preparing compounds containing the 4-thiazolylmethyl radical by syntheses which depend upon direct introduction of the latter by means of 4-chloromethylthia-

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[1] Taken from a thesis submitted by Sidney M. Fox in partial fulfillment of the requirements for the M.A. degree in June, 1947.