138–143° after three recrystallizations from a mixture of benzene and hexane; yield 6.6 g. (27%).

Anal. Calcd. for $C_{11}H_{13}O_4N$: N, 6.27; neut. equiv., 223. Found: N, 6.19; neut. equiv., 213.

The brown oil from the mother liquors solidified on standing. This by reworking with benzene and ligroin gave 4-*t*-butyl-3-nitrobenzoic acid, m.p. 163–164°, neut. equiv. 218 (calcd. 223), whose m.p. was undepressed on admixture of an authentic sample.[5]

2-Amino-4-*t*-butylbenzoic Acid (IV).—A mixture of the above nitro acid III (8 g.), 0.4 g. of platinum oxide catalyst and 150 cc. of absolute alcohol was shaken in an atmosphere of hydrogen until the theoretical amount had been absorbed (45 min.). Two crystallizations of the product from a mixture of alcohol and water gave 4.9 g. (71%) of IV, m.p. 167–168°.

Anal. Calcd. for $C_{11}H_{15}O_2N$: N, 7.25. Found: N, 7.11.

7-*t*-Butyl-2,4-quinazolinedione.—One gram (0.00518 mole) of IV was ground in a mortar with 1.24 g. (0.0207 mole) of urea. The mixture was fused at 140–150° for 3 hours. The cooled mass was dissolved in hot glacial acetic acid. The solution after refrigeration overnight had deposited a crystalline product which was filtered and recrystallized from glacial acetic acid; yield 0.25 g. (22%), m.p. 270–271°. The use of smaller amounts of urea decreased the yield.

Anal. Calcd. for $C_{12}H_{14}O_2N_2$: N, 12.84. Found: N, 12.80.

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(5) C. C. Price and D. C. Lincoln, THIS JOURNAL, **72**, 2807 (1950).

CHEMISTRY DEPARTMENT
UNIVERSITY OF DELAWARE
NEWARK, DELAWARE

Isolation of the Sterols of the White Potato[1,2]

BY JOSEPH J. SCHWARTZ AND MONROE E. WALL

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The sterols of the white potato (*Solanum tuberosum* L.) were investigated at this Laboratory as part of a comprehensive study of potato constituents. Although the steroidal alkaloid solanidine[3] and an unidentified steroidal glycoside[4] have been isolated from potatoes, and Lindemann[5] has reported 3.5% sterols in fat extracted from industrial potato starch, a study of the literature indicated that no information was available on the nature of the free sterols.

A large batch of dried, unpeeled Maine Katahdin potatoes (1950 crop) was extracted with boiling isopropyl alcohol. The unsaponifiable fraction was obtained in the usual manner. Digitonin precipitation yielded an amount of sterols equal to 0.002% of the weight of potatoes on a moisture-free basis. This is close to the value 0.003% calculated from the data of Lindemann.[5] Pyridine cleavage of the digitonides gave 6.7 g. of crude sterol fraction. Conversion to the dinitrobenzoate followed by chromatography on alumina and Florisil[6] removed non-steroidal impurities but accomplished no significant separation of the sterols themselves. Fractional crystallization of the dinitrobenzoates followed by chromatography on silica gel gave two fractions differing about 6° in melting point, of which the higher-melting, less soluble fraction was the minor constituent. Both fractions were hydrolyzed. The major, more soluble, fraction after numerous crystallizations gave β-sitosterol. The sterol was characterized by the melting points and rotations of the free sterol, acetate, benzoate and dinitrobenzoate, which agreed well with literature values. In addition, the infrared spectrum was essentially identical to that given by Dobriner, Katzenellenbogen and Jones.[7]

The minor, less soluble fraction, was identified as stigmasterol. The melting points and rotations of the free sterol and the benzoate were in close agreement with literature values. Further, the infrared spectrum was identical to that of authentic stigmasterol.

Experimental[8]

Isolation of Crude Sterols.—Dried potatoes (276 kg.) containing 8.8% moisture were extracted in 5 batches with a total of 178 gal. of boiling 99% isopropyl alcohol. The residue from the alcohol was saponified with boiling 10% KOH–methanol solution. The mixture was treated in the usual manner, and 46.0 g. of unsaponifiable matter was obtained.

The sterols were isolated by a modification of method F of Sperry.[9] The unsaponifiables, dissolved in 1060 ml. of boiling absolute ethanol, were treated with 21.1 g. of digitonin (Merck) in 716 ml. of 80% ethanol. The mixture was boiled for one minute, 265 ml. of water was added, and the mixture was brought to a boil again. After standing overnight the digitonides were filtered off and washed. They were then treated with pyridine according to the method of Schoenheimer and Dam[10] to obtain the free sterols.

