Although the melting point of this new aminophenoxathiin (81.5–83°) was different than that of either the known[3] 2-amino (93–95°) or the 4-amino[5] (b.p. 209° (5 mm.)) derivatives and a similar reaction in the related heterocycle dibenzothiophene had given rearrangement,[6] additional evidence of the structure was obtained. The new amine was converted to an iodophenoxathiin (m.p. 70–72°) by diazotization and subsequent reaction with potassium iodide. The iodo compound was shown to be different from either the 2-iodophenoxathiin (m.p. 92–93°) or the 4-iodophenoxathiin (m.p. 42.5–43°) by the method of mixed melting points. The 2-iodophenoxathiin had been prepared from 2-aminophenoxathiin through the diazonium salt. It should be noted that both the 2-amino and 3-amino derivatives can be diazotized only with difficulty and special conditions are necessary. Thus, a longer reaction period with sodium nitrite is required and temperatures in the range of 5–10° must be used.

An attempt was made to prepare the desired 3-aminophenoxathiin by nitration of 2-acetaminophenoxathiin followed by deacetylation, diazotization, deamination and reduction of the resulting nitro compound. However, the identity of the nitration product could not be established since a mixture of products resulted.

Experimental Part

4-Iodophenoxathiin.—4-Phenoxathiinyllithium was prepared in essential accordance with the procedure of Gilman, Van Ess, Willis and Stuckwisch[5] from 0.47 mole of *n*-butyllithium and 60 g. (0.4 mole) of phenoxathiin in 600 ml. of anhydrous ether over a period of 20 hours. At the end of this time, the reaction mixture was cooled in an ice-bath and 126.5 g. (0.5 mole) of powdered iodine added in small portions. When the addition was complete, the reaction mixture was allowed to stir for one-half hour or until Color Test I[7] was negative. The excess iodine was removed with bisulfite; the layers were separated; and the ether layer dried over sodium sulfate. After removal of the ether, the heavy viscous oil was distilled under reduced pressure. There was obtained 35 g. of product boiling at 135–170° (2 mm.). Recrystallization from petroleum ether (b.p. 60–90°) gave 27.2 g. (21%) of pure 4-iodophenoxathiin melting at 42.5–43°.

Anal. Calcd. for $C_{12}H_7OIS$: I, 38.92; S, 9.83. Found: I, 39.41; S, 9.78.

There was also obtained a higher boiling fraction (170–190° (1 mm.)) believed to be a mixture of 4-iodophenoxathiin and 4,6-diiodophenoxathiin but separation could not be accomplished.

3-Aminophenoxathiin.—Sodamide was prepared according to directions of Vaughn, Vogt and Nieuwland[8] from 8.1 g. (0.35 g. atom) of sodium and 0.5 g. of ferric nitrate in 300 ml. of liquid ammonia. To this solution was added 38.5 (0.1 mole) of 4-iodophenoxathiin in 100 cc. of benzene over a 20-minute period. The excess sodamide was decomposed with ammonium chloride and the ammonia removed by evaporation. The crude amine that remained was dissolved in benzene and separated from the inorganic salts by filtration. Dry hydrogen chloride was admitted to the benzene solution to precipitate the amine hydrochloride. Treatment of this solid with ammonium hydroxide gave a dark oil that was purified with carbon in a hot 70% methanol-water mixture. After filtering and cooling, there was obtained 8 g. (31%) of product melting at 81.5–83°. A mixed melting point with 2-aminophenoxathiin was depressed.

Anal. Calcd. for $C_{12}H_9ONS$: S, 14.9. Found: S, 14.7.

3-Acetaminophenoxathiin.—One g. (0.005 mole) of crude 3-aminophenoxathiin in 25 cc. of benzene containing 0.5 g. (0.005 mole) of acetic anhydride was refluxed for three hours. At the end of this time the benzene was removed and the crude oil crystallized from methanol to give 0.3 g. (25%) of 3-acetaminophenoxathiin melting at 181–182.5°.

Anal. Calcd. for $C_{14}H_{11}ON_2S$: S, 12.46. Found: S, 12.85.

3-Iodophenoxathiin.—A mixture of 2 g. (0.009 mole) of 3-aminophenoxathiin, 10 ml. of concentrated sulfuric acid (sp. gr. 1.81) and 200 ml. of water was heated to boiling and allowed to cool slowly to room temperature. The reaction flask was then cooled to 5° and 0.7 g. (0.01 mole) of sodium nitrite in 20 ml. of water added over a ten-minute interval. The temperature of the reaction mixture was held between 5–10° during the addition and for another hour after addition was complete. The diazonium salt was then treated with 0.1 g. of urea followed by the addition of 1.5 g. (0.01 mole) of potassium iodide in 20 ml. of water. The bright red solution was warmed to 70° to ensure completion of the reaction. The resulting mixture was extracted with ether and the extracts washed with 5% sodium bisulfite solution. Removal of the ether gave a brown oil that was crystallized from methanol. There was obtained 0.45 g. (15%) of 3-iodophenoxathiin melting at 70–72°. Mixed melting points with both the 2-iodo- and 4-iodophenoxathiin were depressed.

