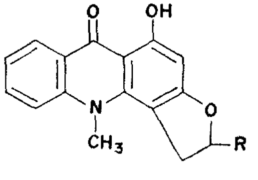
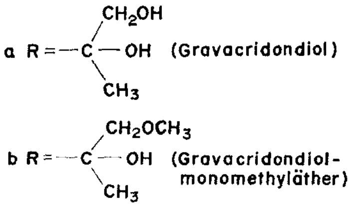
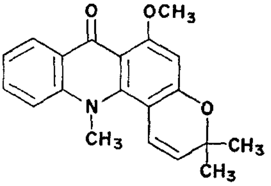


(I)





(II)

Die Strukturen dieser beiden neuen Acridon-Alkaloide deuten darauf hin, daβ in der Pflanzenzelle ähnliche Biotransformationen an den geminalen Methyl-Gruppen eintreten können, wie sie z.B. beim Metabolismus des Acronycins (II) im tierischen Organismus beobachtet wurden.[8]

EXPERIMENTELLE

Über die Isolierung der Acridon-Alkaloide aus *Ruta graveolens* wird ausführlich an anderer Stelle berichtet werden.[9] Gravacridondiol (Arbeitsbez. Rr 15) Schmp.: 224–227° (Zers.) (Aceton) $C_{19}H_{19}O_5N$ (MG 341 m.s.). λ_{max}^{MeOH}: 390; 332; 300; 273; 264; 249; 227; 213 nm: log ϵ: 3,68; 3,86; 4,18; 4,55; 4,46; 4,40; 4,15; 4,16. IR, KBr ν_{max}^{KBr}: 3600–3200; 1640; 1600; 1575; 1550; 1500 cm.$^{-1}$ Gravacridondiol-acetat Schmp.: 221–223° (Benzol).

Gravacridondiol-monomethyläther (Arbeitsbez. Rr 5) Schmp.: 219–221° (Äthylacetat) $C_{20}H_{21}O_5N$ (MG 355 m.s.) λ_{max}^{MeOH}: 390; 332; 299; 272; 265; 249; 227; 213 nm: log ϵ: 3,78; 3,96; 4,33; 4,68; 4,59; 4,52; 4,22; 4,23. IR, ν_{max}^{KBr}: 3600–3200; 1640; 1600; 1580; 1560; 1510 cm^{-1}.

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Key Word Index—Ruta graveolens; Rutaceae; acridone alkaloids; gravacridondiol; gravacridondiol monomethyl ether.

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MONOCOTYLEDONAE

LILIACEAE

ANTHRAQUINONES OF *ASPHODELUS MICROCARPUS*

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Several genera of the family Liliaceae *viz. Aloe*, *Bulpine*, *Asphodeline* were reported[1,2] to contain anthraquinones. The only study of the anthraquinones of *Asphodelus* was that carried out by Oudtshoorn,[1] reporting the presence of chrysophanol and aloe-emodin in *A. albus* Willd.

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[1] M. C. B. VAN RHEEDE VAN OUDTSCHOORN, *Phytochem.* **3**, 383 (1964).

[2] T. J. MCCARTHY, *Planta Med.* **17**, 1 (1969).

The free anthraquinones were prepared by extraction of the defatted tubers with organic solvents, or by treating the alcoholic extract with alcoholic KOH, followed by extraction from the acidic medium with ether. In addition, treatment of the alcoholic extract with dil. HCl gave a brown powder which afforded, after purification, pure free anthraquinones. Extraction of the anthraquinones from the acidic medium gave the purest mixture, while direct extraction (from the defatted tubers) with EtOAc gave the highest yield (2·6%).

Column chromatography, using polyamide separated 3 anthraquinones, while preparative TLC[3,4] using SiO_2 gel G gave the all five components. One anthraquinone (I, in Table 1) was unstable, even when all precautions were taken and gave as a decomposition product 1,8-dihydroxyanthraquinone (II) (TLC, m.m.p., UV, IR, NMR, MS '*m/e* 240', diacetate). The original anthraquinone is thus probably 1,8-dihydroxydianthraquinone. The results obtained from the pharmacological study[5] which showed that this component and bichrysophanol are inactive, while their decomposition products possess spasmogenic effect on the isolated intestine of rabbit, support the proposed structure of the original compound.