Preparation and Purification of Dinitrobenzoates.—The sterols (6.7 g.) were heated two hours on a steam-bath with an equal weight of 3,5-dinitrobenzoyl chloride and 35 ml. of pyridine. The mixture was treated with 1 ml. of water to decompose excess reagent and cooled. Extraction with ether in the usual manner yielded 9.5 g. of solids.

After chromatography on alumina and Florisil, with little improvement in melting point, the dinitrobenzoates were fractionally crystallized from ethyl acetate, and each fraction was chromatographed on a 1:1 mixture of silica gel–Hyflo Supercel.[6] Finally all the fractions were combined into two main fractions A and B. Fraction A, m.p. 204–215°, was less soluble than the lower melting fraction B, m.p. 202–207°.

Saponification and Purification of Sterols.—Fractions A and B were saponified with 5% KOH in methanol, extracted with ether in the usual manner, and crystallized from 95% ethanol. Each fraction was then digested with two small portions of warm light petroleum ether,[11] which removed waxy, non-steroidal impurities. The insoluble residues (A and B) were crystallized six times from 90% ethanol. Fraction B yielded β-sitosterol, 0.67 g., plates, m.p. 138–138.5°, $[\alpha]_D$ −35° (lit.[12] gives m.p. 136–137°, $[\alpha]_D$ −36.6°).

Anal. Calcd. for $C_{29}H_{50}O$: C, 83.99; H, 12.15. Found: C, 84.14; H, 12.36.

β-Sitosteryl Acetate.—The product was prepared from β-sitosterol in the usual manner by heating with acetic anhydride–pyridine for 1 hour at 90; plates from methanol, m.p. 127–129°, $[\alpha]_D$ −45°. (Lit.[12] gives m.p. 125–126°, $[\alpha]_D$ −41.0°.)

Anal. Calcd. for $C_{31}H_{52}O_2$: C, 81.52; H, 11.48. Found: C, 80.93; H, 11.47.

β-Sitosteryl Benzoate: rectangular plates from acetone,

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[1] Article not copyrighted.

[2] This is paper XXIX in a series on steroids and steroidal sapogenins. Paper XXVIII, M. E. Wall, H. E. Kenney and E. S. Rothman, THIS JOURNAL, **77**, Nov. 5 (1955).

[3] G. R. Clemo, *et al.*, *J. Chem. Soc.*, 1299 (1936).

[4] W. Völksen, *Arch. Pharm.*, **283**, 203 (1950).

[5] E. Lindemann, *Die Stärke*, **3**, 141 (1951).

[6] The mention of commercial products does not imply that they are endorsed or recommended by the Department of Agriculture over others of a similar nature not mentioned

[7] K. Dobriner, *et al.*, "Infrared Absorption Spectra of Steroids, an Atlas," Interscience Publishers, Inc., New York, N. Y., 1953, chart 58.

[8] Melting points were obtained with a Kofler hot-stage. Optical rotations were taken in chloroform at 25°.

[9] W. M. Sperry, *J. Biol. Chem.*, **118**, 377 (1937).

[10] R. Schoenheimer and H. Dam, *Z. physiol. Chem.*, **215**, 59 (1933).

[11] G. Soliman and W. Saleh, *J. Chem. Soc.*, 1506 (1954).

[12] E. S. Wallis and P. N. Chakravorty, *J. Org. Chem.*, **2**, 335 (1937).

m.p. 147–148°, $[\alpha]_D$ −13.3°. (Lit.[12] gives 146–147°, $[\alpha]_D$ −13.8°.)

Anal. Calcd. for $C_{36}H_{54}O_2$: C, 83.34; H, 10.49. Found: C, 83.41; H, 10.43.

β-Sitosteryl 3,5-Dinitrobenzoate: Pale yellow plates from benzene–acetone, m.p. 211–213°, $[\alpha]_D$ −12.4°. (Lit.[12] gives 202–203°, $[\alpha]_D$ −10.4°.)

Anal. Calcd. for $C_{36}H_{52}O_6N_2$: C, 71.02; H, 8.61. Found: C, 71.28; H, 8.70.

Stigmasterol.—Fraction A, after two crystallizations from 95% acetone, was converted to the benzoate with pyridine–benzoyl chloride in the usual manner. After crystallization of the benzoate from acetone–benzene, the product was saponified. The free sterol, 0.05 g., was obtained as plates from 95% ethanol; m.p. 166–168°, $[\alpha]_D$ −46°. (Lit.[13] gives m.p. 168–169°, $[\alpha]_D$ −47.3°.)

Stigmasteryl Benzoate.—Plates from benzene–acetone, m.p. 158–161°, $[\alpha]_D$ −25°. (Lit.[13] gives m.p. 160.5–161.5°, $[\alpha]_D$ −24.5°.)

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[13] A. C. Ott and C. D. Ball, THIS JOURNAL, **66**, 489 (1944).

