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Technical Note

The Stability of Cyanohydrins

The hydrolysis of linamarin and lotaustralin, the two cyanogenic glucosides found in cassava (*Manihot esculenta* Crantz) by an endogenous β-glucosidase, linamarase (EC3.2.1.2, linamarin, β-glucoside glucohydrolase), yields acetone cyanohydrin and methylethyl cyanohydrin, respectively (Nartey, 1968; Conn, 1969). Amygdalin, another cyanogenic glucoside usually isolated from almond seeds, yields benzaldehyde cyanohydrin (mandelonnitrile) upon hydrolysis by the β-glucosidase, emulsin (Conn, 1973). Cyanohydrins are compounds generally synthesized by the addition of hydrogen cyanide to ketones and aldehydes.

These cyanogens are stable and release hydrogen cyanide upon treatment with acid only at elevated temperatures (Wood, 1966). Linamarase is inactivated at pH values above or below 5·5 or at temperatures above 72 °C (Joachim & Panditteseker e, 1944). Thus, processing cassava, as is practised in the tropics at low fermentation pH values of about 2–3 or at elevated temperatures of 80–85 °C, inactivates linamarase. Unhydrolysed linamarin and lotaustralin, cyanohydrins and complex glucohydrins formed in side reactions during processing are trapped in cassava products which are ultimately ingested by man and livestock.

Since cyanohydrins are the terminal compounds in the decomposition pathway of these cyanogens and eventually do release hydrogen cyanide. a potent cytotoxin, it is necessary to determine the stability of these compounds in gut-like environments so as to be able to design ways of

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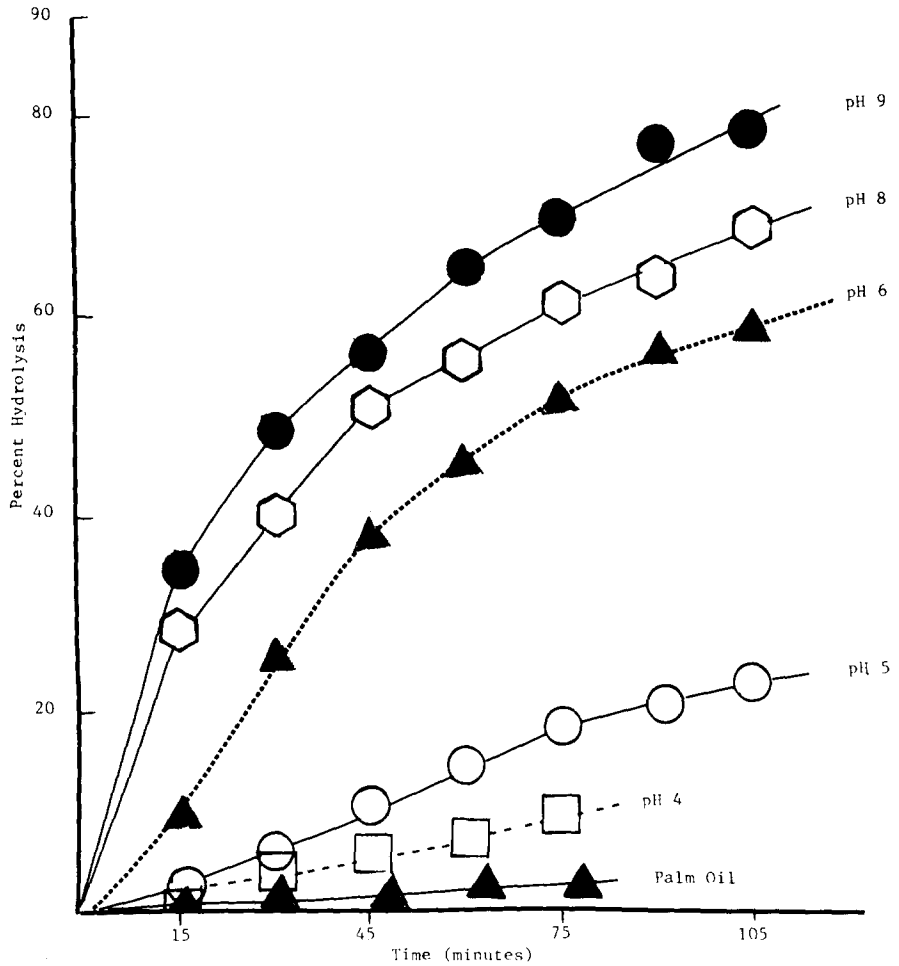

Fig. 1. The per cent hydrolysis of mandelonitrile at 30 °C in 0·05M phosphate buffer at various pHs, measured as released HCN on alkaline-picrate saturated filter paper strips.

eliminating them before they release cyanide to the body. Also, since, in the tropics, cassava is usually ingested with palm oil soups supplemented with palm oil as a source of dietary fat, this study attempts to investigate the stability of acetone cyanohydrin and mandelonitrile at pH 2–9, with and without palm oil.

