T	8	8	4	4	0.85	0.85
V	1.56	2.80	0.91	1.54	5.8264	.49048
P (calculated) ($w = 1$)	19.77	10.15	18.3	9.50	0.355	(.373)
P (calculated) ($w = 1.5$)	20.34	10.31	20.04	10.07	.366	(.379)
P (experimental)	20	10	20	10	.3745	.3745[a]

[a] Used to obtain the relation between y and z.

The use, then, of the Boyle temperature has resulted in a modification of the form of the general equation of state by showing that the logarithmic term is a function of T and it has simplified considerably the determination of the constants of the equation. Using the critical point, the ideal gas value at low pressure, two points on the critical isotherm at high pressure, the Boyle temperature, one point in the liquid phase and the second term maximum at the critical point, an equation

$$PV + \frac{5.3752V + 3.3713}{T^{0.5}V^2 + 0.8973T^{1.8}V + 1.1216T^{-1.88}} = 3.25T + 0.2869P + 1.1972T^{-1.5}\log(P + 1)$$

is found which fits fairly closely at the eight other widely divergent points which were tested.

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[CONTRIBUTION FROM THE DIVISION OF PLANT NUTRITION, UNIVERSITY OF CALIFORNIA]

Age and the Chemical Composition of White Fir Wood

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The effect of age on the chemical composition of wood has been studied by few investigators. The composition of sapwood and heartwood has been compared,[1–4] separate trees examined[4,5] or a single constituent determined in one tree.[6,7] It would seem that differences due to age may be studied best by demarking zones of various ages on a cross-section from a definite height in a selected tree, in order to eliminate environmental factors as far as possible. The material should be examined for all important constituents.

Selection of Material

In the past, little effort has been made to record data on the environment in which the wood to be analyzed was grown. Since there is a possibility that environment and chemical composition may be correlated, such data may be of value in the future.

The wood used for this study was obtained from a white fir tree (*Abies concolor*) growing in a mixed conifer stand near Quincy, California. It was a healthy tree, approximately 100 feet tall and 185 years old. The diameter, breast high, was 23 inches (58 cm.). Classed as a dominant number three,[8] it had a long, pointed crown of medium width. The site was such that a tree dominant throughout its life had an average height of 125 feet (38 meters) at 300 years of age; the elevation 3900 feet (1150 meters); the slope 50%; and the exposure northwesterly. The average annual precipitation is 35 to 40 inches (89 to 101 cm.), with little during the summer season.

(1) E. Gäumann, *Flora*, **23**, 344 (1928).
(2) G. J. Ritter and L. C. Fleck, *Ind. Eng. Chem.*, **15**, 1055 (1923).
(3) G. J. Ritter and L. C. Fleck, *ibid.*, **18**, 576 (1926).
(4) C. G. Schwalbe and E. Becker, *Z. angew. Chem.*, **33**, 14 (1920).
(5) P. Klason, *Cellulosechem.*, **12**, 36 (1931).
(6) G. De Chalmot, *Am. Chem. J.*, **16**, 611 (1894).
(7) B. Johnsen and R. W. Hovey, *J. Soc. Chem. Ind.*, **37**, 132T (1918).
(8) D. Dunning, *J. Agric. Research*, **36**, 755 (1928).

Preparation of Material

A section 7 inches (17.8 cm.) thick and 17 inches (43 cm.) in diameter, without the bark, was sawed from the white fir tree described above, at a point 12 feet (3.66 m.) above the ground level. The age at this point was one hundred and sixty years. This cross-section was carefully marked, following the 15th, 40th, 85th and 125th annual ring from the periphery, thus dividing the piece into five bands or zones. These zones were chiseled to sticks approximately 0.2 × 0.2 × 3.5 inches (0.51 × 0.51 × 8.9 cm.) and after drying at room temperature, chopped in a Wiley mill until all the sawdust passed a 60-mesh screen. In common with standard procedure, all sawdust passing an 80-mesh screen was discarded. Knots and compression wood areas were eliminated.

Data concerning these zones are listed in Table I. The total (T) was mixed from weighted proportions of the zones. The wood was 65.4% sapwood and 34.6% heartwood. The average apparent specific gravity of the sapwood was 0.425 and of the heartwood 0.440.

