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The Isolation of *i*-Inositol from American Flue-cured Tobacco

BY MAX PHILLIPS AND AUBREY M. BACOT

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Shmuk,[1] in 1930, isolated *i*-inositol from fermented Tyk-Kulak, a type of Russian cigarette tobacco. Smirnov,[2] five years later, using a somewhat different procedure, succeeded in isolating *i*-inositol from Russian cigarette tobacco. In connection with a general study of the U.S. Standard grades, repeated attempts made in the Tobacco Standards Laboratory of the USDA to isolate *i*-inositol from American flue-cured tobacco using the procedure of Shmuk, as well as that of Smirnov, have met with failure. However, using the following method, pure crystalline *i*-inositol was isolated for the first time from American tobacco.

Two hundred grams (equivalent to 189 g. of moisture-free material) of American flue-cured tobacco, Type 12, U. S. Grade B4GF, 1949 crop, from which the midribs had been removed, and which had been ground in a Wiley mill fine enough to pass a 1-mm. sieve, were boiled for 2 hours under a reflux condenser with 1800 ml. of distilled water. The mixture was filtered through a Büchner funnel, the residual tobacco was washed with 500 ml. of hot water, and the washings were added to the main filtrate. To this solution, an aqueous solution of neutral lead acetate was added, portionwise, until the precipitation of the lead salts of the acids was complete. The precipitated lead salts were filtered off, and to the filtrate (A) a solution of basic lead acetate was added until precipitation was complete. The basic lead acetate solution was prepared according to the directions given by Browne and Zerban.[3] Instead of precipitating the *i*-inositol in filtrate (A) with basic lead acetate solution, the same could be accomplished by adding to (A) some neutral lead acetate solution and aqueous ammonia. In either case, the precipitated lead complex was filtered with suction on a Büchner funnel and washed with distilled water. The precipitate was then suspended in one liter of distilled water and a stream of hydrogen sulfide was passed in until all the lead complex was decomposed. The lead sulfide was filtered on a Büchner funnel, washed with water and the washings were added to the main filtrate. This filtrate was concentrated under reduced pressure at 50° to a volume of 40 ml. The concentrated solution was heated on the steam-bath to 70° and 3.5 ml. of concentrated nitric acid were added to it portionwise. After each addition of the nitric acid, a fairly vigorous reaction occurred. After the reaction subsided, 160 ml. of 95% ethanol were added to the reaction mixture and the gummy precipitate that separated out was filtered off. To the filtrate, after cooling to room temperature, 40 ml. of ether were added and the mixture was filtered again. The filtrate on standing in the refrigerator (+5°) for several days deposited crystals. These were filtered off and recrystallized from 50% aqueous acetic acid. The crystals melted at 226° (cor.) and when mixed with an authentic specimen of pure *i*-inositol, the mixture also melted at 226° (cor.). The yield amounted to 0.13 g. or 0.07% of the weight of the moisture-free tobacco.

Following the above procedure, *i*-inositol was isolated also from U. S. Grades B5L and H5L of Type 12 tobacco, 1949 crop. The yield in each case was approximately the same as that obtained from U. S. Grade B4GF. The sample of B4GF, when analyzed by the quantitative method of Smirnov,[4] was found to contain 0.55% of *i*-inositol (calculated on moisture-free basis).

(1) A. Shmuk, *State Inst. Tobacco Investigations, Krasnodar* (*U.S.S.R.*) *Bull.*, **69**, 15 (1930).

(2) A. P. Smirnov, *Sbornik Rabot po Khimii Tabaka i Makhorki, Krasnodar* (*U.S.S.R*), *VI*, Bull. 125, 75 (1935).

(3) C. A. Browne and F. W. Zerban, "Physical and Chemical Methods of Sugar Analysis," John Wiley and Sons, Inc., New York, N. Y., 1941, p. 311 (solution II).

(4) Reference 2, pp. 87–105 (1935).

