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THE FORMATION OF 2-HYDROXY-2-CYCLOPENTEN-1-ONES FROM POLYSACCHARIDES DURING KRAFT PULPING OF PINE WOOD*

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ABSTRACT

Small amounts (<0.1% of wood) of 2-hydroxy-2-cyclopenten-1-one (**1**) and its alkyl derivatives were identified by capillary g.l.c.–m.s. in the chloroform extract of the spent liquor obtained from kraft pulping of pine wood. Their formation from polysaccharides was confirmed by experiments on xylan, pectic acid, and hydrocellulose. The most abundant compounds were the 3-methyl and 3,4-dimethyl derivatives of **1**.

INTRODUCTION

Several alkyl derivatives of 2-hydroxy-2-cyclopenten-1-one (**1**) have been detected[1] in the spent liquor ("black liquor") from kraft pulping of pine wood, but most of these compounds were unidentified. The identification of many of these compounds is now reported together with experiments on some representative polysaccharides in order to trace their origins.

EXPERIMENTAL

Materials. — The spent liquor obtained from a laboratory cook of industrial pine-wood chips was similar to that studied previously[1]. The charge of active alkali (as NaOH) was 22%, the sulfidity [100 × Na_2S/(NaOH + Na_2S)] was 30%, and the liquor:wood ratio was 4 L/kg. The time to maximum temperature (20 →170°) was 95 min and the time at 170° was 70 min. The yield of pulp was 47.5%.

Carbohydrate-derived reference samples were prepared by cooking 600 mg each of xylan (Fluka), pectic acid (Nutritional Biochemicals Corp.), or hydrocellulose with 0.7M sodium hydroxide (50 mL) under nitrogen for 30 min at 170° in rotating autoclaves.

A 5-mL sample of the black liquor was freed from cations with Dowex 50W-X8 (H^+) resin. The precipitated lignin was removed, the supernatant solution was

*G.l.c.–m.s. Studies on Pine Kraft Black Liquors, Part IV. For Part III, see *J. Chromatogr.*, 446 (1988) 247–252.

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extracted with chloroform (10 mL), and the extract was concentrated under reduced pressure to 0.5 mL. Samples (10 mL) of the reaction mixtures from the degradation of polysaccharides were treated similarly.

G.l.c. — A Hewlett–Packard 5890A gas chromatograph equipped with a flame-ionisation detector was used. Of the fused-silica capillary columns used (OV-101, SE-54, OV-1701, and OV-351, each 25 m × 0.32 mm i.d.), SE-54 gave the most satisfactory separations. The temperature programme was 2 min at 65°, then 10°/min→180°. The temperature of both the injection port and the detector was 260°. The carrier gas was hydrogen at 2 mL/min.

Mass spectrometry. — E.i.-mass spectra were recorded[2] at 70 eV with a JEOL JMS-DX303 instrument combined with a Hewlett–Packard 5790 A gas chromatograph and the above columns. The temperature programme was similar to that used in g.l.c. The scanning range was 25–300 m.u. with a cycle time of 1 s.

Identification of the 2-hydroxy-2-cyclopenten-1-ones was based on the mass spectra published mainly by Arnarp *et al.*[3], but data from other sources[4–7] were also used.

RESULTS AND DISCUSSION

2-Hydroxy-2-cyclopenten-1-one (**1**) and its 12 alkyl derivatives, including one C_6-compound (**2**), three C_7-compounds (**3–5**), five C_8-compounds (**6–10**), and three C_9-compounds (**11–13**), have been identified in kraft black liquor from pine wood (Table I).

The non-polar columns (OV-101 and SE-54) used for g.l.c. gave good separations of the carbocyclic compounds from each other and from other compounds present in the chloroform extract of the black liquor, *e.g.*, guaiacyl compounds,

