If, on shaking the above mixture with potassium hydroxide, a violet precipitate is formed, the presence of senna is indicated, while with rhubarb or frangula it will be red-violet, and with cascara dark orange-red. Rhubarb and frangula give orange solutions before adding the alkali. The ether layer, after adding the alkali, will become colorless almost immediately, except in the presence of rhubarb, when the red color persists for a time.

IV. If the above tests have not given conclusive evidence as to the composition of the drug, nitrate a portion of the ether extract, and reduce with stannous chloride, keeping at the temperature of boiling water. Senna gives a green residue, aloes a brown one, cascara, red, and rumex, rhubarb and frangula violet-red, the depth of color increasing in the order named. That from phenolphthalein is lemon-yellow throughout the whole process. Frangula residues are much more soluble in alcohol than the others, and on evaporation leave a much deeper violet ring.

Treat the above residues, after washing with water to remove the excess stannous chloride, with U. S. P solution of chlorinated soda. Senna alone will develop a distinct red color, the others turning yellow before decolorization.

Conclusions.

We have been able to devise color tests which will serve to detect rhubarb, senna, and freshly prepared fluidextract of cascara in almost any proportion in which they would be likely to be found in a commercial mixture.

There were already several good tests for aloes, and we have found a way to apply the mercurous nitrate test.

While we have been able to identify pure extracts of frangula and rumex, and frangula in mixtures in which cascara and rhubarb were absent, the identification of these drugs in other mixtures will require the comparison of the colors obtained in a series of tests.

Phenolphthalein responds to the group reaction with sodium, potassium, and ammonium hydroxides, but when the concentration of fixed alkali exceeds 10% the color disappears rapidly. The colors of the emodin drugs are unaffected by an excess of concentrated alkali.

URBANA, ILL.

[CONTRIBUTION FROM THE BUREAU OF PLANT INDUSTRY, DEPARTMENT OF AGRICULTURE.]

NOTES ON THE RUBBER FROM EUCOMMIA ULMOIDES, OLIVER.[1]

BY ARTHUR F. SIEVERS.

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Caoutchouc and caoutchouc-like substances occur rather widely in the vegetable kingdom, but it is doubtful whether it occurs in any plant

[1] Published by permission of the Secretary of Agriculture.

in such a remarkable way as in *Eucommia*. The bark of this tree, and even the young growth like leaves and petioles, contain a network of tiny threads of this material. Probably the bark shows this to the best advantage. A small piece, carefully broken in two, shows a beautiful sheen of silvery, silk-like, elastic threads.

Weiss[1] has made a histological study of these threads, and in regard to their chemical nature he says:

> "I was at first inclined to look upon these threads as of the nature of hardened gum or resin. This, however, is not the case, as they are quite insoluble in alcohol, and both gums and resins are distinguished by their solubility in alcohol from viscin and caoutchouc."

Now, as a matter of fact, gums are insoluble in alcohol, but soluble in water, quite the reverse of resins, and they are frequently distinguished from the latter by that characteristic. In fact one method of extracting gums is to extract the material with water and then precipitate the gums by the addition of alcohol to the extract. The conclusion of Weiss is therefore untenable if based on that point alone because the insolubility of the threads in alcohol does not distinguish them from gums. Their physical characters are such, however, that it is relatively easy to distinguish them from that class of substance.

He states further that viscin and caoutchouc are somewhat similar but that the former differs from the latter by its solubility in ether. In view of this he concludes that:

> "The threads of *Eucommia* consist therefore of caoutchouc, for they are insoluble in alcohol, acids and alkalis, though they become soft when treated with ammonia. They dissolve in chloroform and turpentine and swell up in ether. When heated they melt, and they burn with the characteristic smell of burning rubber."

According to Schmidt[2] ether, benzol, chloroform, carbon disulfide, petroleum, and turpentine penetrate caoutchouc very rapidly, swell it greatly, and gradually dissolve it largely to a sticky, gelatinous mass.

In order to get some definite information regarding the character of the elastic constituent of *Eucommia*, especially with regard to its solubility as compared with other specimens of caoutchouc, a series of tests was made.

Extraction with Ether.—100 g. of coarsely powdered bark were extracted with ether in a Soxhlet extractor. The extract was almost colorless, and the residue after evaporation of the solvent, amounting to 2 g., or 2%, consisted of a rubbery substance which was practically colorless. It should be noted here that apparently the ether acted rapidly because the first quantity that came over the siphon was very thick. This is

[1] Weiss, F. Ernest, "The Caoutchouc-Containing Cells of *Eucommia ulmoides*," Oliver, *Trans. Linnean Soc.*, London, Botany, [2] 3, 243 (1888–94).

[2] Schmidt, *Pharm. Chem.*, [2] 2, 1296 (1901).

interesting in view of the statements found in the literature relative to the solubility of this substance in ether which have already been mentioned.

