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THE ALKALOIDS OF *ASPHODELUS MICROCARPUS*

THE genus *Asphodelus (Liliaceae)* is represented in Egypt by 4 species; two of these, *viz.*, *A. microcarpus* and *A. fistulosus* are common while the other two, *viz.*, *A. viscidulus* and *A. refractus* are rare. Of the two common species *A. microcarpus* is the most widely spread species.

Few *Asphodelus* species have been a subject of interest to investigators particularly their lipids and anthraquinones[1-4]. β-sitosterol and β-amyrin were separated from the seeds of *A. microcarpus* and *A. fistulosus;* while fucosterol was isolated from the tubers of *A. microcarpus*[4].

Only limited investigations of the alkaloidal constituents of the genus *Asphodelus* have been made. Klein and Pollauf[5] recorded evidence for the presence of colchicine in *A. albus*, but this was refuted by Santavy[6]. Initial screening of the seeds of *A. microcarpus* and *A. fistulosus* revealed the presence of alkaloids in both species[3].

The study of the lipids, anthraquinones as well as of certain active constituents of the tubers of *A. microcarpus*, growing in Egypt, had been recently carried out by the authors[4,7-9]. This paper deals with the study of the alkaloids of the tubers.

Experimental and Results.—One kg of the defatted powdered tubers was extracted with ethanol 90% in percolator. The dark brown solvent-free extract was taken with H_2SO_4 5% and filtered. The precipitate (anthraquinones)[7] was filtered off and the filtrate was shaken with successive portions of benzene, chloroform, then with ether and the washings were rejected. The acidulated solution was rendered alkaline with ammonia and then shaken with benzene (A), followed by ether (B) then chloroform (C). The crude yellowish-brown solvent-free residues amounted to 0·05, 0·24 and 0·06 gm respectively; all had the same qualitative picture (TLC) and therefore they were combined.

The alkaline mother liquor was rendered acidic with dil. HCl to pH 2, warmed on a water-bath for 15 minutes, filtered and then treated with 2% aqueous solution of ammonium reineckate. The solution was kept at 0° C overnight, then filtered. The precipitate, on the funnel, was dissolved in acetone and CaO was added. The acetone-free residue was dissolved in methanol (500 ml) and then passed through exchange resin (IR 400) and the eluate was evaporated *in vacuo* at 50° C (D, 1·1 gm).

Both paper and thin-layer chromatography, using different solvents, revealed the presence of 3 constituents in fractions A-C and 2 in fraction D (Table I). The alkaloidal spots were detected by UV, as well as by spraying with modified Dragendorff's[10] and iodoplatinic acid[11] reagents.

TABLE I

The R_f and colour of the components detected in the Alkaloidal Fractions

Component No.	Paper chromatography				Thin-layer chromatography*				Detection		
	A	B	C	D	E	F	G	H	U.V.	Dragendorff	Iodoplatinic acid
I	0·37	0·13	0·16	0·33	0·01	0·01	0·12	0·01	B	Orange	+ ve
II	0·67	0·51	0·52	0·63	0·23	0·21	0·49	0·26	B	,,	− ve
III	0·90	0·83	0·90	0·90	0·90	0·90	0·90	0·90	G	,,	− ve
IV	..	..	0·42	0·40	0·02	0·01	0·01	0·12	..	+ ve	+ ve
V	..	..	0·45	0·48	0·14	0·10	0·36	0·12	..	+ ve	+ ve
Choline (Authentic)	..	..	0·42	0·40	0·02	0·01	0·01	0·12	..	+ ve	+ ve
Stachydrine (Authentic)	..	..	0·45	0·48	0·14	0·10	0·36	0·12	..	+ ve	+ ve

* *Absorbent :* Silica gel G ; G = Green, B = Blue.
Solvents : A—BuOH : ACOH : H_2O (4 : 1 : 5), B—BuOH : ACOH : H_2O (50 : 1 : 49), C BuOH : ACOH : H_2O (49 : 1 : 50), D—BuOH : ACOH : H_2O (50 : 10 : 50) E—Methanol, F—Benzene : Methanol (30 : 70), G—Methanol-Water (60 : 40), H—BuOH-ACOH-Water (4·1 5).

