

a partially *cis*-configuration.¹ This statement refers to flowers which have developed fully under natural conditions on the intact plant. In recent experiments it was found, however, that, if stems with buds were placed in water for several days and exposed only to diffuse light in the laboratory at room temperature, the flowers were noticeably different in tint and paler in color than flowers which developed on the intact plant in the open. Parallel chromatograms of extracts of the two materials established the fact that under these two sets of conditions, the polyene pigment mixtures differed both qualitatively and quantitatively with respect to the components found. The paler flowers contained a greater number of lycopene stereoisomers than the controls. The chromatogram of the paler flowers included considerable quantities of polycopene, C₄₀H₅₆, and pro- γ -carotene, C₄₀H₅₆. The spectral maxima of these pigment fractions in petroleum ether (b. p. 60–70°) were 467, 440 m μ and 461, 431 m μ , respectively. Upon addition of iodine to the solutions, the bands showed the characteristic shift to 500.5, 469.5, 440 m μ and 494, 461 m μ . Both pro-carotenoids have been identified by mixed chromatograms with samples from other sources.

In the light of the above observation, it is possible that polycopene and pro- γ -carotene are precursors of lycopene and γ -carotene in the biosynthesis of the *Mimulus* pigment.

(1) L. Zechmeister, A. L. LeRosen, F. W. Went and L. Pauling, *Proc. Nat. Acad. Sci.*, **27**, 468 (1941); A. L. LeRosen and L. Zechmeister, *This Journal*, **64**, 1075 (1942); L. Zechmeister and W. A. Schroeder, *ibid.*, p. 1173.

GATES AND CRELLIN LABORATORIES OF CHEMISTRY
CALIFORNIA INSTITUTE OF TECHNOLOGY
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Some Physical Constants of N-Octyl-, N-Dodecyl- and N-Cetyl-piperidine

By F. H. STROSS AND R. J. EVANS

There exists little available information on the physical properties of the higher N-alkyl-piperidines. When, in the course of an investigation, it became necessary to prepare N-cetyl-piperidine, only two references^{1,2} were found which mentioned this compound. Its ionization constant was found to be surprisingly low in comparison with the known constants of the lower homologs,

(1) P. Karrer, F. W. Kahnt, R. Epstein, W. Jaffe and T. Ishii, *Helv. Chim. Acta*, **21**, 233 (1938).

(2) H. W. Magnusson and E. R. Schierz, *Univ. of Wyoming, Publications VII*, 1–11 (1940).

and, therefore, the N-dodecyl- and N-octyl-piperidines were also prepared and their characteristic properties measured. The results are given in Table I.

TABLE I
PHYSICAL CONSTANTS OF N-OCTYL, N-DODECYL AND N-CETYL PIPERIDINES

Piperidines	N-Octyl		N-Dodecyl		N-Cetyl
M. p., °C.	89 112 122		141 161		176–177
B. p. {	°C.	1 6 10	1 5	1	1
	Mm.	0.8324	0.8378	0.8468	
d_{20}^{20}	1.4544		1.4588	1.4620	
n _D ²⁰	Calcd.	7.1	5.5	4.5	
	Found	6.9 7.0	5.5	4.4	
Mol. wt. {	Calcd.	197.4	253.5	309.6	
	Found	197	253	304	
pK_H at 27°C.	8.28		5.92	5.8	

While the N-cetyl and N-dodecyl compounds are weak bases of a strength close to that of pyridine, N-octylpiperidine occupies a position intermediate between the higher homologs and the N-methyl- to butylpiperidines. The latter are almost as strong bases as the unsubstituted piperidine, which has a pK_H of 11.1 at 25°.

The bases were prepared by the method described by Magnusson and Schierz.² Aqueous piperidine was refluxed with a slight excess of the alkyl iodide, while an excess of potassium hydroxide was gradually added. The upper of the two layers formed during refluxing was fractionally distilled over solid potassium hydroxide at 2 mm. pressure, yielding a clear distillate. The cetyl-piperidine was yellow, the dodecyl compound had a slight yellow tinge, and the octyl-piperidine was colorless. The analyses were made and the constants determined after redistilling these products.

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Empirical Heat Capacity Equations of Gases

By HUGH M. SPENCER AND GORDON N. FLANNAGAN

Since the publication of empirical heat capacity equations of simple gases,¹ values of thermodynamic functions for many gases have been derived from spectroscopic data.² In the case of

(1) Hugh M. Spencer and John L. Justice, *This Journal*, **56**, 2311 (1934). The heat capacities of bromine and equilibrium chlorine are better represented by equations of form (2). The constants a , $b \times 10^3$, $c' \times 10^{-6}$, maximum and average percentage deviations are 8.911, 0.140, -0.0298, 0.09, 0.02 and 8.764, 0.271, -0.656, 0.24 and -0.11, respectively.

(2) E. B. Wilson, Jr., *Chem. Rev.*, **27**, 17 (1940).