6.30; Br, 19.20; H_2O, 8.65. Found: C, 52.07; H, 6.24; Br, 18.82, 19.64; H_2O, 8.83.

1-Bromocodeine from 1-Bromocodeinone.—Under similar conditions, 101 mg. of 1-bromocodeinone[5] yielded 101 mg. of crude 1-bromocodeine, m.p. 158–160.5°, which on crystallization from ethyl acetate gave 72 mg. (71%) of pure 1-bromocodeine, m.p. 161–163°, whose mixed m.p. with authentic 1-bromocodeine[6] was undepressed.

Its **methiodide** melted at 262.5–264°[7] with decomposition, and did not depress the melting point of the methiodide obtained from authentic 1-bromocodeine.

Anal. Calcd. for $C_{19}H_{23}NO_3BrI$: C, 43.86; H, 4.46. Found: C, 43.89; H, 4.43.

(5) M. Gates and G. Tschudi, THIS JOURNAL, **74**, 1109 (1952).

(6) E. Speyer and H. Rosenfeld, *Ber.*, **58**, 1110 (1925).

(7) E. Vongerichten, *Ann.*, **297**, 204 (1897), has reported the melting point of this methiodide to be 242–244°.

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4-Alkyldiphenylketimine Hydrochlorides and Related Ketones

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RECEIVED MAY 19, 1953

In connection with another investigation which has since been discontinued, the ultraviolet absorption spectra of a series of 4-alkyldiphenylketimine hydrochlorides and the related ketones were determined. Of the compounds examined, four appear to be new. Ketimines were prepared by the method adopted by Pickard and Vaughan.[1] The hydrochlorides were precipitated from ethereal solution with dry hydrogen chloride, repeatedly recrystallized from chloroform solution and washed well with ether. Of the alkyl-substituted benzophenones, the methyl compound was prepared by the Friedel–Crafts reaction and the others were obtained by hydrolysis of the ketime hydrochlorides with 6 *N* hydrochloric acid. Spectral data were obtained with a Hilger "Uvispek" spectrophotometer and the range covered was 2100–3200 Å. Approximately 1×10^{-4} *M* solutions in methanol were used for all compounds. Absorption curves of the alkylated compounds have the simple shape shown by the parent bodies (*e.g.*, see Culbertson[2]).

TABLE I

	Ketone			Ketimine hydrochloride		
4-Substituent	M.p. or b.p., °C.	$\lambda_{max.}$ (Å.)	$\epsilon_{max.} \times 10^{-4}$	M.p.,[a] °C.	$\lambda_{max.}$ (Å.)	$\epsilon_{max.} \times 10^{-4}$
H	M. 48	2520	1.750	310	2755	1.665
Methyl	M. 58	2590	1.745	244	2855	1.570
Ethyl	B. 318–320	2535	1.555	264[b]	2820	1.660
Isopropyl	B. 338–340 (774 mm.)	2570	1.660	260[c]	2875	1.715
t-Butyl[d]	B. 198 (13 mm.)	2585	1.755	280–282[e]	2875	1.680

[a] Visible sublimation occurred to a greater or less extent with each salt, beginning 20–30° below recorded m.p. [b] *Anal.* Calcd. for $C_{15}H_{16}NCl$: N, 5.71; Cl, 14.47. Found: N, 5.58; Cl, 14.30. [c] Calcd. for $C_{16}H_{18}NCl$: N, 5.40; Cl, 13.66. Found: N, 5.44; Cl, 13.55. [d] Calcd. for $C_{17}H_{18}O$: C, 85.70; H, 7.56. Found: C, 85.86; H, 7.86; n^{19} 1.5762. [e] Calcd. for $C_{17}H_{20}NCl$: N, 5.13; Cl, 12.96. Found: N, 5.15; Cl, 12.88.

Analysis of the 4-*t*-butylbenzophenone was carried out by Dr. A. D. Campbell of Otago University.

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(1) P. L. Pickard and D. J. Vaughan, THIS JOURNAL, **72**, 876 (1950).

(2) J. B. Culbertson, *ibid.*, **73**, 4818 (1951).

Pipecolic Acid in *Phaseolus vulgaris:* Evidence on its Derivation from Lysine

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RECEIVED JULY 7, 1953

After the discovery of pipecolic acid as a prominent constituent of the green bean (*Phaseolus vulgaris*) and of other plants, the question of its origin and metabolic relationships arises. Advantage has been taken of the availability of lysine containing radioactive carbon to test the possibility that it may arise from, or be interconvertible with, lysine by a process of ring closure and loss of ammonia. The lysine used in this experiment was prepared synthetically by Dr. R. W. Helmkamp of the University of Rochester and was made available to us through the courtesy of Dr. Leon Miller, also of the University of Rochester.

The lysine was labelled in the ϵ-position and was made available to us dissolved in dilute salt solution. The specific activity of the lysine was 0.85 microcurie per milligram and 10 mg. of L-lysine was dissolved in 0.65 ml. of 0.9% sodium chloride solution.

The plants selected for the experiments were grown in pots and had fruits approximately 10 cm. in length. The morphology of the specimen selected for the first experiment is shown in Fig. 1. It will be noted that there were two developing fruits in the axil of the same leaf which was removed (X in Fig. 1). The main branch bearing the fruits was also decapitated (Y in Fig. 1). The method was to inject with a hypodermic needle, 0.25 ml. of the autoclaved lysine solution into the cavities surrounding the two lower ovules of fruit A (Fig. 1).

After the elapse of an appropriate period (55 hours) the tissue of the injected fruit was dissected and sampled and also the tissue of the adjacent fruit in the same leaf axil (B in Fig. 1).

In sampling the material for analysis, the ovules and carpel walls were treated separately and all the rest of the tissue of the plant examined as a whole. The weights of the organs analyzed are given in Table I.

TABLE I

FRESH WEIGHTS OF TISSUES EXTRACTED

Material	Weight, g.
First Experiment	
Injected fruit	2.468
carpel wall	2.229
ovules	0.239
Uninjected fruit	4.501
carpel wall	3.530
ovules	0.971
Rest of shoot	15.521
Second Experiment	
Stem tissue (F–F)	0.446
Fruit	8.098
carpel wall	5.395
ovules	2.703
Rest of shoot	37.600

(1) Predoctoral Rockefeller Foundation Fellow at Cornell University.