

Formation of Methylcyclopentenolone by Digestion of Spruce Wood or Galactose with Sodium Hydroxide Solutions at 100° C

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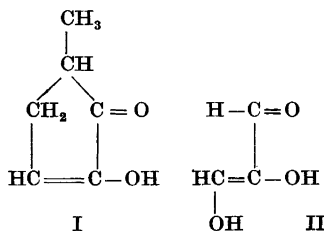
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During studies on the degradation products of lignin¹, spruce wood was digested with 1.7 % sodium hydroxide solution for 6 hours at 100° C under pressure. From the liquor obtained, a crystalline substance could be isolated, which is soluble in ether and in sodium hydroxide but not in sodium bicarbonate solution, and which can be sublimated in vacuum. Its ultraviolet absorption spectrum (Fig. 1) is fairly sharp and shows a strong bathochromic shift on addition of alkali, indicating the presence of an ionizable group. The substance gives a red enol reaction with ferric chloride solution. It has now been identified as 1-methyl-cyclopenten-(3)-ol-(3)-one-(2), (formula 1)²⁻⁵ by elementary analysis and mixed melting point determinations for the substance itself, and for its *bis*-2,4-dinitrophenylhydrazone $C_6H_5[N \cdot NH \cdot C_6H_3(NO_2)_2]_2$. The best yield of crude crystals obtained is 0.06 % of the wood, but of recrystallized, practically pure substance only about 0.016 % has been recovered.

Compound I has previously been found in soluble wood tar⁶⁻⁹, and can also be prepared by synthesis^{5, 10-12}, but it seems never before to have been obtained at so low a temperature as 100° C. Moreover, its isolation after alkaline digestion was rather unexpected, since the compound has been reported not to be very stable in alkaline solution⁴.

Therefore it seemed to be of interest to trace the wood constituent from which it originated.

In Fig. 3 a summary is given of a series of preliminary experiments where spruce wood was treated in different ways and methylcyclopentenolone sought for in the ether extracts of the reaction solutions, ferric chloride and 2,4-



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dinitrophenylhydrazine ("DNPh") being used as testing reagents. No methylcyclopentenolone could be detected after simple boiling of the wood with water. Hence the substance seems not to be present as such in the wood. Treatment of spruce wood with dilute sodium hydroxide at room temperature resulted in a slight positive reaction, and heating of the wood with dilute sodium hydroxide at 100° C led to strongly positive tests. Hence the substance seems to be formed only on treatment of the wood with sodium hydroxide solution.

Since methylcyclopentenolone contains no methoxy-groups and no benzene nucleus, it can hardly be a degradation product of lignin, but must be formed from some substance of carbohydrate nature. A series of experiments with various carbohydrate materials were carried out. Some of the results obtained are given in Table 1, which shows the absorption maxima of ether-soluble, vacuum-sublimated enolic fractions obtained after pressure heating of various materials with sodium hydroxide solutions at 100° C. For comparison, absorption maxima are also given for several known substances. It can be seen that the wave lengths for the absorption maxima of methylcyclopentenolone from spruce wood or from soluble tar are, within the limits of error, the same as for the enol fraction obtained through alkaline digestion at 100° C of a solution of spruce wood polyoses produced by heating the wood with water at 120° C (*cf.*¹³). In contrast, after analogous treatment the corresponding uronic acids gave only a very poor yield of the sublimated enol fraction, and the sublimate had absorption maxima at wave-lengths quite different from those of methylcyclopentenolone. Also the absorption maxima of a series of lignin preparations, represented in Table 1 by thiolignin, and of several lignin model substances, for instance vanillyl alcohol and acetoguaiacone, lie far from the position of the maxima of the spectrum of methylcyclopentenolone.

The extinction values ($E \frac{1\%}{1\text{ cm}}$) reported in Table 1 give essentially the same impression as the wave lengths. It must be observed that the extinction

Table 1. Absorption maxima for ether-soluble, vacuum-sublimated enolic fractions obtained after pressure heating of various starting materials with dilute NaOH solutions at 100° C, compared with the absorption maxima of several known substances.

