give 3.2 g. (0.0158 mole, 87%) of methyl 2-phenylcyclohexyl ketone, m. p. 81–82° (reported, 78–79°,[18] 80–81°[19]).

The 2,4-dinitrophenylhydrazone was prepared according to Shriner and Fuson,[20] m. p. 140–141° (dec.) (reported, 140–141° (dec.)[19]).

2-Phenylcyclohexane-1-carboxylic Acid.—Several attempts to oxidize the methyl 2-phenylcyclohexyl ketone with sodium hypochlorite, sodium hypobromite, sodium hypoiodite, and with chromic acid in acetic acid were unsuccessful. The oxidation was successfully effected by means of alkaline permanganate according to Shriner and Fuson.[21] From 0.50 g. (2.5 mmole.) of the ketone there was obtained 0.15 g. (0.73 mmole., 30%) of crude 2-phenylcyclohexane-1-carboxylic acid, m. p. 98–102°. Crystallization from petroleum ether (b. p. 90–100°) gave an almost colorless product, m. p. 105–107° (reported, 104–105°,[18] 105–107°,[22] 105°[2], (*trans*) 107–108°[23]).

(18) F. S. Kipping and W. H. Perkin, *J. Chem. Soc.*, 304 (1890).

(19) C. D. Gutsche and W. S. Johnson, THIS JOURNAL, **68**, 2239 (1946).

(20) Reference 17, p. 171.

(21) Reference 17, p. 198.

(22) J. W. Cook and C. L. Hewett, *J. Chem. Soc.*, 62 (1936).

(23) C. D. Gutsche, paper presented before the Division of Organic Chemistry of the American Chemical Society in St. Louis, Mo., September, 1948.

BROOKLYN, NEW YORK RECEIVED NOVEMBER 22, 1948

Summary

1-Phenyl-1,3-butadiene has been shown to give *ortho*-substituted cyclohexene derivatives in the diene synthesis with acrylonitrile and methyl vinyl ketone.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF LINGNAN UNIVERSITY]

Chemical Investigation of *Draba nemorosa*, L. The Isolation of Sinapine Iodide

BY H. P. KUNG AND WEI-YUAN HUANG[1]

No chemical work on the Chinese drug, *Draba nemorosa*, L. (Ting Li) has been reported in the literature, although the seed of this plant has been long used in Chinese medicine,[2] and recently has been reported[3] to be effective in the treatment of pleurisy. Chemical work in this Laboratory on this seed has resulted in the isolation of a quaternary ammonium iodide, which degradation and absorption spectra studies indicated to be sinapine iodide, previously isolated from white mustard seed (*Sinapis alba*, L.) and characterized by Gadamer.[4] Since the melting points obtained by Gadamer, however, are generally lower than ours, confirmation was obtained by comparison with authentic sinapine iodide isolated from white mustard seed.

The ultraviolet absorption spectra,[5] here presented in Fig. 1, of sinapine iodide and of sinapic acid show expected similarity with that of *p*-methoxycinnamic acid.[6] The oxidation product of the methyl ether of methyl sinapate was identified as gallic acid trimethyl ether and confirmed by comparison of the spectra.

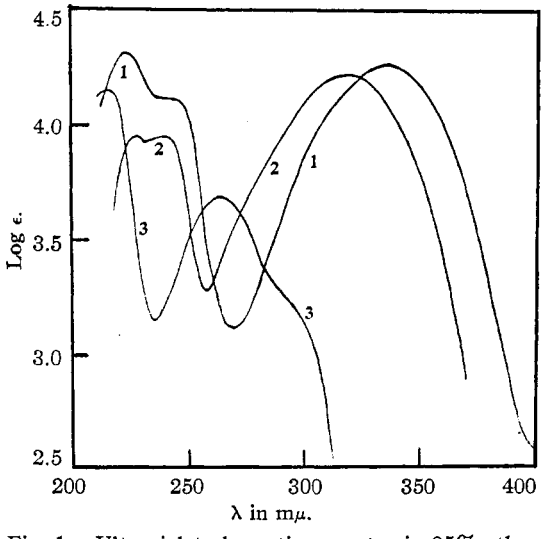


Fig. 1.—Ultraviolet absorption spectra in 95% ethanol of: 1, sinapine iodide; 2, sinapic acid; 3, gallic acid trimethyl ether.