Trials to obtain either of the three former constituents, after fractionation by preparative TLC, in a crystalline form were unsuccessful. The pharmacological screening[9] of them revealed interesting and promising results ; two are spasmolytic and one is spasmogenic.

Colchicine, colchceine, colchamine, demecolcine, jervine, cornigerine and rubjervine were proved to be absent by PC and TLC and by the failure of the alkaloidal extract to give any colour specific for colchicine[12,13].

Fractionation of the Water-Soluble Alkaloidal Fraction (D).—Fraction D was fractionated into the two alkaloids by preparative TLC (using silica gel G) and applying the solvent system methanol-water (60 : 40).

Stachydrine.— The alkaloid possessing the higher R_f, crystallised from absolute ethanol was identified as stachydrine (m.p., m.m.p., 234–235° C). The hydrochloride melted at 219–220° C (undepressed) (Found : C, 46·3 ; H, 7·8 ; N, 7·5 . $C_7H_{13}O_2N$. HCl, m.p., 222° C[14] required : C, 46·8 ; H, 7·8 ; N, 7·8%). The picrate melted at 195–197° C (Lit.[14] 199–200° C).

Choline.—The picrate melted at 245–247° C (Found : C, 39·46 ; H, 4·63 ; N, 16·49. $C_{11}H_{16}N_4O_8$, m.p. 245° C[15] required : C, 39·76 ; H, 4·86 ; N, 16·87%). The chloroaurate melted at 250–252° C (undepressed).

The presence of stachydrine in *Asphodelus microcarpus*, a plant belonging to the family *Liliaceae*, seems to be the first record of this alkaloid in the family.

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A PRELIMINARY NOTE ON FOSSIL POLYCHAETA FROM THE CRETACEOUS ROCKS OF SOUTH INDIA

Fossil record of polychaetes reaches back into the Cambrian period and as in other regions, they are known to occur in Indian subcontinent also in various rock formations. Our geological literature, however, rarely gives more than a mere mention of them as *annelids* or *worms* or *serpulids*. Hardly a dozen species have been so far described in any detailed manner[1-5], seven of them being from the Cretaceous rocks of South India described by Stoliczka[3,4] nearly a hundred years ago.

Recent collections of fossils made by us from the Cretaceous rocks of South India have revealed a rich and varied polychaetan fauna, mostly coming from the Uttattur and Ariyalur Groups. Our study has revealed among them several new species, as also some genera, *e.g.*, *Spirorbula, Rotularia, Glomerula, Serpentula* and *Terebellolites*, which were not known to occur in these South Indian strata. The species which we have so far been able to identify in our collection include : *Serpula filiformis* Sow., *S. ootatoorensis* Stol., *S. hamata* Forbes, *S. rugosa* sp. nov., *S. malburensis* sp. nov., *Ditrupa brevituba* sp. nov., *Glomerula gordialis* (Schloth.), *Serpentula ampullacea* (Sow.), *Rotularia rotuloidea* sp. nov., *R. callosa* (Stol.), *R. discoidea* (Stol.), *Spirorbula crispans* sp. nov., *S. sinuirugosa* sp. nov., *Burtinella concava* (Stol.) and *Terebellolites* sp.

Tubilosteum Stoliczka (now a synonym of *Rotularia* Defrance[6]) and *Burtinella* Mörch are polychaetan and not gastropodous genera as considered by Stoliczka[3].

Morphological features of determinative value available for study in polychaetan fossil material being not many nor easy to study, this group of organisms has been generally neglected by palaeontologists as material not of much use for stratigraphical purposes or for age considerations. However, for these very reasons and accepting the limitations inherent