138–139°. *Anal.* Calcd. for $C_9H_7NH\cdot SCN$: SCN^-, 30.9. Found: SCN^-, 30.9. Greenish-yellow quinolinium selenocyanate, m. p. 99.5–100.5° (dec.). *Anal.* Calcd. for $C_9H_7NH\cdot SeCN$: Se, 33.6. Found: Se, 33.1.

While sulfur and selenium dissolved in aniline–hydrogen cyanide solutions, no solid was deposited on dilution with dry ether. A water solution of anilinium thiocyanate evaporated to dryness on the steam-bath gave a water-insoluble residue which dissolved in hot absolute alcohol and on recrystallization formed colorless glossy plates; m. p. 152–153°. A mixed melting point with an authentic sample of phenyl thiourea was the same. However, no phenyl selenurea was obtained when a solution of anilinium selenocyanate was evaporated nor when a mixture of aniline, hydrogen cyanide, and selenium in equimolar proportions was heated in a sealed tube for two hours at 100°. Solutions of hydrogen cyanide in ethylenediamine reacted vigorously with sulfur and selenium to give products which were difficult to purify but approximated the formulas for ethylenediammonium thiocyanate and selenocyanate. No tellurocyanates were isolated. A very small amount of tellurium dissolved in each of the onium cyanide solutions but separated again as these solutions were diluted with ether.

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The Specific Rotation of *l*-Tyrosine

BY WILLIAM H. STEIN, STANFORD MOORE AND MAX BERGMANN

The values for the specific rotation of *l*-tyrosine obtained in different laboratories show considerable variation. For example, in 4% hydrochloric acid, Schulze and Winterstein[1,2] reported $[\alpha]^{16}D = -16.1°$ and $-16.2°$, Fischer[3] $[\alpha]^{20}D = -13.2°$, Bergmann and Zervas[4] $[\alpha]^{22}D = -12.44°$, and Dudley[5] $[\alpha]D = -11.6°$.

We have had occasion to prepare tyrosine by the following procedures: (a) digestion of casein by pancreatin; (b) hydrolysis of silk fibroin with concentrated hydrochloric acid; (c) recrystallization of a commercial sample of *l*-tyrosine employing hydrochloric acid and ammonium acetate; (d) repeated recrystallization of *l*-tyrosine 4-nitrotoluene-2-sulfonate[6] and regeneration of the amino acid; (e) repeated recrystallization of *l*-tyrosine 3-carboxy-4-hydroxyazobenzene sulfonate[7] and regeneration of the amino acid; (f) resolution of synthetic benzoyl-*dl*-tyrosine[8] and subsequent hydrolysis in the manner described by Fischer.[3] The six samples possessed the same specific rotation, $[\alpha]^{26}D = -10.3° \pm 0.2°$ ($C = 5.00$; 4% HCl). This indicates that the observed rotation is that of pure *l*-tyrosine.

The rotation, −10.3°, was determined at the relatively high temperature of 26°. Consequently the specific rotation of our samples was also determined at lower temperatures. The results are given in the accompanying table. It will be noted that in 4% hydrochloric acid the rotation varies considerably with temperature, and that this variation is approximately linear over the room temperature range. Minor changes in hydrochloric acid or tyrosine concentration, however, are not significant sources of variation. The specific rotation in 20% hydrochloric acid, for which Fischer[3] reported $[\alpha]^{20}D$ −8.64°, is similarly sensitive to temperature. The value of the specific rotation of tyrosine is a function, therefore, not only of the purity of the sample, but also of the adequacy of the temperature control.

TABLE I

Tyrosine concn., %	HCl concn., %	Temp., °C.	$[\alpha]D$
5	4	26 ± 0.3	10.3 ± 0.2
5	4	20 ± .3	11.8 ± .2
5	4	16 ± .3	13.0 ± .2
4	20	26 ± .3	7.0 ± .2
4	20	20 ± .3	8.5 ± .2
4	20	16 ± .3	9.6 ± .2

In connection with these findings, it may be noted that Fischer[3] reported $[\alpha]^{20}D$ −12.56° for a sample of tyrosine prepared from casein after hydrolysis with 20% hydrochloric acid. This value was slightly lower than the specific rotation, $[\alpha]^{20}D$ −13.2°, observed by Fischer for his synthetic *l*-tyrosine. Fischer attributed this difference to the presence of inactive tyrosine in the sample obtained from casein. In view of the sensitivity of the specific rotation of tyrosine to changes in temperature, however, the question

(1) E. Schulze and E. Winterstein, *Z. physiol. Chem.*, **35**, 299 (1902).
(2) E. Schulze and E. Winterstein, *ibid.*, **45**, 79 (1905).
(3) E. Fischer, *Ber. chem. Ges.*, **32**, 3638 (1900).
(4) M. Bergmann and L. Zervas, *Biochem. Z.*, **203**, 280 (1928).
(5) W. H. Dudley and H. E. Woodman, *Biochem. J.*, **9**, 97 (1915).
(6) D. G. Doherty, W. H. Stein and M. Bergmann, *J. Biol. Chem.*, **135**, 487 (1940).
(7) The amino acid salts of carboxyhydroxyazobenzenesulfonic acid will be described in a forthcoming paper.
(8) The benzoyl-*l*-tyrosine obtained as intermediate in this procedure had the same specific rotation as reported by Fischer.

of the racemization by strong acids warrants further investigation.

