Band	Crystals						Solutions in benzene		
	Wave-length (A.)	Approx. diameters (mm.) 1	0·1	0·02	0·003	0·0003	Wave-length (A.)	1 gm. per l.	0·1 gm. per l.
0–0	4050	7	7	16	16	23	3830	—	—
0–1	4250	103	133	162	161	180	4050	180	185
0–2	4450	100	100	100	100	100	4290	100	100
0–3	4750	27	20	25	27	24	4560	29	29

the intensity of the 0–1 band relative to the 0–2 increases as particle size diminishes, and approximates to the ratio for dilute solutions at the smallest particle size examined. Another effect was noticed in comparing similar particles spread on a dry flat surface or embedded in a thick gelatine layer. The spreading produces an orientation which is absent in the gelatine preparation. The greater randomness of the latter crystal positions causes an increase in the ratio of the 0–1 to the 0–2 band.

This effect of particle size and shape in forcing much of the emitted fluorescence light through long distances in the crystal compared with the very small penetration of the exciting light raises the question whether the apparent 'resonance transfer' effect observed in anthracene–naphthacene and similar systems[1] is not due to re-absorption of the primary anthracene fluorescence. To test this, a homogeneous solid solution of anthracene with 8×10^{-3} gm./gm. acridine was prepared by crystallizing about 15 per cent from a benzene solution of the components. In this solid the anthracene fluorescence is reduced to 0·66 of the value for pure anthracene. The absorption band of acridine is only a little to the long-wave side of that of anthracene; if the quenching effect is due to re-absorption of the anthracene fluorescence the 0–1 band should be much more reduced in intensity than the 0–2 band, whereas if the effect is due to resonance transfer the two bands should be equally reduced. No decrease in the 0–1 to 0–2 ratio was observed. Similarly, for anthracene containing naphthacene over the range $1{\cdot}8 \times 10^{-3}$ to $2{\cdot}5 \times 10^{-8}$ gm./gm., where the blue anthracene fluorescence is reduced in intensity, the ratio of the 0–1 to 0–2 bands was constant although somewhat higher than that of pure anthracene of the same apparent crystal size in the higher size range. This small difference is believed to be due to the lesser perfection of the solid solution crystals.

The results, therefore, favour the resonance transfer hypothesis for the effects of acridine and naphthacene on the fluorescence of crystalline anthracene.

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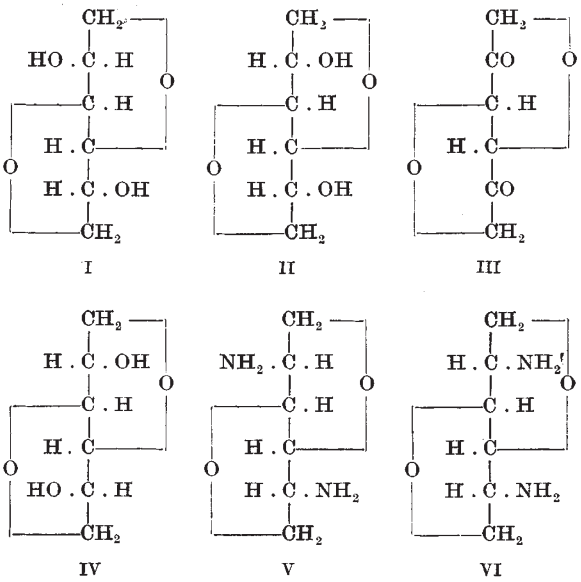
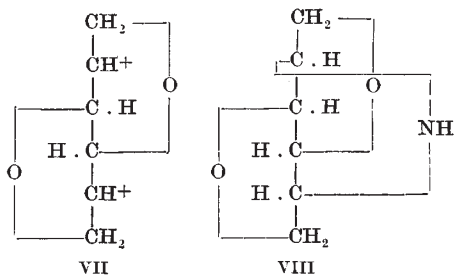
Interconversion of Dianhydro Hexitols and of Saccharic Acids

The conversion of 1 : 4-3 : 6-dianhydromannitol (I) and 1 : 4-3 : 6-dianhydrosorbitol (II) into the 1 : 4-3 : 6-dianhydride of L-iditol (IV) has previously been reported by Fletcher and Goepp[1], who effected the transformation by the dehydrogenation of either dianhydromannitol or dianhydrosorbitol with Raney nickel, followed by the hydrogenation of the intermediate, which is doubtless essentially the diketone (III). We have now effected the same transformation during studies on the deamination of amino-derivatives of sugar[2] and sugar alcohol derivatives.