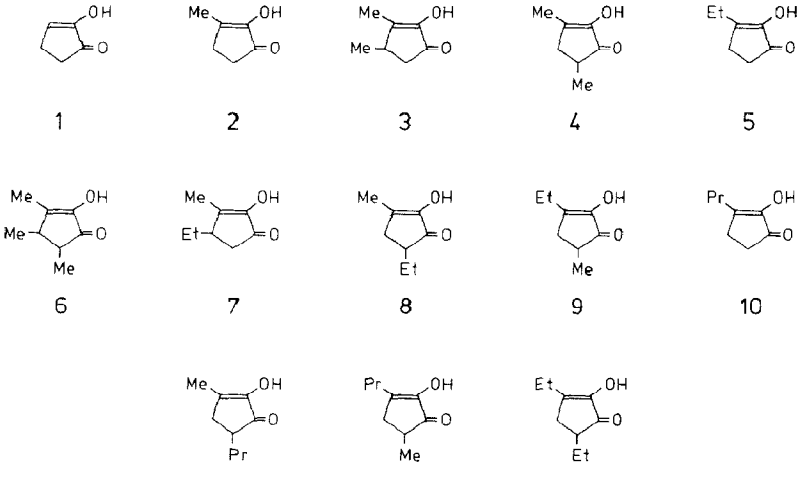


TABLE I

RELATIVE RETENTION TIMES (T) AND ABUNDANCES OF 2-HYDROXY-2-CYCLOPENTEN-1-ONES, IDENTIFIED IN PINE KRAFT BLACK LIQUOR, AND THEIR FORMATION DURING MODEL EXPERIMENTS

	Compound	T[a]	*Abundance*[b]	*Formation from*		
				Xylan	*Pectic acid*	*Cellulose*
1	2-Hydroxy-2-cyclopenten-1-one	0.621	0.6	+	+	+
2	2-Hydroxy-3-methyl-2-cyclopenten-1-one[c]	0.826	23.5	+	+	+
3	2-Hydroxy-3,4-dimethyl-2-cyclopenten-1-one	0.912	39.1	+	+	+
4	2-Hydroxy-3,5-dimethyl-2-cyclopenten-1-one	0.979	3.9	+	+	+
5	3-Ethyl-2-hydroxy-2-cyclopenten-1-one	1.103	3.5	+	+	+
6	2-Hydroxy-3,4,5-trimethyl-2-cyclopenten-1-one	1.042	7.3		+	+
7	4-Ethyl-2-hydroxy-3-methyl-2-cyclopenten-1-one	1.218	0.6			+
8	5-Ethyl-2-hydroxy-3-methyl-2-cyclopenten-1-one	1.192	12.3		+	+
9	3-Ethyl-2-hydroxy-5-methyl-2-cyclopenten-1-one	1.180	5.2		+	+
10	2-Hydroxy-3-propyl-2-cyclopenten-1-one	1.238	0.9	+		+
11	2-Hydroxy-3-methyl-5-propyl-2-cyclopenten-1-one	1.477	0.6			+
12	2-Hydroxy-5-methyl-3-propyl-2-cyclopenten-1-one	1.435	0.6			+
13	3,5-Diethyl-2-hydroxy-2-cyclopenten-1-one	1.444	1.9		+	+

[a]Relative to that (5.2 min on SE-54) of guaiacol (2-methoxyphenol). [b]Percent of total amount of identified 2-hydroxy-2-cyclopenten-1-ones. [c]Until 1970, usually known as "methylcyclopentenelone". Often known as "cyclotene" in food chemistry.

catechols, terpenoids, and thiophene derivatives. The orders of elution of many compounds differed from those reported[3] on a more polar column (Supelcowax 10). Good separations were also obtained for the tautomeric pairs of **8** + **9** and **11** + **12**, which were eluted[3] as one broad peak on Supelcowax 10.

Although only **2** and **3** have previously been identified[1,8] in alkaline pulping liquors, the formation of most of **1–13** from carbohydrate materials under other conditions, usually at elevated temperatures, has been reported. The formation of **2** during pyrolysis or destructive distillation of wood[9–13], during thermal treatment of polysaccharides[14–16], monosaccharides[17,18], and their derivatives[19,20], in Maillard reactions[21–23], and in various food processing systems[24–27] is well known. Since 1972, the presence of **2** in tobacco- or cigarette-smoke condensates has been reported[3,4,6,18,28–32] frequently. Under alkaline conditions, however, only some mono-[8,33–36] and di-saccharides[34,37] have been reported to produce **2**.

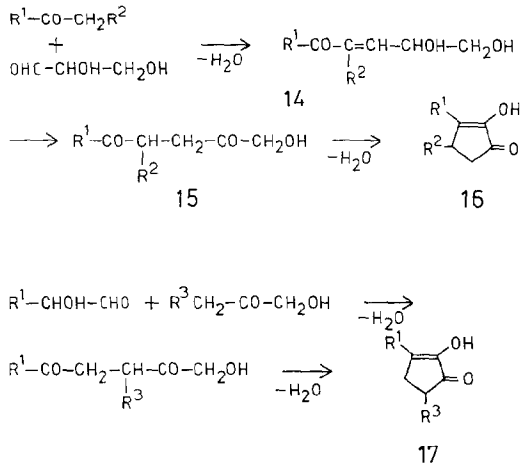
Compound **1** has been found after mild-alkali treatment of certain carbohydrates[38,39], and in tobacco smoke[3,29,31] and a pulp pyrolysate[40]. The C_7-compounds (**3–5**) have been detected in the aroma-complex of roasted coffee[24], in tobacco smokes[3,6,28,32], and after alkali treatment of fructose[35]. Compound **3** has also been identified after alkali treatment of xylose and glucose[36], and after thermal treatment of invert sugar[41], which gave also **5**. In addition, **5** has been found in the volatile products from the processing of molasses[42] and in a pulp pyrolysate[40].