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An Improved Procedure for the Preparation of Glycine

BY WALTER C. TOBIE AND GILBERT B. AYRES

By modifying the Orten and Hill synthesis of glycine,[1] it is possible to improve their yield of 60–64% of pure glycine to 75–77%.

Method.—Pour a solution of 0.5 mole (47.2 g.) of good-quality monochloroacetic acid in 100 cc. of water into a rapidly swirling four-pound bottle of ammonium hydroxide of sp. gr. 0.9 (1.8 kg. or 30 moles). After twenty-four hours (longer standing is not necessary), evaporate the solution to dryness on a water-bath, preferably under reduced pressure. Dissolve the crust in a minimum amount of warm water, and filter out traces of insoluble material. With the aid of vacuum, dry the material as thoroughly as possible in a 2-liter round-bottom flask on a water-bath. Dissolve out the ammonium chloride by refluxing with 1 liter of methanol on a water-bath for about four hours. After cooling to room temperature, filter with suction on a 7-cm. Büchner. Place the glycine (about 36 g. dry weight) in a 500-cc. flask fitted with a condenser, and add just enough water (about 50 cc.) to dissolve the solid completely upon boiling. Discontinue heating and place the flask and condenser under a hood. Slowly add four volumes of methanol (about 200 cc.), keeping the flask swirling. Cool to 30° or less, then suction-filter the material as dry as possible. Repeat the precipitation with the same amounts of water and methanol. Wash the cake with two 50-cc. portions of methanol, allowing it to soak in well before being suctioned off.

When dry, the glycine weighs 28–29 g., 75–77% yield. It contains no chloride and not more than a faint trace of ammonia. Analysis gave 18.54% N (Kjeldahl method), calcd. 18.67%; m. p. 233–236° with decomposition.

Discussion.—Methanol of 99% or more by weight is satisfactory. The yield would probably be slightly reduced if 95% methanol were used. The preliminary removal of ammonium chloride can be done by seven hours of Soxhlet extraction with 500 cc. of methanol on a water-bath at 85°, but 99.5–100% methanol must be used, since even a little water greatly increases the solubility of glycine in warm methanol. The yields are a little lower, about 27–28 g.

However, Soxhlet extraction with 99.5–100% methanol gives excellent results in purifying certain amino acids prepared from the corresponding bromo acids. This is probably due to the fact that ammonium bromide is more soluble in methanol than is ammonium chloride. By treating α-bromo-*n*-butyric acid for twenty-four hours with aqueous ammonia in a 1 to 50 ratio, we obtained a 65% yield of very pure α-amino-*n*-butyric acid by Soxhlet extraction alone, without the necessity of subsequent precipitation from aqueous solution with methanol. An additional 15% of pure amino acid was isolated from the methanol extract through the copper salt.

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(1) Orten and Hill, THIS JOURNAL, **53**, 2797 (1931).

NEW COMPOUNDS

2-Methyl-1,4-naphthoquinone Derivatives

With a view to obtaining derivatives of 2-methyl-1,4-naphthohydroquinone and 2-methyl-1,4-naphthoquinone sufficiently soluble for therapeutic use, the following four compounds were made. The first was not tested for coagulation time, the solution being insufficiently stable. The other three compounds were ineffective at the 12 microgram level in the usual chick assay.

2-Methyl-1,4-naphthohydroquinone Acetate Acid Succinate.—0.5 g. of 2-methyl-1,4-naphthohydroquinone hydrogen succinate[1] was heated on the steam-bath with 3.0 cc. of acetic anhydride for two hours. The mixture was poured into water and left overnight and the product recrystallized twice from ether–pentane mixture. The compound forms white aggregates of tiny needles, melting at 129° and dissolving in dilute sodium hydroxide solution.

Anal. Calcd. for $C_{17}H_{16}O_6$: C, 64.54; H, 5.10. Found: C, 64.55; H, 5.32.

2-Methyl-1,4-naphthoquinone-*p*-carboxyphenylhydrazone.—A solution of 1.5 g. of 2-methyl-1,4-naphthoquinone, 100 cc. of 95% alcohol, 3.5 cc. of acetic acid and 1.6 g. of *p*-hydrazinobenzoic acid[2] was refluxed for two hours, allowing most of the alcohol to evaporate. The solid which separated was taken up in potassium carbonate solution, the solution extracted with ether and the aqueous layer

(1) Baltzly and Buck, THIS JOURNAL, **63**, 882 (1941).
(2) Anchel and Schoenheimer, *J. Biol. Chem.*, **114**, 539 (1936).