

in the chlorination washings, these constants are not to be regarded as proximate constituents but rather as radicals connected with the constituents cellulose and lignin. With the exception noted, these constants may be ignored in the summative analysis of coniferous woods.

SUMMARY

I—A study is made of the distribution of the groups contained in redwood which yield furfural, acetic acid, and methoxy, with the object of learning their relation to the constituents cellulose and lignin.

II—About half of the furfural-yielding groups are associated with the cellulose, but only a small amount with the lignin. The portion present as true pentosan is hydrolyzed and removed during chlorination.

III—The acetic-yielding groups are partly associated with the cellulose, much less so with the lignin. A small amount appears to be detached from either. The results are not conclusive in view of the small amount present in redwood and the analytical difficulties. In the case of coniferous woods acetic acid probably need not be considered as a proximate group.

IV—The methoxy groups are wholly associated with the lignin. They may be partially split off from it by acid hydrolysis.

V—In the summative analysis of coniferous woods, all of the acetic-yielding and methoxy groups and part of the furfural-yielding groups may be disregarded as already accounted for in the cellulose and lignin. The furfural-yielding substances contained in the chlorination washings and representing hydrolyzed pentosans should be estimated.

THE PROXIMATE ANALYSIS OF CONIFEROUS WOODS

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INTRODUCTORY

A method has been recently proposed by the author for the summative proximate analysis of woods.^{1*} Later investigations have shown the advisability of certain modifications of the original scheme which are considered in detail in this paper.

The proposed system for the analysis of wood effected a separation of the wood substance into the following fractions: loss on drying, benzene extract, alcohol extract, water-soluble, soluble in one per cent sodium hydroxide, cellulose, and lignin. Full information as to the composition of these fractions was lacking, but it was believed that the wood constituents were separated into logical groups based upon chemical similarity and economic value.

The scheme was found to account for nearly all of the material of coniferous woods in that the sum of all constituents varied from 96 to 97 per cent for the three conifers examined. With the hardwoods the method was unsuccessful, as 10 to 17 per cent of the constituents remained unaccounted for. The available data seem to indicate that the chemistry of the hardwoods is an entirely separate problem. The woods of the broad-leaved trees have accordingly been omitted

* Numbers refer to Reference, page 479.

from consideration in this investigation and the conclusions are applicable to the conifers only.

DEFECTS IN PROPOSED SCHEME

(1) ITS FAILURE TO GIVE CORRECT RESULTS FOR CELLULOSE AND LIGNIN—It was noted in the original paper¹ that when digestion in one per cent sodium hydroxide was used less cellulose and lignin were obtained than when this treatment was omitted. In a subsequent paper² it was shown that the diminished yield of cellulose was due to partial destruction of true cellulose instead of to greater purity of the product. Accordingly the results for cellulose are incorrect. No direct data are available for lignin, but it has been shown in the preceding paper that lignin readily loses a portion of its methoxy groups when it undergoes acid hydrolysis. Possibly the same effect is produced by alkalis.

(2) THE VAGUE SIGNIFICANCE OF THE WATER-SOLUBLE AND ALKALI-SOLUBLE FRACTIONS—In the absence of detailed studies of the substances contained in these portions, it was believed that they consisted of substances corresponding approximately to König's "proto" and "hemi" forms of cellulose and lignin.³ It is apparent from subsequent studies,² however, that they contain also degradation or hydrolytic products of true cellulose and true lignin. The numerical expression of these fractions has therefore no value as an analytical statement of wood constituents.

(3) THE FAILURE TO EXPRESS THE HEMICELLULOSES—Schorger's studies of mannan⁴ and galactan⁵ have shown that these carbohydrates are found in all conifers, sometimes in considerable quantity. Xylan is well known as a constituent of woods. It is therefore evident that a complete analysis of a wood should take these hemicelluloses into consideration. In the proposed scheme the water- and alkali-soluble portions only partially accounted for these bodies together with other substances.

(4) ORGANIC RADICALS—The original scheme took no account of organic radicals present—the so-called "wood constants." The preceding paper has shown that, with the exception of the furfural-yielding substances soluble in the chlorination washings, these radicals may be disregarded as proximate constituents of coniferous woods.⁶ The original scheme is defective, however, in that it ignores this soluble furfural-yielding substance.

