with 2.5–5% hydrochloric or sulfuric acid.[19] It has been shown by O'Dwyer,[20] Schmidt[21] and co-workers, Schwalbe and Feldtmann[22] and others, that hemicelluloses contain uronic acids. A hemicellulose preparation from the maize plant has been obtained that contains *d*-glucuronic acid.[23]

The authors wish to acknowledge their indebtedness to Dr. Allan Dickson for assistance rendered during the course of this work.

Summary

d-Glucuronic and *d*-galacturonic acids are decarboxylated when heated with either hydrochloric or sulfuric acid of concentrations below 5.0%. In the course of the preparation of these acids from their parent polyuronide substances by hydrolytic procedures, an inevitable destruction occurs. This destruction accounts for the low yields that are usually obtained in the course of the preparation of the uronic acids from their natural source materials, and also contributes to an error in the course of the determination of hemicellulose and pectin in plant physiological studies. Besides carbon dioxide, furfuraldehyde and some reversion products, the action of dilute mineral acids produces a furan derivative whose nature has not been determined.

DEPARTMENT OF AGRICULTURAL CHEMISTRY
MADISON, WISCONSIN

[CONTRIBUTION FROM THE INSECTICIDE DIVISION, BUREAU OF CHEMISTRY AND SOILS]

ROTENONE. V. THE IDENTITY OF ISOTUBAIC AND ROTENIC ACIDS

BY H. L. HALLER AND F. B. LAFORGE

RECEIVED FEBRUARY 18, 1930 PUBLISHED JUNE 6, 1930

When an alcoholic potassium hydroxide solution of rotenone is refluxed for several hours, an acid is obtained in a yield of about 5% which represents approximately half of the rotenone molecule and which is known as tubaic acid. Kariyone, Kimura and Kondo[1] have established the empirical formula $C_{12}H_{12}O_4$ for tubaic acid and this formula has been confirmed by Takei.[2]

Tubaic acid possesses the properties of a phenolcarboxylic acid. It shows an acid reaction to litmus and requires 1 mole of alkali for its neu-

---

[19] Report of Committee on Methods, *Plant Physiology*, **2**, 93–95 (1927).

[20] O'Dwyer, *Biochem. J.*, **17**, 501 (1923); **19**, 694 (1925); **20**, 656 (1926).

[21] Schmidt, Meinel and Zintl, *Ber.*, **60**, 503 (1927).

[22] Schwalbe and Feldtmann, *ibid.*, **58**, 1534 (1925).

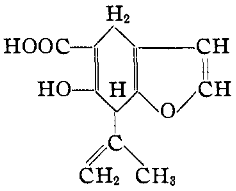
[23] Unpublished data of the senior author to which reference has been made in THIS JOURNAL, **51**, 2506 (1929).

[1] Kariyone, Kimura and Kondo, *J. Pharm. Soc.* (Japan), No. **514**, 1094 (1924); *ibid.*, No. **518**, 377 (1925).

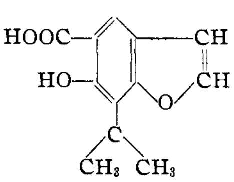
[2] Takei, *Ber.*, **61**, 1003 (1928).

tralization. In alcohol solution it gives a violet color with ferric chloride, and it forms an acetyl derivative. It yields a dimethyl derivative, in which one methyl group is readily saponifiable, and the other is in the form of a methoxyl, replacing the original phenol group. Tubaic acid contains a double bond which is readily reduced with colloidal palladium and hydrogen. It contains no methoxyl group. All attempts to bring the fourth oxygen atom into reaction so far have failed. Tubaic acid yields acetic acid on oxidation in aqueous solution with permanganate, whereas dihydrotubaic acid and rotenic acid, which will be discussed below, yield isobutyric acid.[3]

A tentative structural formula for tubaic acid (I) has been proposed recently by Takei, Koide and Miyajima.[3]



I



II

Tubaic acid is converted by fusion with potassium hydroxide into an isomeric compound known as rotenic acid, for which Takei, Koide and Miyajima have advanced the structural formula II. Rotenic acid can also be prepared by fusing rotenone with solid potassium hydroxide.

According to the Japanese investigators the conversion of tubaic acid into rotenic acid is brought about by a migration of two hydrogen atoms, as a result of which the iso-allyl group is converted into an isopropyl group and a more stable conjugated system is formed.

When rotenone is dissolved in concentrated sulfuric acid and the resulting solution is diluted with water, or when rotenone is boiled with 50% sulfuric acid, an isomer of rotenone is obtained which is known as isorotenone.[2] So far as we know neither Takei nor Butenandt has proposed an explanation of the difference in structure between rotenone and isorotenone. It has been suggested by one of the writers[4] that the iso-allyl group in rotenone has been converted into a trimethylene ring in the formation of isorotenone.

In the course of our investigations on the structure of rotenone we have prepared isotubaic acid by refluxing an alcoholic potassium hydroxide solution of isorotenone and isolating the resulting acid in the same manner that was described for the preparation of tubaic acid.[5] A product melting

---

[3] Takei and Koide, *Bull. Inst. Phys. Chem. Res.*, **8**, No. 6, 64 (1929); also in *Ber.*, **62**, 3030 (1929); Takei and Miyajima, *Bull. Inst. Phys. Chem. Res.*, **8**, No. 6, 61 (1929).

[4] LaForge and Smith, THIS JOURNAL, **51**, 2574 (1929).

