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

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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).

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[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.

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

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

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

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.

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

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-

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[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).