The hydrogenation temperature was controlled by the circulation of water through the jacket surrounding the hydrogenation flask. In the flask were placed freshly distilled menthofuran (I), 3.210 g., (0.0214 mol.), platinum oxide (60 mg.), and acetic acid (30 ml.). At the beginning of the shaking, the hydrogenation mixture should be colorless.[8] After 4 hr., the absorption of hydrogen ceased at 1120 ml. (0.466 mol.; measured at 20°). From the hydrogenation mixture a colorless oil (3.000 g.) was obtained, b.p. 88–100° (18 mm.) which contained 20.1% menthol mixture.

The hydrogenation product was treated with 3,5-dinitrobenzoyl chloride in pyridine and then steam-distilled. The undistilled residue solidified to give the crude 3,5-dinitrobenzoate (0.829 g.). From the distillate, tetrahydromenthofuran (II) was obtained, b.p. 91–92° (20 mm.). α_D^{17} $-20.8°$ (homogeneous), d_4^{25} 0.9286, n_D^{25} 1.4610, MR (calcd.) 45.62, (obsd.) 45.58.

Anal. Calcd. for $C_{10}H_{18}O$: C, 77.86; H, 11.76. Found: C, 77.90; H, 11.81.

The crude 3,5-dinitrobenzoate (100 mg.) was purified by passing an *n*-hexane solution of the 3,5-dinitrobenzoate through a layer of alumina (1 g.). The removal of *n*-hexane from the effluent gave colorless needles (86 mg.), while a resinous substance (9 mg.) adsorbed on the alumina was eluted with ether.

The purified 3,5-dinitrobenzoate (20.0 mg.) was chromatographed on an alumina column (alumina 15 g.; height 15 cm.) using *n*-hexane mixed with 5% ether as developing solvent. The effluent was collected in small fractions and the solvent was removed from each fraction. After the melting points had been determined, as shown in Fig. 1, the fractions were combined into three parts: Fraction I 6.0 mg. (m.p. 150–154°), Fraction II 1.0 mg. (m.p. 85–145°), and Fraction III 12.1 mg. (m.p. 95–99°). From the results obtained by the above preliminary purification and by chromatography, the composition of crude ester was calculated as shown in Table I.

When recrystallized from methanol, Fraction I and Fraction III melted at 154–155° and 99–100° respectively, and were shown to be (+)-*neo*menthyl- and (+)-*neoiso*menthyl 3,5-dinitrobenzoate, by mixed melting point determinations with authentic samples. Fraction II was a mixture of these two isomers.

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Differentiation of Glyceraldehyde from Other Trioses by Means of 2,4-Dinitrophenylhydrazine[1]

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In an effort to identify some oxidation products of glycerides by 2,4-dinitrophenylhydrazone derivatives it was discovered that the literature is rather vague concerning the 2,4-dinitrophenylhydrazone of glyceraldehyde.

Neuberg,[2] using a saturated solution of 2,4-dinitrophenylhydrazine in 2*N* hydrochloric acid at 0°, prepared glyceraldehyde 2,4-dinitrophenylhydrazone which melted at 166–167°. Neuberg and Collatz[3] reported the 2,4-dinitrophenylosazone of glyceraldehyde to melt at 265° (dec.). Later, Neuberg and Strauss[4] reported that the bishydrazone (osazone) of methyl glyoxal can be obtained quantitatively from dihydroxyacetone and glyceraldehyde with 2,4-dinitrophenylhydrazine in hydrochloric acid. This 2,4-dinitrophenylosazone melted at 298°.[5]

In the present investigation two methods were used to study the dinitrophenylhydrazones and osazones of glyceraldehyde, dihydroxyacetone, and pyruvaldehyde (methyl glyoxal). The results appear in Table I.

Infrared spectra of the products melting at 164–166° were all similar with peaks at: 3.05, 6.15–6.20, 6.28, 7.45, 8.18, 8.70–8.90, 9.15–9.35, 10.28, 10.75–10.90, 11.73–11.95, and 12.00 μ. Infrared spectra of the products melting at 297–299° were all similar with peaks at: 3.08, 6.19, 6.27, 6.32, 6.65, 7.40–7.50, 7.60, 7.95, 8.23–8.28, 8.73, 9.20, 9.47, 10.68, 10.92, 11.90–12.00, and 13.43–13.70 μ.

The results show that glyceraldehyde 2,4-dinitrophenylhydrazone can be prepared in hydrochloric acid at 5°, but the 2,4-dinitrophenylosazone of pyruvaldehyde forms at other temperatures. In the case of dihydroxyacetone and pyruvaldehyde, however, the 2,4-dinitrophenylosazone of pyruvaldehyde forms at all the temperatures tried. This osazone which melts from 250–298° can be recrystallized from dioxane or pyridine to melt at 297–299°.