EASTERN UTILIZATION RESEARCH BRANCH
AGRICULTURAL RESEARCH SERVICE
U.S. DEPARTMENT OF AGRICULTURE
PHILADELPHIA 18, PENNSYLVANIA

The Rate of Pyrolysis of Di-(2-ethylhexyl) Sebacate[1]

BY EARL E. SOMMERS AND THOMAS I. CROWELL

RECEIVED JUNE 8, 1955

The rate of decomposition of liquid di-(2-ethylhexyl) sebacate, a synthetic lubricant, has been determined in the temperature range 261–304°. The results given in this paper supplement and confirm other recent studies of the kinetics and mechanism of ester pyrolysis.[2–4]

The reaction, which produced 2-ethylhexene-1, 2-ethylhexyl hydrogen sebacate and sebacic acid, was followed by titration for acid. Because of the high molar concentration of the pure liquid, decomposition of only 1% of the sample was adequate for a complete eight-sample run. Even in the first few tenths of a per cent. of its course, the reaction showed no induction period and was experimentally zero order, though the calculations were made assuming first-order kinetics. Neither concentrated sulfuric acid (1 mole per cent.) nor polished sheet copper catalyzed the reaction.

A plot of log k *vs.* $1/T$ (Fig. 1) is linear, and leads to an experimental activation energy of 47.1 kcal./mole. This result is comparable with the values 44.1 for cholesteryl acetate,[4] 39.2 for *t*-butyl propionate,[2] 38.1 for menthyl benzoate[3] and 45.8 for *t*-amyl acetate, calculated from the data of Menschutkin.[5] (The last three are vapor-phase decompositions.) The entropy of activation, −3.1 cal./deg.-mole, is compatible with a mechanism involving a cyclic transition state.[4,6]

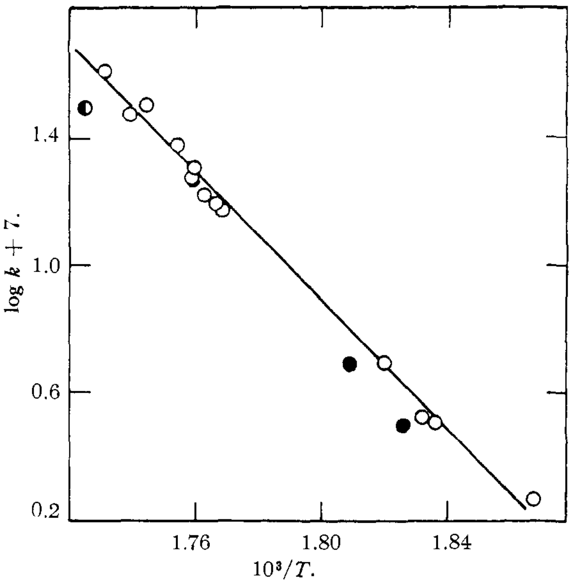

Fig. 1.—Variation of pyrolysis rate with temperature: ◐, Cu added; ●, H_2SO_4 added.

Experimental

Reaction Products.—Commercial diester (98–99%) was heated in a flask at about 300° for 3 hours. The volatile distillate was identified as a branched-chain octene by its physical constants, b.p. 120–121°, d^{20}_4 0.7318, n^{26}_D 1.4120, and assumed to be 2-ethylhexene-1. When the residue in the flask was cooled, sebacic acid precipitated (m.p. after recrystallization from aqueous nitric acid, 133–133.5°; m.p. of N-benzylamide, 165°).

To obtain the monoester, the heating of the diester was carried out for a somewhat shorter time at 280°. The liquid was taken up in ether and extracted with 5% sodium hydroxide. After the extract was washed several times with ether and acidified with dilute hydrochloric acid, an oil separated, which was purified by redissolving in sodium hydroxide and repeating the washing and precipitation. The following analytical data showed the oil to be a fairly pure sample of 2-ethylhexyl hydrogen sebacate: neutral equivalent 93% of theoretical; saponification equivalent 98% of theoretical; calcd. for $C_{18}H_{34}O_4$: C, 68.75; H, 10.90. Found: C, 68.79; H, 10.44.

Kinetics. Method A.—The diester was heated in a 500-ml. flask supplied with a reflux condenser, a magnetic stirrer and a mercury regulator which controlled the Glas-Col heater. Samples were withdrawn by a special pipet. **Method B.**—Sealed Pyrex tubes containing about 1 g. of diester were immersed in a Wood metal thermostat. They were removed at intervals and quenched in cold water before opening.

In both methods, the temperature was observed by means of a Chromel-P Alumel thermel The reference junction was maintained at 0°. The samples were titrated in 95% ethanol with 0.1 M aqueous potassium hydroxide and 1–2 drops of 0.1% phenolphthalein. Duplicate samples were taken in all cases, and except when darkly colored, showed good agreement.

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[1] From the M.S. thesis of Earl E. Sommers, University of Virginia, 1953. This work was done under the financial sponsorship of the Materials Laboratory, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio.

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