	Not alkaline		Alkaline	
	m μ	$E \frac{1\%}{1\text{ cm}}$	m μ	$E \frac{1\%}{1\text{ cm}}$
Enolic fractions from alkaline pressure heating of:				
Spruce wood, washed with acetone	258	729	297	553
Galactose	259	679	298	547
Glucose	260	541	(297)	764
Fructose ^a	260 (305)	164	295	180
Neutral substance from spruce wood				
hemicellulose	261	368	299	464
Uronic acid from same	276 (305)	477	348	1 057
Spectra of known substances:				
Methylcyclopentenolone from soluble wood tar	258	709	295	—
Vanillyl alcohol ²³	230, 281	190 ^b	294	245
Acetoguaiacone ²³	230, 276, 303	513 ^c	248, 348	1 450 ^d
Thiolignin (80°, H ₂ S ²⁴)	(230) 280	161	287	158

^a) In this case the whole ether extract was sublimated instead of the enolic fraction. —

^b) At 281 m μ . — ^c) At 303 m μ . — ^d) At 348 m μ .

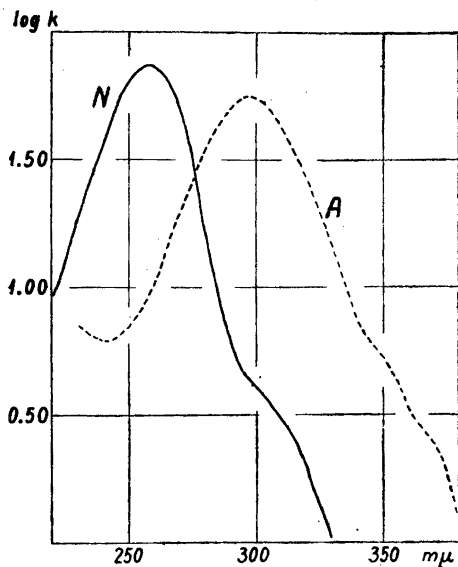


Fig. 1. Absorption spectrum of methylcyclopentenolone obtained by alkaline digestion of spruce wood at 100° C. Substance: expt. 2, "cr, recr.". Concentration: 10 mg/l. Curve N in 96 % ethanol, A in 0.5 N ethanolic KOH. Curve N at 258 mμ: $E_{1\text{ cm}}^{1\%} = 729$.

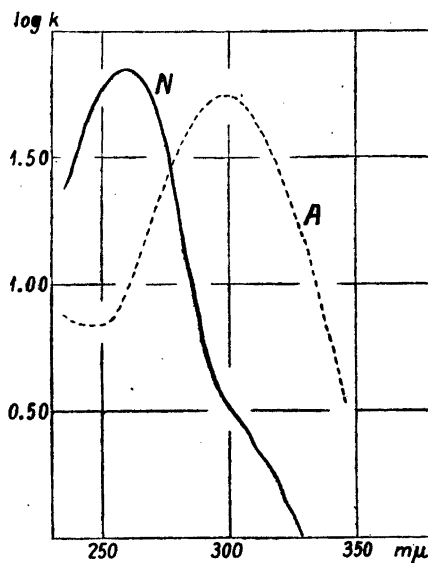


Fig. 2. Absorption spectrum of methylcyclopentenolone obtained by alkaline digestion of galactose at 100° C. Substance: expt. C, sublimate 71–92° C (8 mm). Concentration: 11.8 mg/l. Curve N in 96 % ethanol, A in 0.5 N ethanolic KOH. Curve N at 260 mμ: $E_{1\text{ cm}}^{1\%} = 679$.

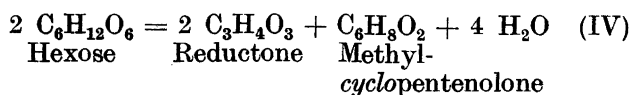
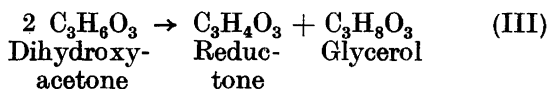
value is dependent on the purity of the substance, and that it decreases if the substance is so unstable that its concentration drops markedly before the measurement can be made. This seems to be the case with methylcyclopentenolone, especially in alkaline solution⁴.