Extraction with Alcohol.—200 g. of material gave 37.78 g. of extract with alcohol, corresponding to 18.89%. The extract was blood red, and upon evaporation of the solvent a reddish brown mass remained which contained none of the caoutchouc-like constituents. The latter is therefore insoluble in alcohol.

Preliminary Solubility Tests.—Small pieces of the material obtained from the ether extraction were placed in test tubes with various solvents and the following results noted:

TABLE I.—SOLUBILITY OF ETHER EXTRACTED CAOUTCHOUC IN VARIOUS SOLVENTS AFTER 24 HOURS.

No.	Solvent.	Remarks.
1.	Toluol	All dissolved. Cloudy solution.
2.	Chloroform	All dissolved. Cloudy solution and thicker than (1).
3.	Carbon disulfide	All dissolved. A clear, thin solution. This appears to be the best solvent.
4.	Turpentine	Slowly dissolving. A quantity still undissolved on the bottom.
5.	Carbon tetrachloride	Dissolving slowly. Some left on sides of tube. Much like (4).
6.	Ether	Slowly dissolving; not quite as fast as (4) and (5).
7.	Gasoline	Almost all dissolved. This is a fair solvent.
8.	Alcohol	Undissolved.

After 48 hrs. the sample in alcohol remained unchanged, the ether having dissolved everything but a few flakes, and the other solvents had dissolved the sample completely. The interesting thing here is that whereas ether dissolved the material fairly rapidly out of the tissues of the bark, it acted quite slowly in this test. The point is, however, that it actually dissolves it.

Quantitative Solubility Tests.—Ten grams of bark were placed in a convenient bottle and shaken frequently with 100 cc. of the solvent for 48 hrs. After that time 40 cc. were filtered off and the amount of extract determined. Six different solvents were used. The experiment was performed on the original bark and also on bark previously extracted with alcohol.

It will be noted here that ether dissolved a fair percentage of the caoutchouc material and the light color of the extract indicated of course that very little other extractive matter was taken out. The darker extracts, with some of the other solvents are no doubt contaminated and this would account for the higher percentages obtained and the sticky character of some of the extracts.

TABLE II.—PERCENTAGE EXTRACTED FROM THE BARK BY EACH SOLVENT.

No.	Solvent.	A—Original bark. % extract.	A—Original bark. Description of extract.	B—Bark exhausted with alcohol. % extract.	B—Bark exhausted with alcohol. Description of extract.
1.	Gasoline	0.825	Almost colorless. Can be rolled up like rubber.	1.06	Clear and colorless. Like A-1.
2.	Ether	1.51	Pale yellow. Readily rolled up.	1.38	Very light color. Rolls up and not sticky.
3.	Carbon disulfide	2.79	More colored than (2), but of same consistency.	1.18	Lighter color than A-3. Very rubbery.
4.	Carbon tetrachloride	2.89	Slightly more colored than (3). Otherwise the same.	1.56	About the same as A-4.
5.	Chloroform	2.72	Light brown. Sticky to touch. Will not roll up.	1.32	Light brown. Rolls up fairly and not sticky like A-5.
6.	Toluene	0.86	Light brown. Rolls up but slightly sticky.	1.01	Only slightly colored. Rolls up. Not sticky.

Action of Solvents with Constant Agitation.—100 g. of original bark were placed in a flat bottle of 1,000 cc. capacity with 500 cc. of solvent and the contents constantly agitated by means of a shaking machine. At various intervals 50 cc. were removed, filtered, and the amount of extract determined. In the table below are given the amounts extracted with various solvents in given periods.

TABLE III.—PERCENTAGE EXTRACTED WITH VARIOUS SOLVENTS IN DIFFERENT PERIODS UNDER CONSTANT AGITATION.

	Percentage of extract, using			
Time shaken.	Gasoline.	Ether.	Toluene.	Chloroform.
1 hr	1.27	1.06	1.35	1.32
4 hrs	1.29	1.89	1.94	1.59
10 hrs	1.57	2.02	1.94	1.90
20 hrs	1.57	2.01	2.08	1.97

