Studies on Xanthorrhoea *Resins. Part I. Isolation of Chrysophanic Acid* (1 : 8-*Dihydroxy*-3-*methylanthraquinone*) *and of* 2′ : 4-*Dihydroxy*-4′-*methoxychalkone.*

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The isolation of chrysophanic acid from bushfire-damaged *Xanthorrhoea* resin, in which it is found as an artifact, is described. 2′ : 4-Dihydroxy-4′-methoxychalkone has been isolated from *X. australis* resin.

The object of the present work is to study the colouring matters of *Xanthorrhoea* resins and possibly throw some light on the nature of the resin itself. Earlier investigations summarized by Tschirch and Stock ("Die Harze," Borntraeger, Berlin, 1935, Vol. II, 135) do not concern themselves with these aspects. Resins from three *Xanthorrhoea* species were examined in a preliminary manner. The first, from an unidentified species growing in the National Park, Sydney, N.S.W., was used for early fractionations. Subsequently resins from *X. resinosa*, Pers. (Peat's Ferry, N.S.W., and Melbourne Botanical Gardens) and from *X. australis*, R.Br. (Mangalore, Vic., Gembrook, Vic., and the Grampians, Vic.) were studied.

After removal of alcohol-insoluble material the resin of unknown origin was largely precipitated from its solution in benzene by the addition of light petroleum. From the material still in solution orange crystals of chrysophanic acid were isolated. Paper chromatograms of the resins of *X. resinosa* (Botanical Gardens) and *X. australis* were simpler than that of the unidentified resin, and it was not possible to show the presence of chrysophanic acid, even after the removal of the bulk of the resin body. As the protruding part of the leaf bases of the unidentified resin had been charred by a bushfire, it appeared likely that chrysophanic acid would only be found in such resin. This was confirmed, for slightly burnt resin samples from both *X. resinosa* and *X. australis* afforded chrysophanic acid. It was also produced by igniting a fresh piece of *X. australis* resin.

As yet no survey of the resins from different *X.* species has been made, but from a comparison of paper chromatograms of resins from *X. resinosa* and *X. australis* it appears likely that some pigments may be species-specific. 2′ : 4-Dihydroxy-4′-methoxychalkone which has now been isolated from *X. australis* may be such a compound, for it could not be found in resins from *X. resinosa*. This appears to be the first time that this chalkone has been isolated from a natural source.

One of the volatile products of prolonged steam-distillation of a strongly alkaline solution of the resins of *X. tateana*, *X. Preissii* (Rennie, Cooke, and Finlayson, *J.*, 1920, **117**, 338), *X. resinosa*, *X. hastilis*, and *X. reflexa* (Finlayson, *J.*, 1926, 2763) is paeonol (2-hydroxy-4-methoxyacetophenone) and it may arise, in part at least, from the decomposition of 2′ : 4-dihydroxy-4′-methoxychalkone, which was shown to produce paeonol under these conditions.

Experimental

X. sp. *Resin from National Park, Sydney, N.S.W.—Purification.* After removal of plant debris by dissolution of the resin in ethanol and filtration, the completely alcohol-free resin (83 g.) was extracted with hot benzene (8 × 250 ml.), and the yellow extract removed by decantation. After some resinous matter had been allowed to settle, the solution was again decanted and left a brittle, somwehat sticky, orange-red resin after evaporation.

Fractional precipitation and isolation of chrysophanic acid. The benzene-soluble portion (17 g.) from the purified resin was dissolved in benzene (200 ml.), and light petroleum (b. p. 40—60°; 200 ml.) was added. The precipitate was removed and the filtrate evaporated to dryness. The residue was dissolved in benzene (25 ml.), and light petroleum (100 ml.) added, giving a further precipitate and material in solution. Evaporation of this solution left an oil to which ethanol was added. Crude chrysophanic acid crystallised and was filtered off warm to prevent the precipitation of a white contaminant. The product (15 mg.) had m. p. and mixed m. p. 193·5° (from ethanol) (Found : C, 70·6; H, 4·1; OMe, 0·0. Calc. for $C_{15}H_{10}O_4$: C, 70·9; H, 4·0%). The diacetate had m. p. and mixed m. p. 207·5—208° (Found : C, 67·6; H, 4·4. Calc. for $C_{19}H_{14}O_6$: C, 67·5; H, 4·2%). The ultra-violet spectrum of chrysophanic acid was in agreement with that of a 1 : 8-dihydroxyanthraquinone (Morton and Earlem, *J.*, 1941, 159), *viz.* : in EtOH, max. at 224, 257, 277, 287, and 430 mμ (log ε 4·54, 4·30, 3·99, 4·03, and 4·01, respectively) ; in EtOH containing NaOEt, max. at 285, 365—380, and 504 mμ (log ε 3·92, 3·28, and 3·94, respectively).