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The Dissociation of 2,2,2-Trinitroethanol in Aqueous Solution[1]

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In a publication by Marans and Zelinski,[2] the preparation and properties of trinitroethanol (TNE) are described and its dissociation is reported to be that shown in equation 1.

$$C(NO_2)_3CH_2OH \rightleftarrows C(NO_2)_3CH_2O^- + H^+ \quad (1)$$

TNE, however, does not demonstrate the properties of an alcohol in many of its reactions. It does not form ethers and does not react with epoxides as would be expected of a strongly acidic alcohol which forms a stable alkoxide ion. This behavior led to the conclusion that the trinitroethoxide ion has only a transitory existence and that equation 2

$$C(NO_2)_3CH_2O^- \rightleftarrows C(NO_2)_3^- + CH_2O \quad (2)$$

represents an instantaneous consecutive process. Thus, equation 3 summarizes the observable equilibrium. The complete conversion of the trinitroethoxide ion to the nitroformate ion is believed to be favored by resonance stabilization of the latter.

$$C(NO_2)_3CH_2OH \rightleftarrows C(NO_2)_3^- + H^+ + CH_2O \quad (3)$$

The differences in the near ultraviolet absorption spectra of nitroformate ion and undissociated TNE (Fig. 1) make it possible to determine nitroformate ion concentration in aqueous TNE solutions. In this manner, the degree of dissociation, α, of TNE to nitroformate ion was determined (Table I, Fig. 2) and an equilibrium constant, $K_s = 3.1 \times 10^{-5}$, was calculated for equation 3 under the assumption that the absorption intensities of undissociated TNE in water and in heptane are not significantly different. A further assumption that the absorbing species is nitroformate ion, and not trinitroethoxide ion, was corroborated by the observation that high concentrations of formaldehyde markedly reduce absorption, and, in fact, the concentration of nitroformate ion in these solutions corresponds very closely to the concentration calculated on the basis of the above equilibrium constant (Table II).

The degree of dissociation was also determined for a number of solutions of TNE from calculations based upon hydrogen ion concentrations. The values of α, and therefore the equilibrium constant, K_{pH} (Table I), obtained in this manner are con-

(1) Presented at the 123rd National Meeting of the American Chemical Society at Los Angeles, Calif., March 1953.

(2) N. S. Marans and R. P. Zelinski, THIS JOURNAL, **72**, 5329 (1950).

TABLE I

Molar concn.	$K_s \times 10^5$	Molar concn.	$K_{pH}{}^a \times 10^5$
1.25×10^{-3}	2.68	9.9×10^{-3}	1.2
2.00×10^{-3}	3.89	2.01×10^{-2}	1.7
4.00×10^{-3}	3.18	3.01×10^{-2}	1.2
5.00×10^{-3}	2.86	4.09×10^{-2}	1.5
8.00×10^{-3}	2.97	5.06×10^{-2}	1.4
2.00×10^{-2}	2.64	6.27×10^{-2}	2.9
4.98×10^{-2}	2.90	7.47×10^{-2}	2.5
7.69×10^{-2}	3.50	7.64×10^{-2}	3.1

[a] $K_{pH} = [H^+]^3/(\text{original TNE concn.} - [H^+])$.

TABLE II

Original TNE concn.	$[NF^-]$ Found	$[NF^-]$ Calcd.
1.00×10^{-2}	5.3×10^{-4}	5.4×10^{-4}
5.00×10^{-3}	3.6×10^{-4}	3.8×10^{-4}
5.08×10^{-3}	3.4×10^{-4}	3.8×10^{-4}

sistently lower than the corresponding values which were calculated from the spectra. This difference is significant because the hydrogen ion concentration would have to be greater than the nitroformate ion concentration if trinitroethoxide ion were present. Since the hydrogen ion concentration is, however, consistently lower, the dissociation represented by equation 1 appears insignificant, if present at all. The inequality of the two concentrations arises from the limiting accuracy of *p*H measurements, but there can be no doubt of the fundamental agreement of the two independent determinations of α.

An attempt was made to determine the degree of dissociation of TNE by utilizing the freezing point depression of a series of aqueous solutions. However, the small freezing point constant of water coupled with the deviation from ideality exhibited by all solutions made it impossible to draw any conclusions from these data.

Experimental

Nitroform.—Nitroform was prepared by a modification of the procedure in the literature.[2]

2,2,2-Trinitroethanol (TNE).—This compound was prepared by a modification of the procedure in the literature[3] (m.p. 72–73°).

Anal. Calcd. for $C_2H_3N_3O_7$: C, 13.27; H, 1.67; N, 23.21. Found: C, 13.30; H, 1.83; N, 22.62.

Determination of the Dissociation from Ultraviolet Absorption Spectra.—Nitroform obeys the Beer–Lambert law in the range of concentrations used. It is completely dissociated in dilute aqueous solution as shown by the fact that the spectrum of a neutral solution coincides with that of a strongly basic solution.