On pressure heating with sodium hydroxide solutions at 100° C, several hexoses gave low yields of ether-soluble enolic substances showing absorption spectra which in the case of galactose and glucose were rather like that of methylcyclopentenolone (Table 1). The closest resemblance was seen with the spectrum of the enolic fraction formed from galactose (*cf.* Figs. 1 and 2). In fact, on sublimation in vacuum, this enolic fraction gave crystals which could be identified with the methylcyclopentenolone of formula I from soluble wood tar by determination of the mixed melting points of the enols themselves as well as of their dinitrophenylhydrazones. The yield of pure crystals of methylcyclopentenolone from galactose was very small, but a calculation from the absorption spectrum of a vacuum sublimate (expt. B, see experimental part) corresponds to a yield of 1.8 % of a substance with a spectrum resembling that of methylcyclopentenolone.

The question arises of what type of reaction can be involved in the formation of methylcyclopentenolone from hexoses. *v.* Euler and Martius¹⁴ have found that hexoses such as glucose, galactose and fructose, as well as dihydroxyacetone and pentoses, give reductones, especially triose-reductone (formula

II), on heating with sodium hydroxide solution at 92°C , *i. e.* under almost the same reaction conditions as are used in the formation of methylcyclopentenolone as described above. In fact, the water solutions obtained on preparation of methylcyclopentenolone by alkaline digestion of spruce wood or galactose were found to give the reactions of reductone with Tillmans' reagent¹⁵ and with iodine in acid solution. Moreover, a solution obtained by boiling the raw spruce wood with water gave no positive test for reductone (expt. a—e).

As two molecules of triose-reductone contain the same number of carbon and oxygen atoms, but four hydrogen atoms less than one molecule of hexose, it seems probable that the reductone is formed as a dehydrogenation product of hexose by a disproportionation reaction. In the case of dihydroxyacetone, v. Euler¹⁶ has presumed that the corresponding hydrogenation product would be glycerol, according to scheme III. However, it seems that the presence of glycerol has not been experimentally proved by him. In the present investigation therefore, tests were made for glycerol in the reaction solution resulting from treatment of galactose with sodium hydroxide at 100°C , but the result was negative. Therefore it seems that the most probable scheme for the formation of methylcyclopentenolone at present would be the disproportionation reaction IV:



Spruce wood is reported to contain about 1.9 % of galactan¹³. Hence it could be thought possible that the methylcyclopentenolone formed on alkaline digestion of spruce wood originates from the galactose produced on hydrolysis of galactan, but it is not impossible that other hexosans also give methylcyclopentenolone.

EXPERIMENTAL

Methylcyclopentenolone from spruce wood

Four experiments were made employing essentially the same procedure: Expt. 1: Spruce wood, ground in a Nelco mill to splits about $1 \times 5 \text{ mm}$, was extracted with acetone until the amount of acetone solubles had decreased to $< 0.1 \%$. 630 g of this wood, calculated on a dry basis, was digested for 6 hours at $100^{\circ} \pm 1^{\circ}\text{C}$ with 1.7 % NaOH solution in a rotating 10 litre digester of stainless steel, in which the air had been replaced by N_2 . Ratio NaOH (g): wood (dry basis, g) = 10 : 100, of liquor (including moisture, ml): wood (dry basis, g) = 6 : 1. After filtration: yield of undissolved wood (dry basis) 83.0 %, containing 30.9 % of Klason lignin¹⁷, 4.96 % OCH_3 and 2.09 % of ash. The filtrate and the wash waters were evaporated in vacuum to about 1 700 ml, acidified with HCl to about pH 3, and filtered. The precipitate (lignin) amounted to 2.3 % of the wood (dry and ash-free basis). The filtrate was thoroughly extracted with ether in an extraction apparatus for liquids. A small amount of ethanol was added in order to obtain good separation of the layers. The ether extract was divided by shaking successively with 21 % NaHSO_3 , 8 % NaHCO_3 and 5 % NaOH¹⁸ in an aldehydic (0.127 %), an acidic (0.335 %), a phenolic-enolic (1.229 g, 0.195 %) and a neutral fraction (0.029 % of the original wood, dry basis).

