

FINSKA SUOMEN
KEMISTSAMFUNDETS KEMISTISEURAN
MEDDELANDEN TIEDONANTOJA

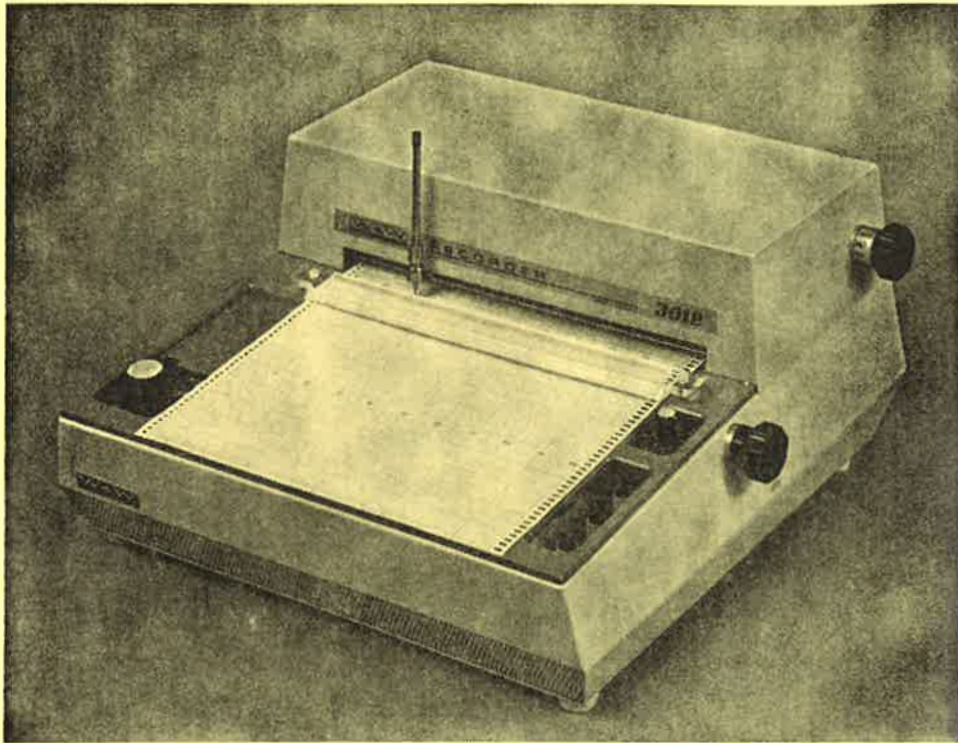
REDAKTÖR — TOIMITTAJA

Gösta Brunow

INNEHÅLL — SISÄLTÖ

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Walter Wahl in memoriam

Finska Kemistsamfundets hedersledamot, professor emeritus Walter Wahl, avled 18 oktober 1970 i den höga åldern av 91 år. Han var kanske den sista företrädaren hos oss för en typ av forskare med gamla traditioner, den ekonomiskt oberoende privatmannen med eget laboratorium och eget bibliotek, som forskar på områden han själv väljer. Han var väl också den sista ledamot som var äldre än Finska Kemistsamfundet självt, han var tolv år när samfundet grundades.

Walter Wahl föddes i Viborg som ättling av en släkt med gamla traditioner på träförädlingens område i östra Finland. Firman Wahl var med på sågverksområdet vid Saima-vattnen redan i början av 1800-talet. Som 20-åring var Walter Wahl bland de studenter, som efter februarimanifestet år 1899 i Finlands bygder insamlade namn på den massadress som av den stora deputationen fördes till Rysslands huvudstad för att hos tsaren protestera mot förryskningsåtgärderna. Två år senare följde Wahl med Wilhelm Ramsay på geologiska exkursioner i Ostkarelen och medverkade på så sätt till uppkomsten av det geologiska begreppet Fennoskandia. År 1906 företog han geologiska exkursioner i Förenta Staterna och Kanada och deltog i den internationella geologkongressen i Mexico. Wahl blev fil. kand. i Helsingfors 1903. Som assistent på Kemicum vid Rege- ringsgatan hörde Wahl till »övre våningens herrar», som på kvali- tativa och kvantitativa avdelningarna företrädde den oorga- niska kemien och under ledning av mineralsyntetikern A. B. af

Schultén stod i ett visst motsatsförhållande till »nedre våningens herrar», organikerna Hjelt och Aschan. Wahl var sedermera väl den sista från Finland som besökte af Schultén i Paris, där denne under åren före första världskriget levde en enstörings liv.

Wahl var till utbildningen egentligen kemist, men inriktade i hög grad sin forskning på mineralogi och geologi och därifrån på studier av meteoriter och kemiska substanser vid höga tryck. Han disputerade 1908 med en avhandling om pyroxenminera- lens kemi och optik. Dessa mineral förekommer såväl i bergarter som i vissa meteoriter. — Wahl arbetade i olika repriser utom- lands. 1911 — 1914 var han stipendiat vid Davy-Faraday-labora- toriet i London, där han fick bestående intryck av kärnkemins genombrott och arbetade med bl.a. syrets och vätets kristallo- grafi och optik i fast tillstånd, alltså vid extremt låga tempera- turer. Han blev ledamot av Royal Institution of Great Britain 1912. — Under livsmedelsbristen 1918 var Wahl ordförande i sta- tens livsmedelsproduktionskommitté och följande år medlem av den till England, Frankrike och U.S.A. sända handelskommissio- nen för import från dessa länder. Åren 1918 — 1924 var Wahl professor i kemi vid den nygrundade Åbo Akademi, de tre sista åren också dekanus vid kemisk-tekniska fakulteten. Vid Hel- singfors universitet blev han docent 1923 och var 1937 — 1947 personlig e.o. professor. Från 1940 till in på 1960-talet var han chefdirektör för familjebolaget Wahl o. Co och var länge sty- relseledamot vid A. B. Centrallaboratorium. Från 1951 var han några år ständigt sekreterare för Finska Vetenskaps-Societeten. Från 1949 var han medlem av den internationella atomvikts- kommissionen och var tio år president i den internationella me- teoritkommissionen. Han hann uppleva landstigningen på månen och analyserna av mineralproven därifrån, som intresserade ho- nom på det högsta. — Under 1920- och 1930-talen publicerade han ett antal arbeten om graniterna i det finska urberget. År 1937 ställde han upp den första masspektrografen i Finland och utförde med den serier av åldersbestämningar på fennoskandiska urbergsmaterial.

