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Note

Metaperiodate — a new structure-specific locating reagent for phenolic compounds

MICHAEL NEWTON CLIFFORD* and JOHN WIGHT

Department of Food Science, University of Strathclyde, Glasgow (Great Britain)

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During chromatographic examination of the quinic acid depsides of green coffee beans the locating reagent of Cartwright and Roberts¹ was employed. To locate quinic acid, quinic acid lactone, and shikimic acid with this reagent the chromatogram is sprayed with a one third-saturated solution of potassium metaperiodate, 20 min later with a solution of sodium nitroprusside (0.4% w/v) and piperazine (0.4% w/v) dissolved in ethanol (85% v/v), and heated for 5 min at 100°.

When the metaperiodate was applied to a chromatogram on which samples of caffeic acid, ferulic acid, caffeoylquinic acid and feruloylquinic acid had been run, a yellow-orange colour was obtained, at R_f values corresponding to the phenolic compounds but at this stage of the procedure quinic acid was not located.

The present work was initiated to investigate the structure specificity of metaperiodate.

MATERIALS AND METHODS

The phenolic compounds listed in Table I were dissolved in propan-2-ol (70% w/v) at a concentration of 5 mg/ml. Saturated 5% w/v and 0.5% w/v aqueous solutions of analytical grade potassium metaperiodate were used as spray reagents.

A sheet of Whatman No. 1 chromatography paper was sprayed with one of the metaperiodate solutions and allowed to dry. Each phenolic solution was applied to the metaperiodate-treated papers at levels of 1, 5 and 10 μ g using a micro-pipette. Failure to produce a detectable colour within 10 min was taken as a negative response.

RESULTS AND DISCUSSION

The results are presented in Table I. Metaperiodate (0.5%) detected microgram quantities of *o*- and *p*-dihydroxyphenols and their monomethyl ethers by producing a yellow-orange colour. This response was essentially independent of other substituents (carboxyl, hydroxyl, methoxyl, propenoic acid), but vanillin, vanillic acid

* Present address: Department of Science and Food Technology, Grimsby College of Technology, Nuns' Corner, Grimsby, Lincolnshire, Great Britain.

TABLE I

RESPONSE OF PHENOLIC COMPOUNDS TO THE PERIODATE REAGENT

Experimental conditions: The phenolic compounds were spotted onto chromatograms already sprayed with the periodate reagent. Responses are indicated as negative if no colour was detected after 10 min.

<i>Phenolic compound</i>	<i>Response</i>
Monohydroxy	
2-Hydroxybenzoic acid	Negative
3-Hydroxybenzoic acid	
4-Hydroxybenzoic acid	
2-Hydroxybenzaldehyde	
3-Hydroxybenzaldehyde	
4-Hydroxybenzaldehyde	
2-Hydroxycinnamic acid	
3-Hydroxycinnamic acid	
4-Hydroxycinnamic acid	
Methyl phenyl ketone	
Tyrosine	
<i>o</i>-Dihydroxy	
2,3-Dihydroxybenzoic acid	Positive
3,4-Dihydroxybenzoic acid	
3,4-Dihydroxybenzaldehyde	
3,4-Dihydroxycinnamic acid	
3,4-Dihydroxybenzene	
DOPA	
3-Caffeoylquinic acid	
5-Caffeoylquinic acid	
1,4-Dicaffeoylquinic acid	
3,5-Dicaffeoylquinic acid	
4,5-Dicaffeoylquinic acid	
Vicinal trihydroxy	
3,4,5-Trihydroxybenzene	Positive
3,4,5-Trihydroxybenzoic acid	
<i>p</i>-Dihydroxy	
1,4-Dihydroxybenzene	Positive
2,5-Dihydroxybenzoic acid	
2,5-Dihydroxybenzaldehyde	
<i>m</i>-Dihydroxy and trihydroxy	
2,4-Dihydroxybenzene	Negative
2,4-Dihydroxybenzoic acid	
2,6-Dihydroxybenzoic acid	
3,5-Dihydroxybenzoic acid	
2,4-Dihydroxybenzaldehyde	
2,4,6-Trihydroxybenzene	
Vicinal hydroxy methoxy	
3-Methoxy-4-hydroxybenzoic acid	Positive
3-Hydroxy-4-methoxybenzoic acid	
3-Methoxy-4-hydroxycinnamic acid	
3-Hydroxy-4-methoxycinnamic acid	

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TABLE I (continued)

<i>Phenolic compound</i>	<i>Response</i>
Vicinal hydroxy methoxy	
3-Methoxy-4-hydroxybenzaldehyde	Positive
3-Hydroxy-4-methoxybenzaldehyde	
3-Methoxy-4-hydroxybenzene	
3,5-Dimethoxy-4-hydroxybenzene	
3,5-Dimethoxy-4-hydroxybenzoic acid	
3,5-Dimethoxy-4-hydroxybenzaldehyde	
3,5-Dimethoxy-4-hydroxycinnamic acid	
3-Feruloylquinic acid	
Methyl vanilloyl ketone	
Methyl syringoyl ketone	
Others	
3-Methoxybenzaldehyde	Negative
3,4-Dimethoxybenzoic acid	
3,4-Dimethoxycinnamic acid	
3,4-Dimethoxybenzaldehyde	

and methyl vanilloyl ketone responded less readily, a 5- μ g loading being necessary to give a positive response. In all other cases a 1- μ g loading was detected.

According to Adler *et al.*² aqueous periodate oxidizes *o*- or *p*-dihydroxyphenols to the corresponding benzoquinone and water. The benzoquinones may dimerize and may be converted to a naphthoquinone and according to Adler and Bergmann³ the mixture of products has a yellow-orange colour. Treatment of a monomethyl ether with aqueous periodate removed the methyl group as methanol and produced the corresponding dihydroxyphenol which entered the reactions outlined above.

CONCLUSION

Aqueous metaperiodate is a valuable locating reagent for detecting microgram quantities of *o*- and *p*-dihydroxyphenols and their monomethyl ethers.

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