The portion of the spectrum used in this study was the near ultraviolet from 370–460 mμ where no interference is encountered from absorption by undissociated TNE. The degree of dissociation, α, was obtained by dividing the apparent molar extinction coefficients of TNE obtained from solutions of different concentrations by the molar extinction coefficient of nitroform (Table I, Fig. 2).

Spectra were obtained for 17 solutions. Comparisons were made with solutions of nitroform of nearly equal optical density at several wave lengths and the values of α were averaged to yield a more accurate value for each concentration. These values could be determined within about 2%.

Solutions were prepared by weighing samples of nitroform and TNE into a glass boat and washing directly into volumetric flasks with a stream of distilled water. The spectra were determined at ambient temperature (22–25°) by means of a Beckman Model DU Quartz Spectrophotometer. The usable range of concentrations was extended by adding matched quartz flats of 0.902 and 0.988 cm. thickness to the standard 1.000 cm. cell.

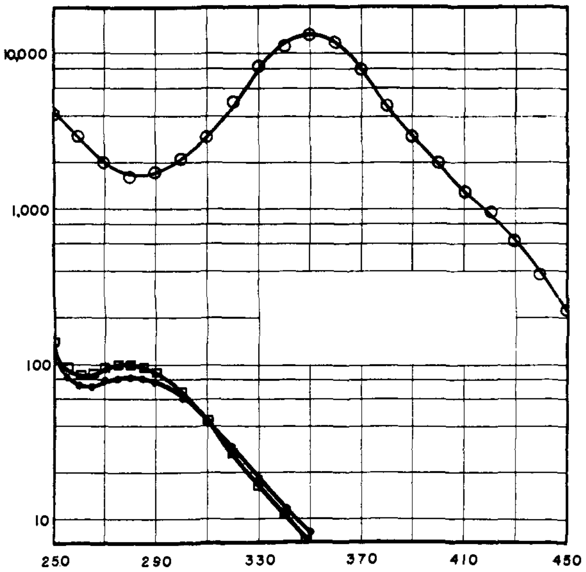

Fig. 1.—Molar extinction coefficient, ϵ, *vs.* wave length in mμ: ○, nitroform in water; ●, nitroform in heptane; □, TNE in heptane.

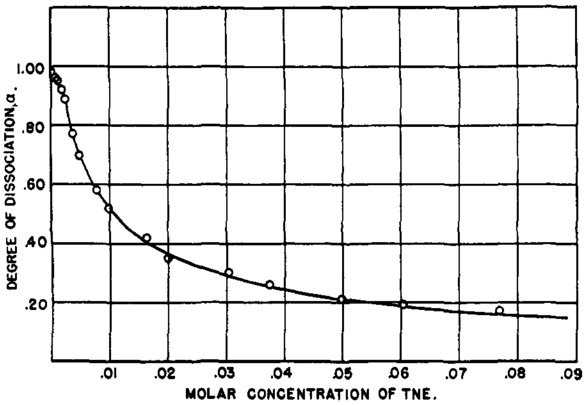

Fig. 2.—Data based on ultraviolet absorption spectra.

The dissociation constant for equation 3 is

$$K_s = \frac{[C(NO_2)_3^-][CH_2O][H^+]}{[TNE]} = \frac{[C(NO_2)_3^-]^3}{[TNE]} = \frac{c^2\alpha^3}{1-\alpha}$$

where c is the original concentration of TNE. A single value for K_s (3.1×10^{-5}) was obtained by determining the arithmetic average of the 17 experimental values. This constant was used to construct the curve shown in Fig. 2.

Effect of Excess CH_2O on Equilibrium.—Solutions of TNE in 1.00 *M* CH_2O[3] were prepared and their nitroformate ion concentration determined from the equation

$$[NF^-] = D/\epsilon_{\text{nitroform}}$$

The calculated nitroformate ion concentration was obtained by solving the quadratic equation

$$3.1 \times 10^{-5} = \frac{[NF^-][H^+][CH_2O]}{\text{original TNE concn.} - [NF^-]} = \frac{[NF^-]^2 \times 1}{\text{original TNE concn.} - [NF^-]}$$

The results are shown in Table II.

Determination of the Dissociation from *p*H Measurements.—The *p*H of a series of TNE solutions was measured

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[3] R. C. Griffin, "Technical Methods of Analysis," McGraw-Hill Book Co., Inc., New York, N. Y., 1927, p. 102.

with standard Beckman pH meters. Glass and calomel electrodes were used.