Utgående från mineralogin intresserade han sig för centrala problem på kemins olika områden, särskilt det stereokemiska. Han arbetade med siliciums och bors valensförhållanden, silika- ternas rymdstruktur och byggnaden hos hemoglobin och kloro- fyll samt undersökte isotopsammansättningen hos koppar och andra metaller i blodet hos olika havsdjur. För detta ändamål bedrev han länge laboratorieundersökningar i Monaco och i Neapel. En tid arbetade han med de kemiska substansernas för- hållande vid extremt höga tryck.

I Finska Kemistsamfundet var han ordförande åren 1929 och 1941 och han har representerat samfundet i Centralrådet för

Finlands Kemister. År 1926 var han generalsekreterare för Nordiska kemistmötet, som då för första gången hölls i Finland.

När Wahl vid ca 80-års ålder sålde sin firma var hans vitalitet ännu obruten. Han föresatte sig att resa till alla de länder han velat besöka men ej fått tillfälle att se. Han reste därefter bl.a. till Tanzania, där han drabbades av malaria, som han botade i Marocko, och sedan jorden runt via Nya Zeeland, Australien och Indonesien. Blott Singapore gick han miste om, till sin stora förtrytelse, på grund av den politiska oron i sydöstra Asien. — Walter Wahl hade under sitt långa liv sett mycket av länder och folk och vetenskapens store. Han hade humor av snarast brittisk typ och kunde berätta mycket fascinerande om sina upplevelser. Så skildrade han hur han i England träffade en ung man, som satt i en laboratoriekorridor på en fastskruvad trampcykel och alstrade elektricitet med muskelkraft för sina experiment. Den mannen var Aston, uppfinnaren av masspektrografen!

Vi ser att Wahl i hög grad hade förmågan att arbeta på egna uppslag på aktuella, okonventionella och betydelsefulla forskningsområden. I detta avseende höll han sig i främsta ledet av den internationella forskningen. Tyvärr är det i våra dagar icke lätt för en mer eller mindre ensam forskare att genomföra program av nödig omfattning. Walter Wahl var dock en forskare av format och hans idériakedom är ett stimulerande föredöme.

Terje Enkvist

Lignin Determination in *Gmelina Arborea*

Femi Odeyemi

Chemistry Department, University of Lagos, Nigeria.

Abstract

The plan to make *Gmelina arborea* a pulpwood in Nigeria calls for an investigation into the determination of the lignin content of the wood species.

Absorptiometric method is used in the estimation of the acid soluble lignin. With respect to the sulphuric acid method the most favourable acid concentration lies between 66 and 74 per cent. A higher percentage (77.1 %) could be used with good results provided the reaction time is less than one hour. The primary hydrolysis reaction could be advantageously carried out under the tropical laboratory room temperature ($29 \pm 1^\circ\text{C}$).

The use of a mixture of sulphuric acid (Sp. gr. 1.84) and hydrochloric acid (Sp. gr. 1.18) in the ratio 2:1 or 1:1 by volume is recommended.

The total lignin in the *Gmelina* samples investigated amounts to 31 ± 1 per cent. The determination of the lignin in the Kraft pulp requires severer conditions.

Purpose of the Investigation

The work of Chittenden et al.¹ has recommended the Nigerian grown *Gmelina arborea* as a pulpwood. Partly upon this recommendation, Nigeria has embarked on a massive cultivation of the species.

While much is known about the silvicultural characteristics of the wood, studies on its chemistry from the point of view of pulping are few. Lignin determination in wood and pulps is essential to a successful pulping. The commonly employed procedure for lignin determination is the Klason or 72 per cent sulphuric acid method. This procedure seems suitable for softwood species which contain no significant amount of the acid-soluble lignin.^{2,3}

But investigations⁴⁻⁶ do show that hardwoods contain varying amounts of the acid-soluble lignin and that the usual acid concentration (72 per cent) is unsuitable for the deciduous woods.⁷ Hence this investigation is designed to seek an acceptable procedure for the determination of the lignin content of *Gmelina arborea* and of the pulp prepared from it.

*Experimental**Wood samples*

The samples of the *Gmelina arborea* used in this investigation were collected from the Federal Forest Research Institutes plantation at Ibadan. Only three year old gmelina trees were randomly selected.

The samples were reduced into sawdust and were stored in plastic bags. The accepted sawdust was the portion which passed through a 40–80 mesh sieve.

Extraction

The sawdust was first extracted with ether for a period of ten hours after which it was extracted with a mixture of benzene and 96 per cent ethyl alcohol in the ratio 2:1 by volume for a period of ten hours.

