yield measurements have shown that 1250 molecules of methyl methacrylate are polymerized per quantum of 3660 Å. radiation in the presence of benzoin. Since benzoin methyl ether appears to be at least equally efficient, this yield appears too high to be consistent with a mechanism involving copolymerization of light-activated benzoin molecules with methyl methacrylate.

Experimental

Preparation of Labeled Benzoin Methyl Ether.—Carbon-14 labeled benzoin methyl ether was prepared from benzoin, carbon-14 labeled methyl iodide and silver oxide by a modification of the method of Wren.[8] The labeled methyl iodide (1 mc. in 1 mm.) was supplied by Tracerlab, Inc., under allocation from the Atomic Energy Commission. The product was recrystallized from petroleum ether.

Polymerization.—Polymerizations were carried out in small tubes of 10-mm. Pyrex brand glass into which freshly distilled methyl methacrylate monomer and labeled benzoin methyl ether were charged as listed in Table I. The tubes were flushed with oxygen-free nitrogen through a long capillary, frozen in Dry Ice–acetone and sealed off under vacuum. They were then brought to room temperature and placed under a reflector holding two BL-360 fluorescent tubes. After polymerization the polymers were precipitated from excess monomer with methanol, dissolved in benzene, and reprecipitated twice. After drying to constant weight, the radioactivity of the polymers was measured by combustion, precipitation as barium carbonate and radioassay in an internal counter. The original tagged benzoin methyl ether was run as a control. The polymers were dissolved and reprecipitated a third time without producing a significant change in activity.

A polymer sample was prepared in the dark by thermal initiation of methyl methacrylate containing benzoin methyl ether and α,α'-azobisisobutyronitrile to determine if exchange or transfer reactions might lead to radioactive products. A 10-mm. Pyrex tube was charged with 7.116 g. of freshly distilled methyl methacrylate, 0.0953 g. of α,α'-azobisisobutyronitrile, and 0.0206 g. of the labeled benzoin methyl ether. This was heated at 50° for 40 minutes in the dark and the polymer recovered as described for the photopolymerizations. Conversion was 9%. The polymer showed no significant radioactivity after two precipitations.

Molecular Weight.—Dry polymers were dissolved in thiophene-free benzene to produce solutions of about 0.1 g. per 100 ml., whose viscosities were measured in Ostwald viscometers. The true intrinsic viscosities were not measured but were estimated from $(\ln \eta_{\text{rel}})/c$ and from $\eta_{\text{sp}}/c = [\eta] + k' [\eta]c$, assuming k' to be 0.4, and viscosity average molecular weights were calculated from the equations of Baxendale and co-workers.[4]

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[8] H. Wren, *J. Chem. Soc.*, **95**, 1585 (1909).

CONTRIBUTION NO. 346
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The Distribution of Triterpenes in Plants. *Chenopodium album*

BY H. J. NICHOLAS,[1] C. L. WADKINS AND R. C. HILTIBRAN

RECEIVED AUGUST 2, 1954

In a previous communication[2] we noted the accumulation of the pentacyclic triterpene oleanolic acid in mature *Plantago major*. None was found in young plants. Djerassi, *et al.*,[3] have listed the known sources of this acid. We wish to report the presence of oleanolic acid in *Chenopodium album*, or Lamb's Quarters.[4] In this plant it accumulates in the mature growth also but its occurrence is limited to the flower parts only. The acid is not present in any part of the young plants selected for examination before the appearance of the flowers. The non-saponifiable portion of alcoholic extracts of the young and mature plant, respectively, contains sitosterol as the sitosterol mixture.

Of a large number of local plants examined for the presence of both the carboxylated pentacyclic triterpenes and sterols (to be published), only *Chenopodium album* and *Plantago major* were found to contain them together.

