solution was refluxed gently for 3 h, during which time the liquid changed from colourless to dark green. Fifty ml. carbon tetrachloride was added and refluxing continued for 30 min. The solution was filtered and the filtrate was evaporated to dryness by a stream of dry air. The yield of *tris*-(hexafluoroacetylacetonato) Cr(III) was 1·85 g (80 per cent based on potassium dichromate). Calculated for $Cr(C_5HF_6O_2)_3$: C, 26·76 per cent; H, 0·45 per cent; F, 50·80 per cent. Found: C, 27·04 per cent; H, 0·68 per cent; F, 51·30 per cent. The infra-red spectrum and melting point (84°) of the compound were determined and agree well with the data of Morris *et al.*[2]

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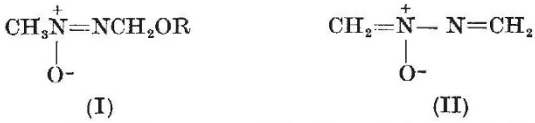
BIOCHEMISTRY

Decomposition and Carcinogenic Activity of Azoxyglycosides

The toxicity of leaves and seeds of cycads to animals and humans is well established (for review, see ref. 1). The toxic constituents are azoxyglycosides of which the simplest are cycasin (I; R = β-D-glucopyranosyl)[2] and macrozamin (I; R = β-primeverosyl)[3,4]. More recently, liver damage[5] and carcinogenesis[6] have been observed to follow ingestion of the seeds or extracts containing the unstable aglycone, methylazoxymethanol (I; R = H) (ref. 5). The latter may theoretically decompose to the alkylating agent, diazomethane, a potent carcinogen[7], and is indeed isomeric with hydroxydimethylnitrosamine through which dimethylnitrosamine may be transformed *in vivo* to the same active carcinogen[8].

That cycasin and macrozamin may be effective methylating agents *in vitro* has now been demonstrated by the production of anisole (40–50 per cent yield, based on azoxyglycoside) when a solution of the glycoside in molten phenol is treated with a drop of concentrated sulphuric acid and warmed until evolution of gas ceases (2–3 min). No reaction occurs in the absence of strong acid, nor is any trace of anisole produced when azoxyglycoside is hydrolysed in hot dilute sulphuric acid containing a large excess of phenol. This behaviour is analogous to that of benzaldazine monoxide[9], and formaldazine monoxide (II) may be an intermediate, formed by loss of water from initially produced aglycone.



(I) (II)

Azoxyglycosides are rapidly degraded by alkali to a variety of products including cyanide ion, ammonia, methylamine, nitrogen and formic acid; the sugar component is liberated even with cold dilute ammonia[3]. The first step is now formulated as (*a*) in the annexed scheme (Fig. 1). A little anisole (*c.* 2 per cent) is produced when cycasin is degraded by aqueous alkali buffered to *p*H 10 by an excess of phenol, so that the postulated intermediate, formaldazine monoxide (II), may break down partly to formaldehyde and free diazomethane in alkali. Most of these products, however, are apparently diverted into acetaldehyde, their product of (perhaps intramolecular) reaction (*b*), as shown by the appearance of iodoform (20 per cent yield) on treatment of cycasin or macrozamin with aqueous alkaline hypoiodite. The presence of acetaldehyde has not been demonstrated directly but the same yield of iodoform was obtained from an equimolar mixture of *N*-nitrosomethylurea and formaldehyde on treatment with alkali followed by hypoiodite, none being obtained by similar treatment of these compounds alone. The iodoform probably does not arise from direct iodination and cleavage of the 'active' methyl group (but see ref. 10) in the aglycone, for the electronically similar nitromethane yields no iodoform under the same conditions.

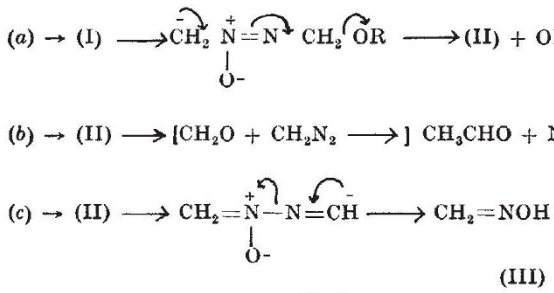


Fig. 1

The formation of cyanide ion in alkali is now postulated to follow an alternative mode (*c*) of decomposition of formaldazine monoxide (II), which finds a close analogy in the base-induced cleavage of aldehyde quaternary hydrazones to nitriles and tertiary amines[11]. The other product expected in the present case, formaldoxime (III), has not been isolated but evidence for its presence is found in (i) the production of formic acid (45 per cent), the hydrolysis product of formaldoxime in dilute acid[12], when the alkaline solution is acidified with dilute sulphuric acid and distilled[3], and (ii) the slow deposition of formaldehyde–dimedone (26 per cent) when the alkaline solution is buffered to *p*H 4 with acetic acid and sodium acetate in the presence of dimedone. The small amounts of methylamine and ammonia produced from macrozamin in boiling alkali[3] may also arise from decomposition of formaldoxime.

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Mechanism of Choline Sulphate Utilization in Fungi

Choline sulphate is synthesized by higher fungi[1], algae[2] and plants[3]. In fungi it is found in high concentration in the mycelium[4] and in spores[5] and is thought to act as a store of sulphur[6,7] and possibly carbon and nitrogen. Synthesis of choline sulphate[6,8] involves activation of inorganic sulphate by the enzymes ATP-sulphate adenylyltransferase (*EC*.2.7.7.4), (ATP-sulphurylase) and ATP-adenylyl 3′-phosphotransferase (*EC*.2.7.1.25), (APS-kinase), to give adenosine 3′-phosphate 5′-sulphatophosphate (PAPS) and the subsequent transfer of the