

In a 2-3% solution with mercury light, specific rotations of -14.5 to -15.0° were found for *l*-epicatechin pentacetate. M. Nierenstein reports -12° for sodium light (concentration not indicated).

The melting points reported by M. Nierenstein and his collaborators³⁰ for the acetates of the so-called *dl*-acacatechin (160°), *d*-gambircatechin (137°), *dl*-gambircatechin (156°) do not correspond to those for our pure substances. The acetates of *dl*-epicatechin, *d*-catechin and *dl*-catechin melt at 169° , $131-132^\circ$, $164-165^\circ$, respectively.^{28a}

Summary

1. The catechin present in the cacao bean is shown to be identical with *l*-epicatechin.
2. Recent work of Dr. Nierenstein is criticized.

³⁰ Ref. 5, p. 1504.

MADISON, WISCONSIN, AND HEIDELBERG, GERMANY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE COLLEGE OF THE OZARKS]

THE PREPARATION OF 5,7-DI-IODOISATIN

BY WARD C. SUMPTER AND LAWRENCE AMUNDSEN

RECEIVED OCTOBER 19, 1931

PUBLISHED MAY 7, 1932

The preparation of 5,7-di-iodoisatin has been described by Kalb and Berrer.¹ These investigators treated an aqueous solution of the sodium bisulfite addition compound of dehydroindigo with iodine monochloride. 5,7-Di-iodoisatin was obtained by treating the resulting solution with a solution of potassium dichromate in aqueous sulfuric acid.

The writers attempted to repeat the work of Kalb and Berrer but were able to obtain only very poor yields of the compound by this method. A procedure was then developed for preparing 5,7-di-iodoisatin from 5,7,5',7'-tetraiodoindigo. The latter compound was oxidized with an aqueous solution of chromic and nitric acids and more satisfactory yields of the di-iodoisatin were obtained.

It has also been stated that 5,7-di-iodoisatin,² as well as a small amount of tetraiodoisatin, is obtained when a solution of isatin in concentrated hydrochloric acid is treated with iodine monochloride. Hill and Sumpter found that this statement³ is in error, 5-iodoisatin being the sole product even when a large excess of iodine monochloride is used.

The writers have further attempted to prepare 5,7-di-iodoisatin by the action of iodine monochloride on isatin and on iodoisatin in methyl alcohol, ethyl alcohol, concentrated sulfuric acid, fuming sulfuric acid and acetic anhydride without success. It appears that iodine cannot be introduced

¹ Kalb and Berrer, *Ber.*, **57**, 2112 (1924).

² German Patent 429,101.

³ Sumpter, Ph.D. Dissertation, Yale University, 1930.

directly into the isatin nucleus in position 7. This is in keeping with the observations of Borsche⁴ and of Kalb and Berrer,¹ who also reported that 5,7-di-iodoisatin could not be obtained by the iodination of isatin.

Experimental Part

5,7,5',7'-Tetraiodoindigo.—This compound was prepared according to the directions given by Kalb and Berrer.⁵ The yields averaged 60% of the theoretical.

5,7-Di-iodoisatin. A. By the Method of Kalb and Berrer.¹—Repeated experiments using 10 g. of the sodium bisulfite addition compound gave yields of 1.7–1.8 g. or about 10% of the theoretical. Kalb and Berrer reported 48% yields.

B. By the Oxidation of Tetraiodoindigo.—Ten grams of tetraiodoindigo was suspended in 20 cc. of water and the mixture heated to boiling. A solution of 8.4 g. of chromic acid in 35 cc. of concentrated nitric acid was slowly added to the mixture and the boiling continued for ten minutes; 100 cc. of water was added to the mixture and the insoluble material filtered off. The residue was digested with 150 cc. of hot 10% sodium hydroxide, the whole diluted to a volume of 1500 cc. by the addition of water, boiled for ten minutes and filtered into an excess of dilute hydrochloric acid. The precipitate of 5,7-di-iodoisatin was filtered off and purified by crystallization from glacial acetic acid. It separated in characteristic red plates, m. p. 261–263°. Kalb and Berrer reported decomposition at 240°. The compound is identical with that which was obtained in poorer yields by the procedure of Kalb and Berrer. The yield was 6.3 g. or 60% of the theoretical.

Anal. Calcd. for $C_8H_3O_2NI_2$: N, 3.50; I, 63.66. Found: N, 3.50, 3.46; I, 62.85.

Oxidation of the di-iodoisatin with 3% hydrogen peroxide in alkaline solution gave 2-amino-3,5-di-iodobenzoic acid (m. p. 230°) as stated by Kalb and Berrer.

Summary

5,7-Di-iodoisatin has been prepared by the action of chromic and nitric acids on 5,7,5',7'-tetraiodoindigo.

CLARKSVILLE, ARKANSAS

⁴ Borsche, Weussman and Fritzsche, *Ber.*, **57**, 1770–1775 (1924).

⁵ Kalb and Berrer, *ibid.*, **57**, 2105 (1924).