the arginine synthesis; yield based on cyanamide was 90%, m. p. 126° uncor. (reported[8] m. p. 127–128°, uncor.).

In a control experiment, using no carbonate, no trace of the yellow-green silver precipitate appeared.

(8) Kapfhammer and Müller, *Z. physiol. Chem.*, **225**, 1 (1934).

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Tenulin. II.[1] Anhydrotenulin and Pyrotenulin

BY HERBERT E. UNGNADE,[2] EDWARD C. HENDLEY[3] AND WALTER DUNKEL[4]

Tenulin (I), $C_{17}H_{22}O_5$, loses water when it is heated for a short time at 300°. The dehydration product, anhydrotenulin (II) $C_{17}H_{20}O_4$, has been purified and analyzed by Clark.[5]

Further investigations have shown that (II) has an ultraviolet absorption spectrum identical with that of tenulin and isotenulin[1,5a] (Fig. 1) which is indicative of an α,β-unsaturated carbonyl group. Such a function is confirmed by the infrared spectra of the compounds which show bands at 5.89–5.92 μ[6] (C=O) and 6.37 μ[7] (C=C, conjugated with C=O) (Fig. 2).

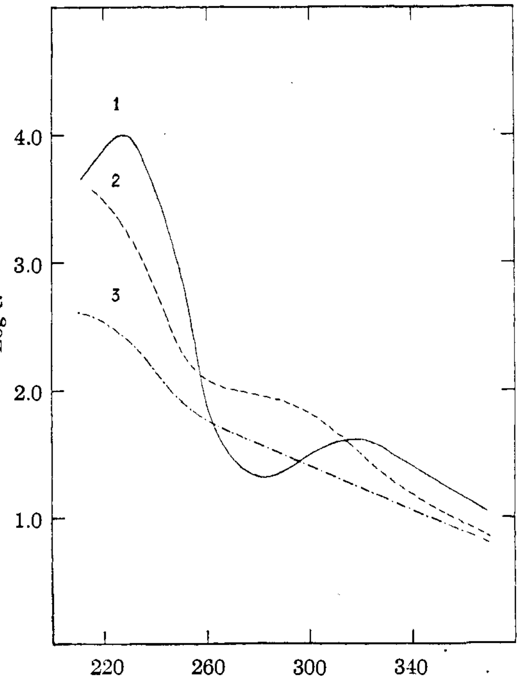

Fig. 1.—Ultraviolet absorption spectra in 95% alcohol: 1, anhydrotenulin (0.000753 mole per liter); 2, pyrotenulin (0.003559 mole per liter); tenulinic acid (0.00263 mole per liter).

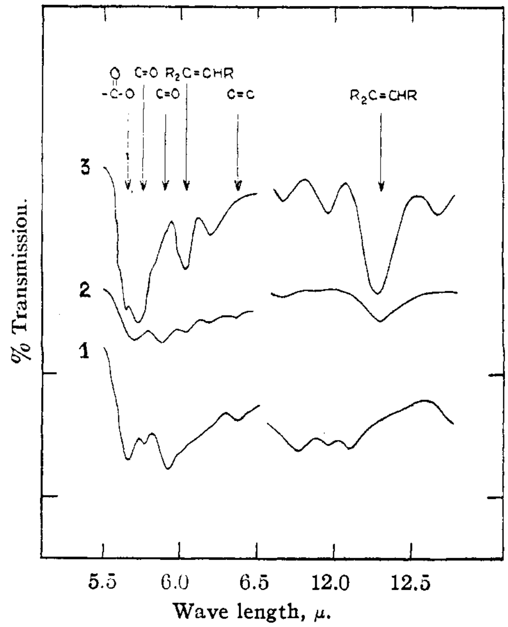

Fig. 2.—Infrared absorption spectra in nujol: 1, tenulin; 2, anhydrotenulin; 3, pyrotenulin.

The oxidation of anhydrotenulin with potassium permanganate yields acetyltenulinic acid ($C_{17}H_{22}O_8$) while hydrogen peroxide oxidation furnishes tenulinic acid in good yields. The same acids are also obtained from tenulin and isotenulin under identical conditions.[8] Since tenulinic acid does not absorb appreciably in the ultraviolet, the α,β-unsaturated carbonyl group is destroyed in these oxidation reactions. The oxidation results with anhydrotenulin are tentatively explained on the basis that the dehydration of tenulin is reversible, *i. e.*, that anhydrotenulin adds a molecule of water during the oxidation.