The sawdust was then washed with hot water and dried in the air.

The lignin determination

For each experiment, about one gram of the sawdust was accurately weighed in a 50ml beaker. This was treated with 15ml (except otherwise stated) of the mineral acid at room temperature ($29 \pm 1^\circ\text{C}$) for two hours (except otherwise stated). After this, the reaction mixture was diluted to 3 per cent, with respect to the mineral acid used, and boiled for 3 hours under a constant volume condition by frequently adding hot water to the solution.

The solution was allowed to cool down. The residue was filtered through a previously weighed Gooch crucible of porosity 4 and washed with hot water. The residue was then dried to constant weight at 105°C in an oven. The residue was expressed as a percentage of the extracted oven dried wood. Each experiment was carried out in duplicate. The lignin residue was not corrected for the ash content.

The estimation of the acid-soluble lignin

In each case, the volume of the filtrate was recorded. The absorbance of the filtrate was determined using Unicam SP 800 Recording spectrophotometer. The absorption maximum which occurred between 215 nm and 220 nm was recorded for the lignin estimation.

The spectrophotometer was calibrated with a sample of thioglignin. From this, the acid-soluble lignin was calculated as a percentage based on the oven dried extracted wood.

ESTIMATION OF ACID-SOLUBLE LIGNIN

Gravimetric Method

Some workers extracted the acid-soluble lignin from the acid hydrolysates with alcohols,⁸⁻⁹ while in some cases the "Zeo-karb 215" column absorption was used to extract the acid-soluble lignin. The column was eluted with alcohol after which the solvent was evaporated and the residue weighed.^{6,11} The gravimetric method is slow and in most cases the procedure is non-specific with respect to lignin isolation.

Absorptiometric method

The estimation of the acid-soluble lignin by the absorptiometric method has resulted from the extensive investigations on some lignin preparates.¹²⁻¹⁷ And several workers have used the method.^{2,5,18-24} The method is rapid.

Lignin usually has absorption maxima in the ultraviolet region about 280 nm, 230 nm, and 215 nm. One of the major sources of error in the method is that the carbohydrate hydrolysis products also absorb in the ultraviolet region especially at 280 nm. This interferes with the lignin absorption.

It has been observed, however, that the absorption of the carbohydrate hydrolysis products is insignificant in the far ultraviolet region.²²⁻²⁴ For this reason, Lorås and Løschbrandt² have recommended the use of the absorbance peak at 220 nm while recently, Pearl and Busche⁵ have estimated the acid-soluble lignin from the absorbance measurement at 208 nm. Kyrklund and Palenius also read the absorbance values at 205 nm.²¹

Having found out that the polysaccharide hydrolysis products have no absorbance at 215 nm, the absorbance peak in this region is chosen for the estimation of the acid-soluble lignin in the present work.

Ultraviolet standard

The search for a satisfactory standard is another problem. In absorptiometric behaviour and in structural composition, an ideal standard must be identical with the acid-soluble lignin.

The milled-wood lignin is believed to be similar to the proto-lignin in wood. Pearl and Busche⁵ have compared the absorption curves of milled-wood lignin and lignosulphonate with that for the acid-soluble lignin and have found them similar. Almost quite arbitrarily they have used lignosulphonate as a standard.

Although the structural relationship between the acid-soluble lignin and the lignosulphonate is not clearly elucidated, some authors have been correcting for the sodium sulphonate component of the lignosulphonate each time it is used as a standard.^{2,21} It seems doubtful that the acid-soluble lignin is a pure compound which is equivalent in molecular weight to a corrected lignosulphonate.

In arriving at a decision as to which lignin preparate to use as the standard, the following have been prepared from the wood sample.

- (a) Alkali lignin,^{25,26}
- (b) thioglignin and ^{25,26}
- (c) sodium lignosulphonate.²⁷

Their ultraviolet absorption curves are compared with that for the acid-soluble lignin in Figure 1. It can be seen that each

one of them has peaks at 280 nm, 240 nm and about 220 nm. The peak at 240 nm is less noticeable for the acid-soluble lignin than for others. While the peak around 220 nm really occurs at 212 nm for the acid-soluble lignin, those for other lignin

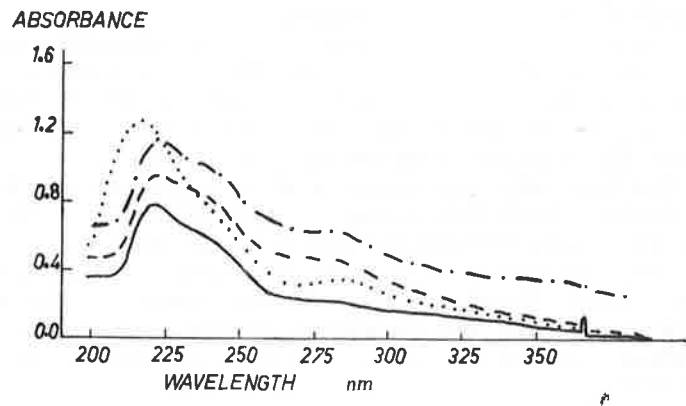


Figure 1. Ultraviolet absorption curves for some lignin preparates.
 — Thiolignin
 - - - Alkali lignin
 - . - . - lignosulphonate (displaced by 0.2 unit upwards).
 Acid-soluble lignin from Klason filtrate.

preparates occur at 222 nm for approximately the same value of absorbance. This observation indicates that all the lignin preparates are similar and that the acid-soluble lignin is different from them as far as the position and shape of the far ultraviolet absorbance peak are concerned. This contradicts the experience of Lorås and Løschbrandt.²

As the concentration of each of the lignin preparates increases the absorbance peak in the far ultraviolet region shifts towards the higher wave lengths. This is also true, to a lesser extent, of the acid-soluble lignin.