The remedies for the above defects are quite evident. The cellulose and lignin determinations should be made reliable by omission of the alkaline hydrolysis. The water- and alkali-soluble fractions would disappear, leaving the hemicelluloses entirely unaccounted for. It would then be necessary to give the hemicelluloses a separate place in the scheme, and methods would be required for their estimation either collectively or individually. The soluble furfural-yielding substance (probably the pentosan, xylan) would be included in the hemicelluloses.

The present investigation is an attempt to revise the original scheme in accordance with the above suggestions. Methods have been applied for the determination of the hemicelluloses. The revised procedure has then been checked by making these and

the other determinations required for a complete summative analysis on the three coniferous woods formerly employed.

EXPERIMENTAL

The woods examined were redwood (*Sequoia sempervirens*), yellow pine (*Pinus ponderosa*), and sugar pine (*Pinus lambertiana*). The original material was in the form of slabs. In the case of the redwood it represented mostly sapwood with a small amount of the outer portion of heartwood. In the case of the pines it represented sapwood only.

The samples were in the form of fine sawdust obtained by making a number of cross-sectional cuts of the slabs and screening the resultant material through a sieve having 50 meshes to the linear inch. As considerable coarse material was rejected, the samples cannot be regarded as strictly representative of the original material. That, however, is of no importance to the purpose of this study which was to determine the applicability of the analytical methods to the woods employed.

ANALYTICAL METHODS

LOSS ON DRYING—Two grams of the wood were dried at 100° C. to constant weight.

BENZENE EXTRACT—Two grams of material dried as above were placed in an alundum thimble and extracted in a Soxhlet apparatus for 6 hrs. with benzene. The solvent was then evaporated and the residual extract dried for 1 hr. at 100° C., and weighed.

ALCOHOL EXTRACT—The residue from the above treatment was extracted for 6 hrs. with 95 per cent alcohol. The solvent was evaporated and the residue dried and weighed as before.

CELLULOSE—Two grams of material after extraction with benzene and alcohol as above were transferred to a Gooch crucible containing a cloth filtering disk and washed with distilled water. The cellulose was determined by the Sieber and Walter method as described in the preceding paper and elsewhere.⁷ The residues were tested for lignin by digestion in 72 per cent sulfuric acid and when appreciable amounts were found, the lignin was filtered off and weighed, and the cellulose corrected for it.

LIGNIN—Two grams of material after extraction with benzene and alcohol were air-dried at low temperature (60° C.) and transferred to a 750 cc. flask. 20 cc. of 72 per cent sulfuric acid were added and the mixture allowed to stand at room temperature for 3.5 hrs. 50 cc. of cold water were added, then 500 cc. of hot water. The residue was filtered off on a tared Gooch crucible, washed thoroughly with hot water, dried, and weighed.

HEMICELLULOSES—The hemicelluloses are apparently contained quantitatively in the chlorination washings,² and it was thought at first that these solutions might be utilized for their determination. They were found to be unsatisfactory for this purpose except in the case of the soluble pentosans. The presence of lignin derivatives interferes seriously with either the collective estimation of the hemicelluloses by reducing sugar methods or the separate mannan and galactan determinations.

SOLUBLE PENTOSANS—The chlorination filtrates and washings from four cellulose determinations representing 8 g. of original material were evaporated to a little less than 500 cc., transferred to a 500 cc. volumetric flask and made up to volume. Aliquot parts of 125 cc. each were placed in the distilling flask of the pentosan apparatus, 30 cc. of concentrated hydrochloric acid added, and the furfural distilled off in the usual manner. The furfural was precipitated as phloroglucide, and the precipitate filtered off, washed, dried, and weighed. The results were calculated to xylan by means of Krober's tables.

MANNAN—The method used was that described by Schorger.⁸ Ten grams of the wood were hydrolyzed by boiling for 3.5 hrs. with 150 cc. of hydrochloric acid (sp. gr. 1.025) in an Erlenmeyer flask under a reflux condenser. The mixture was then filtered and the residue rinsed into a beaker and digested with 100 cc. of water for a few minutes on the hot plate. The solution was poured through the filter and the residue again rinsed back into the beaker and the digestion repeated. This process was continued until about 500 cc. of filtrate were obtained. The filtrate was neutralized with sodium hydroxide and the solution made slightly acid with acetic acid, after which it was evaporated to 150 cc. It was filtered into a glass-stoppered Erlenmeyer flask, and a mixture of 10 cc. of phenylhydrazine and 20 cc. of water acidified with glacial acetic acid was added. The mannanose hydrazone was in every case immediately precipitated. The whole was allowed to stand for 2 hrs. with frequent shaking and then filtered on a Gooch crucible fitted with a filtering disk of mercerized cotton cloth. It was washed several times with cold water and then with acetone, dried at 100° C. and weighed. The weight of residue was calculated to mannan by multiplying by the factor 0.6.