Experimental[5]

Isolation of Oleanolic Acid as the Acetate.—Finely ground dried flower parts (1362 g.) of Lamb's Quarters (*Chenopodium album*) were exhaustively extracted with hot, 95% ethanol. The extract was distilled to low volume, made approximately 2 *N* with concd. HCl and refluxed for 2 hr. The cooled solution was diluted with water and extracted thoroughly with ethyl ether. The latter was washed with water, then extracted thoroughly with 5% $NaHCO_3$ (extracts discarded) and 5% KOH, respectively. The ether was then washed with water and distilled, leaving 44.0 g. of neutral, greenish-black wax (see below). The KOH extracts were acidified (HCl) and filtered. The precipitate was washed and dried leaving 8.5 g. of greenish lumps. This crude product was too contaminated with black gum to obtain any crystalline material from it by direct crystallization or crystallization after acetylation with acetic anhydride and pyridine (room temperature). The acetylated mixture was transferred to a 100-g. alumina column with the aid of a little benzene. The column was washed with low boiling (b.p. 30–60°) petroleum ether and 1% ethanol in petroleum ether, respectively (elutes discarded). Washing with 2% ethanol in petroleum ether eluted 1.5 g. of tan needles, m.p. 245–255°. After several crystallizations from methanol and aqueous acetone feathery needles were obtained, m.p. 268–270° undepressed on admixture with authentic oleanolic acid acetate; $[\alpha]^{27}\text{D}$ +75° ($CHCl_3$).[6]

Anal. Calcd. for $C_{32}H_{50}O_4$: C, 77.06; H, 10.10. Found: C, 77.14, 76.98; H, 9.92, 9.89.

Oleanolic Acid.—Microscopic needles, m.p. 308–310°, undepressed on admixture with authentic oleanolic acid; $[\alpha]^{27}\text{D}$ +78° ($CHCl_3$).

Anal. Calcd. for $C_{30}H_{48}O_3$: C, 78.89; H, 10.58. Found: C, 78.63, 78.67; H, 10.43, 10.32.

Acetyl Methyl Oleanolate.—Glistening scales, m.p. 224–225°, undepressed on admixture with authentic acetyl methyl oleanolate; $[\alpha]^{27}\text{D}$ +60° ($CHCl_3$).

Examination of Mature Plant Parts, Other Than Flowers, and Young Lamb's Quarters.—Mature plant parts, other than flowers, did not contain any oleanolic acid, nor did any part of the young plant, selected before the appearance of the flower parts.

Isolation of Sitosterol.—The neutral fractions from the flower parts and whole young plants, after saponification and chromotography, yielded sitosterol as white flakes, m.p. 137–139°, undepressed on admixture with authentic sitosterol mixture. An acetate was prepared, m.p. 125–127°, undepressed on admixture with authentic sitosterol (mixture) acetate.

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[1] Central Research Department, Anheuser-Busch, Inc., St. Louis, Missouri. Address communications to this author.

[2] R. Hiltibran, C. Wadkins and H. Nicholas, THIS JOURNAL, **75**, 5125 (1953).

[3] C. Djerassi, L. Geller and A. Lemin, *ibid.*, **75**, 2254 (1953).

[4] A prolific weed occurring widespread throughout the United States (J. M. Fogg, Jr., "Weeds of Lawn and Garden," Univ. of Penn. Press, Philadelphia, Pa., 1945, p. 73).

[5] All melting points are uncorrected and were determined on the Fisher–Johns apparatus, with the exception of that of oleanolic acid which was determined by the capillary tube method.

[6] Djerassi, *et al.*,[3] give the following constants: oleanolic acid, m.p. 308–310°; acetyl oleanolate, m.p. 264–267°, $[\alpha]^{22}\text{D}$ +70°; acetyl methyl oleanolate, m.p. 217–219°, $[\alpha]^{22}\text{D}$ +65°.

of the University of Kansas for partial financial support during this investigation.

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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).

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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]

BY JOAN REINHART, JOHN G. MEITNER AND ROBERT W. VAN DOLAH

RECEIVED SEPTEMBER 4, 1953

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).