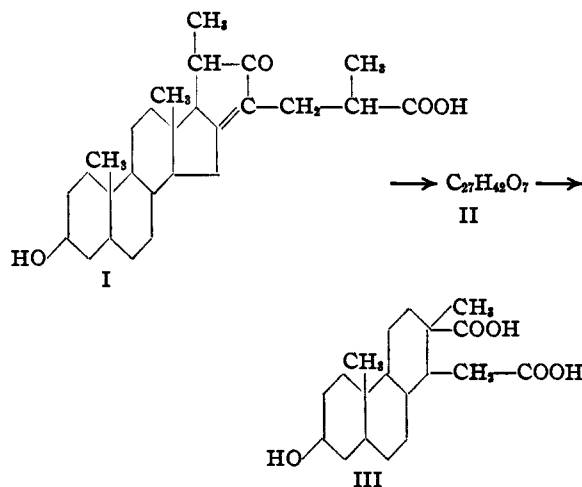


formula, the properties and mixed melting point determination definitely indicate acid III. It should be noted that the hypohalite oxidation is not a simple one. Two treatments are required.



We wish to thank Parke, Davis and Company for assistance.

### Experimental Part

**Haloform Reaction on the Dibasic Acid<sup>2</sup> Obtained from the Potassium Permanganate Oxidation of Anhydrosarsapogenoic Acid.**<sup>2</sup>—The dibasic acid was obtained according to the method described by Fieser and Jacobsen<sup>1</sup> by the oxidation of anhydrosarsapogenoic acid with potassium permanganate in alkali. It gave no silver mirror when heated with ammoniacal silver nitrate. This casts doubt on its being an alpha keto acid<sup>1</sup> and favors the  $\text{C}_{27}\text{H}_{45}\text{O}_7$  formula.<sup>2</sup>

To a solution of 1 g. of the dibasic acid in 15 cc. of dioxane was added 10 cc. of 10% sodium hydroxide solution and the mixture was treated at 60° with iodine-potassium iodide (200 g. of potassium iodide, 100 g. of iodine and 800 cc. of distilled water) until the color persisted for two minutes. No iodoform separated on dilution. The solution was acidified and the acids were filtered. They were dissolved in 15 cc. of 5% sodium hydroxide and heated with the potassium iodide-iodine solution on a steam-bath for five minutes. Water was added and the iodoform was filtered. The alkaline solution was acidified and the product was extracted with ether. The ethereal extract was washed well with water, sodium bisulfite solution and finally again with water. The ether was removed and the residue was treated in acetone with Norite. Upon standing with 50% acetone-water in a refrigerator overnight, a crystalline product separated. It was very soluble in acetone and only a small amount of material was obtained. It was crystallized from chloroform; m. p. 220–222°; yield about 50 mg. When mixed with an authentic sample of 3(β)-hydroxyetio-bilanic acid, there was no depression in melting point.

*Anal.* Calcd. for  $\text{C}_{19}\text{H}_{30}\text{O}_5$ : C, 67.4; H, 8.9; neut. equiv., 169.1. Found: C, 67.2; H, 8.9; neut. equiv., 174.2.

The residue after the evaporation of the above mother liquor was refluxed for thirty minutes with 20 cc. of acetic anhydride. The excess acetic anhydride was vacuum distilled and the residue was sublimed in a high vacuum at 185–190°. The sublimate crystallized from ether as flat prisms; m. p. 202–203.5°. When mixed with an authentic sample of the acetate of the anhydride of 3(β)-hydroxyetio-bilanic acid, m. p. 202–204°, there was no depression in melting point.

*Anal.* Calcd. for  $\text{C}_{21}\text{H}_{30}\text{O}_5$ : C, 69.6; H, 8.3. Found: C, 69.4; H, 8.3.

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### The Absorption Spectra of Para- and Diamagnetic Nickel Complexes

By J. E. MILLS AND D. P. MELLOR

Attention has been drawn recently to what appears to be a correlation between the color and magnetic properties of nickel complexes.<sup>1</sup> Many paramagnetic nickel complexes are some shade of green or blue while diamagnetic complexes, as a rule, have colors ranging from bright red through reddish-brown to various shades of yellow. In the course of an extended survey of the magnetic properties of nickel complexes carried out in this Laboratory, it has become increasingly clear that little reliance can be placed on the above correlation. It has been shown, for example, that vermillion bis-1-hydroxy-acridine-nickel is paramagnetic ( $\mu = 3.2$  Bohr magnetons) and that green bis-formylcamphor-ethylenediamine-nickel is diamagnetic.

In order to determine what influence the magnetic condition of the nickel atom has on the absorption of light by its complexes, a systematic examination of the absorption spectra of para- and diamagnetic complexes in solution has been initiated. Wherever possible, a comparison has been made between the absorption spectrum of the metal-free and the metal-containing compound. Attention has so far been confined largely to complexes in which the nickel atom is linked to (a) two nitrogen and two oxygen atoms as in bis-salicylaldehyde nickel, or (b) to four oxygen atoms as in bis-acetylacetonate-nickel. Complexes belonging to the latter group are always paramagnetic, while those belonging to the former may be either para- or diamagnetic. It was possible with these compounds to search for

(1) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940, p. 122; D. P. Mellor and D. P. Craig, *J. Proc. Roy. Soc. N. S. W.*, **74**, 475 (1940).

differences while keeping to the same solvent, namely, alcohol.

