Am(V) absorption which was accompanied by a rapid growth of the 991 peak (Am(VI)) and Am(III) absorption. Insufficient evidence has been accumulated to establish whether this disproportionation gives Am(IV) in observable amounts.

The authors would like to express appreciation to E. Staritzky for the crystallographic identification and to F. H. Ellinger for the X-ray analysis.

L. B. ASPREY
LOS ALAMOS SCIENTIFIC LABORATORY S. E. STEPHANOU
LOS ALAMOS, N. M. R. A. PENNEMAN

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THE TOTAL SYNTHESIS OF ESTRONE AND THE REMAINING STEREOISOMERS

Sir:

As early as 1935[1] extensive research programs directed toward the total synthesis of the female sex hormone estrone were well under way. These studies have since been continued with increasing interest in laboratories all over the world. In 1942 Bachmann, Kushner and Stevenson[2] succeeded in synthesizing a stereoisomer of the hormone, "estrone a." Using essentially the same synthetic scheme as Bachmann, *et al.*, Anner and Miescher[3] recently were able to isolate additional stereoisomers including *dl*-estrone. Six of the eight possible racemic forms, estrone, a-f, have now been reported.[4]

In the present communication we are reporting a completely new synthesis which has yielded, in addition to the natural product (estrone b), the two remaining stereoisomers g and h. The potassium salt of *m*-methoxyphenylacetylene (prepared from *m*-hydroxyacetophenone) was added to 1,5-decalindione[5] in a 1:1 molecular ratio. The acetylenic bond of the resulting carbinol was hydrogenated over palladium catalyst and the product dehydrated with formic acid. The unsaturated ketone, produced in 70% over-all yield from the diketone, was cyclized with hydrogen chloride and aluminum chloride in benzene, giving an oily mixture from which were crystallized in about equal amounts two stereoisomeric 1-keto-8-methoxy-1,2,3,4,4a,4b,5,6,10b,11,12,12a-dodecahydrochrysenes: α-form, m. p. 168.4–170° (*Anal.* Calcd. for $C_{19}H_{24}O_2$: C, 80.24; H, 8.51. Found: C, 80.60; H, 8.37) and β-form, m. p. 153.4–154.8° (*Anal.* Found: C, 80.11; H, 8.13). The β-isomer gave a benzal derivative,[6] m. p. 152–153.1° (*Anal.* Calcd. for $C_{26}H_{28}O_2$: C, 83.83; H, 7.58. Found: C, 83.49; H, 7.66), which on treatment with potassium *t*-butoxide and methyl iodide afforded two angularly methylated stereoisomers,[6] β^1, m. p. 146.6–147.2° (*Anal.* Calcd. for $C_{27}H_{30}O_2$: C, 83.90; H, 7.82. Found: C, 83.88; H, 7.83) and β^2, m. p. 147.0–147.8° (*Anal.* Found: C, 84.01; H, 7.85). Oxidation of the β^2 benzal derivative[7] with ozone afforded *dl*-homomarianolic acid methyl ether, m. p. 225.2–227.5° (reported,[3] 225–227°), which on heating with lead carbonate yielded *dl*-estrone methyl ether, m. p. 143.2–144.0° (reported,[3] 143–144°). A comparison of the crystals with natural estrone methyl ether[8] indicated that they possess identical form and optical properties. Infrared spectrographic analysis[9] gave identical curves for the two materials. Demethylation with pyridine hydrochloride afforded *dl*-estrone, m. p. 252.8–254.8° (reported,[3] 251–254°), which showed 50% of the activity of U.S.P. estrone in ovariectomized rats.[10] Resolution *via* the *l*-menthoxyacetate gave *d*-estrone *l*-menthoxyacetate, m. p. 132–135°, undepressed on admixture with the ester (m. p. 133.5–135°) prepared from natural estrone.

