	Ten per cent spirit.	
7.84		9.86
9.58		9.85
10.42		9.87
10.68		9.84
Av. 9.63	9.80*	Av. 9.86
	Twelve per cent spirit.	
8.45	11.63	11.75
7.68	11.68	11.77
7.80	11.60	11.80
8.80	11.60	11.82
Av. 8.38	Av. 11.63	Av. 11.79

* Average of fifty determinations by five analysts.

A few assays were conducted using a 5-cc. sample and a 2 per cent reagent. Satisfactory results were obtained when the reagent was freshly prepared. Upon standing over night some of the dinitrophenylhydrazine crystallized out of the 2 per cent reagent, thus indicating its instability. It is the opinion of the author that the percentage yield of hydrazone is dependent upon two factors, *i. e.*, the solubility of the derivative and the equilibrium obtained between the reactants. By increasing the amount of dinitrophenylhydrazine, the reaction can be driven more nearly toward completion, and thus decrease the error.

SUMMARY.

1. It is shown that the official method of preparing dinitrophenylhydrazine reagent and also the assay of camphor in spirit of camphor is unsatisfactory.

2. The results of Plein and Poe have been confirmed and what is considered to be an improvement on their procedure is submitted.

3. In the Plein and Poe method fifteen cc. of ethyl alcohol is added and the sample refluxed for four hours. In the method submitted in this paper the dinitrophenylhydrazine reagent contains twenty-five per cent methyl alcohol which stabilizes the reagent. The time consumed in refluxing is reduced from four to two and one-half hours. The yield of dinitrophenylhydrazone was increased thus reducing the error of the procedure.

THE PREPARATION OF EMODIN FROM CHRYSAROBIN.*

BY JOHN H. GARDNER.[1]

In an earlier paper from this laboratory (1), it was shown that chrysophanic acid can be obtained from chrysarobin by a process consisting in reducing to convert dianthrones into anthrones, boiling under reflux with hydrobromic and acetic acids to demethylate the emodin-anthrone-monomethyl ether, acetylating and crystallizing the chrysophanic acid-anthranol triacetate from acetic acid. From this compound, chrysophanic acid may be prepared by oxidation followed by saponification. Since chrysarobin contains large amounts of reduction products of emodin-

* Presented before the Scientific Section, A. PH. A., Minneapolis meeting, 1938.

[1] From the Chemical Laboratory of Washington University, St. Louis.

monomethyl ether (2), the residual material left after the removal of the chrysophanic acid-anthranol triacetate must contain a considerable quantity of emodine anthranol tetra-acetate. This material was oxidized in acetic acid solution with chromic acid and the oxidation product was saponified. To obtain the emodin, this material was extracted with sodium carbonate solution and the extract was acidified. The product so obtained was found to be quite pure. The yields were from 16 to 31 per cent of the weight of chrysarobin used.

EXPERIMENTAL.

Separation of Chrysophanic acid-9-Anthranol Triacetate.—The mixture obtained after reducing, demethylating and acetylating 25 Gm. of chrysarobin as described in the previous paper (1) was dissolved in 400 cc. of glacial acetic acid and the solution was cooled. The chrysophanic acid-9-anthranol triacetate crystallized and was filtered out. The mother liquor was diluted with water until no more precipitate formed. The precipitate was filtered out and air dried.

Preparation of Emodin.—The dried precipitate was dissolved in about 350 cc. of hot glacial acetic acid and treated with a solution of chromic acid in a small volume of 50 per cent acetic acid, using 0.34 Gm. of chromic acid for each Gm. of the precipitate. The mixture was heated to 100° C. for about fifteen minutes and then diluted with water until no more precipitate formed. The precipitate was filtered out and washed with water until the washings were no longer appreciably acid. After air drying, it was suspended in 250 cc. of alcohol and a solution of 12 Gm. of potassium hydroxide in a little water was added. The mixture was boiled under reflux for three hours, cooled and filtered. The filtrate was diluted to about a liter and acidified to Congo Red with hydrochloric acid. The precipitate which formed was filtered out and then stirred well with 800 cc. of 5 per cent sodium carbonate solution. The mixture was filtered and the emodin precipitated from the filtrate by acidifying with hydrochloric acid. Yield, 4.0 to 7.8 Gm., m. p. 254–256° C., with slight previous softening.

SUMMARY.

A satisfactory method for the preparation of emodin from chrysarobin has been developed.

REFERENCES.

(1) Gardner, JOUR. A. PH. A., 23, 1178 (1934).
(2) Hauser, Dissertation, *Zürich*, 1924.

THE TITRATION CURVE OF METHIONIC ACID.*

PHYLLIS M. BREWSTER[1] AND GLENN L. JENKINS.[1]

Before attempting to prepare stable complex and double salts of methionic acid, it was necessary to study the acid properties of the compound, $CH_2(SO_3H)_2$. If the acid were to behave as a fairly weak dibasic acid, showing two separate dissociations, then it is conceivable that a salt of the type $MM'CH_2(SO_3)_2$ might form easily, depending on its physical properties. Since a solution of such a salt would consist of a mixture of three ions M^+, M'^+ and $CH_2(SO_3)_2^-$ the salt that would crystallize would be determined roughly by the solubilities of the three possible products.

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[1] Contribution from the College of Pharmacy of the University of Minnesota, August, 1937.