product decomposition, and other factors affecting the isolation of a product.

Variation of the specific rate constant with temperature is also shown in Table I (runs 13, 14 and 15). The reaction has a low temperature coefficient which is not particularly surprising for an aldol-type condensation.[2b]

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The Isolation of the Toxic Principles of Mamey

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The insecticidal properties of the various parts of the mamey tree (*Mammea americana* L.) have been recognized for many years.[1] Although the seeds from the fruit of this tree have been the subject of numerous investigations,[2] the isolation of the toxic compounds in pure form has not been previously reported.

Outlined below is a procedure which led to the isolation of one pure, toxic, crystalline compound and to one toxic amorphous solid. These two substances were highly toxic to several species of insects and accounted for 81% of the toxicity of mamey extract. Their powerful action as fish poisons facilitated their isolation since this permitted the use of guppies as the bioassay test animal.

Experimental

Seeds of mature fruit were sectioned, dried at 45° in a forced-draft oven for 24 hours, ground to 80 mesh, and extracted for 8 hours with petroleum ether in a soxhlet type extractor. A light-red, sticky, semi-solid mass, representing 5% of the dried powder, was obtained after evaporation of the solvent. Heating under high vacuum for 2 hours at 100° was required for the removal of the last traces of solvent. Other non-polar solvents served as well as petroleum ether for this extraction. This semi-solid mass was dissolved in the minimum amount of acetone and placed in an ice-bath for 24 hours. A non-toxic white, powdery solid, melting sharply at 78°, was obtained. The yield was 1.5% of the dried extract. The acetone in the filtrate was evaporated under reduced pressure and the residue dissolved in petroleum ether to give a 10% solution. Fifty ml. of this solution, equivalent to 5.0 g. of dried extract, was placed on a 75 × 150 mm. column prepared with silicic acid (Merck 200 mesh) and developed with a 1:10 mixture of ether and petroleum ether. After the initial band had separated into three distinct bands, the silicic acid was extruded, sectioned, and the three bands extracted with ether. The immobile band at the top of the column was not toxic and was discarded. The procedure was repeated five times and the corresponding extracts of the two mobile toxic bands were combined. This gave a preliminary separation.

The ether solution of the leading toxic band was partially evaporated and the remaining ether gradually replaced with petroleum ether while boiling on a steam-bath. Cooling in an ice-bath for 24 hours produced 2.3 g. of well-formed, colorless crystals, representing several crystalline modifications. Numerous recrystallizations from ether–petroleum ether showed these crystals to be a mixture of compound A, m.p. 130–131° (2.1 g.), and several other crystalline compounds which have not yet been obtained in pure form. Compound A showed approximately the same LD_{50} as the original extract, *i.e.*, 1.5 p.p.m., and thus accounted for 7% of the toxicity of the original extract. The mother liquors when combined and partially evaporated yielded 0.5 g. of light-yellow crystals, m.p. 70–90°. This mixture was resolved into three crystalline substances, melting at 82–84°, 101–102° and 114–115°. These last three substances appeared to be solvates, for they effervesced strongly at their melting points.

Compound A dissolved readily in dilute alkali to give a yellow solution and gave positive phenolic tests. This compound added methylmagnesium bromide readily, but did not liberate methane in the Zerewitinoff apparatus. The ultraviolet absorption spectrum obtained with a Beckman model DU spectrophotometer, using 95% alcohol as the solvent, showed maxima at 244, 249, 255, 261 and 334 mμ.

Anal. Calcd. for $C_{18}H_{22}O_4$: C, 71.26; H, 7.33. Found: C, 71.15, 71.10; H, 7.62, 7.56.

The ether solution of the middle toxic band was evaporated and a light-red oil was obtained which was extracted several times with petroleum ether. The tacky residue that remained was taken up in a 1:10 ether–petroleum ether mixture and rechromatographed three times on a silicic acid column as described above. This led to the isolation of 3.1 g. of a highly toxic material. The LD_{50} of this golden-yellow amorphous substance which softened at 170–175°, was 0.25 p.p.m. by the guppy bioassay method[3] and accounted for 74% of the toxicity of the original extract. This LD_{50} of 0.25 p.p.m. indicated that this substance was approximately 20% as toxic as rotenone under the same conditions. The molecular structures of the toxic compounds described above are now being investigated by Professor J. L. E. Erickson, Louisiana State University. A report of this work will be submitted from his laboratory to THIS JOURNAL at a later date.

During the past year this Laboratory received several requests for samples of these pure toxic compounds, indicating a widespread interest in these potential insecticides. A recent press release[4] from the University of Puerto Rico stated that mamey extract contained "antibiotic substances which were active *in vitro* against one or more bacteria."

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[1] D. de Grosourdy, "El Médico Botánico Criollo," Vol. II(2), Paris, (1864), p. 511.

[2] M. A. Jones and H. K. Plank, THIS JOURNAL, **67**, 2262 (1945); H. K. Plank, *J. Econ. Entomol.*, **37** (6), 737 (1944), and refs. cited.

[3] C. Pagán, *ibid.*, **41** (6), 942 (1948).

[4] "Información Oficial," Núm. **19**, Oct. 4, 1951, Universidad de Puerto Rico.

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An Investigation of the Hammick Reaction

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In an attempt to elucidate the nature of the Hammick reaction[1,2] with a view to extending it, we varied the character of the carbonyl reactant by introducing substituents into its nucleus.

The various carbonyl compounds which were successfully coupled with picolinic acid upon decarboxylation are listed in Table I. In initial investigations various solvents such as dibromobenzene, nitrotoluene, bromoanisole, xylene and *p*-cymene, equivalent in amount to the aldehyde used were added to the reaction mixture to determine what effect they might have on the yield. This proved to be very practical for the yield of carbinol was increased in every case. The best yields were ob-

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[1] D. Ll. Hammick and P. Dyson, *J. Chem. Soc.*, 1724 (1937); 809 (1939).

[2] D. Ll. Hammick and B. R. Brown, *ibid.*, 173 (1949); 659 (1949).