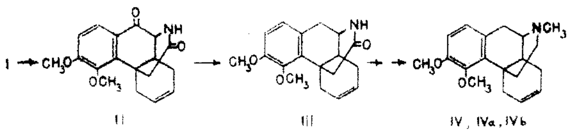
+ 34°, (*c* 0.447, alc.) found, C, 57.21; H, 7.29; tosylate, oil, methiodide, m. p. 165–166°, found, C, 52.45; H, 6.04) yields Δ^6-dihydrodesoxycodeine methyl ether (IVb) (oil, found, C, 75.83; H, 8.44) purified through its characteristic fumarate (2 moles of base to 3 of acid) m. p. 233–235°, found,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



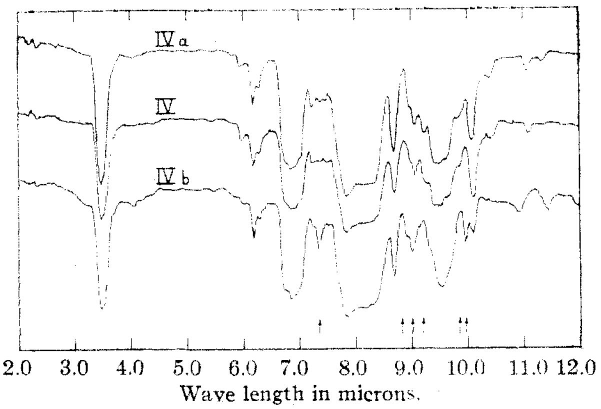


Fig. 1.—Infrared absorption spectra of: IVa, β-Δ^6-dihydrodesoxycodeine methyl ether; IV, synthetic *d,l*-β-Δ^6-dihydrodesoxycodeine methyl ether; IVb, Δ^6-dihydrodesoxycodeine methyl ether; approximately 1.7% in chloroform.

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
UNIVERSITY OF ROCHESTER MARSHALL GATES
ROCHESTER 3, N. Y. GILG TSCHUDI

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
UNIVERSITY OF TORONTO
TORONTO, CANADA A. R. GORDON

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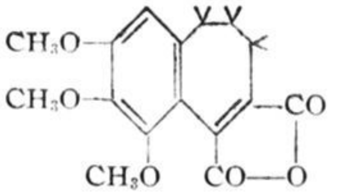
[1] The work carried out at the University of Pennsylvania was aided by a Grant-in-Aid from the American Cancer Society recommended by the Committee on Growth of the National Research Council.

[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).

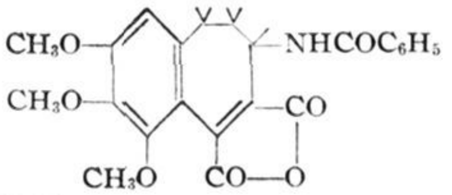
acid anhydride (III). Identity was established by a mixed melting point determination and by comparison of the ultraviolet absorption spectra in chloroform and in aqueous alkali.



(III)

2,3,4 - Trimethoxybenzsuber - 5 - ene - 5,6 - dicarboxylic acid anhydride (III) was prepared by the Bougault cyclization of 3,4,5-$(CH_3O)_3C_6H_2(CH_2)_3$-$CH(COOC_2N_5)COCOOC_2H_5$ which was obtained by two different routes. (A) Ethyl 3,4,5-trimethoxybenzoylacetate was alkylated with ethyl β-bromopropionate and the resulting ester was hydrolyzed to yield γ-(3,4,5-trimethoxybenzoyl)-butyric acid. The keto-acid was hydrogenated[5] with a palladium-carbon catalyst to γ-(3,4,5-trimethoxyphenyl)-valeric acid (m. p. 68–69°; reported[6] m. p. 70°). This acid was converted to the ethyl ester (with ethanol-sulfuric acid) (b. p. 151° at 0.3 mm.). (*Anal.* Calcd. for $C_{16}H_{24}O_5$: C, 64.59; H, 8.11. Found: C, 64.83; H, 8.32.) Condensation of this ester with ethyl oxalate gave an enolic ester which was cyclized with sulfuric-phosphoric acids to yield the anhydride III (m. p. 119.5–120°). (*Anal.* Calcd. for $C_{16}H_{16}O_6$: C, 63.15; H, 5.30. Found: C, 63.28; H, 5.59.) (B) A Reformatsky reaction with 3,4,5-trimethoxybenzaldehyde and methyl γ-bromocrotonate yielded an olefinic ester which was hydrogenated (palladium–carbon catalyst) to provide a saturated ester. From this ester, which was not obtained in analytical purity, it was also possible to prepare III by condensation with ethyl oxalate, followed by cyclization.