Resins from X. resinosa *and* X. australis.—*Isolation of chrysophanic acid from charred* X. resinosa *resin.* The resin (190 g., freed from plant material by extraction with ethanol) was worked up as described above. The ether extract of crude chrysophanic acid was extracted with 2N-sodium carbonate and finally with N-sodium hydroxide. Acidification of the sodium hydroxide extract gave chrysophanic acid (75 mg.), melting at 188—189° (from ethanol). Sublimation (125—130°) at 10^{-4} mm. gave material with m. p. and mixed m. p. 194—194·5° (from ethanol). The diacetate after sublimation (150—160°/10^{-4} mm.) had m. p. and mixed m. p. 208·5—209° (from benzene).

Chrysophanic acid produced by burning X. australis *resin.* A large piece of *X. australis* resin was ignited at one end, the charred portion extracted with ethanol, the ethanol removed, and the residue treated with hot benzene. The solution was decanted and extracted successively with solutions of sodium hydrogen carbonate, sodium carbonate, and sodium hydroxide. The sodium hydroxide extract was red and the precipitate formed on acidification when examined in a circular paper chromatogram (Whatman No. 1 and benzene) showed chrysophanic acid at the solvent front by its red colour in ammonia vapour. The unburnt portion of the resin did not show chrysophanic acid when treated similarly.

Isolation of 2′ : 4-dihydroxy-4′-methoxychalkone from X. australis *resin.* The resin (20 g.) was dissolved in ethanol (250 ml.), partly precipitated by the addition of water (250 ml.), and filtered with the help of Filter-Cel (40 g.). The benzene extract of the filtrate was then shaken successively with saturated aqueous sodium hydrogen carbonate (3 × 100 ml.), 2N-sodium carbonate (8 × 50 ml.), and N-sodium hydroxide (3 × 100 ml.). With sodium carbonate complete extraction was impossible. The extracts were acidified (10N-sulphuric acid) and left overnight to allow the precipitate to coagulate. The material extracted by sodium hydroxide was granular and removed by filtration (0·66 g.). A benzene-insoluble amorphous impurity was removed. The crude pigment melted at 166—167° (0·33 g. of yellow needles from aqueous ethanol). The crystals were redissolved in benzene by warming and the solution repeatedly extracted with 2N-sodium carbonate (7 × 100 ml.) in which the chalkone formed a deep yellow solution. Acidification gave a product (0·29 g.) melting unchanged at 172° (0·25 g. from aqueous ethanol) (Found: C, 71·2; H, 5·0; OMe, 11·7. Calc. for $C_{16}H_{14}O_4$: C, 71·1; H, 5·2; OMe, 11·5%). A synthetic specimen prepared according to the directions of Geissman and Clinton (*J. Amer. Chem. Soc.*, 1946, **68**, 697) melted at 172° and showed no depression when admixed with the natural product. The ultra-violet absorption spectra of the two materials were identical, with maxima (in EtOH) at 240 and 371 mμ and a point of inflection at 309 mμ (log $\varepsilon_{max.}$ 4·07 and 4·53, respectively; log $\varepsilon_{infl.}$ 3·99). In 0·001N-NaOEt maxima occurred at 253, 290 (very broad), and 444 mμ (log ε 4·21, 4·16, and 4·58, respectively).

2′ : 4-Dihydroxy-4′-methoxychalkone is a major pigment constituent of *X. australis* resin with an R_F about 0·8 (Whatman No. 1 and benzene). The spot on paper was yellow in daylight, orange-brown in ultra-violet light, and in the presence of ammonia vapour deep yellow and golden-yellow, respectively. Hydrochloric acid (4 : 1, concentrated hydrochloric acid and ethanol) produced an orange colour which faded to yellow on warming. When its alcoholic solution containing a little boric acid and a drop of hydrochloric acid was evaporated to dryness, a red residue was left, which became blue with sodium hydroxide.

Paeonol from 2′ : 4-Dihydroxy-4′-methoxychalkone.—2′ : 4-Dihydroxy-4′-methoxychalkone (0·106 g.) and potassium hydroxide (0·5 g.) in water (3 ml.) were gently refluxed for 6 hr., then acidified with 10N-sulphuric acid, and the liberated paeonol was steam-distilled. The distillate (15 ml.) was extracted with ether; the residue from the ether extract (0·051 g.) after crystallisation melted at 50—51°.

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