418.9 mg of the *aldehydic fraction* was sublimated in an apparatus with a cup for collection of oily sublimate beneath the finger, at 9 mm Hg and 160° C, measured in the oil bath. Sublimate: 263.1 mg, with 3.95 % OCH₃. Residue: 122.4 mg, with 6.22 % OCH₃. The absorption spectrum of the sublimate was very like that of vanillin.

141.0 mg of the *acidic fraction* was sublimated in a corresponding way at 12 mm Hg, and gave 63.9 mg of a partly crystallizing sublimate containing 4.1 % OCH₃ and showing an absorption spectrum with a maximum in neutral solution at 260 m μ and $E_{1\text{ cm}}^{1\%} = 156$.

488.3 mg of the *enolic fraction* was correspondingly sublimated at about 6 mm Hg. Yields in percent of the wood: 80–160° C in oil bath, crystals on the finger 14.6 mg = 0.0058 %, oil in the cup 51.6 mg = 0.0206 %, with 2.8 % OCH₃, 160–245° C viscous oil 0.0309 %, residue 0.1059 %. The crude crystals showed m.p. about 80° C, and after recrystallization from light petroleum-ethyl ether 100° C.

Expt. 2 gave better yields of crystals: 80–97° C, 24 mm Hg ("cr") 0.051 % of the wood, at 97–150° C 0.012 %, in all 0.063 % of the wood. Color reaction with ferric chloride in neutral solution: red-violet. The substance reduces Fehling's solution and ammoniacal silver nitrate solution. 275.8 mg of "cr" on recrystallization from light petroleum-ethyl ether gave 45.3 mg of a substance "cr recr": M.P. 97–98° C, absorption spectrum in Fig. 1. Analysis (A. Schoeller, Kronach): OCH₃ negative; C 63.97; H 7.12. Calc. for C₆H₈O₂: C 64.25; H 7.20.

Expt. 3: The corresponding recrystallized crystals showed m.p. 104.5° C. A mixture with methylcyclopentenolone (m.p. 103.5–104.5°) prepared from soluble wood tar had m.p. 104.5° C (Rothes app.).

Dinitrophenylhydrazone: 61.0 mg of crude crystals from expt. 3 was dissolved in water. 150 ml of a 0.5 % solution of 2,4-dinitrophenylhydrazine ("DNPh") in 2 N HCl was added. After short heating on the water bath and standing overnight at room temperature the brick red precipitate obtained was washed with HCl (yield 130 mg), purified by recrystallization from warm benzene after passing the benzene solution through a 3 cm layer of aluminium oxide (Brockmann) and finally dried for 2 hours at 100° C and 20 mm Hg. Analysis (K. Salo, Helsingfors): N 23.25 (Dumas); C 46.12; H 3.52. Calc. for C₁₅H₁₆N₂O₆: N 23.73; C 45.74; H 3.42. m.p. 238° C; m. p. of a mixture with the corresponding derivative (m. p. 235° C) of methylcyclopentenolone prepared from soluble wood tar 238° C.

Qualitative tests for methylcyclopentenolone on extracts of wood obtained by various treatments: 40 g of original spruce wood sawdust was digested for 5 hours with 350 ml of distilled water in a loosely stoppered flask on the water bath. Filtration gave the filtrate f1. Thereafter 400 ml of 4 % NaOH solution was added to the sawdust, and the mixture allowed to stand for 3 hours at about 20° C with occasional mixing. Filtration gave the filtrate f2. 100 ml of this was heated in a sealed tube of stainless steel for 4 hours at 100° C (solution s1). Another 100 ml of f2 was refluxed for 4 hours in a glass vessel in a current of N₂ (solution s2).

A sample of spruce wood chips was digested with NaOH solution in a sealed tube of stainless steel for 3 hours at 100° C. Ratio of liquor (ml): wood (dry basis, g) = 4 : 1, of NaOH (g): wood (dry basis, g) = 10 : 100. Filtration gave the filtrate f3.