The infrared spectrum of anhydrotenulin shows new bands at 6.04, 6.20 and 12.30 μ which are regarded as evidence for unsaturation. The bands at 6.04 and 12.3 μ are associated with double bonds of the type $R_2C{=}CHR$.[6b,9]

Anhydrotenulin consumes two moles of alkali on heating with aqueous alcoholic alkali. It contains therefore in addition to the acetoxyl group also the lactone grouping which has been suggested for tenulin.[1]

Strong heating of tenulin causes decomposition beyond simple dehydration. Pyrotenulin (III) $C_{13}H_{16}O_3$[8] can be isolated from the pyrolysis products in 11% yield. Clark's molecular

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[1] Paper I, THIS JOURNAL, **70**, 3921 (1948).

[2] Chemistry Department, New Mexico Highlands University, Las Vegas.

[3] In part from the Ph.D. thesis of E. C. Hendley.

[4] In part from the master's thesis of W. Dunkel.

[5] Clark, THIS JOURNAL, **61**, 1836 (1939).

[5a] Ungnade, *ibid.*, **71**, 4163 (1949).

[6] (a) Cromwell, Miller, Johnson, Frank and Wallace, *ibid.*, **71**, 3339 (1949); (b) Gunthard and Ruzicka, *Helv. Chim. Acta*, **32**, 2130 (1949).

[7] Adams and Herz, THIS JOURNAL, **71**, 2547 (1949).

[8] Clark, *ibid.*, **62**, 598 (1940).

[9] The band at 6.20 μ is thus far unexplained.

formula for this compound has been confirmed. The substance is neutral and consumes only one mole of alkali on heating with alcoholic base. Since the hydrolysis products of pyrotenulin do not contain a volatile acid, the acetoxyl group originally present in tenulin is eliminated in the pyrolysis reaction. The reaction with alkali is ascribed to the lactone grouping which is probably responsible for the absorption band at 5.65–5.70 μ[7,10] occurring in all these compounds.

Pyrotenulin contains a double bond $R_2C{=}CHR$ since its infrared spectrum shows bands at 6.02 and 12.28 μ.[6b] It does not contain an α,β-unsaturated carbonyl group as evidenced by the ultraviolet spectrum and the disappearance of the absorption bands at 5.92 and 6.37 μ. Permanganate oxidation of pyrotenulin yields one mole of volatile acid which has been identified as acetic acid, the unsaturated group may therefore be represented by $R_2C{=}CHCH_3$.

The absorption band at 5.72–5.78 μ is believed to be due to a strained ring carbonyl group[6a,7] in pyrotenulin. While it has not been possible to prepare a pure oxime, pyrotenulin does react with hydroxylamine.

Experimental

All temperatures uncorrected. Analyses by Karl Zilch.

Anhydrotenulin, tenulinic acid, acetyltenulinic acid and pyrotenulin were prepared by the procedures of Clark.[5,8,11]

Anhydrotenulin (II).—Anhydrotenulin (0.1 g., m. p. 171–173°) was saponified by refluxing with 10 cc. of 0.1076 *N* aqueous sodium hydroxide and 20 cc. of ethyl alcohol for one hour in an atmosphere of nitrogen. Titration with 0.1037 *N* hydrochloric acid against phenolphthalein showed a consumption of 1.86 moles of alkali.

Tenulinic Acid.—Anhydrotenulin (0.50 g.) was oxidized with alkaline 30% hydrogen peroxide according to the procedure described for tenulin by Clark.[8] The crystalline acid melting at 338–340° weighed 0.25 g. Further purification gave a constant melting point of 341–343° and a mixed melting point of 341–343° with an authentic sample.

Tenulinic acid was also obtained by permanganate oxidation of anhydrotenulin (0.9 g.), removal of the precipitated manganese dioxide, acidification of the filtrate with sulfuric acid and removal of the volatile acid by steam distillation. The non-volatile residue was extracted with benzene, dried, distilled and crystallized from aqueous methanol; yield 0.108 g.