The gmelina thiolignin is chosen as an ultraviolet standard because if there is any structural similarity at all, the acid-soluble lignin from the Klason filtrate of the wood, would most probably resemble the thiolignin more than the alkali lignin which contains no sulphur and more than lignosulphonate which contains sulphonate groups. It can be seen that my choice is also largely arbitrary.

Acid-soluble lignin as a standard

A preliminary work on employing the acid-soluble lignin as a standard was carried out at the later part of this work. From the Klason lignin obtained in the usual procedure, a known weight was subjected to a second Klason treatment. The Klason

residue got was dried and weighed; and the absorbance of the filtrate was taken. From the loss in weight, the concentration of the acid-soluble lignin in the secondary filtrate was calculated. A graph of concentration of the acid-soluble lignin was plotted against the absorbance. This is shown in Figure 2.

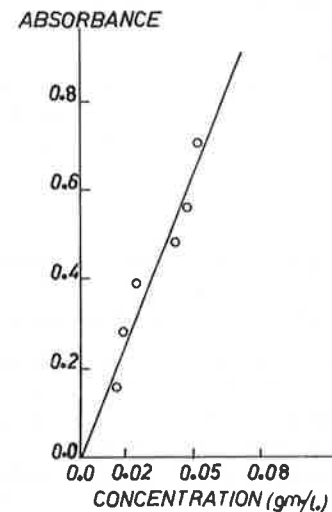


Figure 2. Calibration graph for the acid-soluble lignin.

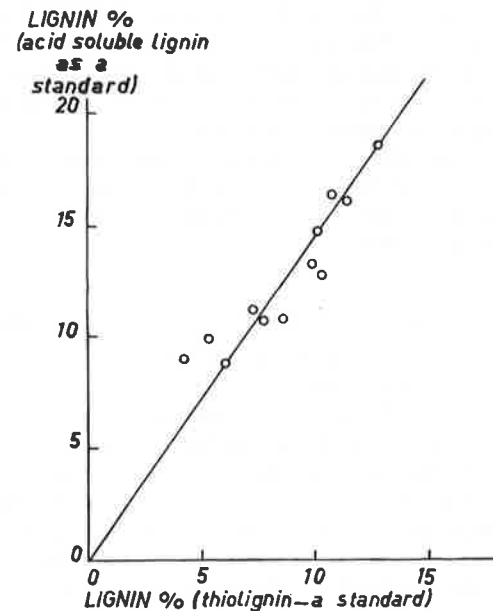


Figure 3. Some acid-soluble lignin values, estimated and plotted on two absorptometric standards: Thiolignin versus acid-soluble lignin.

The relationship between the values obtained with the thiolignin as a standard on the one hand, and with the acid-soluble lignin as a standard on the other hand is depicted in Figure 3. The deviation of some points from the straight line could be due to the error in using thiolignin as a standard.

The acid-soluble lignin as a standard gives a higher lignin value than the thiolignin; for this reason, the thiolignin was used without any correction as this would decrease the values further. All the values for the acid-soluble lignin recorded in this paper are calculated on the thiolignin as a standard because more work is still needed in order to make the acid-soluble lignin a standard.

RESULTS AND DISCUSSION

The Influence of the acid concentration

Table 1 shows the effect of the sulphuric acid concentration, during the primary hydrolysis of the polysaccharides, on the values of Klason lignin and the acid-soluble lignin. For the 65 per cent sulphuric acid, the value of the Klason residue is high. As the percentage of the acid is further decreased, the polysaccharides of the wood is not completely hydrolysed and as a result, the Klason residue increases. Between 66 per cent and 72 per cent, the value of the Klason residue does not vary much. The lowest value (25.9 per cent) recorded is obtained with 68.3 per cent sulphuric acid. For percentages higher than 74, the value of the Klason lignin gradually increases, and the colour becomes darker. This is generally attributed to the sorption of sulphuric acid into the lignin.

With respect to the acid-soluble lignin, however, below 65 per cent, the values decrease. This is due to an incomplete hydrolysis. As the percentage of the sulphuric acid increases, so the acid-soluble lignin decreases.

The time of impregnation with the concentrated sulphuric acid

The effect of time is illustrated in Table 2. It appears that, under the same experimental conditions, the longer the time of impregnation, the higher the value of Klason lignin and the lower the value of the acid-soluble lignin obtained. The darker appearance and the increase in the Klason lignin got with a high concentration (77.1 per cent) can be avoided by reducing the time of impregnation from two hours to one hour or less. From the values of the acid-soluble lignin in Table 2, one tends to infer that the acid-soluble lignin is completely liberated at the initial stage of the reaction and after this, somehow, the

acid-soluble lignin is gradually precipitated out of the solution probably through some form of polymerisation with the Klason residue or other hydrolysis products under the influence of the sulphuric acid.