Anal. Calcd. for $C_{12}H_7OIS$: S, 9.83. Found: S, 10.12.

2-Iodophenoxathiin.—2-Aminophenoxathiin[3] was diazotized in the same manner as described for 3-aminophenoxathiin. Thus, from 3.5 g. (0.016 mole) of the 2-amino compound, 12 ml. of sulfuric acid, 300 ml. of water and 1.2 (0.017 mole) of sodium nitrite, there was obtained 0.55 g. (10.4%) of 2-iodophenoxathiin melting at 92–94° after recrystallization from dilute methanol.

Anal. Calcd. for $C_{12}H_7OIS$: S, 9.83. Found: S, 9.53.

Nitration of 2-Acetaminophenoxathiin.—Nitration of 4 g. (0.016 mole) of 2-acetaminophenoxathiin[3] in 50 ml. of acetic anhydride with 2 ml. of concd. nitric acid (sp. gr. 1.42) at −4° over a 20-minute period gave a crude yellow product which was recrystallized from methanol. There was obtained 0.1 g. of material melting at 174–176.5°. The analytical results indicated that this material might be 2-acetamino-3,8-dinitrophenoxathiin. None of the desired 2-acetamino-3-nitrophenoxathiin could be isolated.

Anal. Calcd. for $C_{14}H_9O_6N_2S$: S, 9.23. Found: S, 9.48.

Nitration of 2-Acetaminophenoxathiin 5-Dioxide.—Attempts to nitrate 2-acetaminophenoxathiin 5-dioxide[3] under a variety of conditions gave only mixtures of products from which no pure material could be isolated.

DEPARTMENT OF CHEMISTRY
XAVIER UNIVERSITY
CINCINNATI, OHIO

---

[5] H. Gilman, J. P. Van Ess, H. B. Willis and C. G. Stuckwisch, THIS JOURNAL, **62**, 2606 (1940).

[6] H. Gilman and J. F. Nobis, *ibid.*, **67**, 1479 (1945).

[7] H. Gilman and F. Schultz, *ibid.*, **47**, 2002 (1925).

[8] T. H. Vaughn, R. R. Vogt and J. A. Nieuwland, *ibid.*, **56**, 2120 (1934).

Crystalline Brucine Salts of Oligogalacturonides[1]

BY ROLLAND M. MCCREADY, ELIZABETH A. MCCOMB AND DALE R. BLACK

RECEIVED JANUARY 22, 1954

During the hydrolysis of polygalacturonic acid with dilute acid or the enzyme polygalacturonase, a series of oligogalacturonic acids is produced. Jermyn and Tomkins, using paper chromatography,[2] tentatively identified galacturonic acid after enzymic hydrolysis. Galacturonic, di-, tri- and tetragalacturonic acids have been obtained in pure form[3-4] and we have succeeded in crystallizing their brucine

---

[1] Presented in part before Division of Carbohydrate Chemistry, 123rd National Meeting of the American Chemical Society, Los Angeles, Calif., March, 1953. Article not copyrighted.

[2] M. A. Jermyn and R. G. Tomkins, *Biochem. J.*, **47**, 437 (1950).

[3] (a) H. J. Phaff and B. S. Luh, *Arch. Biochem. and Biophys.*, **33**, 212 (1951); (b) H. Altermatt and H. Deuel, *Helv. Chim. Acta*, **35**, 1422 (1952); **36**, 340 (1952).

[4] J. K. N. Jones and W. W. Reid, *Chem. and Ind.*, 303 (1953).

salts.[5] The brucine salts are characterized below by analyses and by X-ray diffraction powder photographs. These results offer proof of the crystallinity of these materials.

Experimental

Polygalacturonic acid was hydrolyzed to an extent of 75% with a purified polygalacturonase, and the products were separated by macro paper chromatography with Whatman No. 103[6] or Eaton-Dikeman No. 301 thick filter paper. The chromatographic procedure and methods of crystallization of the salts were previously described.[5] The brucine galacturonate monohydrate was similar to that prepared earlier by Ohle and Berend.[7]

Dibrucine digalacturonate hydrate crystallized from aqueous ethanol solution in plates or spherulitic clusters. Information on the degree of hydration of these crystals is not available. When the wet crystals are dried, they become translucent and crack into fragments. Thus reliable crystallographic data were not obtained from the dry specimens. Upon drying the crystals at 25° and 0.1 mm. *in vacuo* over anhydrous magnesium perchlorate for 24 hours, the salt corresponding to the monohydrate was obtained.

Tribrucine trigalacturonate hydrate crystallized from solution in long slender needles usually arranged in spherulitic clusters. The dried crystals were translucent and showed signs of a change in structure.

The di- and trigalacturonic acids formed macro-crystals as salts of alkaloids such as cinchonine, but not with quinine. Attempts to prepare macrocrystalline oligogalacturonic acids or the sodium, potassium, calcium, strontium, barium, lead, mixed sodium-calcium and mixed sodium-strontium salts, were unsuccessful.