The solutions were prepared as described above and pH was determined at ambient temperature. The pH values were converted to hydrogen ion concentrations with no correction being applied.

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The Infrared Spectra of N-Substituted Trifluoroacetamides

BY JOHN H. ROBSON[1] AND JOAN REINHART

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Several hitherto unreported N-substituted amides have been prepared and their infrared spectra recorded. Of these compounds, the trifluoroacetamides, exhibit the so-called amide I and amide II[2] absorption bands at 5.8–5.9 and 6.35–6.45 μ, respectively. On the other hand, representative formamides and acetamides (Table I) exhibit these amide bands at 6.0–6.2 and 6.4–6.6 μ, respectively.

TABLE I

AMIDE ABSORPTION BANDS (IN μ) OF SOME TRIFLUOROACETAMIDES, FORMAMIDES AND ACETAMIDES

N Substituent(s)	Trifluoroacetamides Amide I	Trifluoroacetamides Amide II	Formamides Amide I	Formamides Amide II	Acetamides Amide I	Acetamides Amide II
Methyl	..	..	5.98^a	6.47^a	...	...
Ethyl	..	..	...	...	6.08^a	6.42^a
Isopropyl	5.88	6.38	...	...	...	...
n-Butyl	5.82	6.37	...	...	...	...
Phenyl	5.89	6.43	6.00^a	6.45^a	6.01^a	6.46^a
Benzyl	5.86	6.42	6.11^a	6.51^a	...	...
Diethyl	5.89	^{b}	5.98	^{b}	6.08	^{b}
Di-*n*-propyl	..	..	5.95	^{b}	6.06	^{b}
Di-isopropyl	5.91	^{b}	5.98	^{b}	...	...
Di-*n*-butyl	5.88	^{b}	5.96	^{b}	6.06	^{b}
Di-isobutyl	5.90	^{b}	...	...	6.05	^{b}

^{a} These data were obtained from H. M. Randall, *et al.*, reference 2. ^{b} Amide II band is not present in N,N-disubstituted amides.

This shift to lower wave lengths of the absorptions attributable to the amide grouping is an expected effect of the electronegative trifluorosubstitution in as much as the increased ionic character of the F_3C–C bond increases the carbonyl stretching frequency. In addition to the amide group shifts, the trifluoroacetamides show extremely strong absorption between 8 and 9 μ attributable to C–F stretching. In general, the two bands arising from the symmetrical and antisymmetrical CF_3 stretching modes are clearly resolved. The degeneracy of the latter mode is often removed to such an extent that three bands appear in this region. Regardless of the shape of the 8–9 μ absorption band, it has proved very useful when considered in conjunction with the shifted amide I and II bands in quickly distinguishing between trifluoroacetamides and other types of amides.

Experimental[3]

The infrared data were obtained by means of a Perkin-Elmer model 21 infrared spectrophotometer, using sodium chloride prisms and cells. All liquids were run as pure liquids and the solids as Nujol mulls or melts.

The benzyl and phenyl substituted trifluoroacetamides were prepared according to Bourne, *et al.*[4] The alkyl trifluoroacetamides were all prepared in the same manner as described for diethyl trifluoroacetamide.

N,N-Diethyltrifluoroacetamide.—A solution of 14.6 g. (0.2 mole) diethylamine in 100 cc. of ether was cooled to −10° and 14 cc. (0.1 mole) of trifluoroacetic anhydride was added at a rate such that the reaction temperature remained at −5 to −10°. After the addition was complete, the mixture was warmed to room temperature and washed with water until the wash was neutral to litmus, dried over Na_2SO_4, and distilled at reduced pressure to yield 11.7 g. (69%) of diethyltrifluoroacetamide boiling at 65–67° (24 mm.) with n^{24}D 1.3782.

Anal. Calcd. for $C_6H_{10}ONF_3$: C, 42.59; H, 5.97; N, 8.28. Found: C, 42.0; H, 6.12; N, 8.21.

N-Isopropyltrifluoroacetamide: b.p., 71–72° (20.5 mm.), m.p. 51.0–52.3°. This compound may be purified either by recrystallization from hexane or by vacuum sublimation. *Anal.* Calcd. for $C_5H_8NOF_3$: C, 38.71; H, 5.20; N, 9.03. Found: C, 39.07; H, 4.73; N, 9.27.

