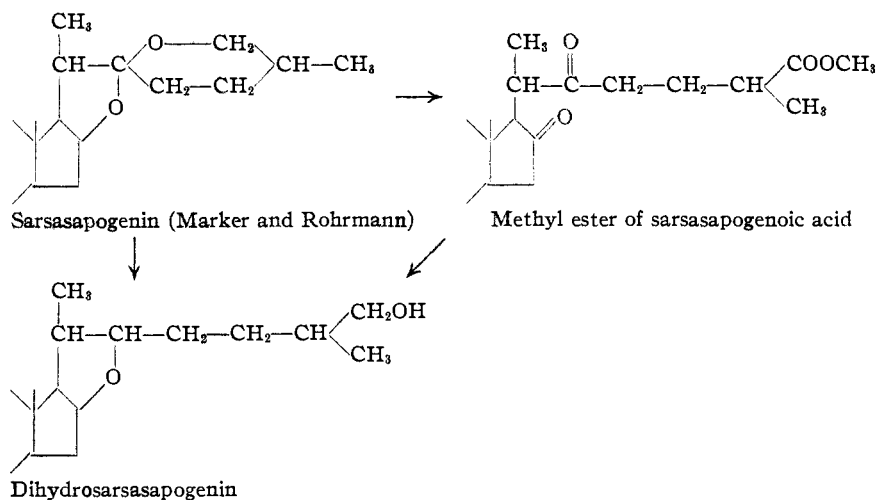


an acid, which after hydrolysis gave a product melting at 187°. According to our structure of the sapsogenin side-chain this acid should be identical with anhydrotetrahydrosarsasapogenoic acid, obtained by Fieser and Jacobsen¹ by the reduction of sarsasapogenoic acid. Although no direct comparisons were made, Fieser, Fry and Jones³ have indicated that the acids prepared by these two methods are different because "their acid (Marker and Rohrmann) is stated to melt at 187° and forms a crystalline methyl ester. Our acid (Fieser and Jacobsen) melts over a characteristi-



cally long range (174–184°) and gives a liquid ester." We have made a direct comparison⁴ of the two acids and their esters and find them to be identical. As additional proof of the identity of the two acids, we have now reduced the methyl ester of sarsasapogenoic acid with sodium and alcohol and have obtained dihydrosarsasapogenin which was identified by mixed melting points with a sample obtained by the catalytic hydrogenation of sarsasapogenin. Their acetates are also identical.

We wish to thank Parke, Davis and Company for their assistance.

Experimental

Methyl Ester of Sarsasapogenoic Acid.—To 4 g. of pure sarsasapogenoic acid in 250 cc. of ether was added a cold ethereal solution of diazomethane in ether. After standing for twenty-four hours at room temperature the solvent was evaporated and the residue was crystallized from methanol as flat plates, m. p. 132–134°.

Anal. Calcd. for $C_{28}H_{44}O_5$: C, 72.9; H, 9.6. Found: C, 72.7; H, 9.8.

(3) Fieser, Fry and Jones, *THIS JOURNAL*, **61**, 1849 (1939).

(4) Marker and Rohrmann, *ibid.*, **61**, 2072 (1939).

Oxime of the Methyl Ester of Sarsasapogenoic Acid.

—A mixture of 1.0 g. of the methyl ester of sarsasapogenoic acid, 0.7 g. of hydroxylamine hydrochloride, 1.0 g. of potassium acetate and 70 cc. of methanol was heated in a bomb tube at 130° for three hours. The solution was diluted with water, extracted with ether and the solvent removed. The residue was crystallized from aqueous methanol as small white needles, m. p. 169–171°.

Anal. Calcd. for $C_{28}H_{46}O_5N_2$: C, 68.5; H, 9.45; N, 5.7. Found: C, 68.6; H, 9.6; N, 5.6.

Reduction of the Methyl Ester of Sarsasapogenoic Acid.

—To a boiling solution of 800 mg. of the methyl ester of sarsasapogenoic acid in 250 cc. of absolute ethanol was added 20 g. of sodium over a period of two hours. The solution was cooled, diluted with water and the precipitated solid was extracted with ether. The ethereal extract was washed with water, evaporated and the residue was crystallized from acetone in needles, m. p. 163–165°. This gave no depression in melting point when mixed with dihydrosarsasapogenin, prepared by the catalytic reduction of sarsasapogenin. A yield of 150 mg. of pure product was obtained.

Anal. Calcd. for $C_{27}H_{46}O_5$: C, 77.4; H, 11.1. Found: C, 77.7; H, 11.2.

When refluxed with acetic anhydride it yielded a diacetate which crystallized from ether-pentane in white prisms, m. p. 116–118°. When mixed with an authentic sample of the diacetate of dihydrosarsasapogenin there was no depression in melting point.

Anal. Calcd. for $C_{31}H_{50}O_5$: C, 74.0; H, 10.0. Found: C, 74.1; H, 10.0.

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On the Structure of Hydrogen Cyanide

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Many arguments have been advanced in support of the hypothesis that hydrogen cyanide is a mixture of tautomers; hydrogen cyanide proper and hydrogen isocyanide. In connection with the recent study of the synthesis of thiocyanates by the reaction of sulfur with organic cyanides,¹ it occurred to us that the presence of any isocyanide might be detected by treatment of ordinary hydrogen cyanide with sulfur, since it was known²

(1) McCrosky, Bergstrom and Waitkins, *THIS JOURNAL*, **62**, 2081 (1940).