TABLE I

MEASUREMENTS ON AGE ZONES

No. of rings from periphery	Symbol	Sap- or heart-wood	Radial width of zone, in.	Area of zone, sq. in.	% of total	% of sap- or heart-wood
1–15	A	S	0.5	23.0	10.1	15.5
16–40	B	S	1.25	60.6	26.8	40.9
41–85	C	S	1.75	64.6	28.5	43.6
86–125	D	H	2.38	57.0	25.1	72.5
126–160	E	H	2.62	21.6	9.5	27.5
1–160	T	..	8.50	226.8	100.0	..

Methods

Methods of the Forest Products Laboratory[9] were used to determine ash. solubility in cold water. hot water, 1% sodium hydroxide. ether. and alcohol–benzene, pentosans (thiobarbituric acid used as precipitant), cellulose and lignin.[10] Nitrogen was determined by the method given in Schorger.[11] The Zeisel method. as modified by Dore,[12] was used to determine methoxyl content. Acetic acid was determined by the toluenesulfonic acid method of Freudenberg.[13]

Carbon dioxide determinations, using Dore's modification[14] of the LeFevre method for the determination of uronic acid, were made on the total sawdust. Mannan was determined on this material by Schorger's method[11] (p. 537).

Results

The averages for all data collected on age zones are gathered in Table II. In each case the value calculated for the total from the zones is listed so that it may be compared with the figure determined experimentally. All results are the average of at least two check determinations. Values are expressed in per cent. of oven-dry (105°) weight of the wood.

TABLE II

SUMMARY OF RESULTS

Zone	Ash	Solubility in Cold water	Hot water	Ether	Alcohol-benzene	1% NaOH	Acetic acid
A	0.38	1.46	2.35	0.21	0.92	11.28	1.64
B	.37	0.51	1.29	.19	.96	10.66	1.70
C	.38	.21	1.19	.20	.94	9.95	1.71
D	.63	2.16	2.83	.26	1.74	11.72	1.33
E	.64	1.55	2.04	.22	1.49	10.77	1.25
T	.43	1.12	1.89	.23	1.43	11.38	1.64
Calcd. T	.46	1.04	1.83	.22	1.20	10.79	1.56

Zone	Methoxyl	Nitrogen	Pentosan	Lignin	Cellulose	Pentosan-in-cellulose
A	4.68	0.08	8.68	26.62	64.63	6.96
B	4.62	.06	8.46	27.29	64.56	6.33
C	4.40	.06	8.62	27.65	64.60	7.18
D	4.68	.06	8.83	27.31	64.53	5.75
E	5.06	.06	10.98	28.00	63.65	9.16
T	4.57	.06	8.86	27.43	64.47	7.31
Calcd. T	4.62	.06	8.73	27.40	64.49	..

The total sawdust contained 5.98% mannan and yielded 0.86% carbon dioxide in the uronic acid determination. The methoxyl content of the lignin isolated from total sawdust was 14.81%, or 4.06% calculated on the total wood. Compared to 4.57%, 89% of the methoxyl content was retained in the lignin.

Discussion

No previous data have been reported in the literature for the proximate analysis of the wood of white fir. The values found for the total wood, *i. e.*, the sample commonly used for analysis, compared favorably with the data recorded for other coniferous woods[11] (p. 34). In many points the composition of white fir resembled that of white spruce.

The carbon dioxide from total sawdust amounted to 0.86%. If the carbon dioxide is assumed to be due principally to uronic acid residues, the value for pentosan must be corrected. The total sawdust yielded 5.09% of furfural (equal to 8.86%, pentosan). The carbon dioxide content of 0.86% is equal to 3.44% uronic anhydride. Norris and Resch[15] found that the furfural resulting from galacturonic anhydride, on distillation with 12% hydrochloric acid, was only 43% of the theoretical, or 23.50% of the uronic anhydride. Using this figure, 0.81% of furfural was due to uronic anhydride. Apparently the difference, 4.28%, was the furfural due to pentosans. Accordingly the pentosan content was 7.33%, instead of 8.86%. Anderson[16] found 1.00% carbon dioxide in the wood of white spruce.

Inspection of the data for the five age zones showed the ash content to be constant within the sapwood and within the heartwood, but the values for the latter were approximately 50% higher than those of the sapwood. Other investigators[1–3] have found ash content higher in the sapwood in some instances and higher in the heartwood in others. The wood from older trees often is lower in per cent. ash than that from a younger tree of the same species.

The values for solubility in cold water, hot water, and 1% sodium hydroxide decreased from the outer to the inner sapwood, then rose sharply in the outer heartwood to their highest value and dropped slightly in the inner heartwood. Solubility in ether and alcohol–benzene had a constant value in the sapwood with an increase in the outer heartwood followed by a slight decrease in the inner heartwood.

