L-pipecolic acid and fluoresced cherry red under ultraviolet light as reported by Morrison.[2] An assay of the pipecolic acid hydrochloride showed that it had a specific activity of 1.21×10^5 disintegrations/min./mmole. Part of the pipecolic acid hydrochloride was converted to the hydantoin[4] and this derivative had a specific activity of 1.23×10^5 disintegrations/min./mmole. These observations afford strong evidence that pipecolic acid is a catabolite of L-lysine in the rat.

The high specific activity obtained suggests that pipecolic acid is involved in the conversion of L-lysine to α-aminoadipic acid, a view in keeping with the finding that under similar experimental conditions, L-lysine, via α-aminoadipic acid, yields glutaric acid with a specific activity of 6.45×10^4 disintegrations/min./mmole.[5]

(4) W. Leithe, *Ber.*, **65**, 927 (1932).
(5) M. Rothstein and L. L. Miller, unpublished results.

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THE MINOR ALKALOIDS OF *GELSEMIUM SEMPERVIRENS*[1]

Sir:

In the course of our work with gelsemine the isolation of the alkaloids of *Gelsemium sempervirens* Ait. has been reinvestigated. The alkaloidal residue obtained from the combined mother liquors left after removal of all the gelsemine and sempervirine was benzoylated to separate the secondary from the tertiary amines. The neutral fraction, after purification by chromatography, crystallized readily. It was hydrolyzed and the recovered base converted to a perchlorate which on repeated recrystallization from methanol–water was separated into a very sparingly soluble crystalline perchlorate and a readily soluble one. The readily soluble perchlorate yielded alkaloid A, m.p. 171–172°, $[\alpha]^{25}D$ −142° (*c*, 0.945 in $CHCl_3$). *Anal.* Found: C, 66.89, 67.27; H, 7.00, 7.31; N, 7.78; OCH_3, 16.47; NCH_3, 3.96. Calcd. for $C_{20}H_{26}O_4N_2$: C, 67.02; H, 7.31; N, 7.82; 2 OCH_3, 17.30; 1 NCH_3, 4.18. The base which contains one C-methyl and one active hydrogen (Zerewitinow) forms a neutral benzoyl derivative, m.p. 235–236°, $[\alpha]^{25}D$ −107° (*c*, 0.97 in $CHCl_3$). *Anal.* Found: C, 70.02; H, 6.50; N, 6.21. Calcd. for $C_{27}H_{30}O_5N_2$: C, 70.11; H, 6.54; N, 6.06. These properties are in agreement with those reported by Chou[2] and by Forsyth, Marrian and Stevens[3] for gelsemicine. Furthermore, the ultraviolet and infrared absorption spectra of alkaloid A were identical with the corresponding spectra determined on a sample of Chou's gelsemicine.[4] In admixture with Chou's gelsemicine (m.p. 164–167°), alkaloid A melted at 168–170°. Alkaloid A, therefore, is identical with gelsemicine.

(1) Issued as N.R.C. Bull. No. 0000.
(2) T. Q. Cohu, *Chinese J. Physiol.*, **5**, 131 (1931).
(3) W. G. C. Forsyth, S. F. Marrian and T. S. Stevens, *J. Chem. Soc.*, 579 (1945).
(4) We are indebted to Dr. Raymond-Hamet of Paris for supplying us with a sample of gelsemicine that he had received from Dr. T. Q. Chou.

The sparingly soluble perchlorate yielded alkaloid B, m.p. 172.6–174°, $[\alpha]^{25}D$ −158° (*c*, 1.35 in $CHCl_3$). *Anal.* Found: C, 69.77, 69.69; H, 7.52, 7.30; N, 8.57; OCH_3, 9.18; NCH_3, 4.22. Calcd. for $C_{19}H_{24}O_3N_2$: C, 69.49; H, 7.37; N, 8.53; 1 OCH_3, 9.43; 1 NCH_3, 4.57. Alkaloid B contained one C-methyl and one active hydrogen (Zerewitinow); it gave a neutral benzoyl derivative, m.p. 251–252°, $[\alpha]^{25}D$ −116° (*c*, 0.99 in $CHCl_3$). *Anal.* Found: C, 72.23; H, 6.55; N, 6.54. Calcd. for $C_{26}H_{28}O_4N_2$: C, 72.20; H, 6.53; N, 6.48. The properties of alkaloid B are quite different from those of gelsemine and of gelsemicine and the infrared absorption spectra of these three bases are quite distinct. Alkaloid B thus appears to be new and it is proposed to designate it as gelsedine. Recently Janot, Goutarel and Friedrich[5] isolated from *G. sempervirens* an alkaloid (m.p. 171°, $[\alpha]D$ −160°) which gave rise to a benzoyl derivative, m.p. 262°, $[\alpha]D$ −117°. They claimed their base to be gelsemicine and assigned to it the empirical formula $C_{19}H_{24}O_3N_2$ which is the same as that now assigned to gelsedine. The properties of gelsedine were the same as those of Janot and co-workers' gelsemicine except for the ten-degree difference in the reported melting point of the benzoyl derivatives. The ultraviolet absorption spectrum of Janot and co-workers' alkaloid resembled that of gelsemine and was the same as that of gelsedine so that the two are probably identical and both are certainly different from gelsemicine.

The basic fraction obtained from the benzoylation yielded a further base (alkaloid C) which was an oil (*Anal.* Found: C, 71.18; H, 7.00. Calcd. for $C_{21}H_{24}O_3N_2$: C, 71.57; H, 6.87), but formed a crystalline perchlorate, m.p. 250–252°. *Anal.* Found: C, 55.75; H, 5.66; N, 6.34. Calcd. for $C_{21}H_{24}O_3N_2 \cdot HClO_4$: C, 55.69; H, 5.56; N, 6.19. This base, which has an empirical formula differing from that of gelsemine by CH_2O, appears to be new.

(5) M. M. Janot, R. Goutarel and W. Friedrich, *Ann. pharm. franc.*, **9**, 305 (1951).

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A SYNTHESIS OF HYDROPEROXIDES FROM GRIGNARD REAGENTS

Sir:

The reaction of aryl and alkyl Grignard reagents with oxygen is well known and has been found to give poor yields of phenols,[1] and good yields of alcohols.[2,3] The sequence

$$RMgX + O_2 \longrightarrow ROOMgX$$
$$ROOMgX + RMgX \longrightarrow 2ROMgX$$

has been proposed[4] for this reaction and is supported by small, but significant peroxide titration values.[5]

We have found that by slow addition of alkyl Grignard reagents to oxygen-saturated ether at −75°, the intermediate ROOMgX can be ob-

(1) F. Bodroux, *Compt. rend.*, **136**, 158 (1903).
(2) L. Bouveault, *Bull. soc. chim.*, [3] **29**, 1051 (1903).
(3) M. T. Goebel and C. S. Marvel, THIS JOURNAL, **55**, 1693 (1933).
(4) C. W. Porter and C. Steele, THIS JOURNAL, **42**, 2650 (1920).
(5) H. Wuyts, *Bull. soc. chim. Belg.*, **36**, 222 (1927).