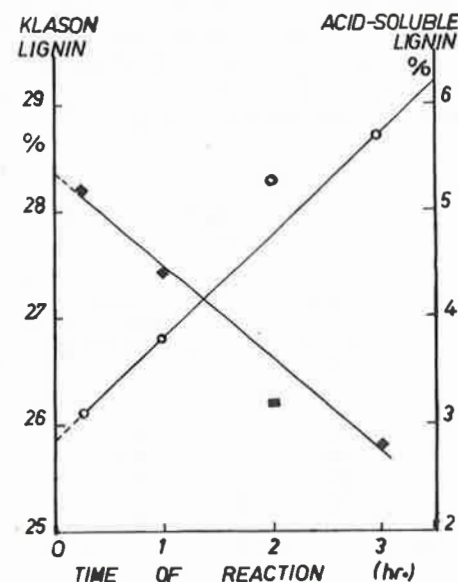


Figure 4. Plot of the Klason lignin and the acid-soluble lignin versus the time of hydrolysis with 77.1 per cent sulphuric acid.

■ — ■ Acid-soluble lignin
○ — ○ Klason lignin

Table 1. The influence of acid concentration on the lignin values.

Sulphuric acid % by weight	Klason residue % on O. D. Wood A	Acid-soluble lignin % on O. D. Wood B	Total A + B % on O. D. Wood
57.2	75.2	9.1	84.3
60.4	73.7	9.5	83.2
65.3	31.6	10.2	41.8
66.5	26.3	—	—
68.3	25.9	8.3	34.2
70.2	27.2	5.2	32.4
71.0	26.0	4.1	30.1
72.0	27.8	3.9	31.7
74.0	28.6	4.6	33.2
76.0	28.9	4.2	33.1
77.1	28.3	3.2	31.5
81.4	30.6	2.1	32.7
83.7	31.2	1.4	32.6
86.4	39.3	1.1	40.4

The Klason residue is plotted against the time of impregnation in Figure 4. The graph is a straight line for the value of the reaction time below three hours. On extrapolating to zero time, the value of the Klason lignin reads 25.85 while the extrapolated value of the acid-soluble lignin is 5.35. This brings the total lignin to 31.2 per cent. The effect of time is also demonstrated by using 68.3 per cent sulphuric acid which gives the lowest value for Klason lignin in Table 1. Below a reaction time of one hour, the hydrolysis is incomplete (Table 3).

Table 2. Time of the sulphuric acid treatment and the lignin values. sulphuric acid concentration: 77.1 %.

Time of acid treatment (hr.)	Klason residue % on O. D. Wood A	Acid-soluble lignin % on O. D. Wood B	Total A + B % on O. D. Wood
0.25	26.1	5.2	31.3
1	26.8	4.4	31.2
3	28.7	2.8	31.5
10	33.5	1.6	35.1
24	37.9	0.9	38.8

Table 3. Time of the sulphuric acid treatment and the lignin values. sulphuric acid: 68.3 %.

Time (HR)	Klason residue % on O. D. Wood A	Acid-soluble lignin % on O. D. Wood B	Total % on O. D. Wood A + B
0.25	66.2	10.4	76.6
0.5	50.5	11.2	61.7
1	26.0	5.8	31.8
1.5	26.4	9.3	35.7

The Temperature of reaction

The Tappi standard Method²⁸ recommends that the temperature of the reaction during the acid treatment be kept at 18 to 20°C. The room temperature in the laboratory at the time of the experiment was 29 ± 1°C. This was also the temperature of the mineral acids used. The experiments whose results are recorded in Table 4 have been carried out to ascertain the effect of using the high tropical temperature in the laboratory.

Table 4. Effect of the reaction temperature on the lignin values using 68.3 % sulphuric acid.

Temperature of reaction °C	Klason residue % on O. D. Wood A	Acid-soluble % on O. D. Wood B	Total A + B % on O. D. Wood
-5	79.2	6.4	85.6
8	71.2	10.1	81.3
18	43.8	8.0	51.8
29	26.0	8.4	34.4

It was observed that on adding the sulphuric acid to the sawdust, the temperature rises from 28°C (the temperature of the sulphuric acid) to 29.8°C. After some minutes, the temperature gradually falls to 28°C. On stirring, the rise in temperature is noticed. To maintain the reaction temperature at 20°C leads to a higher value of Klason lignin.

Action of the hydrochloric acid

The effect of using the 36 per cent (sp. gr. 1.18) hydrochloric acid instead of the usual 38 per cent (sp. gr. 1.19) is also investigated. The result is compiled in Table 5. After 4 days, only about 32 per cent of the wood has gone into solution and the incomplete hydrolysis notwithstanding, the values of the acid-soluble lignin are high. Obviously, 36 per cent hydrochloric acid is too weak for the determination of the lignin content of this species; It appears therefore that the liberation of a high amount of the acid-soluble lignin does not depend on a complete hydrolysis of the polysaccharides as is the case for the use of the sulphuric acid.

Table 5. Action of the concentrated hydrochloric acid (sp.gr. 1.18) on Gmelina wood dust.

Time of reaction (HR.)	Dissolved Substance % on O. D. Wood	Acid-soluble lignin % on O. D. Wood
24	26.6	11.6
48	29.4	11.1
72	31.6	10.9
96	30.6	10.9

Sulphuric acid-Hydrochloric acid lignin

The results of the determination of the lignin with mixtures of sulphuric acid (sp. gr. 1.84) and hydrochloric acid (sp. gr. 1.18) are set out in Table 6. The two acids were first mixed together in a fume cupboard before use.

Table 6. Determination of lignin with mixtures of hydrochloric acid and sulphuric acid.