TABLE 1

Anthraquinone	%*	λ_{max} nm	R_f in TLC (SiO_2)		
			A	*B*	*C*
I†	15·6			0·42	0·00
II (1,8-dihydroxy-anthraquinone)		222,252,285		0·82	0·53
III (bichrysophanol)	17·8			0·45	0·10
IV (aloe-emodin)	22·2	220,255,282		0·50	0·14
V (chrysophanol)	33·3	224,257,277,287	0·94		
VI	11·1			0·80	0·47
VII‡ (chrysophanol glycoside)			0·51		

A—Benzene–methanol (9:1); *B*—Benzene–methanol (8:2); *C*—Light petroleum–ethyl acetate (9:1).

* Calculated on the basis of the free anthraquinones.

† Before decomposition.

‡ The glycoside had R_f 0·64 (TLC) in benzene–ethyl acetate–acetic acid (20:15:0·5) and 0·85 and 0·81 respectively (Paper chromatography) in *n*-propanol–ethyl acetate–water (4:4:3) and *n*-butaol–acetic acid–water (4:1:5).

The other anthraquinones were identified as 5,5′-bichrysophanol (III, m.p., IR, MS '*m/e* 506', tetraacetate and the cleavage product chrysophanol), aloe-emodin (IV, TLC, m.m.p., UV, IR, triacetate and trimethyl ether) and chrysophanol (V, TLC, m.m.p., UV, IR, diacetate) respectively. The last compound (VI) was obtained in small amounts and its identity as an anthraquinone was proved by the Börntrager test.[6,7]

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[3] R. P. LABADIE and A. B. SVENDSEN, *Pharm. Weekblad.* **102**, 169 (1967).

[4] R. P. LABADIE and A. B. SVENDSEN, *Pharm. Weekblad.* **102**, 615 (1967).

[5] H. GHALEB, A. M. RIZK, F. M. HAMMOUDA and M. M. ABDEL-GAWAD, *Qualitas Plantarum et Materiae Vegetabiles* (Holland) **21**, (1972) (In press).

[6] H. BÖRNTRAGER, *Z. Analyt. Chem.* **19**, 165 (1880).

[7] T. ROBINSON, *The Organic Constituents of Higher Plants, their chemistry and Interrelation*, Burgess Publ. Co. (1963).

The glycoside (VII) was prepared by extraction of the tubers with methanol and by precipitation with lead acetate and cholesterol. Chrysophanol-8-mono-β-D-glucoside (PC, TLC, m.m.p., acid hydrolysis) was the sole glycoside detected in the tubers.

EXPERIMENTAL

Plant material. A. microcarpus Salzm et Vivi. was collected from Borg El-Arab, 45 km west Alexandria.

Chromatography. For the free anthraquinones on TLC SiO_2 developed with different solvents[3,4,8–12] were tried. C_6H_6–MeOH (9:1, 2 developments or 8:2) gave the best separation. Attempts to obtain better separations by PC[13,14] were unsuccessful. For glycosides both TLC[15,16] and PC[14,17,18] were applied. Visualization was carried out by UV or by spraying with alcoholic MgOAc[16] or KOH soln.[4] or by exposing to NH_3 vapours and re-examining under UV light.

Preparation of the free anthraquinones Method A. 1 kg of the defatted tubers was extracted with 95% EtOH (perculator), the extract concentrated *in vacuo* at 45° and treated with HCl (10%) giving a precipitate (67 g) purified as follows: *Procedure* 1, 33·5 g in EtOH (500 ml), filtered concentrated to 150 ml and H_2O (180 ml) added. The precipitate (MeOH–H_2O, 98:2) gave yellow orange powder (16 g). *Procedure* 2, 33·5 g in EtOH (500 ml), filtered, concentrated to 150 ml, 100 ml 10% KOH added and the solution extracted with ether,[19] then acidified with HCl and the anthraquinones extracted with Et_2O. *Method B.* About 100 g portions of the defatted tubers were, extracted successively with C_6H_6, $CHCl_3$, Et_2O, EtOAC (yield 0·90, 1·08, 2·26 and 2·6% respectively) and purification achieved by procedure 2 above. *Method C.* 0·5 kg of the defatted tubers were percolated with EtOH and the concentrated extract (200 ml) treated with alc. KOH (200 ml) and the steps of procedure 2 then followed (11·1 g).

Column chromatography. About 5 g of the anthraquinone mixture (method *C*) were chromatographed on polyamide (250 g). Fractions (500 ml each) 53–65 (eluted by H_2O–MeOH 3:7), 71–75 and 76–85 (eluted by MeOH) gave bichrysophanol, aloe-emodin and chrysophanol respectively.