[5] Takei, *Biochem. Z.*, **157**, 1 (1925).

at 186° was obtained which in alcoholic solution gave a blue color with ferric chloride. Rotenic acid[5] according to Takei melts at 182° and gives a blue color in alcoholic solution with ferric chloride. We have prepared rotenic acid by the procedure described by Takei and found its melting point to be 182°. The mixed melting point of a mixture of isotubaic acid and rotenic acid was 185°. G. L. Keenan of the Food, Drug and Insecticide Administration, U. S. Department of Agriculture, has determined the optical properties of isotubaic acid and rotenic acid and was unable to find any difference between them. The acetyl derivative of isotubaic acid was prepared and found to melt at 156°. According to Takei,[2] the acetyl derivative of rotenic acid melts at 155°.

Isotubaic acid is also obtained when tubaic acid is refluxed with 50% sulfuric acid.

It is a surprising fact that rotenic acid (isotubaic acid) is obtained from derritol by the alkali fusion process, details of which will be presented in another communication to follow shortly.

Since isotubaic acid and rotenic acid are identical,[6] the change which takes place when rotenone is converted into isorotenone is the same as when rotenic acid is produced from tubaic acid. Accordingly the theory of the mechanism for the transformation of rotenone into isorotenone advanced by one of the writers or the explanation suggested by Takei and Koide for the change taking place in the conversion of tubaic acid into rotenic acid must be altered. The investigation is being continued.

Experimental

Isorotenone.[2]—Ten grams of rotenone was added to a solution of 330 cc. of concentrated sulfuric acid in 600 cc. of water and the mixture was refluxed for eight hours. After standing at room temperature overnight, the solution was filtered, the isorotenone was washed free of sulfuric acid and then recrystallized from alcohol; it melted at 183°. An equal volume of water was added to the alcoholic filtrate and the precipitate was filtered off and dried. It melted at about 100°. It has not yet been identified.

Isotubaic Acid.—Ten grams of isorotenone was added to a solution of 6 g. of potassium hydroxide in 200 cc. of alcohol. The solution was refluxed for three hours, diluted with water and acidified with dilute sulfuric acid. The precipitate was filtered off and extracted with a 5% aqueous solution of sodium carbonate. This solution was acidified with dilute sulfuric acid and the isotubaic acid was filtered off. It may be recrystallized from dilute alcohol solution, dilute acetic acid or from ether–petroleum ether. It melted at 186°. Mixed with rotenic acid it melted at 185°. For analysis it was dried to constant weight at 110°.

Anal. Subs., 0.0632: CO_2, 0.1518; H_2O, 0.0321. Calcd. for $C_{12}H_{12}O_4$: C, 65.42; H, 5.50. Found: C, 65.53; H, 5.68.

Mr. Keenan states, "Isotubaic and rotenic acids were found to be identical in so far as partial optical data (immersion method) could determine. Both substances

---

[6] The identity of isotubaic and rotenic acids is reported by Butenandt [*Ann.*, **477**, 245 (1930)] and by Takei, Koide and Miyajima [*Ber.*, **63**, 508 (1930)] in recent articles which came to our attention after this paper had been prepared for publication.

were rod-like in habit with a minimum index of refraction of 1.445, which may be considered as α for the acids. The other indices of refraction were found to be very high and not measurable by the liquids available."

Rotenic Acid.—Ten grams of rotenone was intimately mixed with 40 g. of powdered potassium hydroxide and heated in an oil-bath to 180–200°. When fusion was completed, the cooled mass was dissolved in water and the solution was acidified with dilute sulfuric acid. The precipitate was filtered off and dissolved in ether; the ether solution was dried over anhydrous sodium sulfate. The ether was removed and the residue was extracted with petroleum ether, from which the rotenic acid separated on cooling. It melted at 182°. A mixture of rotenic acid and isotubaic acid had a melting point of 185°. The optical data as determined by Mr. Keenan of the Food, Drug and Insecticide Administration were the same as for isotubaic acid.

Isotubaic Acid from Tubaic Acid.—One-tenth gram of tubaic acid was added to 5 cc. of 50% sulfuric acid, and the mixture was refluxed for one hour. After cooling, the solution was exactly neutralized with dilute sodium hydroxide and then extracted with ether. After removal of the ether, the acid was recrystallized from ether–petroleum ether. It gave the characteristic blue color of isotubaic acid in alcohol solution with ferric chloride.

Summary

Isotubaic acid was prepared from isorotenone and was found to be identical with rotenic acid.

The change which occurs when rotenone is converted into isorotenone involves the same groupings as when rotenic acid is formed from tubaic acid.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, SYRACUSE UNIVERSITY]

THE OXIDATION OF INOSITE WITH NITRIC ACID

BY OTTO GELORMINI AND NEAL E. ARTZ

RECEIVED FEBRUARY 20, 1930 PUBLISHED JUNE 6, 1930

The object of this investigation was an attempt to clear up the apparently contradictory results obtained by different investigators in the oxidation of inosite with nitric acid. Maquenne[1] oxidized inosite with three to five times its weight of fuming or concentrated nitric acid in an open dish, on a water-bath. He obtained upon evaporating to dryness, a white residue which was washed with absolute alcohol to remove the trace of oxalic acid formed, and then taken up in water and evaporated on the water-bath. The solution immediately began to turn brown, and soon a brown precipitate which he believed to be tetrahydroxyquinone separated. A solution of the oxidized material when treated with barium chloride, gave barium rhodizonate, which he identified by its red color. When the oxidized material, in water solution, was treated with sodium carbonate, a greenish-black powder separated, which he reported as a mixture of the di-sodium salts of tetrahydroxyquinone and rhodizonic acid. By acidifying he again

---

[1] Maquenne, *Compt. rend.*, **104**, 298 (1886).