The β^1 benzal derivative yielded a new stereoisomer, estrone g (presumably *dl* lumiestrone), m. p. 238.5–240° (*Anal.* Calcd. for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20. Found: C, 79.80; H, 8.22); methyl ether, m. p. 109–110° (*Anal.* Calcd. for $C_{19}H_{24}O_2$: C, 80.24; H, 8.51. Found: C, 80.25; H, 8.44). Similar studies in the α-series yielded what is apparently estrone d, m. p. 180.6–181.4° (reported,[4] 184–186°), methyl ether, m. p. 115–116.2° (reported,[4] oil), derived from the homomarrianolic acid methyl ether, m. p. 169.8–170.5° (reported,[4] 170–171°); and the new estrone h, m. p. 197.0–198.1° (*Anal.* Calcd. for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20. Found: C, 80.14; H, 8.19), methyl ether, m. p. 67–68.3° (*Anal.* Calcd. for $C_{19}H_{24}O_2$: C, 80.24; H, 8.51. Found: C, 80.19; H, 8.49).

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(1) See for example, Robinson and Schlittler. *J. Chem. Soc.*, 1288 (1935).

(2) Bachmann, Kushner and Stevenson, THIS JOURNAL, **64**, 974 (1942).

(3) Anner and Miescher, *Experientia*, **4**, 25 (1948); *Helv. Chim. Acta*, **31**, 2173 (1948).

(4) Anner and Miescher, *ibid.*, **32**, 1957 (1949).

(5) Prepared from 1,5-dihydroxynaphthalene by a modification of the method of Hudson and Robinson, *J. Chem. Soc.*, 691 (1942).

(6) *Cf.* Johnson, THIS JOURNAL, **65**, 1317 (1943).

(7) *Cf.* Johnson *ibid.*, **66**, 215 (1944).

(8) The crystallographic examinations were kindly performed by Dr. R. L. Clarke of the Sterling-Winthrop Research Institute.

(9) Kindly carried out by Dr. R. N. Jones of the National Research Council, Canada.

(10) Tests kindly performed by Drs. R. K. Meyer and E. G. Shipley of the Zoology Department, University of Wisconsin.

LABORATORY OF ORGANIC WILLIAM S. JOHNSON
CHEMISTRY D. K. BANERJEE
UNIVERSITY OF WISCONSIN WILLIAM P. SCHNEIDER
MADISON, WISCONSIN C. DAVID GUTSCHE

RECEIVED FEBRUARY 17, 1950

THE DIELECTRIC CONSTANT OF TRIFLUOROACETIC ACID

Sir:

The dielectric constant of trifluoroacetic acid has been found to increase with increasing temperature in the range of −10 to +30°. This appears to be an unusual property for a liquid, as a search of the literature has failed to disclose any other substances showing this property to this extent.

The dielectric cell had cylindrical electrodes of nickel and had a calibration of 61.5 microfarads. The substitution method was employed for the measurements using the No. 1554 Leeds and Northrup shielded capacitance and conductance bridge with a thousand cycle oscillator. The acid was purified by fractional crystallization, and the material had a melting point of −15.25 ± 0.05°. All manipulation of the pure sample was performed in a vacuum system and without contact of waxes and greases. The values obtained with a probable error of 2% are

Temp., °C.		$g_x \times 10^3$ l./ohms
−11	26.2	1.28
− 6.2	27.2	1.38
− 2.3	28.7	1.49
0	29.5	1.55
12.8	36.1	1.68
14.2	36.0	1.72
21.5	40.2	2.03
27.7	43.4	2.33

The third column of the above table gives the determined conductances. The cell constant was approximately 0.007 cm.$^{-1}$. A slightly impure sample of the acid with a higher conductance was measured at 0°. The dielectric constant found was 26.9 and the conductance in the above units 1.69 showing that in the method of making the measurements an increase in conductivity resulted in a lower determined number for the dielectric constant. The same technique was employed using the same bridge and cell with nitrobenzene, and values were obtained which agreed with those recorded in the literature to better than 1%.

THE FLUORINE LABORATORIES
THE PENNSYLVANIA STATE COLLEGE J. H. SIMONS
STATE COLLEGE, PENNSYLVANIA K. E. LORENTZEN

RECEIVED JANUARY 18, 1950

STUDIES ON LIGNIN AND RELATED PRODUCTS. II.[1] 5-CARBOXYVANILLIC ACID IN THE BISULFITE-SOLUBLE FRACTION FROM THE SILVER OXIDE OXIDATION OF FERMENTED SULFITE SPENT LIQUOR[2]

Sir:

In a recent paper on the silver oxide oxidation of basic calcium lignosulfonate[1] the isolation of substantial amounts of a 21% sodium bisulfite-soluble fraction which contained only small percentages of vanillin was noted. The bisulfite-soluble fraction from a similar silver oxide oxidation of a *Torulopsis utilis* fermented sulfite spent liquor has been found to contain at least 50% 5-carboxyvanillic acid.