From each of the five solutions obtained, a volume corresponding to 2 g of wood was acidified with hydrochloric acid and extracted with ether. The ether solutions were all evaporated to the same small volume. 5 drops of each solution was put on strips of filter paper, the ether allowed to evaporate and the spots obtained tested with a 0.5 % solution of DNPh in 2 N HCl. An orange color was regarded as a positive test. The rest of the ether solutions were evaporated at room temperature, the residues dissolved in water, neutralized with dilute ammonia and tested with dilute FeCl₃ solution. A red or violet color reaction was taken as a positive test.

The tests with DNPh and with FeCl₃ gave the same results, positive or negative, for each extract tested. The findings are given in Fig. 3.

Alkaline digestions of wood polyoses

A sample of 1 000 g, calculated on a dry basis, of spruce wood sawdust was digested with 8 l of distilled water for 8 hours at 120° C in a rotating digester of stainless steel. The sawdust was filtered off and washed with water. The aqueous solution obtained had a

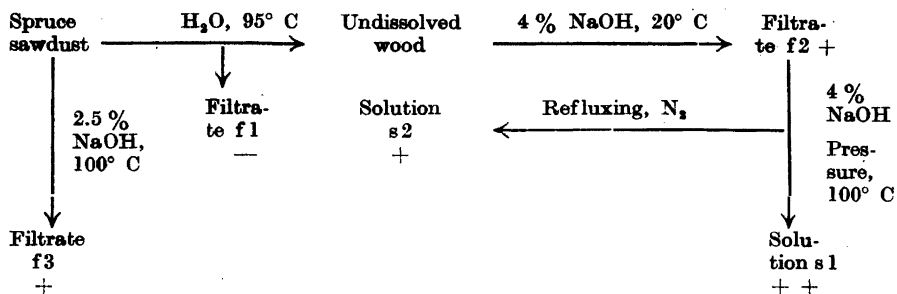


Fig. 3. Tests on methyleclopentenolone with DNPh and $FeCl_3$ on ether extracts obtained by various treatments from spruce wood.

volume of 9.08 l. 8.58 l of this was evaporated *in vacuo* in an evaporator in accordance with Bartholomew's method¹⁹ to a volume of 690 ml. This concentrated solution was allowed to pass an anion exchanger containing the strongly basic exchange resin "Levatis II". The pH of the solution after this treatment was 6.9. On evaporation to dryness of a sample of the solution, it was found to give a brown, transparent solid (neutral part of the hemicellulose) corresponding to 11.9 % of the original wood. 108.8 g of NaOH dissolved in water was added to the bulk of the solution, which contained the same amount by weight of organic solids. This solution was evaporated in vacuum at 40–60° C to a volume of 350 ml and heated for 15 hours at 100° C in a tube of stainless steel. After cooling, the solution was acidified with dilute H_2SO_4 , extracted with ether, and the enolic fraction (347.1 mg) of the ether extract was isolated as in the case of NaOH digestion of wood (Expt. 1). 317 mg of the enolic fraction was sublimated. The fraction obtained at 68–100° C and 8–10 mm weighed 6.1 mg and contained some crystals. Its absorption maximum in ultraviolet light is given in Table 1.

The uronic acid fraction was eluted from the anion exchanger with 40 ml of 4 % and 80 ml of 2 % NaOH solution and finally with 380 ml of water. The eluate was evaporated to 325 ml and heated for 15 hours at 100° C in a tube of stainless steel. An ethersoluble enolic fraction was isolated in an amount of 50 mg, which, on sublimation at 8–10 mm Hg gave only 0.15 mg of sublimate at 67–100° C. For absorption maximum of sublimate see Table 1.

Table 2. Alkaline digestions of various monosaccharides.

