684. Solanum *Alkaloids. Part IX.** *The Relation between Constitution and Basicity in Solasodine, its Derivatives, and Solanidine.*

By H. Bloom and Lindsay H. Briggs.

A relation exists between the constitution of bases in this series and their basicity, depending on the presence or absence of the oxide ring.

Utilising Ingold's micro-procedure (*Helv. Chim. Acta*, 1946, **29**, 1929) for estimation of the dissociation constants of bases, already employed in constitutional studies of polymethyleneimines (Prelog *et al.*, *ibid.*, 1948, **31**, 1325; 1949, **32**, 544) and strychnine bases (Prelog and Häfliger, *ibid.*, 1949, **32**, 1851) we have measured the basicity of the following compounds in terms of their $\mathrm{p}K_b$ values. The results are recorded in the following Table.

	Compound	$\mathrm{p}K_b$		Compound	$\mathrm{p}K_b$
I	Solasodine	6·30, 6·32	VII	Dihydrosolasodenol	4·36
II	Solasonine	6·26	VIII	Dihydrosolasodanol	4·28
III	Solmargine	6·25, 6·36	IX	Dihydrosolaso-3 : 5-diene [2]	4·16
IV	Solasodamine [1]	6·18, 6·23, 6·32	X	Dihydro-*N*-methylsolasodenol [2]	5·50, 5·66
V	Solasodanol	6·36	XI	Solanidine	5·38
VI	Solaso-3 : 5-diene	6·20			

[1] A new tetrasaccharide derivative of solasodine isolated from *S. sodomaeum*, *S. auriculatum*, and *S. marginatum*, constituted as rhamnose–rhamnose–galactose–glucose–solasodine, with probable sugar linkages, 1 : 1,4 : 1,4 : 1,6, respectively (forthcoming publications).

[2] New compounds to be described in detail later.

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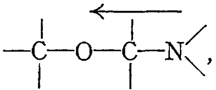
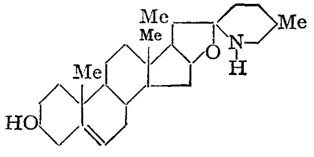
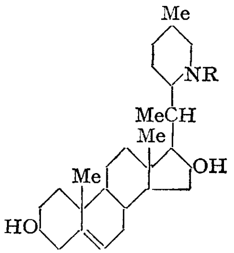
* Part VIII, preceding paper.

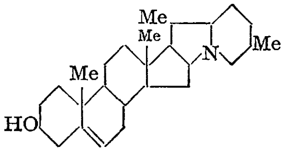
Solasodine (I) and all its derivatives with the oxygen bridge intact, *viz.*, (II), (III), (IV), (V), and (VI), are relatively weak bases with an approximate pK_b value of 6·2—6·3. This weak basicity is obviously due to the inductive effect of the ether-oxygen atom attached to the same carbon atom as the nitrogen atom, *i.e.*,  $\overleftarrow{-\overset{|}{\underset{|}{C}}-O-\overset{|}{\underset{|}{C}}-N}\!\!<$, an effect weaker than that occurring in amides, and it explains why *O*-acetylation occurs in solasodine in preference to *N*-acetylation and why *O*-benzoyl derivatives may be obtained and not *N*-benzoyl derivatives (cf. Part VII, *J.*, 1952, 1654).



(I)



(VII; R = H) (X; R = Me)



(XI)

When the oxide ring is broken, however, as in dihydrosolasodenol (VII) and its derivatives, *viz.*, (VIII) and (IX), no such inductive effect occurs and these bases are much stronger, with a pK_b value of 4·2—4·3. In contrast with the first series of compounds no difference can be detected in the ease of acetylation or benzoylation of the secondary hydroxyl and amino-groups (cf. Part VII, *loc. cit.*).

When dihydrosolasodenol is converted into the tertiary base, dihydro-*N*-methylsolasodenol (X), the basicity decreases and the pK_b value (5·5) is comparable with that of the tertiary base, solanidine (XI).

EXPERIMENTAL

Solutions of 50—100 mg. of the compounds in 60% alcohol–water (carbon dioxide-free) were titrated at 19·5—20·5° with 0·1N-hydrochloric acid by use of a semimicro-burette. pH readings were carried out with a Cambridge pH meter with an accuracy of ±0·02 pH unit. The pH at half-neutralization was estimated from the plot of pH against the volume of hydrochloric acid added, within ±0·05 unit.

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