Preparative TLC. 2 g of the anthraquinones were fractionated on 40 plates coated with SiO_2 gel G (1 mm thick) applying the system C_6H_6–MeOH (9:1, 2 developments). The anthraquinone zones were extracted with $CHCl_3$–MeOH (9:1).

Anthraquinone (I). The decomposed product (MeOH–H_2O) gave 1,8-dihydroxyanthraquinone, m.p., m.m.p. 191–192° (Lit.[20] 191–192°). (Found: C, 70·00; H, 3·10, $C_{14}H_8O_4$ (240) required: C, 70·00; H, 3·33%.) The *diacetate* (Ac_2O–pyridine refluxed 0·5 hr) (MeOH) m.p. 230–232° (Lit.[20] 231–232°). (Found: C, 66·62; H, 3·61. $C_{18}H_{12}O_6$ required: C, 66·67; H, 3·73%.)

5,5′-Bichrysophanol (II) (EtOH) decomposed at 318–319° (Lit.[21] 321°). (Found: C, 71·18; H, 3·67. $C_{30}H_{18}O_8$ (506) required: C, 71·14; H, 3·56%.) The *tetraacetate* (Ac_2O at 100°, 2 hr) (MeOH–H_2O) m.p. 248–250° (Lit.[21] 244–248°). *Cleavage* of II (50 mg treated with 10 ml 85% HCOOH, left at room temp. for 48 hr and the formed precipitate extracted with C_6H_6) gave chrysophanol (TLC, m.m.p., IR).

Aloe-emodin (III) (*toluence*) melted at 222° (undepressed). The *triacetate* (Ac_2O-pyridine, refluxed 5 hr) (MeOH) m.p. 175–178° (Lit.[22] 175–178°). (Found: C, 63·80; H, 4·52. $C_{21}H_{16}O_8$ required: C, 63·60; H, 4·20%.) The *trimethylether* (7 hr reflux with Me_2SO_4 and K_2CO_3 in acetone followed by refluxing the residue with 5% KOH for 0·5 hr) (AcOH) melted at 162° (Lit.[20] 163°).

Chrysophanol (V) (MeOH–$C_6H_5CH_3$) had m.p. 192° (undepressed) (Lit.[23] 194–195°). (Found: C, 70·80; H, 3·87. $C_{15}H_{10}O_4$ (254) required: C, 70·87; H, 3·95%.) The *diacetate* melted at 202–204° (Lit.[23] 204–205°). (Found: C, 67·62; H, 4·31. $C_{19}H_{14}O_6$ required: C, 67·50; H, 4·20%.)

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[23] F. E. KING and M. F. GRUNDEN, *J. Chem. Soc.* 4580 (1952).

Preparation of the anthraquinone glycoside. Method 1. 0·5 kg. of the defatted powder was first extracted with Et_2O, then with MeOH. The concentrated extract was treated with H_2O, filtered and the filtrate concentrated *in vacuo*. *Method* 2. 0·5 kg of the defatted tubers was extracted with MeOH and the concentrated extract was taken with hot H_2O (100 ml), left at 0° for 48 hr, filtered and the filtrate treated with 10% basic lead acetate. The orange precipitate was suspended in EtOH (1 l.) and after removal of Pb by H_2S was concentrated, left at room temp. and the precipitated yellow powder was further purified (MeOH–H_2O, 1:1). *Method* 3. 0·5 kg of the defatted tubers was refluxed with 80% EtOH. To the hot concentrated extract (300 ml) was added a boiling solution of cholesterol (6 g) in 95% EtOH (80 ml), the mixture was stirred for 15 min, H_2O (100 ml) was added and left to stand at room temp. for 3 days. The precipitated complex was dissolved in dry pyridine (10 ml), refluxed at 100° for 2 hr and filtered. After cooling Et_2O (200 ml) was added to precipitate the anthraquinone glycoside, which was washed with Et_2O (0·7 g). Purification from MeOH–H_2O (1:1) gave a yellow powder (0·4 g).

Chrysophanol-8-mono-β-D-glucoside [TLC, m.p., m.m.p., acid hydrolysis at 100° with 2 N HCl and detection of chrysophanol (TLC, m.m.p.) and glucose (PC) (MeOH–H_2O)] was the sole glycoside detected in the plant.

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Key Word Index—*Asphodelus microcarpus*; Liliaceae; anthraquinones; chrysophanol; aloe-emodin; bichrysophanol; 1,8-dihydroxyanthraquinone; chrysopahnol-8-mono-β-D-glucoside.