The higher homologues (**6–13**) have been detected mainly in tobacco smoke[3,6]. The formation of **7** and **10** during heating of aqueous solutions of invert sugar has been reported[41], although the mass-spectral data given indicate[3] that the latter compound is probably **6** instead of **10**.

Routes of formation. — The generation of **1–13** during alkaline pulping of wood is proposed to take place by the routes outlined in Scheme 1 (*cf.* refs. 33 and 35). In the first stage, carbohydrates are degraded to reactive carbonyl compounds which can undergo an aldol-type condensation to give unsaturated intermediates of type **14**. Such compounds readily isomerise[43] to the corresponding keto compounds (1-hydroxy-2,5-alkanediones, **15**). Finally, these are converted[44,45] into the carbocyclic compounds (**16**) by intermolecular condensation.

According to the positions of the alkyl substituents, most of **1–13** can be allocated to three main categories, namely, 3-alkyl, 3,4-dialkyl, and 3,5-dialkyl derivatives of **1**. The formation of the 3,4-dialkyl derivatives (**16**) can be traced to the condensation of 2-alkanones and glyceraldehyde (upper route in Scheme 1), whereas the 3,5-disubstituted compounds (**17**) might be formed from 2-hydroxyalkanals and 1-hydroxy-2-alkanones (lower route in Scheme 1). Both of these routes yield 3-alkyl-substituted compounds and **1**, although an alternative mechanism for the formation of **1** has also been described[38].

The most probable precursors of **1–13** have been summarised in Table II. Of these, 2-alkanones[46–48], glycolaldehyde, and glyceraldehyde[49] are known to be formed during alkaline pulping of wood. Since acetol and hydroxybutanones (hydroxybutanals) have often been identified after alkali treatment of carbo-



Scheme 1

hydrates in other connections (*e.g.*, refs. 16, 35, 37, and 50), it is reasonable to assume that they are formed, in small amounts, also during the alkaline pulping of wood.

Although the condensation reactions outlined in Scheme 1 provide a logical explanation for the formation of the carbocyclic compounds, it should be pointed out that their validity has so far been confirmed only by the detection of **2** after alkali treatment[33] of acetone and glyceraldehyde, and by the detection of **3–5** after alkali treatment[35] of a mixture of hydroxybutanones and acetol. Thus, there still exists the possibility of some other (unknown) reaction routes.

The most abundant compounds were **2** and **3**, which together constituted >60% of the compounds identified (Table I). The presence of some compounds,

TABLE II

THE MOST PROBABLE CARBONYL PRECURSORS OF **1–13**

Compound	*Precursors*
1	Acetaldehyde + glyceraldehyde, glycolaldehyde + acetol
2	Acetone + glyceraldehyde, 2-hydroxypropanal + acetol
3	2-Butanone + glyceraldehyde, 3-hydroxy-2-butanone + acetol
4	1-Hydroxy-2-butanone + 2-hydroxypropanal
5	2-Butanone + glyceraldehyde, 2-hydroxybutanal + acetol
6	1-Hydroxy-2-butanone + 3-hydroxy-2-butanone
7	2-Pentanone + glyceraldehyde
8	1-Hydroxy-2-pentanone + 2-hydroxypropanal
9	1-Hydroxy-2-butanone + 2-hydroxybutanal
10	2-Hydroxypentanal + acetol, 2-pentanone + glyceraldehyde
12 + 11	1-Hydroxy-2-butanone + 2-hydroxypentanal
13	1-Hydroxy-2-pentanone + 2-hydroxybutanal

such as **1** and **5**, in much smaller proportions than perhaps would be expected, may be due to their relatively poor stability[51,52]. Detailed discussion of the role of cellulose or of various hemicelluloses as sources of **1–13** is not reasonable at present, although the degradative experiments with xylan, pectic acid, and hydrocellulose gave all of these compounds (*cf.* ref. 39). Previously, some attempts have been made to characterize[53,54] the chromogens formed during alkaline degradation of polysaccharides, but it is unclear whether they are cyclic compounds of type **1**.