2 : 5-Diamino dianhydromannitol (V) and 2 : 5-diamino dianhydrosorbitol (VI)[3] have each been treated with nitrous acid. Deamination proceeded smoothly, but the product in each case was 1 : 4-3 : 6-dianhydro-L-iditol (IV). Just as in the case of the hydrogenation of the diketone (III), any of the configurations L-iditol, D-mannitol or D-sorbitol is theoretically possible, so in this case, since the intermediate is doubtless the carbonium cation (VII), any of these three configurations may arise. That, in fact, the system takes on the L-iditol configuration both in this case and that recorded by Fletcher and Goepp indicates a certain configurational stability peculiar to L-iditol. This behaviour is paralleled by the ready epimerization of both 2 : 4-3 : 5-dimethylene-D-gluco- and -D-mannosaccharic acids to the corresponding derivative of L-idosaccharic acid[4]. Alternatively, the isolation of iditol or idosaccharic acid derivatives in the above instances, in which



three epimerically related substances are possible of formation, may be explained merely by the fact that the iditol or idosaccharic acid derivatives isolated may be more easily crystallizable or more insoluble than the isomeric materials.

This interconversion of dianhydro hexitols and also that of the saccharic acids is amenable to a theoretical interpretation on classical lines, whereas a mechanism for the conversion of mannitol and sorbitol into dulcitol recently described by Bladen, Owen, Overend and Wiggins[5] is difficult to envisage. In this case change of configuration occurred with sorbitol at C_4 and with mannitol at C_2 and C_4.

In an effort to determine whether, on deamination, 2 : 5-diamino 1 : 4-3 : 6-dianhydro-L-iditol would yield solely 1 : 4-3 : 6-dianhydro-L-iditol, attempts have been made to prepare this diamine. 2 : 5-Ditosyl 1 : 4-3 : 6-dianhydro-L-iditol was obtained and treated with methyl alcoholic ammonia under pressure in the manner found successful for the preparation of the diamines of dianhydro-mannitol and -sorbitol. No diamino derivative of dianhydro-L-iditol was obtained, however, and, instead, a secondary amine of m.p. 99–100° (found: C, 56·4; H, 6·9; N, 10·7; mol. wt. (Rast) 136. $C_6H_9O_2N$ requires C, 56·6; H, 7·0; N, 11·0; mol. wt. 127) was isolated. This, from the analytical data, appeared to be a compound possessing six carbon atoms and one nitrogen atom in the molecule. It formed a crystalline nitroso derivative and was characterized by the formation of well-defined salts. It was, therefore, 2 : 5-imino : 1 : 4-3 : 6-dianhydro 2 : 5-dideoxyhexitol. Since this has been derived from L-iditol, one would expect this configuration to be retained. Other evidence shows that the diamines derived from 2 : 5-ditosyl 1 : 4-3 : 6-dianhydro-mannitol and -sorbitol do, in fact, retain the configuration of the parent hexitols. Scale models show, however, that the imine derived from dianhydro L-iditol cannot possess the iditol configuration, and, in fact, that the only 1 : 4-3 : 6-dianhydro hexitol which can accommodate an imine bridge across C_2 and C_5 is dianhydro-D-mannitol. Such a contention involves Walden inversion at C_2 and C_5. This inversion is theoretically possible because the hydrolysis of a toluene-*p*-sulphonyl group does take place through the ionic scission of a carbon–oxygen bond, thus allowing the formation of an intermediate carbonium cation. We tentatively propose that the imine obtained by the ammonolysis of 2 : 5-ditosyl dianhydro-L-iditol is, in fact, 2 : 5-imino-1 : 4-3 : 6-dianhydro 2 : 5-dideoxy-D-mannitol (VIII).

