

\*AQUA HAMAMELIDIS N. F.—HAMAMELIS WATER, WITCH HAZEL WATER, DISTILLED EXTRACT OF WITCH HAZEL.

BY S. L. HILTON.

"The subject I wish to discuss is one that enters into the daily sales of the pharmacist; he is constantly called upon by the laity for it—Witch Hazel.

"What is Witch Hazel?—The National Formulary says Hamamelis Water is clear and colorless, having a characteristic odor and taste. It is neutral, or only faintly acid to litmus.

"It is made by the distillation of witch hazel twigs gathered in the fall of the year, macerated in water and distilled; 150 cc. of ethyl alcohol are added to 850 cc. of distillate.

"Little is known or has been determined about its constituents; it seems, however, to have some medicinal value, although there are some that contend it has no value; thousands of gallons are made and consumed every year.

"The U. S. P. VIII, gave a process for its manufacture and required that each 850 cc. of distillate should contain the volatile products of 1000 Gm. of witch hazel twigs, to which was added 150 cc. ethyl alcohol.

"The U. S. P. IX, provided that it should be a saturated aqueous liquid obtained by distilling with steam or water the bark, twigs, smaller stems or the entire shrub collected in autumn; no definite amount of witch hazel was designated, but it required that 150 cc. of alcohol should be added to 850 cc. of distillate.

"The U. S. P. X, dropped Aqua Hamamelidis and it was then included in N. F. V. This standard provides that 1000 Gm. be used to obtain 850 cc. of distillate to which is to be added 150 cc. of alcohol. The description and tests for purity are the same as was contained in U. S. P. IX.

"I was the chairman of the N. F. sub-committee to which this preparation was referred. I found one manufacturer who desired that the amount of twigs to be used should be doubled. I endeavored to have the strength increased accordingly, but was overruled by the committee. I had nothing to do with providing tests for purity; after the N. F. V was published my attention was called to the test as given, and that the test for formaldehyde was not satisfactory; this seemed to be true from the results obtained by a firm of chemists in New York and led me to conduct an investigation.

"Late in the fall of 1928, after distillation was started, a leading manufacturer submitted to me for investigation six samples—first run without alcohol, first run with 15% alcohol added; middle run without alcohol, middle run with 15% alcohol; last run without alcohol and last run with 15% alcohol added—these I have carefully examined, together with two other brands on the market, and I have found some interesting data, all of which have been tabulated in this paper.

"The alcoholic content of all of the samples show very close results: Sample 1, 18.58% by volume at 20° C.; Sample 2, 18.58% by volume; Sample 3, 18.43%; these samples were obtained in the open market and contained pure ethyl alcohol."

*N. F. V Test for Formaldehyde.*—Add 8 drops of an aqueous solution of resorcinol (1 in 200) to 5 cc. Hamamelis Water and carefully superimpose this upon 5 cc. sulphuric acid, contained in a test-tube. After standing for three minutes a rose-red

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ring does not appear at the line of contact of the liquids, nor does a distinct white layer appear above this zone.

Samples.	A.	B.	C.	D.	E.	F.	Control, 0.5% formaldehyde.
Sp. gr. 25° C.	0.99492	0.97384	0.99500	0.97384	0.99506	0.97366	
N. F. test for Formald.	Slight rose, milky	Slight rose, milky	Slight rose	Slight rose	Slight rose	Slight rose	Deep rose milky
After 15 hrs.	Deep, milky	Deep, milky	Deep, slight milky	Slight rose-red	Deep, slight milky	Deep slight milky	Very deep rose, milky
Silver nitr. and ammon.	Neg.	Neg.	Neg.	Neg.	Neg.	Neg.	Positive
Acidity NaOH N/10	3.6 cc.	2.8 cc.	3.2 cc.	2.2 cc.	6.2 cc.	5.0 cc.	...

METHODS OF A. O. A. C.

