(20S,22S,25S)-5α-*Furostan-22,25-epoxy-3β,26-diol-3-monoacetate* (**2**). Needles from MeOH, mp 206–208°; IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3440 (OH), 1740 (C=O), 1240 (ester), 990, 970, 955, 915, 895, 875 (spiroketal chain); MS *m/z* (rel. int.): 474 $[\mathrm{M}]^+$ (2), 443 $[\mathrm{M}-\mathrm{CH_2OH}]^+$ (14), 386 (29), 344 (14), 315 (49), 255 (18), 155 (100), 137 (9).

Acetylation ($\mathrm{Ac_2O}$–$\mathrm{C_5H_5N}$) of **2** gave the diacetyl derivative **2a** as colourless needles, mp 183–186° (MeOH). The IR spectrum showed the disappearance of the free hydroxyl group band.

(20S,22R,25R)-5α-*Spirostan-3β,25-diol monoacetate* (**3**) was crystallized from MeOH, mp 211–213°; IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3500 (OH), 1730 (C=O), 1250 (ester), 1030, 990, 925, 890, 850 (spirostan); MS *m/z* (rel. int.): 474 $[\mathrm{M}]^+$ (1), 443 $[\mathrm{M}-\mathrm{CH_2OH}]^+$ (70), 389 (7), 386 (79), 344 (16), 329 (13), 315 (68), 255 (30), 155 (100).

(20S,22R,25S)-5α-*Spirostan-3β,25-diol monoacetate* (**4**), mp 230–232° (MeOH) (lit. [3] mp 240°). IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3580 (OH), 1730 (C=O), 1240 (ester), 970, 955, 940, 905, 880, 850 (spirostan); MS *m/z* (rel. int.): 474 $[\mathrm{M}]^+$ (3), 443 $[\mathrm{M}-\mathrm{CH_2OH}]^+$ (12), 389 (9), 386 (99), 344 (15), 329 (9), 315 (30), 255 (13), 155 (100). Its ^{1}H NMR and ^{13}C NMR spectra (see Tables) resembled those of 5α,6-dihydroisonuatigenin (isocaelagenin) [3, 10].

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DISTRIBUTION OF ANTHRAQUINONE PIGMENTS IN *RUMEX* SPECIES OF KENYA

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Key Word Index—*Rumex*; Polygonaceae; anthraquinones; chrysaphanol; emodin; physcion; nepodin; distribution.

Abstract—A correspondence between pigment structures and leaf morphology has been found in Kenyan *Rumex* species.

The genus *Rumex* is represented in Kenya by five species [1, 2]. Of the Kenyan species listed in Table 1, only *R. abyssinicus* has attracted chemical study on two occasions previously. In 1962, it was reported to contain chrysophanic acid (chrysophanol) [3]. More recently work in our laboratories has revealed the existence of chrysophanol, physcion and emodin [4]. We now investigated all five Kenyan species including *R. abyssinicus* which was collected in another locality than the plants formerly [4] analysed in order to characterize their pigments. Results are presented in Table 1.

EXPERIMENTAL

Plant materials. The plants were collected from different parts of the high altitude areas of Kenya and authenticated at the

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Table 1. Levels of quinone pigments in *Rumex* species of Kenya (g/kg dry wt)

	Leaf type	Nepodin		Chrysophanol		Physcion		Emodin		
		Free	Bound	Free	Bound	Free	Bound	Free	Bound	Total
R. usambarensis	*									
Roots		—	—	0.263	0.098	0.156	0.073	0.127	0.064	0.78
Seeds		—	—	0.049	0.075	0.036	0.049	0.023	0.086	0.32
Leaves and stem		—	—	0.014	0.034	0.027	trace	0.013	0.039	0.13
R. abyssinicus	*									
Roots		—	—	2.07	0.067	1.15	0.03	9.49	0.102	12.91
Seeds		—	—	0.340	0.057	0.29	0.03	0.31	0.078	1.11
Leaves and stem		—	—	0.60	0.025	0.073	trace	0.069	0.040	0.81
R. bequaertii	†									
Roots		0.071	0.010	0.089	0.042	0.144	0.029	0.093	0.093	0.57
Seeds		0.046	0.031	0.082	0.063	0.079	0.031	0.089	0.061	0.48
Leaves and stem		0.02	trace	0.028	trace	0.032	trace	0.02	0.06	0.16
R. ruwenzoriensis	†									
Roots		3.35	0.208	0.319	0.034	0.117	trace	0.217	0.078	4.32
Seeds		1.17	0.035	0.499	0.154	0.145	0.051	0.126	0.142	2.32
Leaves and stem		0.234	trace	0.352	0.032	0.048	trace	0.120	0.036	0.82
R. crispus	†									
Roots		1.66	0.055	0.933	0.089	0.164	0.055	0.545	0.079	3.58
Seeds		0.498	0.016	0.280	0.031	0.041	0.017	0.164	0.024	1.07
Leaves and stem		0.116	0.004	0.056	0.006	0.008	0.004	0.038	0.006	0.24

*Hastate or sagittate.
†Oblong.

Kenya National Herbarium, Nairobi. *R. usambarensis*, *R. abyssinicus* and *R. crispus* were obtained within the environs of Nairobi (2000 m). *R. bequaertii* was found on a stream near Nyeri town (2700 m) while *R. ruwenzoriensis* was on the moorland of the Aberdare range (3400 m). They were brought into the laboratory and for the purposes of the study divided into roots, seeds and stems and leaves. These three portions for each plant were cut up and dried under a Phillips 250 W lamp immediately to avoid mould. The dried samples were ground into fine powder before solvent extraction.

Solvent extraction and hydrolysis of glycosides. All the parts (200–300 g) were extracted by continuous process in a Soxhlet with petrol (bp 40–60), $CHCl_3$ and MeOH successively. Petrol and $CHCl_3$ fractions, usually quite similar, were combined before chromatography. The MeOH fractions, black viscous masses, were hydrolysed with 2 N HCl under reflux for 1.5 hr. The filtrates of the hydrolysates were partitioned into benzene which was evaporated *in vacuo* to release the bound aglycones.

Chromatography. Complete separation of the components was achieved using Merck silica gel (70–230 mesh ASTM, 1:30 by weight ratio of sample and silica gel respectively) under gravity elution, with petrol (bp 60–80), $CHCl_3$ and MeOH. Analytical TLC was with hexane–EtOAc–HOAc (17:4:1) which gave the following R_f values: chrysophanol 0.64; physcion 0.56; nepodin 0.48 and emodin 0.28. With extracts containing nepodin this compound was obtained first, mp 163–164° (petrol bp 40–60) lit. [5] 164–65°; MS m/z: 216 (M^+, 76), 201 (100), 155 (29) and 126 (22). ^{1}H NMR: δ2.64 singlet (3H), δ2.74 singlet (3H), δ7.20 multiplet (4H) and δ10.25 (H); IR (KBr) 1630 (C=O stretch). The other compounds chrysophanol (mp 197–198°, MeOH) physcion (mp 204–205° MeOH) and emodin (mp 257–258°, MeOH) followed in that order and their spectroscopic properties were similar to those reported before [4].

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