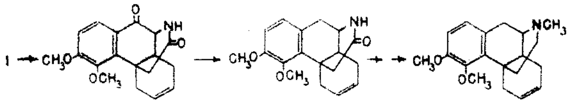
+ 34°, (*c* 0.447, alc.) found, C, 57.21; H, 7.29; tosylate, oil, methiodide, m. p. 165–166°, found, C, 52.45; H, 6.04) yields Δ^6-dihydrodesoxycodeine methyl ether (IVb) (oil, found, C, 75.83; H, 8.44) purified through its characteristic fumarate (2 moles of base to 3 of acid) m. p. 233–235°, found, C, 63.41; H, 6.58).



II III IV, IVa, IVb

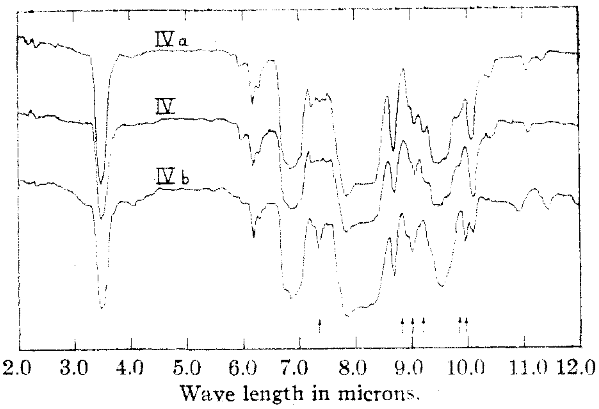


Fig. 1.—Infrared absorption spectra of: IVa, β-Δ^6-dihydrodesoxycodeine methyl ether; IV, synthetic *d,l*-β-Δ^6-dihydrodesoxycodeine methyl ether; IVb, Δ^6-dihydrodesoxycodeine methyl ether; approximately 1.7% in chloroform.

The infrared absorption spectra of IV and IVa (Fig. 1) are virtually superimposable and demonstrate conclusively that IV is the racemic modification of IVa. The spectrum of IVb is similar but unmistakeable differences are shown at the points indicated.

This synthesis provides an unequivocal demonstration that the point of attachment of the ethanamine side chain in the morphine alkaloids is at C_{13}.

DEPARTMENT OF CHEMISTRY
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RECEIVED AUGUST 23, 1950

DIFFUSION COEFFICIENT OF SUCROSE IN SUPERSATURATED SOLUTION

Sir:

In an important paper, English and Dole[1] have recently reported measurements by the Gouy method of the diffusion coefficient of sucrose in highly concentrated solutions. This communication is in no sense a criticism of English and Dole's beautiful measurements; it is intended merely to remove an apparent misconception as to the basis and applicability of the so-called Gordon equation, their Eq. 1

$$D = D^0(1 + d \ln f/d \ln c)(\eta^0/\eta)$$

This relation, as far as the relative viscosity factor is concerned, is entirely empirical, and was originally intended[2] merely as a possibly convenient device for interpolation and extrapolation; it would therefore seem inadvisable to use it as a criterion for normal diffusion. That it cannot be valid over wide ranges of concentration can be readily demonstrated.

Consider a system of two non-electrolytes, miscible in all proportions. The equation may be written for component No. 1 (see Eq. 4a of ref. 2)

$$D_1 = (D_1^0/RT)(n_1\partial\mu_1/\partial n_1)(V/n_2\bar{V}_2)(\eta_2^0/\eta) \qquad \text{(A)}$$

Here D_1^0 is the limiting diffusion coefficient of 1 in pure 2, μ_1 is the thermodynamic potential of 1 in the solution, η_2^0 is the viscosity of pure 2, and $\bar{V}_2$ is the partial volume of 2 in the solution. A similar expression may be written down for the diffusion coefficient D_2 of component 2 in the solution merely by interchanging 2 and 1 in Eq. A. Now in the Gouy method, the flow is measured relative to a fixed frame of reference, so that D_1 and D_2 must be identical. A comparison of the two expressions shows that this can only be true if $D_1^0\eta_2^0/\bar{V}_2 = D_2^0\eta_1^0/\bar{V}_1$—a condition that obviously cannot generally hold.

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[1] English and Dole, THIS JOURNAL, **72**, 3261 (1950).

[2] Gordon, *J. Chem. Phys.*, **5**, 523 (1937).

CHEMISTRY DEPARTMENT
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RECEIVED AUGUST 17, 1950

COLCHICINE. STRUCTURE OF WINDAUS' ANHYDRIDE[1,2]

Sir:

It has been shown by Windaus[3] that the oxidation of N-benzoyltrimethylcolchicinic acid with alkaline permanganate affords a compound, $C_{23}H_{21}O_7N$, designated as N-benzoylcolchinic anhydride (I). The Windaus structure for (I) was that of a dihydronaphthalene derivative; however, recent work[4] indicates that deaminocolchinic anhydride (II), obtained by the deamination of I is not a substituted naphthalene.

We have carried out the Cook degradation of N-benzoylcolchinic anhydride with phosphorus pentoxide in boiling xylene to obtain deaminocolchinic anhydride (m. p. 172.5–173°; reported[4] m. p. 170–171°). (*Anal.* Calcd. for $C_{16}H_{14}O_6$: C, 63.57; H, 4.67. Found: C, 63.86; H, 4.51.) This, on hydrogenation over a palladium catalyst, gave dihydrodeaminocolchinic anhydride (m. p. 119.5–120°) which was identical with synthesized 2,3,4-trimethoxybenzsuber-5-ene-5,6-dicarboxylic

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[1] The work carried out at the University of Pennsylvania was aided by a Grant-in-Aid from the American Cancer Society recommended by the Committee on Growth of the National Research Council.

[2] This investigation was supported (in part) by a research grant from the National Cancer Institute, of the National Institutes of Health, Public Health Service.

[3] Windaus, *Ann.*, **439**, 59 (1924).

[4] Cook, Johnston and Loudon, *J. Chem. Soc.*, 537 (1950).