(2) *Nef, Ann.*, **270**, 312, 328 (1892); **280**, 296 (1894); **287**, 325 (1895).

that alkyl and aryl isocyanides react to form isothiocyanates, and it would be reasonable to expect this reaction to proceed to completion because the resulting isothiocyanic acid, HNCS, initially formed would rearrange to thiocyanic acid, HSCN, and this in turn would form the degradation polymer, perthiocyanic acid, $H_2C_2N_2S_3$. The following series of experiments were carried out to check this possibility.

To demonstrate that thiocyanic acid would undergo polymerization, solutions of pure, dry thiocyanic acid in toluene³ were heated in sealed tubes at 100–110° and 150–160°. A characteristic orange-red deposit of perthiocyanic acid was observed to form on the walls of each tube.

Sealed glass tubes containing 4–5 cc. of hydrogen cyanide purified by passage over calcium chloride and phosphoric anhydride, and 0.5-g. individual samples of sulfur crystallized twice from carbon disulfide, and of selenium and tellurium, were allowed to stand for two days at room temperature. One cc. of the colorless filtered liquid removed from the tube containing sulfur produced no red coloration with a few drops of 5% ferric nitrate solution, while the same amount of liquid from each of the other tubes deposited no selenium or tellurium when acidified with hydrochloric acid. These experiments were then repeated with the addition of 5 cc. of water to the mixtures remaining in each tube, the tubes being resealed, and allowed to stand as before. Tests on the filtrates again indicated that no reaction had occurred.

Experiments with hydrogen cyanide and sulfur were then repeated at higher temperatures. One tube was heated at 100–120° and the other at 150–160° for one hour. The liquid from each tube was colorless and produced no definite red coloration with ferric nitrate. The sulfur appeared to be unchanged, and that recovered amounted to the original weight within 0.01 g. A mixture of dry toluene, hydrogen cyanide and sulfur treated under the same conditions also indicated no reaction. These experiments demonstrated that no thiocyanic or perthiocyanic acids were formed.

In the second series of experiments, 5 cc. of water was added to each of the two tubes containing hydrogen cyanide and sulfur and these mixtures were heated for one hour, one at 110–120°, and the other at 150–160°. Most of the sulfur was unchanged, but a sample of the colorless

liquid filtered from each tube gave a brilliant red coloration with ferric nitrate. Evaporation of the remaining filtrate gave a small amount of a colorless crystalline material which was identified as ammonium thiocyanate. It would appear that hydrogen cyanide was hydrolyzed in these experiments to form some ammonium formate and cyanide, the latter subsequently reacting with sulfur to produce ammonium thiocyanate.

These results indicate that hydrogen isocyanide cannot be present in pure hydrogen cyanide except in extremely small concentrations over the temperature range of 25 to 160°.

It is, however, well known that cyanide ions readily give rise to complex metalocyanides and are responsible for the cyanhydrin addition of aldehydes and ketones and the addition of hydrogen cyanide to α,β -unsaturated compounds. It is also well-known that in the presence of bases hydrogen cyanide readily polymerizes to form complex materials, while the pure substance can be kept indefinitely without alteration. The enhanced reactivity of hydrogen cyanide under basic conditions (cyanides) was shown by the following experiments.

Hydrogen cyanide prepared from 5 g. of potassium cyanide was bubbled for three hours at room temperature into a mixture of 10 cc. of dry pyridine and 5 g. of sulfur in a 50-cc. Erlenmeyer flask, with stirring and with the exclusion of air. In the first ten minutes most of the sulfur dissolved and this process was accompanied by a temperature rise of nearly thirty degrees. The final product was a clear, pale yellow, sirupy liquid with a little unreacted sulfur. The reaction product was filtered through glass wool and added drop by drop to 100 ml. of anhydrous ether. The colorless crystals which separated were washed with ether until the disappearance of the pyridine odor and were then dried *in vacuo*; m. p. 99.5–101°; yield 2.5–3 g. *Anal.* Calcd. for pyridinium thiocyanate, $C_5H_5NH \cdot SCN$: SCN^- , 42.0. Found: SCN^- , 42.3.

Similar experiments were made using a combination of selenium, hydrogen cyanide, and pyridine, also using combinations of sulfur or selenium with quinoline and hydrogen cyanide. Crystalline compounds isolated from these reaction mixtures were: colorless pyridinium selenocyanate, m. p. 76–78° (dec.). *Anal.* Calcd. for $C_5H_5NH \cdot SeCN$: Se, 42.7. Found: Se, 42.3. Cream colored quinolinium thiocyanate, m. p.

(3) Ruck and Steinmetz, *Z. anorg. Chem.*, **82**, 84 (1912).

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

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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 $[\alpha]^{16D} = -16.1^\circ$ and -16.2° , Fischer³ $[\alpha]^{20D} = -13.2^\circ$, Bergmann and Zervas⁴ $[\alpha]^{22D} = -12.44^\circ$, and Dudley⁵ $[\alpha]_D = -11.6^\circ$.

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-sulfonate⁶ and regeneration of the amino acid; (e) repeated recrystallization of *l*-tyrosine 3-carboxy-4-hydroxyazobenzene sulfonate⁷ and regeneration of the amino acid; (f) resolution of synthetic benzoyl-*dl*-tyrosine⁸ and subsequent hydrolysis in the manner described by Fischer.³ The six samples possessed the same specific rotation, $[\alpha]^{26D} = -10.3^\circ \pm 0.2^\circ$ ($C = 5.00$; 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 Fischer³ reported $[\alpha]^{20D} -8.64^\circ$, 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 Fischer³ reported $[\alpha]^{20D} -12.56^\circ$ for a sample of tyrosine prepared from casein after hydrolysis with 20% hydrochloric acid. This value was slightly lower than the specific rotation, $[\alpha]^{20D} -13.2^\circ$, 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.*, **33**, 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.