Sulphuric acid: 98 % Sp. Gr. 1.84
 Hydrochloric acid: 35 % Sp. Gr. 1.18
 Volume of the mixture: 30 ml.
 Time of reaction: 2 hours

Mixture				Residue % on O. D. Wood (A)	Acid-soluble lignin (B)	Total A + B % on O. D. Wood
Sulphuric acid		Hydrochloric acid				
* %	Vol.	%	Vol.			
by wt.	(ml.)	by wt.	(ml.)			
9.8	2	32.1	28	70.8	11.0	81.8
23.3	5	27.5	25	62.5	10.0	72.5
42.9	10	20.2	20	27.9	10.8	38.7
59.7	15	14.1	15	25.0	12.8	37.8
74.4	20	8.7	10	29.6	4.3	33.9

* Percentage on the total weight of the mixture.

When the percentage of the sulphuric acid in the mixture, is low (probably below 30 per cent), the hydrolysis is not complete. With a concentration higher than 40 per cent of the mixture, the values obtained indicate that the reaction has gone to completion. It is of interest to note that when the percentage of the sulphuric acid is raised to 74.4 per cent, the effect of the hydrochloric acid (8.7 %) is not noticeable because the results obtained are similar to those obtained with 74 per cent sulphuric acid (Table 1). The influence of the hydrochloric acid is most significant when 10ml. of sulphuric acid (42.9 % on the total weight) is mixed with 20ml. of the hydrochloric acid (20.2 %). The total content of the two acids in the mixture amounts to 63.1 per cent. This mixture yields a lignin residue of 27.9 per cent, and this value is lower than that obtained with the pure 65.3 per cent sulphuric acid. Hydrochloric acid, it appears, possesses some catalytic behaviour.

The lowest value of lignin residue is obtained with a ratio of 1:1 by volume. In this mixture, the sulphuric acid amount to 59.7 per cent and the hydrochloric acid is 14.1 per cent of the mixture. From Figure 5, one also has the impression that the hydrochloric acid acts as a catalyst. The two acids amounts to 73.8 per cent of the mixture and this gives 25.0 per cent lignin — a value which is considerably lower than the value for the 74 per cent sulphuric acid (Table 1). But the value of the acid-soluble lignin is high.

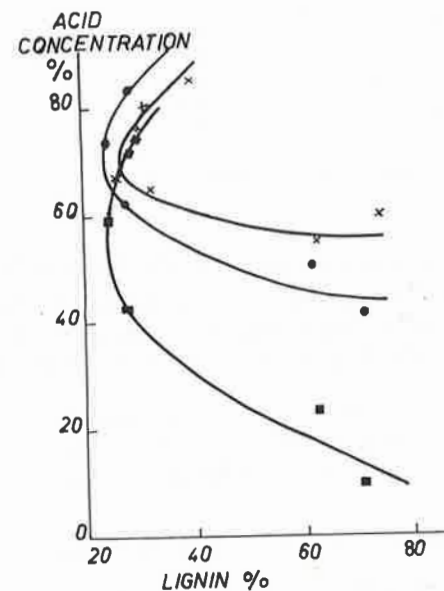


Figure 5.

- × — × Klason method: Acid concentration versus Klason residue.
- — ● Total acid concentration (HCl-H₂SO₄) in the mixture of hydrochloric acid and sulphuric acid versus the lignin residue.
- — ■ Percentage of the sulphuric acid component of the mixture versus the lignin residue.

Table 7 emphasises the same observation about the catalytic action of the hydrochloric acid.

Table 7. Determination of lignin with mixtures of hydrochloric acid and sulphuric acid.

Sulphuric acid: 72 %
 Hydrochloric acid: 36 %
 Total volume of mixture: 50 ml.

Mixture				Residue % on O. D. Wood	Acid-soluble lignin % on O. D. Wood	Total A + B % on O. D. Wood
Sulphuric acid		Hydrochloric acid				
* %	Vol.	%	Vol.			
<i>by wt.</i>	<i>ml.</i>	<i>by wt.</i>	<i>ml.</i>	A	B	
9.4	5	31.3	45	38.6	9.3	47.9
18.2	10	26.9	40	33.0	7.0	40.0
34.2	20	18.9	30	29.4	5.7	35.1
41.5	25	15.3	25	29.1	6.2	35.3
54.7	35	9.3	15	28.6	6.7	35.3

* Each component is expressed as a percentage by weight of the whole mixture.

Lignin determination in the Kraft pulp

The Kraft pulp was produced in Jebba by the Nigerian Paper Company. The unbleached pulp has a Kappa number of 40.3. On the basis of the Tappi 236m - 60 method, the Klason lignin would be 6.05.

Table 8 shows the effect of the concentration of the sulphuric acid. The lowest value of Klason lignin is obtained with 72 per cent for a reaction time of 4 hours. A comparison between

Table 8. Determination of lignin in the Kraft pulp of Gmelina.

Volume of acid: 15 ml.
 Time of reaction: 2 hours

Sulphuric acid concentration %	Klason residue % on O.D. pulp
68.3	9.3
66.5	11.4
65.3	31.2
60.4	82.3
Volume of acid: 30 ml. Time of reaction: 4 hours	
72.0	6.6
68.3	7.3
66.5	10.1

Table 8 and Table 1 shows that the determination of the lignin content in the Kraft pulp requires stronger conditions.

The mixtures which give good results in Table 6 have been tried on the pulp. The results are in Table 9. A mixture of the sulphuric acid and the hydrochloric acid in the ratio 1:1 by volume gives a good result.

Table 9. Treatment of the Kraft pulp with the mixtures of sulphuric acid and hydrochloric acid.