Degradative,[7] spectroscopic,[8] and synthetic[9] data are now available which show that the conversion of N-acetylcolchinol methyl ether to dihydrodeaminocolchinol methyl ether *via* the deamino compound does not involve an alteration in the size of the seven-membered B ring. Further, both N-acetylcolchinol and colchiceine (the N-*acetyl* analog of N-benzoyltrimethylcolchicinic acid) can be oxidized to the same product,[4] presumably N-acetylcolchinic anhydride. From this it may be concluded (1) that N-benzoylcolchinic anhydride has the structure I, in which the position of the benzoylamino group is chosen in accord with the findings of Rapoport, *et al.*,[9] and (2) that the B-ring of I may be correctly assigned to colchicine itself.



(I)

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF PENNSYLVANIA
PHILADELPHIA, PA.
RESEARCH DIVISION
SMITH, KLINE AND
FRENCH LABORATORIES
1530 SPRING GARDEN ST.
PHILADELPHIA, PA.

E. C. HORNING
M. G. HORNING
J. KOO[10]
M. S. FISH[11]
J. A. PARKER[12]
G. N. WALKER[11]
R. M. HOROWITZ[13]
G. E. ULLYOT

RECEIVED SEPTEMBER 14, 1950

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[5] Horning and Reisner, THIS JOURNAL, **71**, 1036 (1949).

[6] Haworth, Moore and Pauson, *J. Chem. Soc.*, 1050 (1948).

[7] Barton, Cook and Loudon, *J. Chem. Soc.*, 176 (1945); Buchanan, Cook, Loudon and MacMillan, *Nature*, **162**, 692 (1948).

[8] Horowitz, Ullyot, Horning, Horning, Koo, Fish, Parker, and Walker, THIS JOURNAL, **72**, 4330 (1950).

[9] Rapoport, Williams and Cisney, *ibid.*, **72**, 3324 (1950).

[10] American Cancer Society Postdoctoral Fellow.

[11] American Cancer Society Research Assistant.

[12] National Institutes of Health Predoctoral Fellow.

[13] Research Associate.[2]

EIGHT LIQUID PHASES IN STABLE EQUILIBRIUM

Sir:

Hildebrand[1] has reported the construction of a system of seven liquid layers in stable equilibrium. This system consisted of heptane, aniline, water, perfluorokerosene, white phosphorus, gallium and mercury. The authors have discovered that an eight-layer system can be constructed by a suitable modification of the Hildebrand system. The eight layers (in order of increasing densities) are paraffin oil, silicone oil, water, aniline, perfluorodimethylcyclohexane, white phosphorus, gallium and mercury. After mixing, the eight layers reappear upon centrifuging. The system is stable indefinitely at 45°. This temperature is required to melt the gallium and phosphorus.

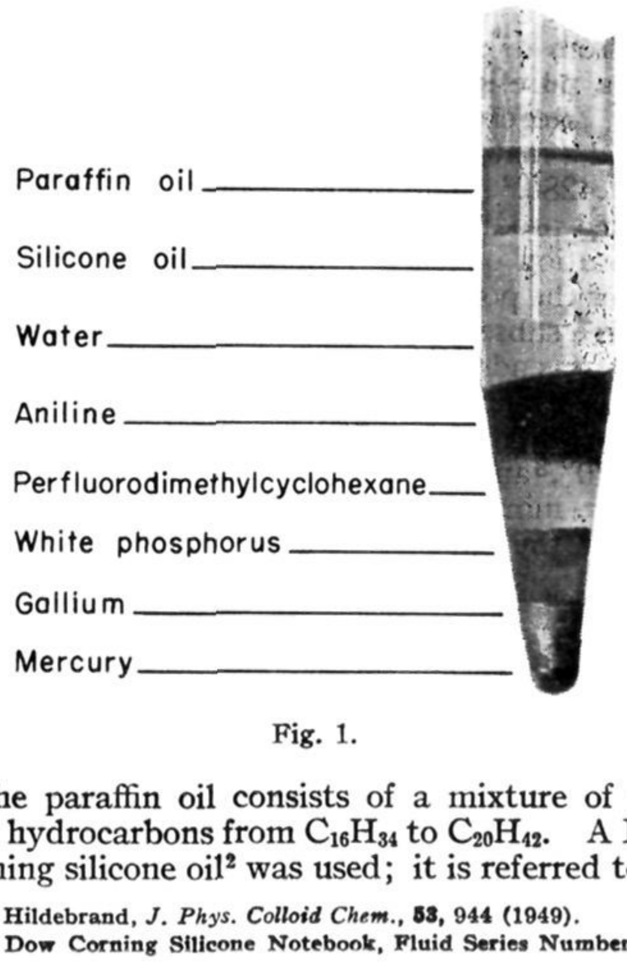

Fig. 1.

The paraffin oil consists of a mixture of paraffin hydrocarbons from $C_{16}H_{34}$ to $C_{20}H_{42}$. A Dow Corning silicone oil[2] was used; it is referred to by

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[1] Hildebrand, *J. Phys. Colloid Chem.*, **53**, 944 (1949).

[2] Dow Corning Silicone Notebook, Fluid Series Number 3, 21 (1948).