oxide (0.15 g.) rapidly took up one equivalent of hydrogen. The product boiled at 166–169° at 19 mm., and crystallized on cooling; m. p. 69–70°.

Anal. Calcd. for $C_{13}H_{18}O$: C, 82.0; H, 9.5. Found: C, 82.0; H, 9.2.

4-Amino-2-cyclohexyl-5-methylphenol.—A cold suspension of cyclohexylcresol (5.7 g.) in aqueous sodium hydroxide was mixed with a solution prepared by diazotizing 6.3 g. of sulfanilic acid. After it had stood for one hour. the mixture was treated with a solution of 14 g. of sodium hydrosulfite and then warmed until reduction was complete. The product was removed by filtration and crystallized from benzene. It formed colorless nodules (4.8 g. 78%) that became pink at 170° and melted to a brown liquid at 182°.

Anal. Calcd. for $C_{13}H_{19}NO$: C, 76.0; H, 9.3. Found: C, 76.3; H, 9.3.

2-Cyclohexyl-5-methylquinone.—A solution of the aminophenol in hot dilute sulfuric acid was poured into a solution of potassium dichromate in water. The mixture was cooled, and the product was separated by filtration (yield nearly quantitative). Crystallized from ethanol, the quinone formed bright yellow plates that melted at 60–61°.

Anal. Calcd. for $C_{13}H_{16}O_2$: C, 76.4; H, 7.9. Found: C, 76.3; H, 7.9.

Reduced with granulated zinc in acetic acid, the quinone yielded **2-methyl-5-cyclohexylhydroquinone,** which formed colorless plates that melted at 146–148°; yield, 95%.

Anal. Calcd. for $C_{13}H_{18}O_2$: C, 75.7; H, 8.8. Found: C, 75.7; H, 8.7.

2-Cyclohexyl-5,8-methano-4a-methyl-4a,5,8,8a-tetrahydro-1,4-naphthoquinone (II).—A solution of 2.6 g. of 2-cyclohexyl-5-methylquinone and 2 g. of cyclopentadiene in 10 ml. of methanol was boiled for one hour and then cooled. The product was separated by filtration and recrystallized from methanol. It formed light yellow needles (3.3 g., 96%) that melted at 75–77°.

Anal. Calcd. for $C_{18}H_{22}O_2$: C, 80.0; H, 8.2. Found: C, 80.1; H, 8.2.

No trimolecular product was formed in the addition; when 1.5 g. of the product and 5 g. of cyclopentadiene were boiled for one hour in xylene, and the solvent was then distilled, there was obtained 0.9 g. of cyclohexylmethylquinone.

Reduction of the addition product with zinc and acetic acid gave a colorless product which separated from methanol in the form of nodules that melted at 71–78°. This substance has not been investigated further.

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Preparation of D-Galacturonic Acid from Pectin*

By E. Rietz and W. D. Maclay

Pectin is composed principally of polymers of D-galacturonic acid and at present constitutes the most readily available source material for the preparation of this compound. Members of the medical profession are displaying considerable interest in the biological properties of not only galacturonic acid but certain of its derivatives. Due to the instability of uronic acids in hot mineral acid, enzymic hydrolysis of pectic acid has proved the most satisfactory method of preparation for galacturonic acid. Ehrlich[1] reported an enzymic method giving high yields. Mottern and Cole,[2] employing the domestically-available materials, pectic acid and "Pectinol 46 AP,"[3] obtained the uronic acid in a yield of approximately 25 per cent. Manville, Reithel and Yamada[4] modified the method of Mottern and Cole to give a maximum yield of 36%. Pigman[5] further modified this method by using methanol in place of ethanol as an extracting solvent and obtained yields in excess of 67% of the weight of the uronic anhydride content of the pectic acid employed as a source material.

The preparation of D-galacturonic acid directly from pectin instead of from pectic acid was undertaken because of the somewhat laborious intermediate preparation of the pectic acid when carried out in the laboratory and the non-uniformity of commercially-available pectic acid. A number of commercial pectins have been used and yields of D-galacturonic acid ranging from 74 to 80%, based on the uronic anhydride content of the pectin, are readily obtainable. Included in these were 285- and 300-grade apple pectins and 170-, 185- and 200-grade citrus pectins with average yields of 78, 78, 80, 78, and 74%, respectively, of the uronic acid.

Experimental

Four 100-g. lots of a 300-grade apple pectin (uronic anhydride content 76.6%) were each dispersed in 2000 ml. of water by means of a Waring Blendor and adjusted to a *p*H of 3.7 by the addition of 20 ml. of 3 *N* sodium hydroxide. The pectin solutions were transferred to 3-liter Erlenmeyer flasks, 10 g. of Pectinol 46 AP was added to each, and the surfaces were covered with toluene. The reaction mixtures were placed in a 30° room for ten days, the course of the hydrolysis being observed by hypoiodite oxidations. Normally, over 50% of the hydrolysis occurs during the first twenty-four hours, and 75 and 95% within three and

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* Not copyrighted.

(1) F. Ehrlich, "Abderhaldens Handbuch der biologischen Arbeitsmethoden," Abt. 1, Teil II, 1617 (1936).

(2) H. H. Mottern and H. L. Cole, This Journal, **61,** 2701 (1939).

(3) Röhm and Haas Pectinol 46 AP, standardized with diatomaceous earth.