Expt.	Mono-saccharides	Alkali	Heating vessel	Heating		Yield of ether solubles ^c , as % of sugar used
				°C	Time	
D	Galactose, 1 g	4% NaOH, 30 ml	Glass flask	100	8 h	3.6
E	» 2 g	8% NaOH, 62.5 »	Steel ^a tube	100	3 h	3.5
F	» 2 g	—»—	—»—	170	3 h	2.9
G	» 2 g	71% KOH, 28 g	Ni crucible ^b	100	3 min	10.5
H	» 2 g	—»—	—»—	170	3 »	3.9
I	Glucose, 100 g	5% NaOH, 600 ml	Steel ^a tubes	100	46 h	6.6 ^d
K	Fructose, 5 g	4 » » 150 »	—»—	100	8 h	6.0 ^e
L	Mannose, 1 g	4 » » 150 »	Glass flask	100	8 h	2.3
M	Arabinose, 1 g	4 » » 30 »	—»—	100	8 h	2.0
N	Xylose, 1 g	4 » » 30 »	—»—	100	8 h	2.9

a) Stainless. — b) As in exp. B. — c) After acidification. — d) Enolic ether fraction isolated and sublimated in vacuum. Yield of sublimate at about 100° (9 mm) 0.013 % of the glucose used. Spectrum: Table 1. — e) Ether extract sublimated in vacuum. Yield of sublimate at 80–100° (10 mm) 0.026 % of the fructose used. Absorption spectrum: Table 1.

Alkaline digestions of galactose solutions

Expt. A: 150 g of galactose were heated in a sealed tube of stainless steel with 4 500 ml of 4 % NaOH solution for 8 hours at 100° C. After cooling, the reaction solution was evaporated *in vacuo* to a volume of about 1 000 ml and acidified with HCl. The ether-soluble enolic fraction was isolated in the manner described. The ether was evaporated *in vacuo* at room temperature, H₂ being led through the capillary tube. Sublimation at 10–12 mm: until 70° C, 48.6 mg of yellow oil; 70–95° C, 70.2 mg, white crystals and yellow oil. The crystals were recrystallized 5 times from ethyl ether-light petroleum, each time allowing them to stand on porous clay *in vacuo*; m.p. thereafter 100–102° C; m. p. of a mixture with methylcyclopentenolone of m. p. 99–101° C, isolated from soluble wood tar, was found to be 99–101° C.

Negative test for glycerol: 2 l of the acidified aqueous solution, which had been extracted with ether, was treated with 25 g of charcoal, filtered and evaporated *in vacuo*. Some NaCl crystallized and was filtered off. Blank tests showed that galactose alone could give the color reactions of glycerol (conversion to acrolein, test with sodium nitroprussiate and piperidine²¹; oxidation with bromine water to dihydroxyacetone, color reactions with resorcinol and codeine, respectively, according to Dénigés²⁰). Therefore the carbohydrates were removed according to the method of Fresenius²²: 25 g of CaCO₃ were added to the concentrated solution, from which the water was evaporated. The dry residue was ground to a fine powder and digested twice with 50 ml of a mixture of ethanol (2 vol.) and ethyl ether (1 vol.). The solvent was evaporated, but no residue was left. Glycerol was thus found to be absent.

Expt. B: 80 g of KOH was dissolved in 32 ml of water in a nickel crucible. 8 g of galactose, which had been washed with ethyl ether, was introduced into the crucible in a current of N₂ at 78° C. The heat of reaction raised the temperature to 97° C and the crucible was further kept for 3 min. at 100° C. After dissolving in 160 ml of water, the solution was acidified with 2 N HCl and extracted with ethyl ether. Weight of the ether extract: 1.216 g, which on sublimation at 60–95° C at 6–8 mm gave 494 mg of a dark orange-brown oil, which showed the absorption spectrum of Fig. 4 and gave a precipitate with DNPh in hydrochloric acid solution. Calculation of the content of methylcyclopentenolone: It is assumed that the absorption at 259 m μ in neutral solution is due to this compound exclusively, that the value of $E_{1\text{ cm}}^{1\%}$ at that wave-length is proportional to the content of methylcyclopentenolone and that the $E_{1\text{ cm}}^{1\%}$ for the pure compound is 729 (Fig. 1). Thus the observed $E_{1\text{ cm}}^{1\%} = 209$ corresponds to 142 mg of methylcyclopentenolone, or 1.8 % of the original galactose.

Expt. C: 20.04 g of galactose, which had been washed with ethyl ether, was heated for 8 hours at 100° C with 600 ml of 4 % NaOH solution in a sealed tube of stainless steel.

