

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-nickel² and bis-salicylaldimine-nickel, the maximum of this last band is at 405 $m\mu$. In two other diamagnetic complexes, namely, bis-salicylaldoxime-nickel³ and bis-formylcamphor-ethylenediamine-nickel,³ 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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RECEIVED OCTOBER 7, 1941

(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.¹ 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,² 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.

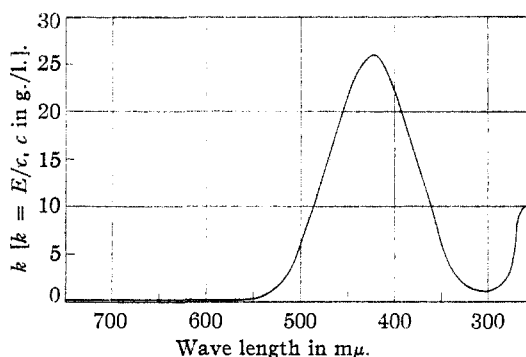


Fig. 1.—Absorption spectrum of tripterine in ethanol.

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).

separate in amorphous form. Tripterine melts at 205° with decomposition.

Recently Gisvold³ isolated from the root bark of bitterweet a red pigment which he named "celastrol." From the description of its properties, it appeared to be identical with tripterine, and from a sample of celastrol kindly furnished by Dr. Gisvold the identity of the two compounds has been confirmed. A mixture melting point of celastrol and tripterine shows no depression. Both are dissolved by dilute alkali or carbonate solution with the formation of a dark red solution which is slowly oxidized by air and readily by permanganate, with the formation of a yellow amorphous acid. Lower fatty acids, such as formic, acetic, or propionic, are absent in the oxidation products. Both compounds are readily reduced by catalytic hydrogen and by sulfurous acid, and the original red color is restored on exposure to air or when the solution is boiled to remove sulfur dioxide. Both give a green color with alcoholic ferric chloride.

Conclusive proof that the compounds are the same is given by the identity of the absorption spectrum of tripterine in ethanol as given in Fig. 1 with that of a sample of celastrol furnished by Gisvold over the range of wave lengths, 400 to 750 millimicrons.⁴

The absorption maximum at 420 millimicrons is of interest because many orthoquinones exhibit a maximum in the range of 400–450 millimicrons.⁵ However, these compounds also possess a maximum at about 333 millimicrons owing to the $-C=C-C=O$ grouping.^{5,6} Its absence in the spectrum of tripterine may be accounted for by the possible presence of a hydroxyl group in the *peri* position, since it has been shown that such groups suppress or modify the maximum due to the conjugated carbonyl grouping.⁶ Such an interpretation would lend support to one of the structures proposed by Gisvold for celastrol,

(3) Gisvold, *J. Am. Pharm. Assoc.*, **28**, 440 (1939); **29**, 432 (1940).

(4) Grateful acknowledgment is made to R. Stewart, of the U. S. Food and Drug Administration, for the absorption spectra of tripterine and celastrol taken from 400–750 millimicrons with a recording spectrophotometer, and to R. E. Davis, of the Bureau of Animal Industry, for the visible and ultraviolet absorption spectrum of tripterine taken from 260–500 millimicrons with a quartz Littrow spectrograph.

(5) Cooke, Macbeth and Winzor, *J. Chem. Soc.*, 878 (1939). The data of these authors indicate that the presence of a maximum in the range 400–450 millimicrons having $\log \epsilon = ca. 3.25-3.30$ in conjunction with a maximum due to the conjugated keto group at about 330 millimicrons is fairly good evidence of a β -naphthoquinone structure.

(6) Macbeth, Price and Winzor, *ibid.*, 330 (1935).

namely, a *peri*-hydroxy-*o*-naphthoquinone derivative.

BUREAU OF ENTOMOLOGY AND PLANT QUARANTINE
U. S. DEPARTMENT OF AGRICULTURE
WASHINGTON, D. C. RECEIVED SEPTEMBER 29, 1941

The Polymorphism of *d*-Galactose Diethylmercaptal Pentaacetate*

BY LLEWELLYN H. WELSH AND GEORGE L. KEENAN

A recent attempt to prepare *d*-galactose diethylmercaptal pentaacetate by the procedure of Wolfrom¹ yielded a product having properties at considerable variance with those recorded for this compound. Although *d*-galactose diethylmercaptal pentaacetate has been used by several investigators in the carbohydrate field, we were unable to find any description of its properties other than those reported by Wolfrom¹ and Wolfrom and Thompson,² who have described the substance as prismatic needles melting between 77 and 79°, and having a specific rotation of +9.7–9.9° in U. S. P. chloroform.

In the course of establishing the identity of our product with an authentic specimen from Dr. Wolfrom's laboratory, it was found that the compound may exist in three forms³ which exhibit different melting point behavior and optical crystallographic properties. By choice of seed crystals, it was possible to obtain from the same solution hexagonal prisms, rectangular plates or elongated prisms. When melting points were determined in the usual manner in capillary tubes, the hexagonal and elongated prism forms underwent volume changes or incipient melting at 76.5–77° and 80.5–81°, respectively, but did not melt completely until the temperature was raised to 90.5–91°. Both forms completely melted in tubes plunged into a bath heated to one or two degrees above their respective shrinkage points, and occasionally slowly solidified and remelted at 90.5–91°. When melting points of these two forms were determined on a Fisher micromelting point apparatus, complete melting occurred at the temperatures at which shrinkages had taken place in capillary tubes, and there was no tendency toward resolidification unless large amounts

* Not copyrighted.

(1) Wolfrom, *THIS JOURNAL*, **52**, 2464 (1930).

(2) Wolfrom and Thompson, *ibid.*, **56**, 880 (1934).

(3) Private communication has revealed that dimorphism of this substance has been recognized independently by Drs. S. B. Hendricks and G. E. Hilbert of the Bureau of Agricultural Chemistry and Engineering, U. S. Department of Agriculture. This note was submitted with their approval.