Heebner's test	Neg.	Neg.	Neg.	Neg.	Neg.	Neg.	Positive
Leach test	Neg.	Neg.	Neg.	Neg.	Neg.	Neg.	Positive
Phenylhydraz. HCl	Neg.	Neg.	Neg.	Neg.	Neg.	Neg.	Positive
Phenylhydraz. and nitroprus	Neg.	Neg.	Neg.	Neg.	Neg.	Neg.	Positive
Phenylhydraz. and ferricyan.	Neg.	Neg.	Neg.	Neg.	Neg.	Neg.	Positive
Phenylhydraz. and FeCl <sub>3</sub>	Neg.	Neg.	Neg.	Neg.	Neg.	Neg.	Positive
Phlorglucinol	Neg.	Neg.	Neg.	Neg.	Neg.	Neg.	Positive
Schiff's test	Neg.	Neg.	Neg.	Neg.	Neg.	Neg.	Positive
Morphine sulphate 100 cc. evap. to 10 cc. with ammon.	Neg.	Neg.	Neg.	Neg.	Neg.	Neg.	Positive
	Trace	Neg.	Trace	Neg.	Trace	Neg.	Positive

SAME SAMPLES AS FORMER TABLE 150 CC. DISTILLED, RECOVERING 100 CC.

	A.	B.	C.	D.	E.	F.	Control, 0.5% formal.	Control, 15% alcohol.
N. F. test	Pos.	Pos.	Pos.	Pos.	Pos.	Pos.	Pos.	Neg.
After 15 hrs.	Pos.	Pos.	Pos.	Pos.	Pos.	Pos.	Pos.	Neg.
Heebner's test	Neg.	Neg.	Neg.	Neg.	Neg.	Neg.	Pos.	Neg.
Phenylhydraz. HCl	Neg.	Neg.	Neg.	Neg.	Neg.	Neg.	Pos.	Neg.
Phenylhydraz. and nitroprus.	Neg.	Neg.	Neg.	Neg.	Neg.	Neg.	Pos.	Neg.
Phenylhydraz. and FeCl <sub>3</sub>	Neg.	Neg.	Neg.	Neg.	Neg.	Neg.	Pos.	Neg.
Phenylhydraz. and ferricyan	Neg.	Neg.	Neg.	Neg.	Neg.	Neg.	Pos.	Neg.
Phlorglucinol	Neg.	Neg.	Neg.	Neg.	Neg.	Neg.	Pos.	Neg.
Schiff's test	Neg.	Neg.	Neg.	Neg.	Neg.	Neg.	Pos.	Neg.
Morphine sulphate 100 cc. evap. to 10 cc. with ammon.	Neg.	Neg.	Neg.	Neg.	Neg.	Neg.	Pos.	Neg.
	Trace	Neg.	Trace	Neg.	Trace	Neg.	Pos.	Neg.
After 15 minutes	Trace	Trace	Trace	Trace	Trace	Trace	Pos.	Neg.

It has been shown that hammelin-tannin is present in witch hazel and is converted into Gallic Acid by hydrolysis, "National Dispensatory."

Richter's Chemistry speaks of pinene and pinol; it is quite clear that witch hazel contains traces of one or the other and that these substances do not react with phenylhydrazine hydrochloride.

Weak solutions of those substances were used as controls comparing same with the middle run containing 15% alcohol, also control of 0.5% formaldehyde solution and testing for gallic acid.

Sample.	Middle run with alcohol.	Pine from Oil <i>Pinus p.</i>	Pinene from oil turp.	Gallic acid.	Control, 0.5% formaldehyde.
N. F. test	Pos.	Pos.	Pos.	Slight milkiness	Pos.
After 15 hours	Pos.	Pos.	Pos.	Slight milkiness	Pos.
Heebner's test	Neg.	Slight red	Brownish yellow	Reddish brown	Pos.
Leach test	Neg.	Slight red	Brownish yellow	Reddish brown	Pos.
Phenylhydrazin	Neg.	Slight red	Brownish yellow	Reddish brown	Pos.
Phenylhyd. and nitroprus.	Neg.	Slight red	Brownish yellow	Reddish brown	Pos.
Phenylhyd. and FeCl <sub>3</sub>	Neg.	Slight red	Brownish yellow	Characteristic iron reaction	Pos.
Phenylhyd. and ferricyan	Neg.	Slightly red	Slightly red	Deep red	Pos.
Phlorglucinol	Neg.	Negative	Negative	Slight brown	Pos.
Schiff's test	Neg.	Negative	Negative	Slight brown	Pos.