The absorption curves were obtained by using a quartz spectrograph in conjunction with a rotating sector photometer and a condensed tungsten steel spark as light source.

The following is a brief statement of some of the results obtained. The diamagnetic complexes in which the four atoms linked to nickel are two nitrogen and two oxygen atoms exhibit the following features: (1) the bands of the coordinated chelate molecule are slightly displaced, usually to longer wave lengths, and (2) a band of appreciable intensity (molecular absorption coefficient of maximum  $>3000$  and, in some complexes, as much as 7000) is observed which must be attributed to the nickel. In three of the diamagnetic complexes examined, namely, bis-salicylaldehyde-propylenediamine-nickel, bis-nicotinylacetone-ethylenediamine-nickel<sup>2</sup> and bis-salicylaldehyde-nickel, the maximum of this last band is at 405  $m\mu$ . In two other diamagnetic complexes, namely, bis-salicylaldehyde-nickel<sup>3</sup> and bis-formylcamphor-ethylenediamine-nickel,<sup>3</sup> the maximum of the band is at 385  $m\mu$ . On the other hand, in the range 650–250  $m\mu$  the paramagnetic complexes of nickel show no band, or at least no band of intensity comparable to (2) above, which can be attributed to nickel. The absorption bands of the paramagnetic complexes appear to be those of the organic chelate molecule displaced, sometimes appreciably, to longer wave lengths and also considerably broadened. The paramagnetic complexes examined included bis-salicylaldehyde-nickel, bis-8-hydroxyquinoline-nickel, bis-1-hydroxyacridine-nickel, bis-formylcamphor-nickel and bis-acetylacetone-nickel. It is of interest to note that the absorption bands of the paramagnetic complexes of nickel in alcohol solution bear a striking resemblance to those of the chelate molecules themselves in alcoholic sodium hydroxide.

Further details of this work relating to nickel and cobaltous compounds will be published shortly.

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(2) We are indebted to Dr. F. Lions for a specimen of this substance which is to be described shortly.

(3) In addition to the band at 385  $m\mu$  this substance shows at 620  $m\mu$  a much weaker band which can also be attributed to the nickel.

## Identity of the Red Pigment in the Roots of *Tripterygium wilfordii* and *Celastrus scandens*

BY MILTON S. SCHECHTER AND H. L. HALLER

For centuries the powdered roots of the thunder-god vine, *Tripterygium wilfordii* Hook f. have been used in China as an insecticide. *Tripterygium wilfordii* is a perennial twining vine belonging to the family *Celastraceae*. In foliage and manner of growth it is much like that of our North American bitter-sweet, *Celastrus scandens* L.

About ten years ago, entomological reports from China containing scientific data began to appear, and shortly thereafter chemical studies on the root, which had for their objective the isolation of the insecticidal principle, were published.<sup>1</sup> The insecticidal principle is reputed to be an alkaloid, but little is known regarding its nature. Dulcitol and an insecticidally inert red pigment, designated tripterine,<sup>2</sup> also have been obtained from extracts of the root.

At the suggestion of W. T. Swingle, of the Bureau of Plant Industry, the Bureau of Entomology and Plant Quarantine has undertaken a study of *Tripterygium wilfordii*. The roots were obtained from plants growing at the Plant Introduction Garden of that Bureau at Glenn Dale, Md.

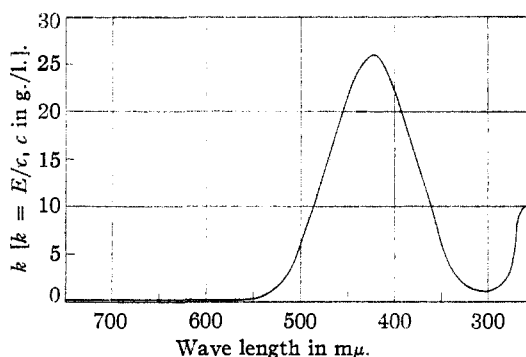


Fig. 1.—Absorption spectrum of tripterine in ethanol.

From the petroleum ether extract of the root, a small quantity of tripterine was obtained. It crystallized from the concentrated extract that had been allowed to stand overnight, the crystals being parallelepipeds which appeared almost cubical. The pigment was soluble in most organic solvents. It was recrystallized from petroleum ether containing about 5% of ethyl ether with some difficulty, as there was a tendency for it to

(1) Swingle, Haller, Siegler and Swingle, *Science*, **93**, 60 (1941); contains a list of the more important Chinese papers and reports on *Tripterygium wilfordii*.

(2) Chou and Mei, *Chinese J. Physiol.*, **10**, 529 (1936).