We gratefully acknowledge the support of the Colonial Products Research Council during this investigation.

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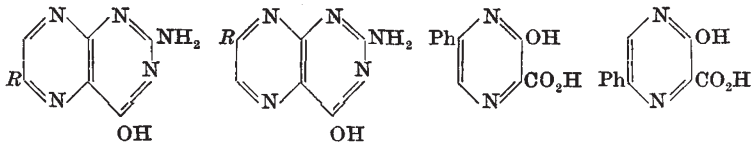
Application of Halogeno-Ketones to the Synthesis of Pteridines, including Pteroic Acid

Pteroic and pteroylglutamic acids were first synthesized from 2 : 4 : 5-triamino-6-hydroxypyrimidine (I), 1 : 2-dibromopropionaldehyde and *p*-aminobenzoic or *p*-aminobenzoylglutamic acids[1]. The action of an α-halogenocarbonyl compound on a 4 : 5-diaminopyrimidine introduces a new variation of the general method of pteridine synthesis remarkable for the spontaneous oxidation of the dihydropteridine initially obtained during the course of the reaction. It has been observed, however, that the formation of an intermediate dihydro derivative can sometimes be troublesome in that the hydrogen eliminated may effect the reduction of substituents[2]. The use of 1 : 1-dihalogeno-aldehyde or -ketone would, if successful, avoid this difficulty; but apart from Purrmann's somewhat analogous synthesis of xanthopterin from dichloracetic acid and the pyrimidine (I)[3], it is a modification not hitherto investigated.

We find that in marked contrast to the condensation of dichloracetic acid and the pyrimidine, which requires drastic conditions and gives xanthopterin in an over-all yield of only 6 per cent, 1 : 1-dichloracetone and 2 : 4 : 5-triamino-6-hydroxypyrimidine dihydrochloride buffered with sodium acetate in aqueous ethanol afford 53 per cent of 2-amino-6-hydroxy-8-methylpteridine at room temperature. The reaction between ω : ω-dichloroacetophenone and the pyrimidine occurred only slowly and heating was necessary, but again the yield of 2-amino-6-hydroxy-8-phenylpteridine was comparatively high (60 per cent).



The orientation of the product as the 8-phenylpteridine (II; R = Ph) rather than the 9-phenyl-isomer (III; R = Ph) rests on the identification of the pteridine from 1 : 1-dichloroacetone as the 8-methyl derivative (II; R = Me), by oxidation to the 8-carboxylic acid[4]. Both (II; R = Me) and (II; R = Ph) differ from the products obtained from the pyrimidine (I) and methyl- and phenyl-glyoxal, which are, therefore, respectively the 9-methylpteridine (III; R = Me) (see Forrest and Walker[5]) and the 9-phenyl compound (III; R = Ph).

Both phenylpteridines have similar physical properties, but may be distinguished by degradation with 25 per cent aqueous sodium hydroxide at 170°. In this manner was obtained from the 9-phenyl compound (III; R = Ph) a mixture of 2-hydroxy-6-phenylpyrazine-3-carboxylic acid (IV), m.p. 208–209° (ethyl ester, m.p. 112°), with a small amount of the corresponding 2-amino-6-phenylpyrazine-3-carboxylic acid (decarboxylated in 80 per cent sulphuric acid at 200° to 2-amino-6-phenylpyrazine). On the other hand, alkali degradation of the 8-phenylpteridine (II; R = Ph) gave entirely 2-hydroxy-5-phenylpyrazine-3-carboxylic acid (V), m.p. 200° (ethyl ester, m.p. 158–159°).

The preparation of pteroic acid by this modified pteridine synthesis requires a 1 : 1 : 3-trihalogeno-