Acetic acid values were constant within the sapwood and within the heartwood but were ap-

(9) M. W. Bray, "Chemical Analysis of Pulps and Pulp Woods," Mimeographed, Forest Products Laboratory. Madison, Wisconsin. 1928.

(10) G. J. Ritter, R. M. Seborg and R. L. Mitchell, *Ind. Eng. Chem., Anal. Ed.*, **4**, 202 (1932).

(11) A. W. Schorger. "Chemistry of Cellulose and Wood." McGraw-Hill Book Co., Inc., New York, 1926, p. 507.

(12) W. H. Dore. *J. Ind. Eng. Chem.*, **12**, 472 (1920).

(13) K. Freudenberg, *Ann.*, **433**, 230 (1923).

(14) W. H. Dore. THIS JOURNAL, **48**, 232 (1926).

(15) F. W. Norris and C. E. Resch, *Biochem. J.*, **29**, 1590 (1935).

(16) E. Anderson, *J. Biol. Chem.*, **91**, 559 (1931).

preciably higher in the former. This holds in all American conifers examined.[2,3] When the sapwood sawdust or the total sawdust was heated with absolute alcohol and *p*-toluenesulfonic acid in the Freudenberg method, a violet coloration first appeared. The reaction which caused this is unknown but the coloration suggests a possible method for distinguishing sapwood from heartwood in doubtful cases.

The methoxyl and pentosan values were practically constant in the four outer age zones, but both showed a sharp rise in the inner heartwood. This trend in the methoxyl content paralleled, to a certain extent, that of lignin, especially in regard to the final rise in the inner heartwood.

Nitrogen content was practically the same throughout the section but was slightly higher in the outer sapwood. One might expect this since most of the living cells were in this zone and conduction of nitrates occurred there also.

The lignin content showed appreciable increase from the periphery to the pith.

The cellulose content was nearly constant in the four outer zones but showed a considerable decrease in the inner heartwood. The pentosan in cellulose was irregular. Johnsen and Hovey[7] determined the cellulose in a balsam fir 10.5 inches (26.6 cm.) in diameter with 64 annual rings and found an increase from pith to sapwood, as follows: pith to 15th ring, 51.14%, 20th to 35th, 53.26% and sapwood, 54.21%.

Since in most determinations the values calculated for the total wood from the data of the individual age zones agreed very well with the values determined experimentally (compare last two rows, Table II), it was decided to calculate values for the sapwood and heartwood so that they might be compared with values found by Ritter and Fleck for other American conifers.[2,3] This was done from the data in Table I, Column 7.

In the American conifers they examined, Ritter and Fleck[2,3] found that the cold-water, hot-water, ether and alkali-soluble components were higher in the heartwood than in the sapwood and that, with the exception of lignin in white cedar, the cellulose and lignin contents were lower in the heartwood. White fir showed similar results for the extractives and cellulose but the lignin behaved like that of white cedar and was higher in the heartwood. Apparently, then, white cedar and white fir can be classed in a separate group from the others examined. Acetic acid was also higher in the sapwood of white fir as it was in all the woods they analyzed. In white fir both methoxyl and pentosan values were higher in the heartwood. Ritter and Fleck found fluctuations for these determinations. In general, the calculated sapwood and heartwood values agree with the data reported for American conifers.

TABLE III

CALCULATED VALUES FOR SAPWOOD AND HEARTWOOD (% Oven-dry Weight)

Determination	Sapwood	Heartwood
Ash	0.38	0.63
Cold water	.53	1.99
Hot water	1.41	2.61
Ether	0.20	0.25
Alcohol–benzene	.94	1.67
1% NaOH	10.45	11.46
Determination	Sapwood	Heartwood
Acetic acid	1.70	1.31
Methoxyl	4.53	4.78
Pentosan	8.56	9.42
Nitrogen	0.06	0.06
Lignin	27.34	27.50
Cellulose	64.59	64.29

Comparison of our data for *Abies concolor* with those of Gäumann for *Abies pectinate*,[1] although different methods were used, showed the ash, lignin and solubility in ether to be higher in the heartwood in both cases. Gäumann found other extractives to be higher in the sapwood while the opposite was true in white fir. The values he found for pentosan and cellulose fluctuated throughout the year.

Summary

The effect of age on the chemical composition of white fir wood was studied. Values, calculated from the age zone data, for the composition of the sapwood and heartwood agree in general with the data reported by other investigators for American conifers.

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