Anal. Calcd. for $C_{15}H_{20}O_7$: C, 57.68; H, 6.46; mol. wt., 312. Found: C, 57.48; H, 7.02; neut. equiv., 316.

Saponification of tenulinic acid with aqueous alcoholic sodium hydroxide showed the consumption of 1.94 moles of base.

The volatile acid from the steam distillation was titrated with 0.02 *N* sodium hydroxide against phenolphthalein. The amount of base used corresponded to one mole of acid per mole of anhydrotenulin. The neutral solution was evaporated and the residual salt was converted to the anilide which gave a melting point and a mixed melting point of 114° (micro) with authentic acetanilide.[12]

Acetyltenulinic Acid.—Anhydrotenulin (0.7 g.) was oxidized with potassium permanganate as described for tenulin by Clark.[6] The acid melting at 210–214° weighed 290 mg. Further purification gave a product with a constant melting point of 232–234° and a mixed melting point of 232–234° with authentic acetyltenulinic acid.

Pyrotenulin.—Crude pyrotenulin, m. p. 174–194° (dec.), was purified by two successive sublimations at 180° (2 mm.) which raised the melting point of the material to 209° (dec.). The analytically pure substance (from 300 mg. of tenulin) weighed 25 mg. It was soluble in benzene, acetone and chloroform, slightly soluble in methanol and insoluble in water and Skellysolve C.

Anal. Calcd. for $C_{13}H_{16}O_3$: C, 70.88; H, 7.32; mol. wt., 220.25. Found: C, 70.60; H, 7.70; mol. wt. (Rast), 220; sapn. value, 236.

The *p*H of its alcoholic solution was 6.82.

The oxidation of 0.00305 mole of pyrotenulin with aqueous permanganate (1.5 g.) in acetone gave 0.0031 mole of volatile acid as determined by titration of the steam distillate. The anilide of the acid (0.00079 mole) melted at 113° and did not depress the melting point of acetanilide.

Absorption Spectra.—Ultraviolet and infrared absorption spectra were determined by Dr. E. E. Pickett, University of Missouri.

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[10] Rasmussen and Brattain, THIS JOURNAL, **71**, 1076 (1949).

[11] Clark, *ibid.*, **62**, 600 (1940).

[12] The acetic acid was undoubtedly formed in the hydrolysis of acetyltenulinic acid during the steam distillation.

Crystal Structure of Cesium Pentachloromonoaquothallate, $Cs_2TlCl_5H_2O$

BY TOKUNOSUKÉ WATANABÉ AND MASAO ATOJI

As an extension of our research on tervalent thallium complexes, we have investigated the crystal structure of cesium pentachloromonoaquothallate, $Cs_2TlCl_5H_2O$. In the course of the research, two papers, the one on the crystal structure of ammonium pentachloromonoaquoferrate, $(NH_4)_2FeCl_5H_2O$,[1] and the other on ammonium pentachloromonoaquoindate, $(NH_4)_2InCl_5H_2O$,[2] were published. It was found that the crystal structure of cesium pentachloromonoaquothallate is isomorphous with the two crystals mentioned above, and a brief account of our research will be given below.

Crystals of cesium pentachloromonoaquothallate were prepared by slow evaporation from aqueous solutions containing thallic chloride and a large excess of cesium chloride (gravimetric ratio, $CsCl:TlCl_3 = 10:1$). According to Wallace,[3] the crystal belongs to the orthorhombic bipyramidal class with the axial ratios $a':b':c' = 0.9690:1:1.4321$, and its density is 3.879 g./cc. at 20°.

Crystals selected for the present study were 0.8 × 0.8 × 0.4 mm. in dimensions and showed no remarkable cleavage.

Laue, oscillation and powder photographs were taken using Cu-Kα radiation. The identity periods obtained from oscillation photographs around the *a*-, *b*- and *c*-axes were refined by the powder photographic method and are listed in Table I, together with those of the two crystals,

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[1] I. Lindqvist, *Arkiv Kemi, Mineral. Geol.*, **24A**, 1 (1946).

[2] H. P. Klug, E. Kummer and L. Alexander, THIS JOURNAL, **70**, 3064 (1948).

[3] R. C. Wallace, *Z. Krist.*, **49**, 427 (1911).