GALACTAN—Five grams of the material were placed in a 100 cc. beaker, and 60 cc. of nitric acid (sp. gr. 1.15) were added. The beaker was placed in a water bath and the liquid evaporated to about 20 cc., care being taken not to allow the temperature of the water bath to exceed 87° C. The mixture was then diluted to about 75 cc. with hot water, and filtered. The residual cellulose was washed until the filtrate came through practically colorless. A total volume of about 250 cc. was generally thus obtained. The filtrate and washings were evaporated on the water bath at 87° C. to a volume of about 10 cc. The residue was set aside for several days to allow the mucic acid to separate out. Large crystals (possibly oxalic acid) always formed at first, then a day or two later fine flakes of mucic acid separated out. At this point the mixture was stirred vigorously to facilitate the precipitation. About 24 hrs. after the mucic acid appeared the mixture was diluted with 20 cc. of cold water. The larger crystals redissolved leaving the mucic acid unaffected. After a further 24 hrs. standing, the mucic acid was filtered off on a tared asbestos Gooch crucible and washed with about 50 cc. of water, 60 cc. of alcohol, and several times with ether. It was then dried at 100° C. for 3 hrs. and weighed. Galactan was calculated by multiplying the weight of residue by the factor 1.2.

RESULTS

By the foregoing methods the following results were obtained for the three coniferous woods examined. The figures are in every case averages of two or more determinations. In the first three columns are given the results on air-dry material as found by analysis; in the second three, the same results are recalculated to the oven-dry basis.

SAMPLE NO.....	ANALYSES OF WOODS (Results in Percentages)					
	—AIR-DRY BASIS—			—OVEN-DRY BASIS—		
	1	2	3	1	2	3
	Red-wood	Yellow Pine	Sugar Pine	Red-wood	Yellow Pine	Sugar Pine
Loss on drying at 100° C.	11.62	8.98	9.84
Benzene extract.....	0.30	2.02	2.56	0.34	2.22	2.84
Alcohol extract.....	3.88	1.36	1.71	4.39	1.49	1.90
Cellulose.....	48.51	52.54	53.36	54.89	57.72	59.18
Lignin.....	30.49	26.82	26.60	34.50	29.47	29.50
Soluble pentosans (as xylan).....	3.24	3.18	1.68	3.67	3.49	1.86
Mannan.....	2.84	5.80	5.98	3.21	6.37	6.63
Galactan.....	0.44	0.71	0.45	0.50	0.78	0.50
TOTAL.....	101.32	101.41	102.18	101.50	101.54	102.41

DISCUSSION OF METHODS

CELLULOSE—It has been previously shown that the method here practiced (omission of preliminary hydrolysis) gives the maximum yield of cellulose free from hemicelluloses and lignin. The process therefore conforms to the requirements of an accurate cellulose method and the product to the proposed definition of a true cellulose derived from lignified material.²

LIGNIN—The term "lignin" has not yet been defined with sufficient precision to permit a comparison of the product with exact specifications. Lignin is generally understood to denote the non-cellulose portion of the wood tissue proper and this conception implies its freedom from extractives, hemicelluloses, and cellulose. The most accurate method for lignin is therefore the one that yields the greatest amount of the substance with the highest purity according to the above standards.

It is believed that there is sufficient evidence to justify the claim that the method used conforms to these requirements. Both acid and alkaline hydrolysis result in diminished yield of product and it has been shown that this is due (at least in the former case) to a partial splitting off of the methoxy groups which are characteristic portions of the lignin complex. Accordingly, only by the complete omission of hydrolysis is the full yield of lignin obtainable.

Inasmuch as the lignin disappears completely on being submitted to the alternate action of chlorine gas and sodium sulfite solution, it is free from cellulose which would otherwise remain as a residue. On hydrolyzing with 2.5 per cent sulfuric acid no reducing sugars were obtained, so the material is free from hemicelluloses. The preliminary treatment with benzene and alcohol precludes the possibility of the presence of extractives. The residue may be therefore considered "pure" in accordance with the requirements outlined.