Mixture		Residue % on O. D. pulp
Sulphuric acid % of total wt.	Hydrochloric acid % of total wt.	
42.9	20.2	8.5
59.7	14.1	6.8

The ultraviolet absorption curve of the filtrate has only one peak at 280 nm and this is generally believed to belong to the carbohydrate hydrolysis products. The sulphate pulp does not contain any acid-soluble lignin.

The investigation is being continued.

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Studies on Components in Wood

4. Mass Spectrometric Identification of Sandaracopimaric Acid in the Oleoresin of Norway Spruce (*Picea abies*)

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Abstract

Sandaracopimaric acid has been identified in the resin acid fraction in the oleoresin from Norway spruce by a technique of gas chromatography and mass spectrometry.

Introduction

The resin acids are tricyclic terpenoid compounds with either an abietane or a pimarane skeleton (fig. 1) occurring as the major nonvolatile constituents in the oleoresin of coniferous species. The acids of the former type are characterized by an isopropyl side chain at carbon atom number 13 while the acids of the latter type have methyl and vinyl substituents at that position.¹ The determination of the composition of the resin acids in oleoresin and other sources has been complicated by their similarity in structure and the lack of analytical methods suitable for the separation of such complex mixtures. Kahila² used the classic method of amine salt precipitation and ultraviolet spectroscopy to determine the resin acid composition of oleoresin from Norway spruce and reported the occurrence of five acids of the abietic type and two of the pimaric type (see table 1). Using partition chromatography Bruun and coworkers^{3,4} isolated a new acid of the abietic type, palustric acid, from spruce oleoresin. They also confirmed the presence of the acids reported by Kahila, with the exception of dihydroabietic acid (see table 1), and also reported the percentage composition found. In studies on the gas chromatographic separation of resin acids as methyl esters Pensar and Bruun^{5,6} also examined samples of oleoresin from Norway spruce obtaining seven compounds in the chromatogram. By comparing the relative retention times for the peaks with those for pure methylated resin acids six of the compounds were easily identified (see table 1). The seventh compound was eluted as a peak with a retention time corresponding either to methyl dihydroabietate or methyl sandaracopimarate. Thus the peak could represent the acid reported

by Kahila or be a new resin acid not found before in the oleoresin of Norway spruce. Therefore it was of interest to verify the identity of the compound giving rise to the peak in question. This identification was made possible by means of a combined technique of gas chromatography and mass spectrometry as here reported.

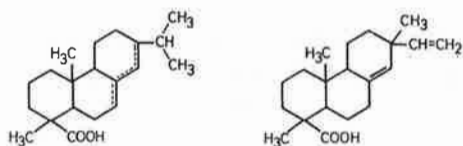


Fig. 1. Dihydroabietic acid (left) and sandaracopimaric acid (right).

Table 1. Composition of the oleoresin from Norway spruce.

Resin acid	Kahila ²	Bruun and co-workers ^{3,4}	Pensar and Bruun ^{5,6}
Abietane skeleton			
Abietic acid	+	+	+
Neobietic acid	+	+	+
Dehydroabietic acid	+	+	+
Levopimaric acid	+	+	+
Palustric acid		+	+
Dihydroabietic acid	+		?
Pimarane skeleton			
Pimaric acid	+	+	+
Isopimaric acid	+	+	+
Sandaracopimaric acid			?

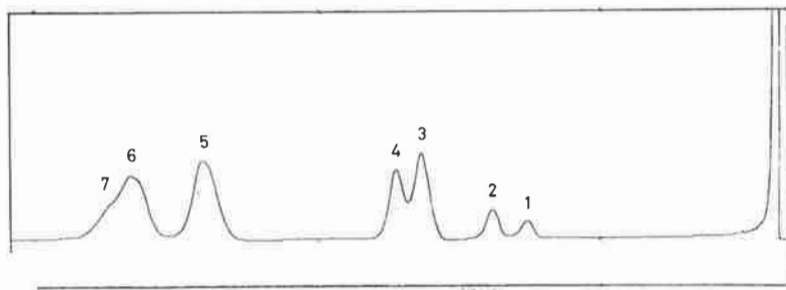


Fig. 2. Gas chromatographic separation of the resin acid fraction from spruce oleoresin. The peaks represent the methyl esters of (1) pimaric acid, (2) unknown acid, (3) palustric acid and levopimaric acid, (4) isopimaric acid, (5) abietic acid, (6) dehydroabietic acid and (7) neobietic acid.

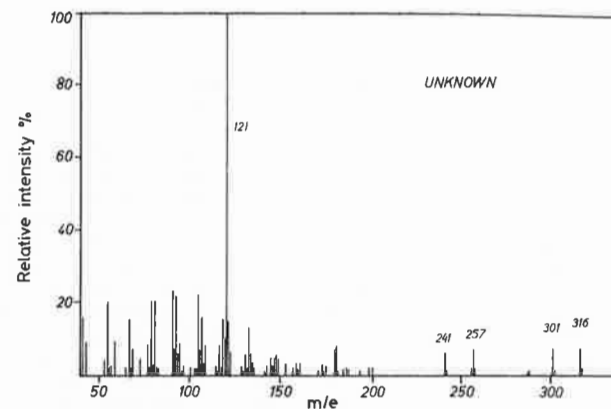


Fig. 3. Mass spectrum of the unknown component in the resin acid fraction.