Analyses of the crystalline brucine salts, after drying *in vacuo* at 0.1 mm. at 25° for 24 hours over anhydrous magnesium perchlorate, are presented in Table I. Nitrogen analyses were made by the method of White and Long,[8] anhydrouronic acid contents were measured with a colorimetric method,[9] and rotations were measured using the sodium D line at 2% aqueous concentrations in a 1-decimeter tube at 25°. The nitrogen and anhydrouronic acid analyses compare well with those calculated for monohydrates. The dissolved salts showed no changes in rotation upon standing in solution for 2 minutes to 24 hours. Mutarotation either did not occur under these conditions or was achieved very rapidly; consequently, it is not known whether these oligogalacturonides crystallized in the α- or β-configuration.

TABLE I

ANALYSES OF THE CRYSTALLINE BRUCINE SALTS OF GALACTURONIC AND OLIGOGALACTURONIC ACIDS

Galacturonate monohydrate	Nitrogen, % Found	Nitrogen, % Calcd.	Anhydrouronic acid, % Found	Anhydrouronic acid, % Calcd.	Specific[a] rotation
Brucine	4.58	4.63	29.0	29.1	− 7.5°
Dibrucine di-	4.64	4.77	30.9	30.0	+25
Tribrucine tri-	4.64	4.82	31.7	30.3	+35

[a] $[\alpha]^{25}\text{D}$ (*c* 2% water).

X-Ray diffraction powder photographs were made on the brucine galacturonate monohydrate, dibrucine digalacturonate mononydrate and air-dried tribrucine trigalacturonate hydrate of 15% water content. The results are given in Table II.

The photographs were obtained with CuKα radiation (λ 1.542 Å.). X-Ray diffraction powder photographs not presented here of the dibrucine digalacturonate hydrates showed different spacings for the wet crystals, the air-dried crystals and the monohydrate, thus indicating that definite changes of structure occurred. The tribrucine trigalacturonate hydrate (15% water) was dried to a composition corresponding to a monohydrate, but much of the crystallinity disappeared.

TABLE II

X-RAY DIFFRACTION POWDER DATA

(CuKα; λ = 1.542 Å.)

d_{hkl}	Relative intensity[a]	d_{hkl}	Relative intensity[a]
Brucine galacturonate monohydrate			
14.27	MS	3.97	MS
9.26	VW	3.84	MS
7.72	W	3.75	MW
7.39	W	3.46	MS
6.92	S	3.33	MW
6.53	MS	3.10	MS
6.32	W	2.81	M
6.06	VS	2.72	MW
5.33	MW	2.63	VW
4.91	MW	2.48	W
4.56	M	2.40	W
4.34	M	2.31	W
4.11	M	2.22	W
Dibrucine digalacturonate monohydrate			
9.58	M	4.43	MW
9.05	MS	4.36	MW
8.02	MS	4.20	M
7.56	S	3.93	M
7.35	MW	3.77	MS
6.84	VS	3.65	S
6.19	W	3.51	M
5.98	M	3.36	W
5.81	MS	3.10	D
5.24	M	2.91	VW
5.01	MS	2.80	W
4.65	MS	2.66	VW
Tribrucine trigalacturonate hydrate (15% water)			
12.98	VW	5.16	M
11.47	MW	4.40	W
10.15	MW	4.17	VW
8.99	S	3.97	VW
8.56	MS	3.77	MW
7.57	VS	3.62	S
6.55	MS	3.49	VW
5.67	VW		

[a] VS = very strong, S = strong, MS = medium strong, M = medium, MW = medium weak, W = weak, VW = very weak, D = diffuse.

Acknowledgment.—The authors thank L. M. White and Geraldine Secor for the nitrogen analyses, F. T. Jones for aid in the microscopic identification of some of the salts, and K. J. Palmer for many helpful suggestions.

FRUIT PROCESSING SECTION
WESTERN UTILIZATION RESEARCH BRANCH
U. S. DEPARTMENT OF AGRICULTURE
ALBANY 5, CALIFORNIA

---

[5] R. M. McCready and E. A. McComb, *J. Agric. Food Chem.*, **1**, 1165 (1953).

[6] Mention of manufacturers or of trade names of products or equipment does not imply that they are recommended by the Department of Agriculture over others not mentioned.

[7] H. Ohle and G. Berend, *Ber.*, **58**, 2585 (1925).

[8] L. M. White and M. C. Long, *Anal. Chem.*, **23**, 363 (1951).

[9] E. A. McComb and R. M. McCready, *ibid.* **24**, 1630 (1952).

Addition of Hydrogen Chloride to Propenylbenzene

BY W. R. R. PARK AND GEORGE F WRIGHT

RECEIVED JANUARY 21, 1954

Addition of hydrogen chloride to styrene[1] (I) or to 2-methyl-1-phenyl-1-propene[2] (II) occurs read-

---

[1] J. Schramm, *Ber.*, **26**, 1710 (1893).

[2] R. H. Hall, R. G. Pyke and G. F Wright, THIS JOURNAL, **74**, 1597 (1952).