SOLUBLE PENTOSANS—Dilute alkaline solutions have been recommended for extracting xylan or wood gum from the hard woods.⁹ It has been asserted, however, that the wood gum of coniferous woods is much less readily soluble in alkaline solvents than that from the wood of the broad-leaved trees.¹⁰ For this reason it

appeared to be desirable to use the chlorination liquors for the determination of soluble pentosans.

MANNAN—The method gave results that were in good agreement with each other and consistent with those given by Schorger¹¹ for the corresponding woods. Small portions of the residue, recrystallized by alcohol, gave a melting point of 188° C.

GALACTAN—In their paper on the galactan of the western larch, Schorger and Smith¹² report only traces of soluble galactans in the coniferous woods examined. In their experiments 100 g. of the material were digested several times in hot water and the resulting solution evaporated nearly to dryness and treated with nitric acid in the usual manner. Other investigators,¹³ however, have reported the presence of galactan in sulfite waste liquors, indicating that galactans are contained in some of the paper-making woods. It therefore seemed probable that galactans are present in not readily soluble form. Accordingly no attempt was made in the present investigation to extract the galactan as such from the wood by means of solvents. Instead the procedure of attacking the wood directly with nitric acid was decided upon as the best means of giving the full galactan content of the wood.

The evaporation of the wood substance with nitric acid results in the production of a large amount of insoluble oxycellulose which interferes with the separation of the mucic acid. This difficulty was overcome by the procedure devised by Miyake¹⁴ in which the mixture, after evaporation, is diluted, and the solution containing the mucic acid is filtered off from the insoluble matter and again evaporated.

The author has pointed out the uncertainty of yield of mucic acid by the usual process when only small amounts of galactan are present.¹⁵ Schorger and Smith¹⁶ have shown that much better results are obtained if the temperature is not allowed at any time to exceed 87° C., instead of maintaining the bath at 94° to 96° C., as prescribed in the official method for galactan.¹⁷ The use of the lower temperature has accordingly been adopted.

Considerable difficulty was encountered at first in obtaining a crystallization of the mucic acid after evaporation. This appeared to be due chiefly to the interfering action of oxalic acid or other substances contained in the solution. When the latter was evaporated to the usual volume of 20 cc., no separation of mucic acid occurred even after several days' standing. By evaporating to a smaller bulk clear crystals separated out after one or two days. These crystals on standing increased in size and a day or two later the characteristic mucic acid flakes were precipitated. After the last precipitation was judged to be complete, the larger crystals were easily removed by diluting the solution to the usual volume of 30 cc. The amounts of residue were always too small to permit of a melting-point determination but the appearance of the precipitate was such as to leave little doubt that it was actually mucic acid.

Considering the nature and difficulties of the method, the agreement of results may be considered satisfactory. Redwood gave 0.40 and 0.47 per cent; yellow

pine gave 0.96, 0.66, 0.43, and 0.80 per cent; sugar pine gave 0.55 and 0.35 per cent of galactan. It is believed that the described procedure gave approximately correct results. A critical study of the whole galactan method is still much needed, however.

DISCUSSION OF RESULTS

It is believed that analyses of coniferous woods made by the methods described account for all important constituents of those woods. The sum is in every case slightly over 100 per cent but not more so than might be expected from the character of the methods employed. A variation of several tenths of a per cent between duplicate determinations is usual. The cellulose and lignin are probably always slightly overestimated on account of the practical impossibility of getting complete contact between all particles of the material and the attacking reagents. This difficulty could be partly overcome by better mechanical condition of the wood.

The possibility of overlapping of values due to certain constituents being included in more than one determination has received careful consideration throughout these investigations. It is believed that such double estimations have been largely avoided. Most of the proximate groups can be shown to be free from any of the constituents contained in the other groups. It has already been pointed out that this is true in the case of cellulose and lignin. Mannan and galactan determinations depend upon reactions too specific to admit of the inclusion of other constituents.

By improving the mechanical condition of the sample in respect to fineness, better results should be obtained in all the determinations. Some of the determinations, particularly that of galactan, could probably be made more accurate and reliable. These changes would no doubt give a considerably better summation and a consequently more satisfactory accounting of the constituents of the coniferous woods.