(1) Abbott Laboratories Research Fellow.

(2) Li Shi-Chen, Pan Tsao Kang, Mu. See also Stuart, "Chinese Materia Medica," 1911, p. 155.

(3) Dr. Y. T. Tsang, private communication.

(4) Gadamer, *Arch. Pharm.*, **235**, 44 (1897).

Experimental

Isolation of Sinapine Iodide.—The 95% ethanol (hot) extract of 1 kg. of ground seeds was concentrated and defatted by repeated extraction with ether. A 95% alcoholic solution of the fat free residue after decolorization by activated alumina was concentrated to a sirupy residue, and an equal volume of aqueous (15%) hydriodic acid was added. On standing, sinapine iodide trihydrate separated in clusters of needles. Recrystallization from hot water and drying over calcium chloride yielded 2.2 g. (0.22%) of the anhydrous compound as a white powder, m. p. 186.2–187.4°[7] (Gadamer, 178–179°). Its aqueous solution turned yellow in alkali and gave a deep red color with strong nitric acid.

Anal. Calcd. for $C_{16}H_{24}O_5NI$: C, 43.94; H, 5.56; N, 3.20. Found[8]: C, 43.72; H, 5.59; N, 3.00.

Sinapic Acid.—A mixture of 415 mg. of sinapine iodide, 3.6 g. of potassium hydroxide, and 10 ml. of water was refluxed for fifteen minutes, and distilled into a 1% hydrochloric acid solution in an atmosphere of nitrogen gas. An amine in the distillate was identified as trimethylamine through its picrate (m. p. 215°) and chloroplatinate (m. p. 234° dec.) in mixed melting point determinations with authentic specimens of the corresponding trimethylamine derivatives.

(5) Determined with a Beckman spectrophotometer, model DU.

(6) Landolt-Börnstein, "Physikalish-chemische Tabellen," Erg. III, 1935, p. 1349.

(7) All melting points are corrected, using a Hershberg melting point apparatus.

(8) Microanalyses by Mr. E. F. Shelberg, through the kindness of Abbott Laboratories.

On cooling, the alkaline decomposition residue gave yellow crystals, probably potassium sinapate. The free sinapic acid, resulting on acidification, was recrystallized from acetone, yielding cream-colored crystals (161 mg.), decomposing at 193.6–195.6° (Gadamer 191–192°) with evolution of carbon dioxide.

Anal. Calcd. for $C_{11}H_{12}O_5$: C, 58.92; H, 5.40; 2-(OCH_3), 27.69; neut. equiv., 224.21. Found: C, 58.97; H, 5.48; OCH_3, 26.2; neut. equiv., 214; *pK*, 4.5.

Sinapic acid gives a pink precipitate with ferric chloride and forms a monoacetate, m. p. 198–200° (Gadamer, 181–187°).

Methyl Sinapate Monomethyl Ether.—A suspension of 120 mg. of sinapic acid in 1 ml. of ether was treated with excess diazomethane at a temperature below 10°. The gummy residue obtained on concentration of the ethereal solution was washed several times with small volumes of 1% sodium hydroxide solution, and then with water. Recrystallization from aqueous acetone gave the monomethyl ether of methyl sinapate as colorless prisms (51 mg.), m. p. 96.4–98° (Gadamer, 91–91.5°).

Oxidation of Methyl Sinapate Monomethyl Ether.—Fifty milligrams of methyl sinapate monomethyl ether was treated with saturated potassium permanganate solution on a steam-bath, until the purple color persisted. The oxidation mixture was acidified with hydrochloric acid, and the manganese dioxide was destroyed by sulfur dioxide. The resulting solution was extracted with several 1-ml. portions of ether, and the ethereal extract was evaporated to a gummy residue, which when recrystallized from acetone, produced colorless plates (15 mg.), m. p. 166.4–168.4°. A comparison of this compound with gallic acid trimethyl ether in melting point, neutralization equivalent, absorption spectrum showed identity. Demethylation of the oxidation product yielded a crystalline material which was identified as gallic acid by its melting point, color reactions[9] and absorption spectrum.[10]

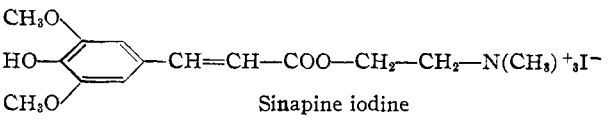
Sinapine Iodide from White Mustard Seed.—Following the same procedure as given above, sinapine iodide was isolated from white mustard seed for comparison with our sample. Identical ultraviolet absorption spectra were obtained from both samples. The melting point of the iodide from mustard seed was 184–186° (Gadamer 178–179°) and on admixture with *Draba* seed iodide gave no depression.