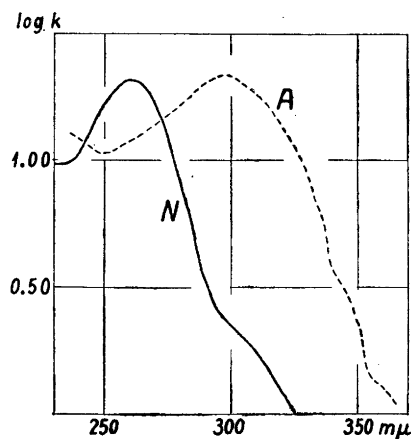


Fig. 4. Absorption spectrum of sublimate of total ether extract obtained after alkaline digestion of galactose (expt. B). Concentration: 10 mg/l. Curve N: in 96 % ethanol, A in 0.5 N ethanolic KOH. Curve N at 259 m μ : $E_{1\text{ cm}}^{1\%} = 209$.

After cooling, the solution was acidified and the enolic ether-soluble fraction isolated as before. It weighed 53.8 mg and, on sublimation at 8 mm between 71 and 92° C, gave a sublimate which partly crystallized. Absorption spectrum in Fig. 2. The sublimate was dissolved in ethanol, and on addition of DNPh in 2 N HCl gave a 2,4-dinitrophenylhydrazone, which was crystallized from benzene; m. p. 235–236° C; m. p. of a mixture with dinitrophenylhydrazone of methylcyclopentenolone prepared from soluble wood tar (m. p. 229–230° C) was 229–231° C.

Alkaline digestions of various monosaccharides

Several monosaccharides were digested with alkali in excess, in some cases with concentrated KOH solution in a current of N₂ in an open nickel crucible, in others with dilute NaOH in sealed tubes of stainless steel. After digestion, the solutions were acidified and extracted with ether. Table 2 shows the results. The maxima of the absorption spectra of vacuum sublimates of some of the ether extracts are given in Table 1. Before the vacuum sublimation, the ether extracts showed very flat absorption curves. Even then, the curve from experiment D with galactose was the sharpest.

Titrations of reductone

Expt. a: 1.01 g of galactose, 10 g of KOH and 4 ml of H₂O were digested in a nickel crucible in a current of N₂ for 3 min. at 100° C. The content of the crucible was then dissolved in water and diluted to 350 ml. 20 ml samples of the solution were titrated with dichlorophenolindophenol (Tillmans' reagent "TR") after addition of phosphoric acid to pH 9, and with 0.1 N I₂ solution after acidification with about 2 N acetic acid.

Expt. b: The experiment was repeated in the same way with another 1.0 g of galactose, but with the difference that the titration with TR was made at pH 5.

Expt. c was made in a corresponding way, but heating the crucible only 2.5 min. at 92° C (cf. ¹⁴).

Expt. d: 5 g of raw air-dry spruce sawdust (moisture content 7.5 %) was boiled 5 min. with 100 ml of distilled water. The mixture was filtered and after addition of Na₂HPO₄ to pH 9 the filtrate was titrated with TR and I₂.

Expt. e: 5 g of raw sawdust of the kind used in expt. d was refluxed for 30 min. with 100 ml of 4 % NaOH solution. The mixture was filtered, and samples of the filtrate treated and titrated in a way corresponding to that of the experiments a and b.

The results are given as mg reductone/g of original galactose or sawdust: expt. a) TR 39 mg at pH 9, I₂ 85 mg. — b) TR 67.7 mg at pH 5, I₂ 55.3 mg. — c) TR 16.5 mg at pH 9, I₂ 33.3 mg. — d) TR 0 at pH 9, I₂ 0. — e) TR 1.7 mg at pH 9, I₂ 3.1 mg.

SUMMARY

Methylcyclopentenolone (Formula I) could be isolated in low yields after digestion of spruce wood or of pure galactose with sodium hydroxide solution at 100° C. It could not be found in the raw wood, but seems to be formed from galactan and perhaps also from other neutral wood polyoses on alkaline digestion. The mechanism of the formation of methylcyclopentenolone is discussed.

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