Acetone cyanohydrin and mandelonitrile were synthesized according to the method of Vogel (1978). For the hydrolysis, 0·2 ml of each cyanohydrin was added to 0·5 ml phosphate buffer, or 0·5 ml palm oil or

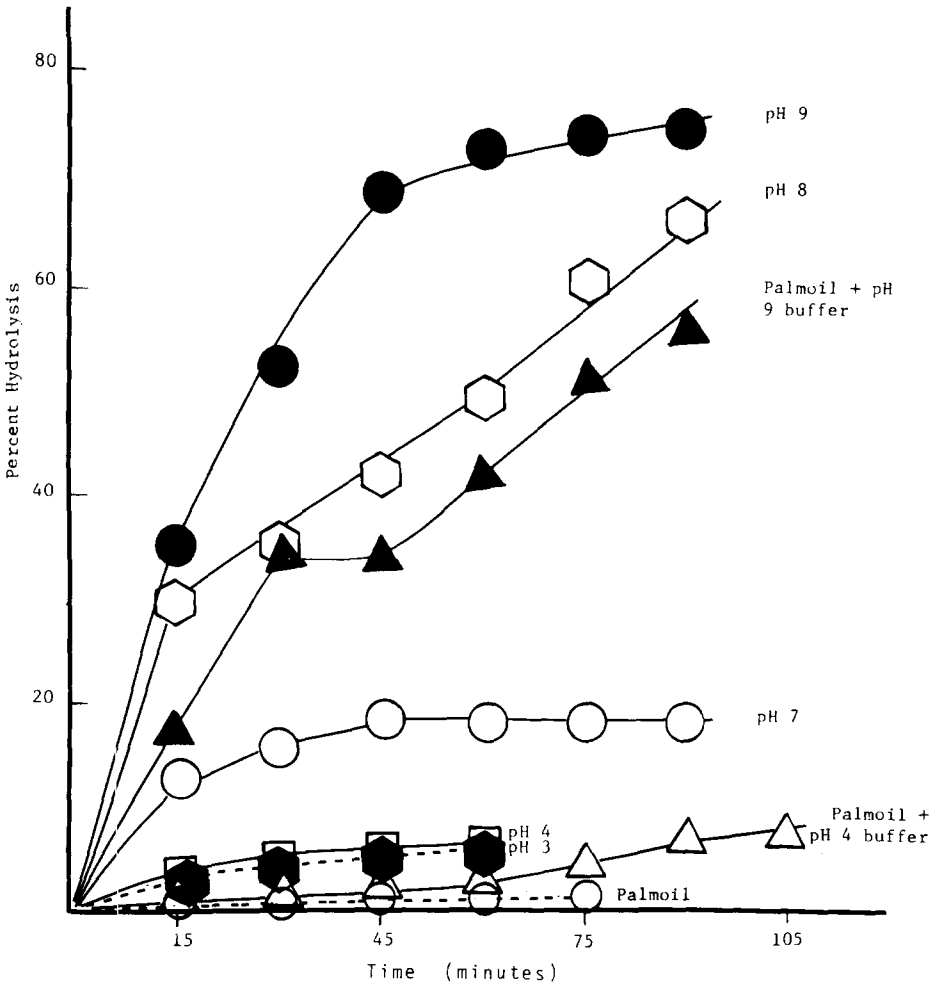

Fig. 2. Per cent hydrolysis of acetone cyanohydrin at 30 °C in 0·05M phosphate buffer at various pHs, measured as released HCN on alkaline-picrate saturated filter paper strips.

a mixture of 0·25 ml phosphate buffer and 0·25 ml palm oil, within the pH range 2–9. The amount of hydrolysis was measured as released hydrogen cyanide using alkaline picrate-saturated Whatman No. 1 filter paper strips according to the method of Gilchrist *et al.* (1967).

The results are shown in Figs 1 and 2. At pH 4 and 5 the hydrolysis of mandelonitrile is very low (10–20 %) and almost follows a straight line, whereas, at higher pH values, it is high (55–80 %) and could be regarded as a smooth curve. With acetone cyanohydrin, hydrolysis was very low

between pH 3 and 7 (5–15 %) and gave a curve which tended to flatten out after about 30 min. At pH 9 the hydrolysis followed the same pattern as that for mandelonitrile, but, at pH 8, the curve was irregular and difficult to explain. Neither compound hydrolysed in palm oil and hydrolysis in palm oil/buffer mixture was lower than in the buffer alone. The non-hydrolysis of these compounds in palm oil reflects the non-alkalinity of this medium. In addition, the inconsistent hydrolysis of cyanohydrin in oil/buffer mixtures, at pH 4 and 9, respectively, may be due to the immiscibility of the two liquids at both pH values. In the gut, palm oil is emulsified during digestion and the fate of these compounds under these conditions is being investigated.

In the tropics cassava is made into foodstuffs by fermentation for about 3 days. During this period, the pH falls from about 5·8 to 3·0. At the initial stage, hydrolysis by linamarase proceeds readily to glucose and cyanohydrin and subsequently to hydrogen cyanide and acetone. However, because of the high stability of cyanohydrin at low pH values, coupled with the deactivation of linamarase at low pH values, less free cyanide (HCN) will be released, resulting in 'fixation' of cyanide in the product. Ingestion would therefore result in the release of cyanide in the body.

However, the stability of these products at low pH values and their extreme solubility in water can be used effectively in the processing of cassava by employing several water changes during fermentation. This would remove most of the cyanohydrins, the unhydrolysed linamarin and the lotaustralin. The similarity in reactivity of acetone cyanohydrin and mandelonitrile suggests that the metabolism of various glucosides and their breakdown products in the gut or at the molecular level should follow the same pathway, although differences in the chemical structures of these compounds may affect the reaction rate.

The implication of the above observations in terms of reactivity in the digestive tract may be that, within the pH ranges of 2 to 4 in the stomach, virtually no cyanide would diffuse into the body. At pH 6 in the duodenum and pH 8 in the intestines, a greater hydrolysis of these compounds would mean diffusion of the cyanide into the blood stream.

A further examination of the effect of palm oil in *garri*, a fermented cassava product, revealed that *garri* fried with palm oil contained less cyanide than *garri* fried without palm oil (Olarewaju & Baszormenyi, 1975). This could be explained on the basis that the trapped linamarin, lotaustralin and cyanohydrins decompose by thermal reaction as palm oil

allows higher temperatures to be reached during drying. Thus, using several changes of water and employing palm oil for frying may remove residual cyanohydrins in cassava products and make them safer for consumption.

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