N-*n*-Butyltrifluoroacetamide: b.p., 100–101° (28.5 mm.), n^{25}D 1.3805. *Anal.* Calcd. for $C_6H_{10}NOF_3$: C, 42.60; H, 5.96; N, 8.28. Found: C, 42.8; H, 6.22; N, 8.12.

N,N-Di-isopropyltrifluoroacetamide: m.p. 52–52.5°. *Anal.* Calcd. for $C_8H_{14}ONF_3$: C, 48.72; H, 7.17; N, 7.10. Found: C, 48.7; H, 7.58; N, 7.38.

N,N-Di-*n*-butyltrifluoroacetamide: b.p. 106° (16.0 mm.), n^{25}D 1.3997. *Anal.* Calcd. for $C_{10}H_{18}NOF_3$: C, 53.32; H, 8.06; N, 6.22. Found: C, 53.3; H, 8.59; N, 5.94.

N,N-Di-*i*-butyltrifluoroacetamide: b.p. 89.0–89.5° (13.4 mm.), n^{25}D 1.4017. *Anal.* Calcd. for $C_{10}H_{18}NOF_3$: C, 53.32; H, 8.06; N, 6.22. Found: C, 52.9; H, 8.47; N, 6.45.

N,N-Diethylacetamide was prepared by the method of Pictet,[5] b.p. 179–181° (700 mm.), 88.5–91.0° (31.0 mm.), n^{25}D 1.4333.

Di-*n*-propylacetamide was prepared by the method of Chancel[6]; b.p. 94.5° (12.0 mm.), n^{25}D 1.4411.

N,N-Di-*n*-butylacetamide was prepared by the procedure used for diisobutylacetamide; its boiling point (238° (705 mm.), 116.5° (8.0 mm.)) checked that reported by Sowa and Nieuwland[7]; n^{25}D 1.4451.

N,N-Di-isobutylacetamide.—To 240 cc. (2.3 moles) of purified acetic anhydride was added 106 cc. (0.82 mole) of distilled di-isobutylamine, the temperature being allowed to rise to 110°. This solution was distilled at atmospheric pressure to remove 170 cc. of acid and excess anhydride, then at 9.3 mm. to yield 75.3 g. (72%) of amide boiling at 99–102°. A second fractionation through a 12-inch Vigreux gave a product b.p. 102.5–103.0° (9.8 mm.), n^{25}D 1.4434.

Anal. Calcd. for $C_{10}H_{21}NO$: C, 70.09; H, 12.35; N, 8.22. Found: C, 70.6; H, 12.6; N, 7.84.

This compound was previously reported[8] to be a solid, melting at 74°. Our compound could not be caused to crystallize. Since the product of Chute, *et al.*, resulted from a nitration reaction, it probably was di-isobutylnitramine; the latter compound was prepared[9] and found to melt at 81–82°.

Diethylformamide was made by the method of Ott[10]; b.p. 69° (15.0 mm.), n^{25}D 1.4296.

Di-isopropylformamide.—To 46.0 g. (1.0 mole) of 98–100% formic acid in 200 cc. of m-xylene was added with cooling 101 g. (1.0 mole) of distilled di-isopropylamine, while the temperature was maintained below 60°. The resulting two-phase liquid was refluxed 48 hours and water continuously removed in a side-arm trap. The solution, now homogeneous, was distilled at atmospheric pressure

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[1] University of Toronto, Toronto, Ontario, Canada.

[2] H. M. Randall, R. G. Fowler, N. Fuson and J. R. Dangl, "Infrared Determination of Organic Structures," D. Van Nostrand Co., Inc., New York, N. Y., 1949, p. 11.

[3] All temperatures are uncorrected.

[4] E. J. Bourne, S. H. Henry, C. E. M. Tatlow and J. C. Tatlow, *J. Chem. Soc.*, 1041 (1952).

[5] A. Pictet, *Ber.*, **23**, 3013 (1890).

[6] M. F. Chancel, *Bull. soc. chim.*, [3] **11**, 935 (1894).

[7] F. J. Sowa and J. A. Nieuwland, THIS JOURNAL, **59**, 1202 (1937).

[8] W. J. Chute, *et al.*, *Can. J. Research*, **26B**, 114 (1948).

[9] J. H. Robson, unpublished work.

[10] E. Ott, G. Dittus and H. Meissenburger, *Ber.*, **76B**, 84 (1943).