THE ISOLATION OF CHRYSOPHANIC ACID AND PHYSCION FROM *RUMEX HYMENOSEPALUS* TORR.*

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The tubers of *Rumex hymenosepalus* Torr. (known as canaigre) contain about 25 per cent. of tannin and they have been considered as a commercial source of this material (Rogers and Russell 1944). Recently, investigations were made to ascertain whether they could be grown as an economic crop in certain Australian localities. The roots were analysed for tannin by leaching with acetone : water (1 : 1) at 60 °C by the method of Luvisi and Rogers (1948). In the initial stages of the leaching, the liquor from some samples deposited a bright yellow substance. This was identified as a mixture of chrysophanic acid (1,8-dihydroxy-3-methylanthraquinone) and physcion (6-methoxy-1,8-dihydroxy-3-methylanthraquinone). Chrysophanic acid has been isolated from

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this and other *Rumex* species and " emodin monomethyl ether " (presumably physcion) from several other *Rumex* species (Wehmer 1929). Although emodin (1,6,8-trihydroxy-3-methylanthraquinone) has been reported as the anthraquinone present (U.S. Committee of Agriculture 1878) no trace of it was found.

At least two distinct strains of canaigre are known and they differ in colour, in tannin content, and also in their behaviour in leaching experiments (Rogers 1950–51). In this present work at least two strains were encountered in the 25 samples, one lot of dried tubers were pink-fawn, the other yellow-fawn and the latter deposited most of the anthraquinones. There was a tendency that those tubers which gave the greatest amounts of yellow deposits showed the least vigorous growth and in view of this, it is interesting to note that a 1,4-dihydroxyanthraquinone (quinizarin) retarded the root growth of garden cress (*Lepidium sativum*) whilst certain polyhydroxyanthraquinones containing a 1,2-dihydroxy grouping increased the root growth (Flaig and Otto 1951). As chrysophanic acid and physcion lack a 1,2-dihydroxy grouping they may be associated with the retarded growth of certain canaigre tubers.

Experimental

(*a*) *Isolation of Anthraquinones.*—The tubers of *R. hymenosepalus* grown at Merbein, Vict., were sliced, air-, and finally vacuum-dried at room temperature, and then ground in a Wiley mill to pass a 10 mesh sieve. The samples were extracted in a Soxhlet apparatus with benzene for 3 days to give between 1·2 and 0·3 per cent. extractives. The order of the samples within these limits was about the same as the qualitative assessment of the amount of yellow crystals precipitated during the determination of tannin by the method of Luvisi and Rogers (1948).

The anthraquinones could be recovered from the benzene extracts by sublimation at 125 °C/0·003 mm. The mixture from this source or from Merck " chrysophanic acid " could be partly separated into the acid and physcion by fractional sublimation at 110 °C/0·003 mm. At first a bright orange amorphous substance collected on the condenser and towards the end a yellow substance appeared as a felt of very fine needles. The first fractions were resublimed at 150 °C/1 mm and the orange platelets of chrysophanic acid recrystallized from ethanol. The felts of yellow needles of physcion were resublimed at 110 °C/0·003 mm. Both materials appeared homogeneous by paper chromatographic examination.

The components were obtained in a pure form by applying a streak of an acetone solution of the canaigre root extract to a Whatman No. 3 MM paper (22 by 18 in.). The chromatogram was developed at 22 °C by capillary ascent for 18 hr with a solvent prepared by saturating methanol with *n*-hexane at 10 °C (this was more reliable than the solvent of Shibata, Takito, and Tanaka 1950). The paper was examined under ultraviolet light immediately it was removed from the tank and the orange (R_F 0·71) and the yellow band (R_F 0·56) outlined and cut out. The components were eluted with cold acetone from the strips obtained from 30 papers, filtered, and evaporated under vacuum at room temperatures, and both sublimed at 110 °C under high vacuum and crystallized from ethanol. The acetate of the material with R_F 0·71 did not depress the melting point of authentic chrysophanic acid diacetate, and the material with R_F 0·56 did not depress the melting point of physcion.

(*b*) *Identification of Chrysophanic Acid.*—The sample obtained by sublimation dissolved in conc. H_2SO_4 to give a purple-red colour, and in 2N NaOH to give a red solution, it slowly dissolved in strong NH_3 solution to give a blue-red colour. It was insoluble in cold 5 per cent. Na_2CO_3 and an alcoholic solution became more strongly yellow with ferric chloride, m.p. and mixed m.p. with authentic chrysophanic acid was 192–194 °C. A 0·00004M methanolic solution exhibited maxima at 427, and 283 mμ (log ε 4·05, and 4·03) when measured in a Unicam Model SP 500 Quartz Spectrophotometer.

Chrysophanic acid (50 mg) was acetylated with acetic anhydride (3 ml) and perchloric acid (1 drop ; 70%) overnight. The product obtained by pouring the mixture into water was recrystallized from ethanol, m.p. 200–203 °C, yield 55 mg. After sublimation (150–160 °C/10^{-3} mm) and several recrystallizations from ethanol, the pale yellow plates of the diacetate had m.p. of 207–208 °C, mixed m.p. unchanged (Found : C, 67·7 ; H, 4·2%. Calc. for $C_{19}H_{14}O_6$: C, 67·5 ; H, 4·2%).

(c) *Identification of Physcion.*—The felt of yellow needles obtained at the end of the sublimation gave colour reactions identical with those given by chrysophanic acid when examined simultaneously. It had m.p. and mixed m.p. 205–206 °C (Found : C, 67·8 ; H, 4·4%. Calc. for $C_{16}H_{12}O_5$: C, 67·6 ; H, 4·2%). A 0·00004M methanolic solution exhibited maxima at 427 and 280 mμ (log ε 4·12 and 4·19).

The substance (3 mg) was acetylated with acetic anhydride (1 ml) and perchloric acid (1 drop ; 70%) for 3 hr. The product obtained by pouring the mixture into water was recrystallized four times from methanol, m.p. 187·5–188 °C (lit. for physcion diacetate, m.p. 186–187 °C (Ashley, Raistrick, and Richards 1939 ; Seshadri and Subramaman 1949)).

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