

## CHAKSINE.<sup>1</sup> PART II.—PYROLYSIS OF CHAKSINE<sup>2,3</sup>

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In the course of studies in the constitution of chaksine, the principal alkaloid of *Cassia Absus Linn*, Siddiqui et al. observed the formation of a cyanide and an odorous product with a characteristic caraway-like smell on the thermal degradation of the salts of the base. As a result of further studies in this direction, it has been noted by the present authors that the odorous product obtained on heating chaksine iodide with Cu-bronze (Merck's) at 310°-320°C. in nitrogen atmosphere, gives on hydrolysis with 20% methanolic potassium hydroxide mainly phthalic acid along with a very small quantity of a light petroleum soluble acid (m.p. 116°C.) which analyses for  $C_{10}H_{12}O_2$ . On the other hand, hydrolysis of chaksine iodide with copper filings or silver powder (40-80 mesh) at the same temperature range, yields an oily product, which on hydrolysis gives the light petroleum soluble acid m.p. 116°C. as the major constituent. This acid has been identified as *p*-isopropylbenzoic acid.

During the hydrolysis with methanolic potassium hydroxide, ammonia was evolved indicating the formation of the acid through a nitrile. The characteristic caraway-like smell, on the other hand would indicate the presence of *p*-isopropylbenzaldehyde which on hydrolysis should furnish the corresponding acid through a Cannizzaro reaction, but it was not possible to isolate the aldehyde from the pyrolysate.

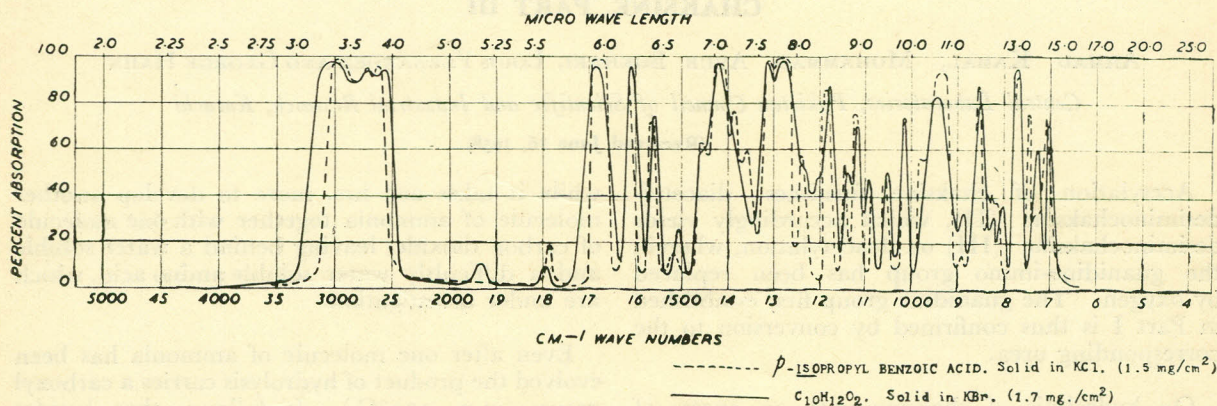
### Experimental

All melting points are corrected.

**Pyrolysis of Chaksine Iodide.**—Chaksine iodide (1 g.) and copper bronze (1 g., Merck's) were thoroughly mixed and placed in a distillation flask (cap. 25 ml.) attached to a receiver tube. The mixture was heated to at 310-320°C. in a metal-bath under a slow current of nitrogen. The flask was removed after 25 minutes heating and the cooled contents extracted with ether repeatedly. The ethereal extracts were combined with the ethereal washings of the receiver flask, dried and the ether removed. The residual oil, deep brownish red in colour, had a characteristic caraway-like smell. Yield between 0.19-32 g. in different experiments.

The crystalline, ether-insoluble material collected from the receiver tube was identified as ammonium bicarbonate.

The oil (0.8 g.) was taken up in 20% methyl alcoholic potassium hydroxide (10 ml.) and refluxed on water-bath, ammonia being evolved in the process. After 10-12 hrs. heating methyl alcohol was removed in vacuum, the residue was taken up in water (5 ml.) and extracted with ether. The aqueous alkaline solution was acidified with dilute hydrochloric acid and repeatedly extracted with light petroleum (60-80°C.), and



Infrared absorption spectrum.



then with ether. Removal of light petroleum left an oily residue which on keeping gave a minute quantity of an acid which on several crystallisations from water melted at 116°C. and was identical with the acid described in the subsequent experiment.

Drying and removal of the ether gave material which crystallised from water (m.p. 196°C. dec.) with evolution of gas. Yield 0.12 g. It was identified as phthalic acid with which it gave no depression in melting point. On melting it gave the anhydride which was purified by sublimation. m.p. 130°C., undepressed with an authentic sample of phthalic anhydride. On heating with water gave phthalic acid m.p. 196°C.

**Acid C<sub>10</sub>H<sub>12</sub>O<sub>2</sub>.**—Chaksine iodide (1.0 g.) thoroughly mixed with copper or silver filings (1 g. 40-80 mesh) was heated, in the manner described above, for 25 minutes. Yield of ether soluble red oil with characteristic caraway-like smell varied between 0.2-0.25 g. In one experiment 0.39 g. of the oil was obtained.

The ether soluble oil (0.85 g.) was taken up in 20% methyl alcoholic potassium hydroxide solution (10 ml.) and refluxed for 12 hrs. Methyl alcohol was removed in vacuum, the residue was acidified with dilute hydrochloric acid and repeatedly extracted with light petroleum (60-80°C.). Drying and removal of the solvent yielded an oil (0.18 g.) which crystallised on standing, m.p. 106°C. Crystallisation from

water (twice) gave colourless prismatic needles, m.p. 116°C., (70 mg.). The compound is an acid and is soluble in all the usual organic solvents.

Calculated for C<sub>10</sub>H<sub>12</sub>O<sub>2</sub>: C, 73.17; H, 7.32; O, 19.51; m.w., 164. Found: C, 73.39; H, 7.3; O, 19.38; m.w., 165.5; equivalent wt., 165.

On admixture with an authentic sample of *p*-isopropylbenzoic acid (m.p. 116°C.) the melting point was undepressed.

#### Acknowledgement

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#### References

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### CHAKSINE. PART III

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Acetylation of chaksine furnishes diacetyl-desiminochaksine (II), which accordingly yields desiminochaksine (III) on deacetylation, wherein the guanidine-imino group has been replaced by oxygen. The guanidine group first established in Part I is thus confirmed by conversion to the corresponding urea.

On hydrolysis of chaksine with an excess of aqueous barium hydroxide one molecule of ammonia is evolved within approximate 48 hrs.

while it takes 200 hrs. more to develop another molecule of ammonia together with one molecule of carbon dioxide, leaving behind a water soluble and a difficultly water soluble amino acid, which are under investigation.

Even after one molecule of ammonia has been evolved the product of hydrolysis carries a carboxyl group (m.p. 123°C.). It follows, that besides the replacement of the guanidine-imino group by oxygen a carbonyl group containing, hydro-