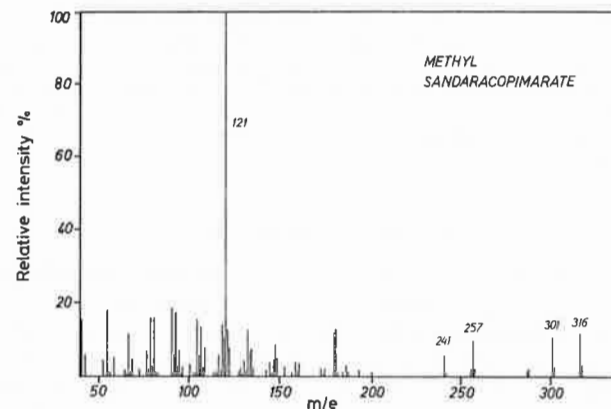


Fig. 4. Mass spectrum of an authentic sample of methyl sandaracopimarate.

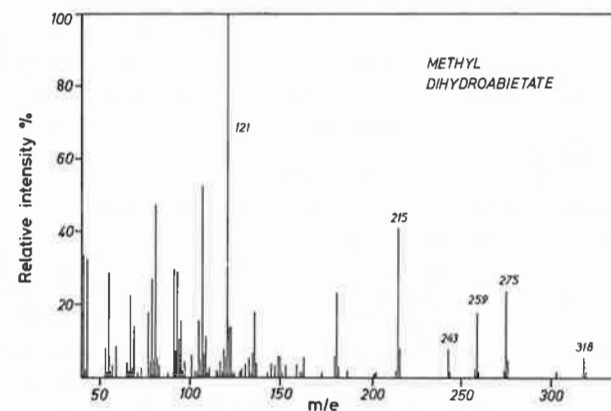


Fig. 5. Mass spectrum of an authentic sample of methyl dihydroabietate.

Experimental

Using small glass capillaries a sample of oleoresin was collected direct from the resin canals in a cross section of a trunk of a 35 year old spruce (*Picea abies*). This cross section was taken at the height of two meters from a trunk of a tree cut in February in the south of Finland (Kotkanniemi). The sample was dissolved in petroleum ether and the resin acid fraction was isolated in a two-step separation on thinlayer plates coated with silica, using the "micro-transfer" technique earlier described⁷. In the first step the crude oleoresin was fractionated with a solvent composed of petroleum ether-diethyl ether-acetic acid (85:15:1, vol/vol). The fraction with a R_f -value corresponding to that of a sample of pure resin acids chromatographed on the same plate, was scraped off and eluted from the adsorbent with methanol-diethyl ether (1:9, vol/vol) and the treated with fresh diazomethane for methylation of the acids. In the second step, this "crude" fraction of resin acids was chromatographed with petroleum ether-diethyl ether as solvent (95:5, vol/vol) for isolating the resin acids from nonacidic components. The spot containing the methylated resin acids was scraped off, the acids were eluted from the adsorbent and taken into a syringe for instantaneous injection into a gas chromatograph on-line coupled to a mass spectrometer. An LKB-9000 instrument was used to achieve the separation of the individual resin acids and record their mass spectra. The gas chromatograph was equipped with a 10' \times 1/8" glass column packed with Chromosorb W (80/100 mesh), coated to 5 % by ethylene glycol succinate. The separation was performed isothermally at 175 °C and the helium carrier gas had a flow rate of 20 ml/minute. The mass spectra were recorded under the following conditions: electron energy 70 eV, ion source temperature 270 °C and scan speed m/e 10—m/e 350 in 3 seconds.

Results and Discussion

The gas chromatographic separation of the methylated resin acids from the spruce oleoresin is shown in figure 2. The peak 2 in the chromatogram represents the unknown compound, which judged from its retention time could be either methyl sandaracopimarate or methyl dihydroabietate. A mass spectrum recorded from the effluent corresponding to this peak is shown in a normalized form in figure 3. Spectra of authentic samples of the two methylated resin acids, recorded under the same conditions are given in figures 4 and 5. The similarity between the spectra of methyl sandaracopimarate and the unknown compound is nearly perfect. Both show a molecular ion peak at $m/e = 316$ (Mwt of methyl sandaracopimarate = 316) and the fragmentation pattern is the same. The most abundant peak, the base peak, is found at $m/e = 121$ and the high mass ends of the two spectra show intense peaks at m/e 301, 257 and 241. On the other hand methyl dihydroabietate gives a mass spectrum with a molecular ion peak at $m/e = 318$ (Mwt of methyl dihydroabietate = 318), the base peak being at m/e 121. Intense peaks are found at m/e 275, 259, 243 and 215, whereas no correspondence at these mass numbers can be found in the spectrum of the unknown compound. Thus the unknown peak in the gas chromatogram of the resin acids from spruce oleoresin is proved to be solely due to the methyl ester of sandaracopimaric acid. The

occurrence of minor amounts of this acid in the oleoresin of various species among the coniferes has been reported by Gough⁸ and by Joye and Lawrence⁹. The finding of sandaracopimaric acid also in the oleoresin of Norway spruce confirms that this acid probably must be considered a normal component of conifer oleoresin.

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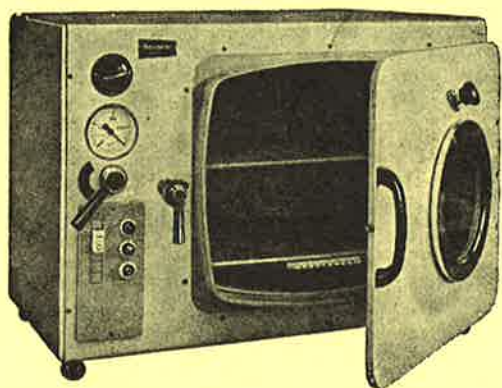
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