

Summary

The fatty acids liberated by the hydrolysis of cassava starch free from extraneous fatty material have been found to be palmitic, oleic, linolic and linolenic.

The detection of small amounts of linolenic acid in the presence of oleic and linolic acids by bromination is a more delicate method than by oxidation.

This is the first time that linolenic acid has been found in a starch.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

FURAN REACTIONS. I. THE PYROLYSIS OF FURAN

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Two possibilities of pyrolysis suggest themselves in the pyrolysis of furan. Either it should yield difuryl, a change analogous to the transformation of benzene into diphenyl, or it should break into carbon monoxide and gaseous hydrocarbons. Since no difuryl was found, the C-H union must be stronger than the C-O bond. Actually, the products formed were carbon monoxide and hydrocarbons. Because of the high temperature required (about 700°) it is interesting that methylacetylene was identified and that evidence was also obtained for cyclopropene: $C_4H_4O \longrightarrow CO + C_3H_4$. In addition, acetylene, ethylene, propylene, methane and butadiene were identified.

Preliminary work¹ in this Laboratory demonstrated the stability of furan at 600° if the hot contact time was less than one second. This is higher than the value of 450–490° reported by Sinkinson² as the "initial conducting temperature." It may be noted³ that with a nickel catalyst (nickel on pumice, the oxide being reduced in a hydrogen stream at 280°) furan started to decompose at 360° when the contact time was thirteen to twenty seconds.

Furan was forced by displacement with mercury into an unpacked quartz tube (43 × 2 cm.) which was heated electrically for 32 cm. of its length. Within the tube was a glass-encased thermocouple. To condense the vapors, two empty flasks, cooled to -15°, were connected to the exit end of the tube, following which was a condensing coil at -80°.

Using 31–33 g. samples of furan it was found that by changing the duration of the experiment from 405 minutes to 110 minutes (a change of 59 to 15.6 sec. contact time) the percentage decomposition at 670–680°

¹ With F. D. Pilgrim.

² Sinkinson, *Ind. Eng. Chem.*, 17, 31 (1925).

³ From results obtained with John W. Garrett.

dropped from 41 to 12%. Similarly, at 740°, a change from 154 to 20 minutes (19.4 to 2.59 sec. contact time) diminished the decomposition from 74 to 17%. In the last two cases, the volumes of gas produced, respectively, were 9.3 and 1.5 liters.

In the 670° experiments, the gas was approximately three-fourths carbon monoxide, one-eighth saturated hydrocarbons and hydrogen, one-eighth unsaturated hydrocarbons. In the 740° experiments, analysis showed less carbon monoxide and more saturated hydrocarbons and hydrogen.

The Unsaturated Hydrocarbons.—The 11% of unsaturated hydrocarbons in the off-gas of the 740° and 2.59 sec. experiment was composed⁴ of 3.1% acetylenes, 5.5% ethylene and 2.4% propylene admixed with undetermined amounts of allene, cyclopropene and butadiene. Longer contact times lowered the acetylene content but did not influence materially the others. That the acetylene content was largely methylacetylene was proved by liquefaction at -80° and conversion to dipropinylmercury, (CH₃C≡C)₂Hg, with alkaline potassium iodomercurate. With one crystallization from alcohol this derivative⁵ melted at 196–204°. A small amount of acetylene resisted liquefaction. It gave the characteristic dull red cuprous derivative, Cu₂C₂.

Since methylacetylene is known⁶ to pyrolyze into allene and since barium furoate has been reported⁷ to yield cyclopropene, it is reasonably certain that both of these C₃H₄ gases were present. There is good evidence from an analogous study of furfural that butadiene was probably present also.

Benzene was definitely identified (as *m*-dinitrobenzene) in the liquid products of the reaction. Only 0.2 cc. of it was found in the experiment at 670° and 59 seconds, but 1.3 cc. was found in the experiment at 740° and 19.4 seconds. These aromatic liquids are traceable as secondary products through the unsaturated hydrocarbons mentioned above.

Summary

Furan decomposes at 670–740° in a quartz tube as contrasted with a temperature of 360° when heated in the presence of catalytic nickel. The pyrolysis proceeds by rupturing the nucleus into gaseous products. A condensation reaction leading to difuryl was not observed.

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⁴ Analysis by method of Hurd and Spence, *THIS JOURNAL*, **51**, 3357 (1929).

⁵ Johnson and McEwen, *ibid.*, **48**, 469 (1926).

⁶ Hurd and Meinert, *ibid.*, **52**, 4543 (1930).

⁷ Freundler, *Compt. rend.*, **124**, 1157 (1897); *Bull. soc. chim.*, [3] **17**, 613 (1897).