#### SAMPLES BOUGHT ON MARKET, NOS. 1, 2 AND 3.

	No. 1.	No. 2.	No. 3.	Control 15% alcohol	Formaldehyde 0.5% sol.
Sp. gr. 25° C.	0.97384	0.97782	0.97628		
N. F. test	Pos. milky layer	Pos. milky layer	Pos. milky layer	Neg.	Pos.
After 15 hrs.	Deeper color	Heavy reaction	Heavy reaction	Neg.	Pos.
Silver nit. test	Neg.	Neg.	Neg.	Neg.	Pos.
Acidity NaOH N/10	3.2 cc.	1 cc.	5 cc.		
Heebner's test	Neg.	Neg.	Neg.	Neg.	Pos.
Leach test	Neg.	Neg.	Neg.	Neg.	Pos.
Phenylhyd. HCl	Neg.	Slight	Neg.	Neg.	Pos.
Phenylhyd. and nitroprus.	Neg.	Neg.	Neg.	Neg.	Pos.
Phenylhyd. and ferricy.	Neg.	Neg.	Neg.	Neg.	Pos.
Phenylhyd. and FeCl <sub>3</sub>	Neg.	Neg.	Pos.	Neg.	Pos.
Phlorglucinol	Neg.	Neg.	Neg.	Neg.	Pos.
Schiff's test	Neg.	Neg.	Neg.	Neg.	Pos.
Morphine test	Neg.	Neg.	Neg.	Neg.	Pos.
100 cc. evaporated to 10 cc. with ammon.	Neg.	Trace	Pos.	Neg.	Pos.

#### CONCLUSIONS.

"From the research I have conducted I am convinced that the test for formaldehyde as given in the National Formulary V, is not satisfactory, as it gives a decided reaction for pinene, a normal constituent of witch hazel, and will be mistaken for formaldehyde. None of the samples shows formaldehyde by the tests as given in the methods of analysis of the Association of Official Agricultural Chemists.

"This paper is offered to the new Committee of Revision of the N. F. VI, for thorough study and I recommend that the test for formaldehyde be changed to one

or more of the tests of the Association of Official Agricultural Chemists, as the present test gives an unfair reaction.

- Samples A Dickinson's first run without alcohol
- B Dickinson's first run with 15% alcohol
- C Dickinson's middle run
- D Dickinson's middle run with 15% alcohol
- E Dickinson's last run
- F Dickinson's last run with 15% alcohol

Other samples, open market: No. 1, Dickinson's; 2, Humphrey's; 3, Ponds. No other samples were available on the market in Washington.

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## A STUDY OF THE EMODIN-BEARING GROUP OF CATHARTICS. PART I.

BY PETER VALAER, JR.

For the past twenty years the writer has been interested and fascinated by what is regarded by many to be the most baffling group of crude drugs. The principal members of this group are cascara, rhubarb, frangula, aloes and senna. They are known to many as emodin-bearing drugs, whose cathartic action depends perhaps upon certain oxymethyl-anthraquinones for their activity. The word "perhaps" is projected into this paragraph for reason that there are eminent members of the pharmaceutical chemical profession who do not share this opinion. Their reasons will be discussed later along with certain chemical data.

The writer has planned to divide the "Study of the Emodin-Bearing Group" into five parts discussing each group member separately. Cascara is the best known and most widely used of this group.

There has been developed in the chemical laboratory of the Bureau of Prohibition a method by which the presence of emodin-bearing drugs are detected and estimated. It is based on the Bornträger reaction (*Z. anal. Chem.*, 19 (1880), 165). When the group of drugs whose virtues depend principally upon the resinous hydroxyanthraquinone bodies and other anthraquinone compounds in the solution are made acid and are extracted with ether and the ether extract made strongly alkaline with ammonia, a red color of a certain shade is caused to develop. Application is made of this test as a basis for the quantitative estimation of, for instance, cascara in medicinal preparations under examination. Under certain carefully observed conditions the depth of color extracted by the ether and the color developed on the treatment with ammonia varies almost directly in proportion to the amount of cascara or other emodin-bearing drugs present.

Twenty-five cc. of the medicine is measured with a pipette into a 250-cc. separatory funnel, 2 cc. *N/10* acid introduced to make the material acid, 50 cc. of sulphuric ether is then added and the funnel shaken for exactly five minutes. The material is allowed to settle, the acid liquid is then drawn off; the funnel shaken and allowed to stand and the process of shaking and drawing off repeated until all the aqueous liquid remaining in the funnel is completely stripped out. If any emodin-bearing drugs are present, the upper layer is yellow; rhubarb causing the deepest shade, and aloes the smallest amount of color from a given amount of material. (See a future paper concerning emodin drugs other than cascara.)