

Note

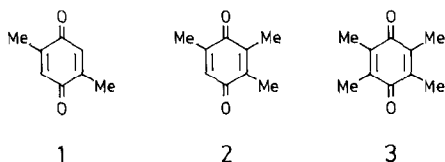
Alkyl-substituted benzoquinones formed on the degradation of pectic acid with alkali

KLAUS NIEMELÄ

Laboratory of Wood Chemistry, Helsinki University of Technology, SF-02150 Espoo (Finland)

(Received April 1st, 1989; accepted for publication, June 3rd, 1989)

Treatment of pectic acid with aqueous alkalis at $>100^{\circ}$ produces¹ hydroxy acids, mainly hydroxydicarboxylic acids, in high yield. Likewise, minor amounts of 2-hydroxy-2-cyclopenten-1-ones are formed² from pectic acid and other polysaccharides. More detailed analysis of the mixtures of products obtained from pectic acid has now resulted in the identification of three alkyl-substituted benzoquinones (**1–3**), which were not found after similar treatments² of xylan and hydrocellulose.



The yields of **1–3** are given in Table I. The most abundant compound was phlorone (**1**), which has also been identified³ after treatment of sucrose with alkali and after liquefaction of cellulose with alkali^{4,5}. *p*-Pseudocuminoquinone (**2**) has also been obtained³ by treatment of sucrose with alkali, and duroquinone (**3**) has been detected as a semiquinone anion radical in the spent liquor from the alkaline pulping of wood⁶.

The routes of formation of **1–3** remain obscure, although the generation of **1** and **3** by alkali-catalysed condensation of 2,3-butanedione (**4**) and 2,3-pentanedione (**5**), respectively, has been reported^{5,7–10}, so that the generation of **2** from **4** + **5** might be possible. In addition to **1**, the corresponding hydroquinone should be formed⁵ from **4**, but no hydroquinones were found after treatment of pectic acid with alkali. It might be assumed that **4** and **5** could react via a benzilic acid rearrangement to give 2-hydroxy-2-methylpropanoic and 2-hydroxy-2-methylbutanoic acids, respectively, but these acids could not be detected. However, the treatment of cellulose under identical¹¹ or more drastic^{12,13} conditions gave appreciable

TABLE I

RELATIVE RETENTION TIMES (*T*) AND YIELDS OF BENZOQUINONES OBTAINED ON TREATMENT OF PECTIC ACID WITH SODIUM HYDROXIDE AT 170°

<i>Benzoquinone</i>	<i>T</i> ^a	<i>NaOH</i>		
		0.3M	0.7M	1.0M
		<i>Yield</i> ^b		
2,5-Dimethyl-2,5-cyclohexadiene-1,4-dione (1)	0.68	0.7	1.1	0.6
2,3,5-Trimethyl-2,5-cyclohexadiene-1,4-dione (2)	0.83	0.1	0.2	0.1
2,3,5,6-Tetramethyl-2,5-cyclohexadiene-1,4-dione (3)	1.03	<0.1	<0.1	<0.1

^aRelative to that (9.5 min) of 2-hydroxy-3-methoxybenzaldehyde. ^bFigures are given as mg/g of pectic acid.

amounts of these hydroxy acids, but neither **1–3** nor the corresponding hydroquinones were detected. Although the formation of **1–3** from pectic acid through condensation of **4** and **5** could thus not be confirmed, no alternative routes for their formation are apparent.

In addition to **1–3** and 2-hydroxy-2-cyclopenten-1-ones², the present samples were also found to contain, among others, 2-methyl, 3-methyl, 2,3-dimethyl, 2,5-dimethyl, 2,3,4-trimethyl, and 3,4,5-trimethyl derivatives of 2-cyclopenten-1-one (*cf.* ref. 13).

EXPERIMENTAL

Samples (600 mg) of pectic acid^{1,2} (Nutritional Biochemicals Corp.) were treated with 0.3, 0.7, or 1.0M sodium hydroxide (50 mL) under nitrogen for 30 min at 170° in rotating autoclaves. Cyclic compounds were extracted with chloroform (10 mL) from the reaction mixtures (10 mL), after adding 2-hydroxy-3-methoxybenzaldehyde (0.1 mg) as the internal standard and after lowering the pH to 2 with 2M hydrochloric acid. The extracts were concentrated to 0.5 mL for g.l.c. and g.l.c.–m.s. investigations.

G.l.c. — A Hewlett–Packard 5890 A gas chromatograph was used with a flame-ionisation detector and an SE-54 fused-silica capillary column (25 m × 0.32 mm i.d.). The temperature program was 2 min at 60° and then 10° min^{–1} to 240°, which allowed the separation of **1–3** in 10 min without any tailing¹⁴ of their peaks. The temperature of the injection port and the detector was 260°. The carrier gas was hydrogen at 2 mL.min^{–1}.

E.i. (70 eV)-mass spectrometry. — A JEOL JMS-DX303 instrument was used in combination with a Hewlett–Packard 5790 A gas chromatograph and the above column. Identification of **1–3** was based on the use of an automatic library search (NIH/EPA, 31,000 spectra), and was confirmed with the help of the literature data¹⁵.

Hydroxy acids were analysed¹² as their trimethylsilyl derivatives.

ACKNOWLEDGMENTS

The author thanks Professor E. Sjöström for his interest in the work, and Miss E. Orban for assistance with the experimental work.

REFERENCES

- 1 K. NIEMELÄ AND E. SJÖSTRÖM, *Carbohydr. Res.*, 144 (1985) 87–92.
- 2 K. NIEMELÄ, *Carbohydr. Res.*, 184 (1988) 131–137.
- 3 H. KATO, M. MIZUSHIMA, T. KURATA, AND M. FUJOMAKI, *Agric. Biol. Chem.*, 37 (1973) 2677–2678.
- 4 D. A. NELSON, P. M. MOLTON, J. A. RUSSELL, AND R. T. HALLEN, *Ind. Eng. Chem., Prod. Res. Dev.*, 23 (1984) 471–475.
- 5 D. A. NELSON, S. D. LANDSMAN, AND P. M. MOLTON, *Carbohydr. Res.*, 128 (1984) 356–360.
- 6 I. ŠIMKOVIC, A. EBRINGEROVÁ, J. TIŠO, J. PLAČEK, Z. MAŇASEK, AND L. ŽILKA, *Holzforschung*, 40 (1986) 15–18.
- 7 H. VON PECHMANN, *Ber.*, 21 (1888) 1411–1422.
- 8 H. VON EULER AND H. HASSELQUIST, *Ark. Kemi*, 1 (1949) 325–330.
- 9 L. SCHOTTE, *Acta Chem. Scand.*, 5 (1951) 969–970.
- 10 P. R. C. GASCOYNE, M. C. R. SYMONS, AND J. A. McLAUGHLIN, *Int. J. Quantum Chem., Quantum Biol. Symp.*, 10 (1983) 123–132.
- 11 K. NIEMELÄ, *Proc. Int. Symp. Wood Pulping Chem., Vth, Raleigh, NC, U.S.A., 1989*, pp. 336–338.
- 12 K. NIEMELÄ AND E. SJÖSTRÖM, *Biomass*, 11 (1986) 215–221.
- 13 K. NIEMELÄ, *J. Chem. Technol. Biotech.*, in press.
- 14 H. J. MÖCKEL AND D. VELTWISCH, *Fresenius Z. Anal. Chem.*, 291 (1978) 222–223.
- 15 J. H. BOWIE, D. W. CAMERON, R. G. F. GILES, AND D. H. WILLIAMS, *J. Chem. Soc., B*, (1966) 335–339.