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] an-

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

hydrouronic 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.

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

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.

corresponding to a monohydrate, but much of the crystallinity disappeared.

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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).

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Addition of Hydrogen Chloride to Propenylbenzene

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

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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).

ily at 0° to give 1-phenyl-1-chloroethane and 2-chloro-2-methyl-1-phenylpropane, respectively. Since the addend thus disposes itself oppositely upon these two alkenes it is of interest to consider the addition rate and disposition of hydrogen chloride to propenylbenzene (III), which is intermediate in type between I and II.

The elements of hydrogen chloride have been added to propenylbenzene previously[3] but, since aluminum chloride was used in the reaction and the products were not completely accounted for (our repetition gave a 66% yield), it is not possible to compare this addition with that of styrene and 2-methyl-1-phenyl-1-propene. Consequently we have imposed an identical condition of reaction (0° and 18 hours) on all three alkenes and find that no addition to propenylbenzene occurs. Only when the system is sealed and allowed to remain at 25° for four days can 43% of the chloride be obtained, the remainder being unchanged propenylbenzene.

In view of the opposite disposition of hydrogen chloride to styrene and 2-methyl-1-phenyl-1-propene we have sought to ascertain whether the chloride from propenylbenzene is a mixture. Like the product reported by Shamshurin ours seems to be 1-chloro-1-phenylpropane. In order to make certain that it is not a mixture we have prepared a Grignard reagent from it and then have treated it with carbon dioxide. This process yields only 2-phenylbutanoic acid, and proves that a detectable amount of 2-chloro-1-phenylpropane is not present. It is necessary to employ this characterization *via* the Grignard reaction because the hydrolytic conditions by which 1-chloro-1-phenylethane and 2-chloro-2-methyl-1-phenylpropane may be converted to the alcohols cause partial dehydrohalogenation of 1-chloro-1-phenylpropane.

Experimental[4]

1-Chloro-1-phenylethane.—A solution of 6.40 g. (0.0615 mole) of styrene (b.p. 48° at 19 mm.) in 50 ml. of anhydrous peroxide-free diethyl ether at 0–1° was saturated with dry hydrogen chloride and then allowed to remain at 0° for 18 hours. Distillation yielded 7.30 g. (84%) of 1-chloro-1-phenylethane, b.p. 74–75° (14 mm.), $n^{20}D$ 1.5273, d^{20}_4 1.058. This halide was characterized by hydrolysis with 1% aqueous sodium hydroxide to an 85% yield of 1-phenylethanol; the crude urethan melts at 104–105° and thus is essentially pure.

Under comparable conditions the yield of 2-chloro-2-methyl-1-phenylpropane from 2-methyl-1-phenyl-1-propene was only 18% (62% after 40 hours) and no detectable amount of 1-chloro-1-phenylpropane was obtained from propenylbenzene during 40 hours.

1-Chloro-1-phenylpropane.—A solution of 23.6 g. (0.20 mole) of the equilibrium mixture (14:86) of *cis*- and *trans*-propenylbenzene (b.p. 59–61° at 14 mm., $n^{20}D$ 1.5494) in 140 ml. of anhydrous peroxide-free ether was saturated at 0° with dry hydrogen chloride and then sealed off. After four days at 25° the solution was distilled. The first fraction, b.p. 54–72° (10 mm.), $n^{20}D$ 1.5409, 13.5 g., represents 57% of impure recovered propenylbenzene. On redistillation, 11.9 g., b.p. 58–62° (11 mm.), $n^{20}D$ 1.5492, m.p. −38 to −34°, was obtained; a mixture melting point with the equilibrium mixture of *cis*- and *trans*-propenylbenzene was now lowered.

The second fraction from distillation of the reaction system boiled at 72–79° (10 mm.), $n^{20}D$ 1.5246, and weighed 13.2 g., and is thought to be a 43% yield of 1-chloro-1-phenylpropane.

2-Phenylbutanoic Acid.—A Grignard reagent was prepared during seven hours from 8.6 g. (0.35 atom) of magnesium, 250 ml. of ether and 11.0 g. (0.071 mole) of the 1-chloro-1-phenylpropane obtained as described above. After this reagent was saturated with carbon dioxide it was hydrolyzed with 200 ml. of 12% hydrochloric acid. After the etherous layer was extracted with alkali and then evaporated, the residue (1.4 g.) was halogen-free.

The chilled alkaline extract was acidified with hydrochloric acid and extracted thrice with 30-ml. portions of ether. The water-washed extract, dried with magnesium sulfate, was distilled, finally at 148–149° (10 mm.), 9.14 g. (78.4%), m.p. 39–42°. Crystallization from petroleum ether raised this m.p. of 2-phenylbutanoic acid to 42.0–43.0°. It was characterized by conversion to its amide (m.p. 83.5–84.8°) in 65% yield.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF TORONTO
TORONTO, CANADA

(3) A. A. Shamshurin, *Trudy Uzbekskogo Gosudarst Univ. Sbornik Rabot Khim.*, **15**, 75 (1939); *C. A.*, **35**, 3984 (1941).

(4) Melting points have been corrected against reliable standards.

The Biosynthesis of Radioactive Senecioic Acid (β-Methylcrotonic Acid) in Particle-free Extracts of Rat Liver[1]

BY JOSEPH L. RABINOWITZ

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During a study of precursors in cholesterol biosynthesis to be published elsewhere,[2] it became apparent that senecioic acid (β-methylcrotonic acid) or closely related substances might be involved. Experiments were undertaken in which 1-C^{14}-acetate was added to aqueous, particle-free extracts of rat liver along with carrier non-radioactive senecioic acid. After incubation, senecioic acid was recovered and found to be radioactive.

The production of senecioic acid by rat liver may well be accounted for as a result of a decarboxylation and dehydration of β-hydroxy-β-methylglutaric acid[2] which has been shown recently to be formed by rat liver. The role of senecioic acid in the biosynthesis of cholesterol is as yet unknown. It has been frequently conjectured that senecioic acid may be a precursor of terpenes.[3–6]

The method of isolation, extraction and preparation of derivatives is described in the Experimental part. The results are presented in Table I.

TABLE I

INCORPORATION OF 1-C^{14}-ACETATE INTO CHOLESTEROL AND SENECIOIC ACID BY AQUEOUS EXTRACTS OF RAT LIVER

	Radioactivity recovered		
Expt.	Senecioic acid, c.p.m./mg. C	Cholesterol, c.p.m./mg. C	Dibromoisovaleric acid, c.p.m./mg. C[b]
1	437	137	473
2	784	238	lost
3[a]	856	112	884
4	234	122	297

[a] No carrier (senecioic acid) during incubation. [b] Corrected for dilution.

Experimental

Aqueous, particle-free extracts (7 ml.) of rat liver[2] were incubated with 1 mg. each of adenosine triphosphate, diphosphorpyridine nucleotide and 1-C^{14} potassium acetate

(1) The radioactive materials were obtained on allocation from the United States Atomic Energy Commission.

(2) J. L. Rabinowitz and S. J. Gurin, *Biol. Chem.*, in press (1954).

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(6) J. Bonner and A. W. Galston, *Botanical Rev.*, **13**, 581 (1947).