(4) I. Manville, F. Reithel and P. Yamada, This Journal, **61,** 2973 (1939).

(5) W. W. Pigman, *J. Research Natl. Bur. Standards,* **25,** 301 (1940).

five days, respectively. The alkali originally added was neutralized with equivalent amounts of sulfuric acid, and the reaction mixtures were filtered, combined, and concentrated *in vacuo* in a water-bath at 50° to a thick sirup. Extraction of the sirup with methanol was carried out according to the directions of Pigman,[5] the extracts being combined and treated with 30 g. of decolorizing carbon. The colorless filtrate was concentrated *in vacuo* on a water-bath at 40° to a thick sirup. Ethanol (25 ml.) was added and the solution was seeded and reconcentrated *in vacuo* at room temperature for eighteen hours or until the mass had become crystallized. The crystalline mass was then triturated with 150 ml. of methanol–ethanol (60/40) and allowed to stand at −30° for twenty-four hours, yielding 248 g. (74%) of the uronic acid monohydrate. The galacturonic acid was of good purity, sintering at 108–110° and exhibiting a specific rotation $[\alpha]^{20}\text{D}$ +50.3° (*c*, 4) in water.

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The Formation of Ergostatetraene-B During the Acetylation of Ergosterol

BY HARRY A. STANSBURY, JR.

It has been frequently observed in this Laboratory that the acetylation of ergosterol by means of boiling acetic anhydride gives an unsatisfactory yield of ergosteryl acetate, and that the physical properties of the crude product indicate the presence of low melting by-product of positive optical rotation. This by-product has now been shown to be a hydrocarbon formed by the dehydration of ergosterol. It is identical with ergostatetraene-B, which had previously been prepared by the action of acetic anhydride[1] or maleic anhydride[2] on ergostatetraene-A, and by the dehydration of ergosterol with *p*-toluenesulfonyl chloride in pyridine.[2]

Experimental

In a typical experiment 200 g. of ergosterol was refluxed for thirty minutes with 2 liters of acetic anhydride. After cooling the crude acetate was filtered, washed with glacial acetic acid and methanol, and recrystallized from ethyl acetate. A total of 160 g. of ergosteryl acetate of m. p. 171° was thus obtained. The mother liquor from this crystallization was concentrated to a small volume, and then diluted with ethanol. Upon cooling, 3.5 g. of fine, colorless needles was obtained which after recrystallization from ether–alcohol showed m. p. 101.5° and $[\alpha]^{25}\text{D}$ +97°. *Anal.* Calcd. for $C_{28}H_{42}$: C, 88.8; H, 11.2. Found: C, 88.7; H, 11.0. When mixed with an authentic sample of ergostatetraene-B, m. p. 101–101.5°; $[\alpha]^{23}\text{D}$ +100°, prepared according to the directions of Stoll,[2] the hydrocarbon showed no depression of the melting point. Fractional recrystallization of the ergosterol used in the present experiments failed to reveal the presence of this hydrocarbon.

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[1] Rhyg, *Z. physiol. Chem.*, **185**, 99 (1929).

[2] Stoll, *ibid.*, **202**, 235 (1931).

Catalytic Degradation of Heptaldehyde in Vapor Phase

BY T. J. SUEN AND SIMONE FAN

In a previous paper[1] the authors reported that when heptaldehyde was hydrogenated with a nickel catalyst at 250° under atmospheric pressure, *n*-hexane was obtained, together with some *n*-heptyl alcohol. In order to ascertain whether the presence of hydrogen is essential for the degradation reaction, heptaldehyde was pyrolyzed over the nickel catalyst without the admixture of hydrogen. The experimental procedure and operating conditions were the same as described previously, except that an additional trap filled with active carbon was inserted between the first trap and the wet gas meter to retain the hydrocarbon vapor uncondensed. It was subsequently stripped with live steam and combined with the other portions of the liquid products.

When analyzing the liquid products, it was found that a considerable amount of unsaturated hydrocarbons was present, and their content was determined in the following manner. Ten ml. of the liquid product fractionated over between 66–70° was shaken with 30 ml. of 96% sulfuric acid for about five minutes in a glass-stoppered buret. After standing, the volume of the oil layer was read. The decrease in volume was considered as the content of the unsaturated hydrocarbons. It was noted that the refractive index of the liquid was lowered by the acid treatment, and this agrees with the assumption that unsaturates were present.[2] The treated and redistilled product gave physical constants essentially the same as those of *n*-hexane.

It was also observed that when no hydrogen was used during the reaction, the catalyst deteriorated quite rapidly. The yield of the degradation products became lower and lower. Unreacted heptaldehyde was also found present in the products, as determined by the bisulfite method.[3]

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[1] Suen and Fan, THIS JOURNAL, **64**, 1460 (1942).

[2] For *n*-hexane, $n^{20}\text{D}$ 1.37506; hexene-1, $n^{20}\text{D}$ 1.3886; hexene-2, $n^{20}\text{D}$ 1.3958; hexene-3, $n^{20}\text{D}$ 1.3942. See Egloff, "Physical Constants of Hydrocarbons," Vol. I, Reinhold Publishing Corp., New York, N. Y., 1939.

[3] Parkinson and Wagner, *Ind. Eng. Chem.*, *Anal. Ed.*, **6**, 433 (1934).