These data show that by the use of 2,4-dinitrophenylhydrazine in 2*N* hydrochloric acid at 5° glyceraldehyde can be differentiated from the other trioses.

EXPERIMENTAL

Preparation of dinitrophenylhydrazones and osazones. Two methods were used to study the dinitrophenylhydrazones and osazones of glyceraldehyde (Nutritional Biochemicals #6559), dihydroxyacetone (Nutritional Biochemicals #4386), and pyruvaldehyde (methyl glyoxal), (K&K #2995L 30% soln.). The first was that of Brady and Elsmie[6] in which a saturated solution of 2,4-dinitrophenylhydrazine in 2*N* hydrochloric acid was added to an aqueous solution of the triose. The second method was that of Allen[7] as modified

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[1] This Communication has been authorized for publication on October 15, 1958, as Paper No. 2302 in the Journal Series of the Pennsylvania Agricultural Experiment Station.

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TABLE I

PROPERTIES OF VARIOUS PRODUCTS PREPARED FROM TRIOSES WITH 2,4-DINITROPHENYLHYDRAZINE

Method	HCl	HCl	HCl	H_2SO_4	H_2SO_4	H_2SO_4
Temperature	5°	20°	35°	5°	20°	35°
PPt. color						
Gly[a]	Yellow	Yellow-orange	Orange	Orange	Orange	Orange
DHA[b]	Orange	Orange	[e]	[e]	Orange	[e]
Pyr[c]	Orange	[e]	[e]	[e]	Orange	[e]
Solubility in hot (1:1) 50% C_2H_5OH/C_2H_5OAc						
Gly	Complete	*ca.* 50%	*ca.* 50%	Trace	Trace	Trace
DHA	Trace	Trace			Trace	
Pyr	Trace				Trace	
M.p. material recrystallized by above						
Gly	166	166	164	—	—	—
DHA	—	—			—	
Pyr	—				—	
M.p. residue from solubility tests						
Gly	—	284[d]	289	298	298	298
DHA	253[d]	280[d]			284[d]	
Pyr	299				289[d]	

[a] Gly, glyceraldehyde. [b] DHA, dihydroxyacetone. [c] Pyr, pyruvaldehyde. [d] Recrystallized from dioxane to melt at 298°. [e] Not performed.

by Brady[8] in which 2,4-dinitrophenylhydrazine was dissolved in a small amount of concentrated sulfuric acid and the solution diluted with ethanol. This solution was added to an alcoholic solution of the triose. Each procedure was run at 5°, 20°, and 35°. The solutions were held at the required temperature for 2 hr. before mixing, and then allowed to react for 12 hr. Only the first crops of precipitate were retained.

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The Identification of $C_{12}H_8N_4O$, an Oxidation Product from α-Pyridil Monohydrazone[1]

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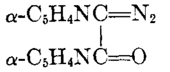
Treatment of α-pyridil (I) with tosyl hydrazide and the resulting derivative with aqueous alkali gives a product, $C_{12}H_8N_4O$, incorrectly identified as "azipyridil" (II).[2] Chemical and physical evidence require the formulation to be that of 1-α-picolinoylpyridotriazole (III, R = α−C_5H_4NCO).

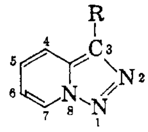
$(\alpha\text{-}C_5H_4NCO)_2$

I



$$\begin{array}{l}\alpha\text{-}C_5H_4NC{=}N_2\\ \quad\quad\quad\ \ |\\ \alpha\text{-}C_5H_4NC{=}O\end{array}$$

II



III

In acid solution pyridotriazole (III. R = H) and, at higher temperatures, 1-phenylpyridotriazole (III. R = C_6H_5) react with carboxylic acids to form esters of corresponding α-pyridylcarbinols.[3] In its resistance to attack by carboxylic acids, III (R = α-C_5H_4NCO) further demonstrates lack of triazole ring reactivity towards acids when electron withdrawing groups are at the 1-position. In boiling aniline, III (R = α − C_5H_4NCO) undergoes degradation of the triazole ring and the product,[2] di(α-pyridyl) acetanilide, suggests an intermediate formation of II. Transformation of III (R = α − C_5H_4NCO) into II apparently occurs more readily in the presence of iodine or bromine, each of which gives rise to the formation of α,α-dihaloketones as nitrogen is liberated.[2]

Hydrazine hydrate combines with III (R = α − C_5H_4NCO) to bring about the formation of the corresponding hydrazone (IV) and, if air is present, its oxidation product 1,1′-bipyridotriazole(V).[4]

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(1) Partial support of this work under a National Institutes of Health Grant No. CY-2895 is gratefully acknowledged.

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