Quantitative determination of the carbocyclic compounds was outside the scope of this study. However, the previous study[1] suggests that the total concentration of **1–13** was ~150 mg/L in the spent liquor, corresponding to ~0.07% of the original wood. Thus, the formation of **1–13** is of negligible technical importance, although the transfer of **2** into light tall oil has been observed[55]. Enkvist *et al.*[8] obtained **2** from spruce wood with a yield of 0.02–0.06%.

The identification of **1–13** in kraft black liquor from pine wood reflects the complex nature of the degradation reactions taking place during alkaline pulping. It may be expected that the carbonyl compounds, which are regarded as important intermediates, will react also with lignin fragmentation products or lignin macromolecules. Some compounds supporting both of these assumptions have been identified[56,57], and many unidentified guaiacyl compounds, recently[1] detected, may be products of such reactions.

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REFERENCES

1 K. NIEMELÄ, *Holzforschung*, 42 (1988) 169–173.
2 K. NIEMELÄ AND E. SJÖSTRÖM, *Holzforschung*, 40 (1986) 361–368.
3 J. ARNARP, C. ENZELL, K. PETERSSON, AND T. PETTERSSON, *Acta Chem. Scand., Ser. B*, 40 (1986) 839–854.
4 H. ELMENHORST, *Beitr. Tabakforsch.*, 6 (1972) 205–209.
5 Y. NAOSHIMA, Y. HAYASHI, I. ICHIMOTO, AND H. UEDA, *Agric. Biol. Chem.*, 38 (1974) 1393–1397.
6 S. S. HECHT, R. L. THORNE, R. R. MARONPOT, AND D. HOFFMANN, *J. Natl. Cancer Inst.*, 55 (1975) 1329–1336.
7 W. BALTES AND G. BOCHMANN, *Z. Lebensm. Unters. Forsch.*, 185 (1987) 5–9.
8 T. ENKVIST, B. ALFREDSSON, M. MERIKALLIO, P. PÄÄKKÖNEN, AND O. JÄRVELÄ, *Acta Chem. Scand.*, 8 (1954) 51–59.
9 J. MEYERFELD, *Chem.-Ztg.*, 36 (1912) 549–552.
10 A. W. GOOS AND A. A. REITER, *Ind. Eng. Chem.*, 38 (1946) 132–135.
11 V. P. SUMAROKOV AND M. G. PERSHANOVA, *Zh. Prikl. Khim. (Leningrad)*, 27 (1954) 656–661.
12 M. T. GALCERAN AND L. EEK, *An. Quim.*, 31 (1977) 319–328.
13 O. BEAUMONT, *Wood Fiber Sci.*, 17 (1985) 228–239.
14 A. VAN DER KAADEN, J. HAVERKAMP, J. J. BOON, AND J. W. DE LEEUW, *J. Anal. Appl. Pyrolysis*, 5 (1983) 199–220.
15 K. UMANO AND T. SHIBAMOTO, *Agric. Biol. Chem.*, 48 (1984) 1387–1393.

