

844. *The Constitution of Piceatannol*

Comment on a Paper by Cunningham, Haslam, and Haworth \*

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In the publication mentioned above, Cunningham and his co-workers have described the isolation of 3,3',4,5'-tetrahydroxystilbene (I) from the *cortex* of spruce and suggested that this compound is the same as that isolated by us from the *phloem* of spruce and which we have named piceatannol.<sup>1</sup>

By degradation and synthesis we have established that the molecular constitution of piceatannol is that shown by structure (II).



Cunningham and her co-workers did not mention our proof of this constitution; they only stated that adipic acid, isolated by us in the course of degradation, may have had its origin in the perlon powder used for chromatographic isolation of the compound; they overlooked the fact that perlon is  $\epsilon$ -aminocaprolactam, containing no adipic acid.

We have established by direct comparison, using material kindly supplied by Professor Haworth, that the compound isolated by him and his co-workers is not piceatannol, despite the fact that the C, H, acetyl, and bromoacetyl analyses for the two compounds are similar and that there are certain similarities in the u.v. spectra and the behaviour in chromatographic systems. The substances have different melting points (piceatannol 216°, compound (I) 229°) and have different  $R_F$  values in some chromatographic systems (Table). Moreover, they behave differently under oxidising conditions. The products isolated by Cunningham, Haslam, and Haworth are described as stable (redox potential  $E_0$  ca. 700 mv) whereas piceatannol is extremely unstable ( $E_0$  ca. 400 mv)

$R_F$  values of piceatannol and compound (I) on thin-layer polyamide

Solvent	$R_F$ values	
	(Tetrahydrofuran)	(Pyridine-acetic acid)
Piceatannol (II) .....	0.70	0.49
3,3',4,5'-Tetrahydroxystilbene (I) .....	0.62	0.45

We have worked up separately the phloem and the phloem-free cortex of a spruce tree felled in June. The mixtures of aglycones, prepared from the ethyl acetate extracts by enzymatic hydrolysis, were examined by chromatography on thin-layer polyamide plates. The main component of the phloem-free bark was shown, by chromatography in various solvents, to be the stilbene (I). In addition two unidentified compounds with light blue fluorescence were shown to be present. The major component of phloem was piceatannol (II); there was also a very small quantity of the stilbene described by Cunningham, Haslam, and Haworth, together with the two fluorescent substances isolated from the phloem-free bark.

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\* I. Cunningham, E. Haslam, and R. D. Haworth, *J.*, 1963, 2875.

<sup>1</sup> W. Grassmann, G. Deffner, E. Schuster, and W. Paucker, *Chem. Ber.*, 1956, **89**, 2523. W. Grassmann, H. Endres, and W. Paucker, *Chem. Ber.*, 1958, **91**, 134.