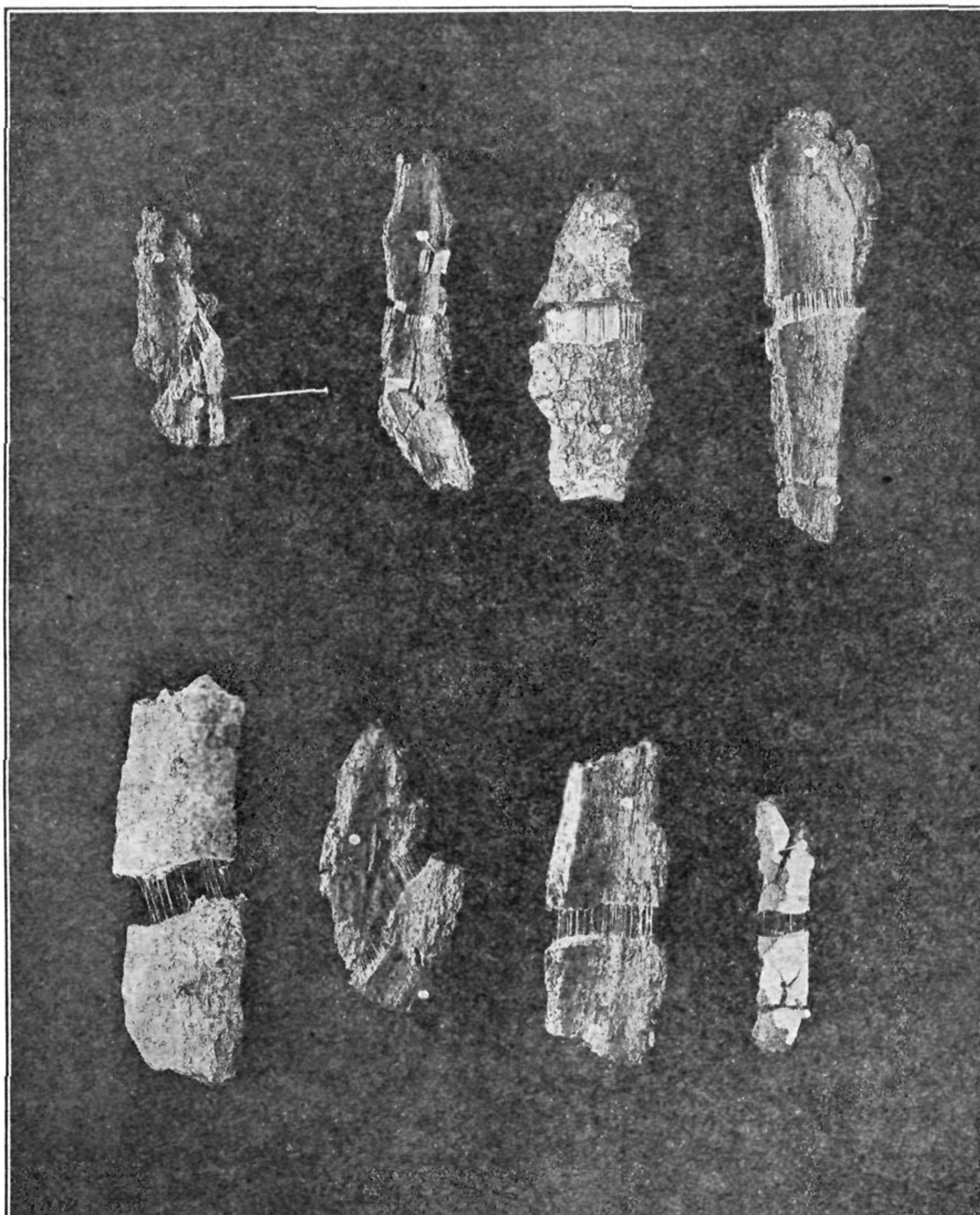
The results indicate that, with constant agitation, the maximum solvent action is practically obtained in ten hours and that very little more is dissolved during the second ten hours. Here again the ether is an efficient solvent when compared with the others that were used.

Solubility of the Caoutchouc from Eucommia as Compared with Other Specimens of Rubber.

Two specimens of crude rubber were obtained, one from Siam and one from Ceylon[1]. For the purpose of comparing the solvent action of the

[1] The Ceylon sample was a specimen of Para rubber from South America, culti-

various organic solvents on these specimens with their action on the caoutchouc from *Eucommia*, small blocks of the rubber weighing 0.25 g. were placed in bottles and constantly agitated with 100 cc. of solvent. This



Specimens of fractured bark of *Eucommia ulmoides* showing the threads of the elastic constituents.

vated in Ceylon. The Siam specimen was obtained from a large creeper, probably one of the *Ficus* species. The samples were secured through the courtesy of Mr. P. L. Ricker and Mr. G. N. Collins, of the Bureau of Plant Industry.

was done with each of the two true specimens and that from *Eucommia*. The following table shows the result:

TABLE IV.—COMPARATIVE EFFECT OF VARIOUS SOLVENTS ON CAOUTCHOUC FROM *Eucommia* AS COMPARED WITH GENUINE SPECIMENS OF CRUDE RUBBER.