The light brown crystalline bisulfite-soluble fraction (6.8 g.) was covered with 100 ml. of dry ether, heated to boiling, and filtered. The clear solution was treated with 50 ml. of dioxane and distilled slowly from a water-bath until all the ether was removed. After cooling and standing, the crystals were filtered, washed with cold dioxane, and dried. The yield of almost colorless crystals melting at 276–277° was 2.8 g. Concentration of the combined dioxane filtrate and washings yielded 0.6 g. of similar crystals. Repeated recrystallization from water raised the melting point to 281°. The product was identical with 5-carboxyvanillic acid reported by Freudenberg, Klink, Flickinger and Sobek,[3] who obtained it by partially hydrolyzing either 5-cyanoveratric acid or 5-carboxyveratric acid with hydrochloric acid.

Anal. Calcd. for $C_9H_8O_6$: C, 50.93; H, 3.80; CH_3O, 14.63. Found: C, 50.80; H, 3.88; CH_3O, 14.65.

The synthesis, degradation, derivatives, and significance to the structure of lignin of 5-carboxyvanillic acid will be discussed in forthcoming papers.

(1) For Part I of this series, see THIS JOURNAL, **71**, 2196 (1949).

(2) This paper represents a portion of the results obtained in the research program sponsored by the Sulphite Pulp Manufacturers' Research League and conducted for the League by The Institute of Paper Chemistry. Acknowledgment is made by the Institute for permission on the part of the League to publish these results.

(3) Freudenberg, Klink, Flickinger and Sobek, *Ber.*, **72**, 224 (1939).

THE INSTITUTE OF PAPER CHEMISTRY
APPLETON, WISCONSIN IRWIN A. PEARL

RECEIVED JANUARY 16, 1950

ACID DEGRADATION OF AMYLOPECTIN TO ISOMALTOSE

Sir:

Considerable indirect evidence exists for C6 as the point of branching in amylopectin but it is desirable to place this on a more definitive basis through degradative experiments involving the isolation of crystalline products of known structure. Action of the α- and β-amylases of malt on amylopectin does not yield isomaltose,[1] although levoglucosan is found in the hydrolyzate[2] (on subsequent treatment with the mold enzyme mentioned below). Isomaltose is isolable in crystalline form, and as the crystalline β-D-octaacetate, in the hydrolysis of amylopectin with an enzyme system of mold origin (a Takadiastase type from *Aspergillus oryzae*).[3] We report herein the isolation of isomaltose, as its crystalline β-D-octaacetate, from the acid hydrolyzate of amylopectin. Evidence is cited that this disaccharide is not an acid reversion product.

Following the procedure employed with glycogen,[4] amylopectin (waxy maize starch, 20.0 g.) in 0.4% concentration was hydrolyzed at 100° in 0.08 *N* hydrochloric acid for ten hours (degree of hydrolysis *ca.* 85%). After ion removal with exchange resins (Duolite C-3 and A-4), the amorphous solid obtained on solvent removal was acetylated with hot acetic anhydride and sodium acetate. A portion (5.9 g.) of the resultant sugar acetate mixture (39.0 g.) was chromatographed[5]

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(1) M. L. Wolfrom, L. W. Georges, A. Thompson and I. L. Miller, THIS JOURNAL, **69**, 473 (1947); **71**, 2873 (1949).

(2) Edna M. Montgomery and G. E. Hilbert, *ibid.*, **68**, 916 (1946).

(3) Edna M. Montgomery, F. B. Weakley and G. E. Hilbert, *ibid.*, **69**, 2249 (1947); **71**, 1682 (1949).

(4) M. L. Wolfrom and A. N. O'Neill, *ibid.*, **71**, 3857 (1949).

(5) M. L. Wolfrom, L. W. Georges and I. L. Miller, *ibid.*, **71**, 125 (1949).