SUMMARY

1—An improved procedure is described for the summative analysis of coniferous woods. Methods are given for the estimation of the following constituents: loss on drying, benzene extract, alcohol extract, cellulose, lignin, soluble pentosans, mannan, and galactan.

2—By the omission of preliminary hydrolysis, more reliable results are obtained in the cellulose and lignin determinations than by methods previously used.

3—Soluble pentosans are determined in the chlorination liquors, mannan and galactan on separate portions of the original material. Improvements in the galactan determination are described.

4—Complete analyses of redwood, yellow pine, and sugar pine are carried out by these methods. A summation of slightly over 100 per cent is obtained in every case.

5—The results indicate that overlapping of the proximate groups, *i. e.*, partial inclusion of any constituent in more than one group, has been largely avoided.

6—Analyses by the proposed scheme probably

account for all important constituents of coniferous woods.

REFERENCES

- 1—THIS JOURNAL, 11 (1919), 556.
- 2—*Ibid.*, 12 (1920), 264.
- 3—*Z. Nahr. Genussm.*, 28 (1914), 177.
- 4—THIS JOURNAL, 9 (1917), 748.
- 5—Schorger and Smith, *Ibid.*, 8 (1916), 494.
- 6—Dore, preceding paper, p. 472.
- 7—Sieber and Walter, *Chem. Abs.*, 8 (1914), 1202; Johnsen and Hovey, *Paper*, [23] 21 (1918), 36; *J. Soc. Chem. Ind.*, 37 (1918), 1321.
- 8—THIS JOURNAL, 9 (1917), 748.
- 9—Cross and Bevan, "Cellulose," p. 187.
- 10—Klason, Cross and Bevan, "Researches on Cellulose," 3, 105; Schorger, THIS JOURNAL, 9 (1917), 562.
- 11—*Ibid.*, 9 (1917), 749.
- 12—*Ibid.*, 8 (1916), 499.
- 13—Lindsey and Tollens, *Ann.*, 267, 341; Klason, *Loc. cit.*; Hagglund, *Biochem. Z.*, 70 (1915), 416.
- 14—*Chem. Abs.*, 6 (1912), 2958; 8 (1914), 2007.
- 15—THIS JOURNAL, 7 (1915), 721.
- 16—*Ibid.*, 8 (1916), 498 (footnote).
- 17—U. S. Department of Agriculture, *Bulletin* 107, 55.

THE DETECTION OF ARSENIC IN SULFUR

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A certain sample of sulfur was reported to contain arsenic. It had been tested by a method first devised by Schaeppi¹ and later accepted by many authorities.² We found that the sulfur contained no trace of arsenic, but that when it was tested by Schaeppi's method, a decided qualitative test for arsenic was obtained. On further investigation it was found that this method contains a fundamental error which makes it useless as a test for small quantities of arsenic.

The method as described by Schaeppi consists essentially in first digesting the sulfur with dilute nitric acid for the purpose of removing calcium chloride, sulfate, and sulfide. The sulfur washed free from acid is now treated with dilute ammonia solution for 15 min. at 70° to 80° C. Schaeppi assumes that any arsenic present in the sulfur must exist as sulfide, mainly arsenious sulfide, and will be dissolved by the ammonia. The arsenic is then estimated indirectly through determination of the amount of sulfide by precipitation with silver nitrate in neutral solution.

"For very rough estimations, it is sufficient to treat 10 g. of finely ground sulfur with nitric acid, to extract with ammonia, and to add silver nitrate. From the intensity of the color or the quantity of the precipitate of silver sulfide, it may be judged whether the sulfur is approximately free from arsenic or is strongly contaminated."³

Schaeppi endeavored to test the accuracy of his method by dissolving known amounts of pure arsenious sulfide in ammonia solution, carefully neutralizing with nitric acid, and titrating with decinormal silver nitrate using chromate as indicator. His results showed fairly good agreement between the quantities of arsenic taken and those found. However, his results would have

¹ *Chem. Ind.*, 4 (1881), 409.

² Crooks, "Select Methods of Chemical Analysis," 4th ed., 416; Lunge, "Technical Methods of Chemical Analysis," 1 (1908), 267; Lunge, "The Technical Chemist's Handbook," 1916, 107.

³ Crooks, *Loc. cit.*