16 D. A. NELSON, P. M. MOLTON, J. A. RUSSEL, AND R. T. HALLEN, *Ind. Eng. Chem., Prod. Res. Dev.*, 23 (1984) 471–475.
17 R. H. WALTER AND I. S. FAGERSON, *J. Food Sci.*, 33 (1968) 294–297.
18 Y. SAINT-JALM AND J. GOY, *Ann. Tab., Sect. 1*, 18 (1981) 41–48.
19 F. D. MILLS, *J. Agric. Food Chem.*, 27 (1979) 1136–1138.
20 J. VELIŠEK, J. DAVIDEK, V. KUBELKÁ, Z. ZELINKOVA, AND J. POKORNÝ, *Z. Lebensm. Unters. Forsch.*, 162 (1976) 285–290.
21 K. OLSSON, P.-Å. PERNEMALM, T. POPOFF, AND O. THEANDER, *Acta Chem. Scand., Ser. B*, 31 (1977) 469–474.
22 P. E. SHAW AND R. E. BERRY, *J. Agric. Food Chem.*, 25 (1977) 641–644.
23 S. K. BERRY AND J. W. GRAMSHAW, *Z. Lebensm. Unters. Forsch.*, 182 (1986) 219–223.
24 M. A. GIANTURCO, A. S. GIAMMARINO, AND R. G. PITCHER, *Tetrahedron*, 19 (1963) 2051–2059.
25 V. J. FLIPIC, J. C. UNDERWOOD, AND C. O. WILLITS, *J. Food Sci.*, 30 (1965) 1008–1015.
26 O. W. PARKS AND C. ALLEN, JR., *J. Dairy Sci.*, 56 (1973) 328–330.
27 T. MATSUI AND S. KITAOKA, *J. Nutr. Sci. Vitaminol.*, 27 (1981) 563–572.
28 J. N. SCHUMACHER, C. R. GREEN, F. W. BEST, AND M. P. NEWELL, *J. Agric. Food Chem.*, 25 (1977) 310–320.
29 S. ISHIGURO AND S. SUGAWARA, *Agric. Biol. Chem.*, 42 (1978) 1527–1531.
30 S. S. HECHT, S. CARMELLA, AND D. HOFFMANN, *J. Agric. Food Chem.*, 29 (1981) 401–404.
31 M. MATSUKURA, K. TAKAHASHI, M. KAWAMOTO, S. ISHIGURO, AND H. MATSUSHITA, *Agric. Biol. Chem.*, 49 (1985) 711–718.
32 T. JANSSON, M. CURVALL, A. HEDIN, AND C. R. ENZELL, *Mutat. Res.*, 169 (1986) 129–139.
33 G. I. FRAY, *Tetrahedron*, 14 (1961) 161–163.
34 T. ENKVIST, *Finska Kemistsamfundets Medd.*, 71 (1962) 104–108.
35 P. E. SHAW, J. H. TATUM, AND R. E. BERRY, *J. Agric. Food Chem.*, 16 (1968) 979–982.
36 I. FORSSKÅHL, T. POPOFF, AND O. THEANDER, *Carbohydr. Res.*, 48 (1976) 13–21.
37 P. E. SHAW, J. H. TATUM, AND R. E. BERRY, *J. Agric. Food Chem.*, 17 (1969) 907–908.
38 R. KOETZ AND H. NEUKOM, *Carbohydr. Res.*, 42 (1975) 365–368.
39 M. H. JOHANSSON AND O. SAMUELSON, *J. Appl. Polym. Sci.*, 22 (1978) 615–623.
40 A. YAMAZAKI AND K. MAEDA, *Jpn. Tappi*, 39 (1985) 1164–1172.
41 H. ITO AND M. DEKI, *Nippon Shokuhin Kogyo Gakkaishi*, 25 (1978) 549–555.
42 J. F. T. OLDFIELD, M. SHORE, N. W. BROUGHTON, C. W. HARVEY, R. PARSLOW, AND J. C. BAILEY, *C. R. Assem. Gen. Commun. Int. Tech. Sucr.*, 16 (1979) 273–324; *Chem. Abstr.*, 95 (1981) 155627.
43 H. PINES AND W. M. STALICK, *Base-Catalyzed Reactions of Hydrocarbons and Related Compounds*, Academic Press, New York, 1977.
44 T. SHONO, Y. MATSUMURA, AND H. HAMAGUCHI, *Chem. Commun.*, (1977) 712–713.
45 H. STETTER AND W. SCHLENKER, *Tetrahedron Lett.*, 21 (1980) 3479–3482.
46 P. O. BETHGE AND L. EHRENBORG, *Sven. Papperstidn.*, 70 (1967) 347–350.
47 D. F. WILSON AND B. F. HRUTFIORD, *Tappi*, 54 (1971) 1094–1098.
48 B. R. BLACKWELL, W. B. MACKAY, F. E. MURRAY, AND W. K. OLDHAM, *Tappi*, 62 (10) (1979) 33–37.
49 E. SJÖSTRÖM, *Wood Chemistry, Fundamentals and Applications*, Academic Press, New York, 1981.
50 H. G. LENTO, J. C. UNDERWOOD, AND C. O. WILLITS, *Food Res.*, 25 (1960) 750–756.
51 W. DIECKMANN, *Ber.*, 35 (1902) 3201–3217.
52 C. M. LEIR, *J. Org. Chem.*, 35 (1970) 3203–3205.
53 I. ZIDERMAN, J. BEL-AYCHE, A. BASCH, AND M. LEWIN, *Carbohydr. Res.*, 43 (1975) 255–263.
54 M. LEWIN, I. ZIDERMAN, N. WEISS, A. BASCH, AND A. ETTINGER, *Carbohydr. Res.*, 62 (1978) 393–398.
55 J. B. BREDENBERG, *Soc. Sci. Fennica, Comment. Phys.-Math.*, 24 (1959) No. 1.
56 J. GIERER AND S. WÄNNSTRÖM, *Holzforschung*, 38 (1984) 181–184.
57 K. NIEMELÄ, *Holzforschung*, 42 (1988) 175–176.