Other components present in the seed of *Draba nemorosa*, L., are being investigated.

We are grateful to the Abbott Laboratories, and to Mr. N. Y. Leung, for grants of equipment in support of this research.

Summary

1. A quaternary ammonium iodide has been isolated from the Chinese drug, *Draba nemorosa*, L., and identified as



Sinapine iodine

2. Ultraviolet absorption spectra of the iodide, of sinapic acid and of gallic acid trimethyl ether are presented.

(9) Huntress and Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, New York, N. Y., 1941, p. 174.

(10) Landolt-Börnstein, "Physikalisch Chemische Tabellen," Erg. III, 1935, p. 1383.

CANTON, CHINA RECEIVED JANUARY 13, 1948

[CONTRIBUTION FROM ELECTROCHEMICALS DEPARTMENT, E. I. DU PONT DE NEMOURS & CO.]

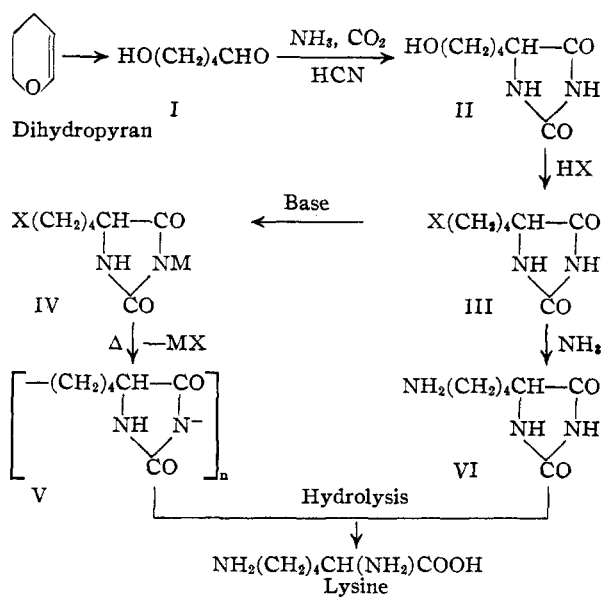
The Synthesis of DL-Lysine from Dihydropyran

BY A. O. ROGERS, R. D. EMMICK, L. W. TYRAN, LILLIAN B. PHILLIPS, A. A. LEVINE AND N. D. SCOTT

During the past three years, a process for the synthesis of *dl*-lysine using dihydropyran as starting material was developed in this Laboratory. A similar synthesis, developed independently, has recently been reported by Gaudry.[1] Since our study differs in several important respects from that of Gaudry, publication of our results appears desirable.

Dihydropyran was prepared and converted to δ-hydroxyvaleraldehyde as described by Paul.[2]

In preparing 5-(4-hydroxybutyl)-hydantoin (II), we omitted any intermediate isolation of δ-hydroxyvaleraldehyde (I) or its cyanhydrin and proceeded directly from the crude aqueous solution of the hydroxyaldehyde (I) to the hydantoin. The conversion of 5-(4-hydroxybutyl)-hydantoin (II) to the corresponding chloro- or bromobutylhydantoin (III) was effected by treatment in the fused state with gaseous hydrogen halide. To avoid thermal decomposition, the melting point of the hydroxybutylhydantoin (II) was depressed by mixing with preformed halobutylhydantoin or



by adding a small quantity of water. When hydrogen chloride was used in this step, the use of

(1) Gaudry, *Can. J. Research*, **26B**, 387 (1948).

(2) Paul, *Bull. Soc. Chim. France*, [4] **53**, 1489 (1933); [5] **1**, 971 (1934).