

Separation and identification of methylol derivatives of 3-pentadecylphenol by thin-layer chromatography

The products formed initially in the condensation reaction of phenols with formaldehyde are the methylol derivatives of the phenols, and the presence or absence of a specific methylol in the reaction mixture governs the subsequent course of the reaction. Rapid and efficient analytical methods for the identification of methylol derivatives in the initial reaction mixture would therefore be very useful.

Various techniques^{1,2} have been employed to separate and identify the reaction products of simple phenols and various lower substituted alkylphenols with formaldehyde under alkaline conditions. BAKSHI AND KRISHNASWAMY^{3,4} have used thin-layer chromatography (TLC) on silica gel for the separation and identification of some of the methylol derivatives of cardanol and 3-pentadecylphenol. These C₁₅-*meta*-substituted phenols derived from indigenously available cashewnut-shell liquid are expected to be trifunctional in their reactivity, like *meta*-cresol.

The present communication describes the separation by TLC of the theoretically possible methylol derivatives of 3-pentadecylphenol, synthesized by appropriate routes using 3-pentadecylphenol and tetrahydroanacardic acid as starting materials.

Experimental

Preparation of the materials. 3-Pentadecylphenol was prepared by the hydrogenation of cardanol using palladium on carbon as catalyst⁵. Anacardic acid and tetrahydroanacardic acid were prepared as described by PILLAY⁶. The 2-monomethylol derivative was prepared by reducing tetrahydroanacardic acid with lithium aluminium hydride. The 6- and 4-monomethylol derivatives were prepared by the Gattermann aldehyde reaction of 3-pentadecylphenol, and the pure 6- and 4-aldehydes obtained were subsequently reduced with lithium aluminium hydride to the corresponding methylols. The Gattermann reaction with tetrahydroanacardic acid followed by the lithium aluminium hydride reduction of the total reaction mixture gave a mixture of the 2-monomethylol and 2,4- and 2,6-dimethylol derivatives. The 4,6-dimethylol derivative was obtained either by reacting 3-pentadecylphenol with paraformaldehyde and sodium ethoxide at 0–5° for 3 days or by reacting 1 mole of 3-pentadecylphenol with 3 moles of formalin (37–41 %) at room temperature for 8 days with an alkali catalyst. The 2,4,6-trimethylol derivative was obtained by reacting 1 mole of the 4,6-dimethylol derivative of 3-pentadecylphenol with 1 mole of formalin in alkaline aqueous dioxane for 4 h (ref. 7).

Thin-layer chromatography. Glass plates were coated by spreading a slurry of Silica Gel G using a Camag applicator as described previously⁸. Ether solutions of the materials were spotted and the plates developed with a mixture of petroleum ether (b.p. 60–80°)–diethyl ether–dimethylformamide–glacial acetic acid (75:85:5:1). The developed plates were sprayed with sulphuric acid and heated in an air oven at 120° for 1h, when the methylol derivatives appeared as brown or black spots against the white background.

Results and discussion

TLC with Silica Gel G has been used for the separation of all the methylol derivatives of 3-pentadecylphenol using the above solvent system. Fig. 1 shows

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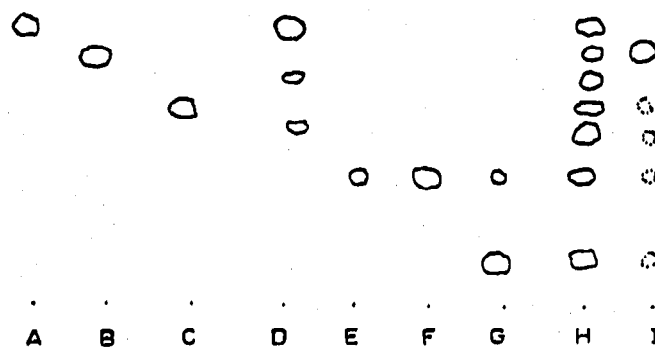


Fig. 1. Chromatogram of the methylol derivatives of 3-pentadecylphenol on Silica Gel G. Solvent system: petroleum ether (b.p. 60–80°)–diethyl ether–dimethylformamide–glacial acetic acid (75:85:5:1). Methylol derivatives: A = 2-monomethylol; B = 6-monomethylol; C = 4-monomethylol; D = mixture of 2-monomethylol and 2,6- and 2,4-dimethylol; E = 4,6-dimethylol; F = 4,6-dimethylol; G = 2,4,6-trimethylol; H = mixture of all the synthetic methylol derivatives; I = 6-monomethylol obtained by the method of JONES AND ROBSON⁹

the separation of all these derivatives individually and in a mixture. A condensation product⁹ of 3-pentadecylphenol with formaldehyde is also included for comparison. Spots A, B and C refer to the 2-, 6- and 4-monomethylol derivatives, D to a mixture of the 2-monomethylol and 2,6- and 2,4-dimethylol derivatives, and E to the 4,6-dimethylol derivative of 3-pentadecylphenol. The separation of the 2-monomethylol (A) from the 6-monomethylol derivative (B) could be attributed to the hindered position of the former substituent between the adjacent phenolic hydroxyl group and the long aliphatic side chain and to its less polar nature compared with the 6-monomethylol derivative ($hR_F = 50$ and 45 , respectively). Unlike the 2- and 6-monomethylol derivatives, the 4-monomethylol derivative exhibits higher polarity for it is not influenced either by steric factors or by chelation. Among the 2,6-, 2,4- and 4,6-dimethylol derivatives, the 2,6-dimethylol derivative exhibits the highest migration ($hR_F = 41$), higher even than the 4-monomethylol derivative ($hR_F = 36$). This is due to the presence of two methylol groups *ortho* to the phenolic hydroxyl group. The 2,4- and 4,6-dimethylol derivatives ($hR_F = 32$ and 24 respectively), exhibit higher polarity than the 2,6-dimethylol derivative because the first is only influenced by steric and chelation and the second by chelation factors. The least migrated ($hR_F = 8.4$) material (G) exhibiting the highest polarity, evidently because of the increased number of methylol groups, may be the 2,4,6-trimethylol derivative of 3-pentadecylphenol. All these methylol derivatives are separable, even in a mixture (H).

In this study, it was observed that the 3-pentadecylphenol–formaldehyde condensation product obtained according to the method of JONES AND ROBSON⁹

after crystallisation contains mainly the 6-methylol accompanied by minor quantities of the 4-, 2,4- and 4,6 dimethylol and 2,4,6- trimethylol derivatives (I). The separation of all the methylol derivatives occurs in the order 2-monomethylol, 6-monomethylol, 2,6-dimethylol, 4-monomethylol, 2,4-dimethylol, 4,6-dimethylol and 2,4,6-trimethylol ($hR_F = 50, 46, 41, 36, 32, 24$ and 8.4 , respectively). This technique was later successfully used in kinetic rate studies of the reaction of formaldehyde with cardanol and 3-pentadecylphenol separately, in order to examine various methylol derivatives formed in the initial reaction products at different temperatures.

Regional Research Laboratory,
Hyderabad-9 (India)

N. HEMALATHA ISAIAH
J. S. AGGARWAL

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Received June 23rd, 1971

J. Chromatogr., 62 (1971) 473-475