Solvent.	Action of solvent on		
	Specimen from Siam.	Specimen from Ceylon.	Specimen from *Eucommia*.
Ether	All dissolved after 3 hrs. 45 mins.	After 7 hrs. only a few flakes remained. Solution cloudy.	Very soft after 1 hr. 30 mins. All dissolved after 2 hrs. 30 mins.
Petroleum ether	All dissolved after 3 hrs. 45 mins.	Still undissolved after 15 hrs.	All dissolved after 1 hr. 30 mins.
Toluene	About half dissolved after 4 hrs.	Contained some undissolved lumps after 7 hrs.	All dissolved after 1 hr. 30 mins.
Chloroform	All dissolved after 3 hrs. 45 mins.	All dissolved except a few fine flakes after 7 hrs.	All dissolved after 1 hr. 30 mins.
Carbon disulfide	All dissolved after 3 hrs. 45 mins.	All dissolved except a few fine flakes after 7 hrs.	All dissolved after 1 hr. 30 mins.
Carbon tetrachloride	Partially dissolved after 3 hrs. 45 mins.	All dissolved except a few small pieces after 7 hrs.	All dissolved after 1 hr. 30 mins.

In order to indicate which solvents acted with the greatest rapidity, the following brief table was submitted:

TABLE V.—TABLE SHOWING RELATIVE RAPIDITY OF SOLVENT ACTION OF VARIOUS ORGANIC SOLVENTS ON THREE SPECIMENS OF RUBBER.

Rank (fastest to slowest).	Siam specimen.	Ceylon specimen.	*Eucommia* specimen.[1]
1..........	Petroleum ether	Chloroform	Chloroform
2..........	Carbon disulfide	Carbon disulfide	Carbon disulfide
3..........	Ether	Ether	Petroleum ether
4..........	Chloroform	Carbon tetrachloride	Carbon tetrachloridc
5..........	Carbon tetrachloride	Toluene	Toluene
6..........	Toluene	Petroleum ether	Ether

It should be noted here that the action of the solvents on the Ceylon specimen is entirely different from that on the other two. The little squares of Ceylon rubber swelled tremendously in all the solvents. For example, the specimen in carbon disulfide, which underwent the greatest swelling, was originally only $8 \times 8 \times 3$ mm. in size, but under the influence of the solvent increased to $^1/_2 \times 2 \times 2$ cm. in size. In other words, the volume increased from 192 to 2,000 cu. mm., or 940%. The Siam specimens did not swell nearly as much, and the specimens from *Eucommia* underwent an entirely different change; they became very soft and spread over the bottom and sides of the bottle when allowed to

[1] All the solvents except ether acted very nearly the same on this specimen. Ether, as shown in Table IV, acted somewhat slower.

settle. The other specimens retained their shape. Furthermore these *Eucommia* specimens left no flakes of undissolved material like the Ceylon specimens. It is possible that these flakes consist of foreign matter, since the specimens of crude rubber used are no doubt less free from foreign material than the extracted sample from *Eucommia.*

It is evident that the literature dealing with the solubility of caoutchouc, especially the solubility in ether, is confusing. It is further evident that investigators of the elastic constituent of *Eucommia ulmoides* have not determined clearly the exact nature of that substance. Its solubility in ether is clearly established in the foregoing experiments, and yet Weiss considered the substance to be caoutchouc, and not viscin, because it only swelled up and did not dissolve in ether. Again, two genuine samples of crude rubber were found to be soluble in ether, not as rapidly as carbon disulfide perhaps, but still distinctly soluble.

It is possible that all the confusion is due to variation in the specimens used by the various investigators. Crude rubber, for instance, comes from several different sources, and the coagulation of the latex in the preparation of such rubber is not always accomplished in the same way. As regards the material from *Eucommia* it must be remembered that the foregoing notes deal entirely with the elastic constituent from the bark. The leaves, twigs and smaller branches may contain a principle of somewhat different chemical properties. In complex substances like caoutchouc, age, for instance, probably has an important modifying influence. If it were possible to secure material from all parts of the individual tree, and study the elastic principle with reference to its solubility in organic solvents, the results might go far towards removing the confusion which at present exists.

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[CONTRIBUTION FROM THE DEPARTMENT OF AGRICULTURAL CHEMISTRY OF THE UNIVERSITY OF NEBRASKA EXPERIMENT STATION.]

ON THE DUCLAUX METHOD FOR THE ESTIMATION OF THE VOLATILE FATTY ACIDS.

BY FRED W. UPSON, H. M. PLUM AND J. E. SCHOTT.

Received January 8, 1917.

The Duclaux[1] method for the determination of the volatile fatty acids is based upon the fact that each of the acids of the series $C_nH_{2n+1}COOH$ has a constant rate of vaporization when distilled under given conditions. For example, if a definite volume of a dilute solution of any one of the lower fatty acids is subjected to distillation and the distillate collected in 10 cc. fractions, the amount of acid in any one fraction will bear a definite relation both to the total amount of acid in the original

[1] Duclaux, *Ann. chim. phys.*, **2**, 289 (1874); *Ann. inst. Pasteur*, **9**, 265 (1895).