

## Condensed Tannins: Preferential Substitution at the Interflavanoid Bond by Sulphite Ion

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The reaction of loblolly pine (*Pinus taeda* L.) bark tannins with sodium hydrogen sulphite gave sodium epicatechin-(4 $\beta$ )-sulphonate (1) and sodium epicatechin-(4 $\beta$  → 8)-epicatechin-(4 $\beta$ )-sulphonate (2) in high yield with only a minor amount of sodium 1-(3,4-dihydroxyphenyl)-2-hydroxy-3-(2,4,6-trihydroxyphenyl)-propane-1-sulphonate (3).

Condensed tannins used in leather tanning,<sup>1</sup> mud additives for oil well drilling,<sup>2</sup> and wood adhesives,<sup>3</sup> are often sulphonated to increase their solubility and reduce their viscosity in water. Despite studies spanning many decades,<sup>4-9</sup> sulphonation of condensed tannins is not fully understood. A commonly held view is that the pyran ring is opened with sulphonation occurring at C-2 resulting in polymeric sulphonic acid derivatives.<sup>1-3</sup> This report establishes that this reaction occurs to only a minor degree and that cleavage of the interflavanoid bonds with the formation of sodium epicatechin-(4 $\beta$ )-sulphonate and oligomeric procyanidin-4-sulphonic acid derivatives is the main reaction between procyanidin-based tannins and sodium hydrogen sulphite.

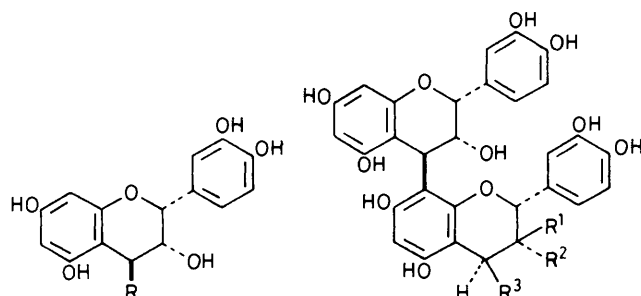
Treatment of loblolly pine bark tannins<sup>10-14</sup> with sodium hydrogen sulphite at pH 5.5 and 100 °C for 20 h gave sodium

epicatechin-(4 $\beta$ )-sulphonate (1) in a yield of about 20% of the tannin. The structure of (1) was readily apparent from elemental analyses, fast atom bombardment mass spectroscopy, and its <sup>1</sup>H and <sup>13</sup>C n.m.r. spectra (Table 1). The dimeric procyanidin sulphonate derivative, sodium epicatechin-(4 $\beta$  → 8)-epicatechin-(4 $\beta$ )-sulphonate (2) and other oligomeric flavan-

**Table 1.** Selected <sup>13</sup>C n.m.r. chemical shifts (in p.p.m.) for sulphonated flavan derivatives and related compounds.<sup>a</sup>

Compound	Carbon number				
	C-2	C-3	C-4	C-6	C-8
(7) <sup>b</sup>	79.1	66.8	28.6	96.7	96.0
(1)	75.9	66.8	60.5	99.1	97.1
(4) <sup>b</sup>	76.6	72.6	36.5	96.5	95.7
(5) <sup>b</sup>	74.4	70.3	42.9	96.4	95.2
(8) <sup>b</sup>	76.6	72.8	36.7	96.5	96.0
	79.1	66.2	29.1	97.4	107.7
(2)	76.5	72.5	36.8	96.7	96.2
	76.0	66.2	61.0	99.7	108.3
(3) <sup>c</sup>	71.4	73.4	30.8	96.2	96.2

<sup>a</sup> Recorded with a Varian FT-80A spectrometer, chemical shifts  $\delta$  from (CD<sub>3</sub>)<sub>2</sub>CO at 30.3 p.p.m. in D<sub>2</sub>O-(CD<sub>3</sub>)<sub>2</sub>CO (1:1). <sup>b</sup> Ref. 17. <sup>c</sup> For ease of comparison numbering of this compound retains that of the parent flavan-3-ol.



(1) R = SO<sub>3</sub>Na

(2) R<sup>1</sup> = H, R<sup>2</sup> = OH, R<sup>3</sup> = SO<sub>3</sub>Na

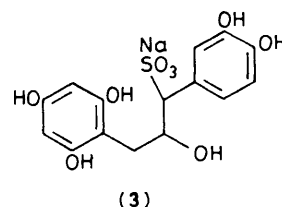
(4) R =

(6) R<sup>1</sup> = OH, R<sup>2</sup> = H, R<sup>3</sup> = H

(8) R<sup>1</sup> = H, R<sup>2</sup> = OH, R<sup>3</sup> = H

(5) R = -S-CH<sub>2</sub>-Ph

(7) R = H



C-4-sulphonates were also isolated in about 6% yield. The constitution of the sulphonate dimer (2) was derived from its  $^{13}\text{C}$  n.m.r. spectrum and from degradation studies. Treatment of (2) with an excess of phloroglucinol under acidic conditions gave epicatechin-(4 $\beta$   $\rightarrow$  2)-phloroglucinol (4) and (1). With phenylmethanethiol, (2) gave epicatechin-(4 $\beta$ )-benzyl sulphide (5) and (1). The C-SO<sub>3</sub>Na function is resistant to substitution since treatment of (1) with either phloroglucinol or phenylmethanethiol in the presence of acetic acid resulted in recovery of only starting materials.

The  $^{13}\text{C}$  n.m.r. spectra of (1) and (2) show the C-4 bearing the sulphonate moiety as a resonance at about  $\delta$  61.0 p.p.m. (Table 1). The upfield shift (ca. 3.15 p.p.m.) of the C-2 resonance of the epicatechin unit in both (1) and (2) shows that the sulphonate group must be *trans* to the 3-hydroxy group because of the  $\gamma$ -*gauche* effect between the axial proton at C-2 and the sulphonate group at C-4.<sup>15</sup>

Also isolated, but in much lower yield (ca. 1%), is the pyran ring opened product, sodium 1-(3,4-dihydroxyphenyl)-2-hydroxy-3-(2,4,6-trihydroxyphenyl)propane-1-sulphonate (3). This compound was previously shown to be a product of the reaction of (+)-catechin with sodium hydrogen sulphite<sup>9</sup> and evidently results from sulphonation of catechin generated from the terminal unit of the polymer. No other C-2 sulphonated products were isolated. The chemical shift of C-2 bearing a sulphonate function occurs at  $\delta$  71.4 p.p.m. (Table 1), and is sufficiently isolated from other signals to have been readily observed. Additionally, the reaction of epicatechin-(4 $\beta$   $\rightarrow$  8)-catechin (6) with sodium hydrogen sulphite gave sodium epicatechin-(4 $\beta$ )-sulphonate (1), catechin, and *ent*-epicatechin only. As in the reaction of (+)-catechin with sodium hydrogen sulphite, epimerization of catechin with the production of *ent*-epicatechin clearly predominates over the formation of 2-sulphonate derivatives.

The marked improvement in water solubility of tannin isolates and the reduction in solution viscosity resulting from sulphonation of condensed tannins can now be explained by cleavage of the interflavanoid bonds with the generation of lower molecular weight procyanidin-4-sulphonate derivatives. These results also emphasize the importance of restricting the severity of this reaction in production of leather tanning agents

since dimeric and trimeric procyanidins possess poor tanning properties.<sup>16</sup> Applied as wood adhesives, it is apparent that the decrease in polymer size during sulphonation would require higher proportions of cross-linking agents in order to obtain cured resins. The ease with which epicatechin-4-sulphonate is formed suggests that the sulphonation of condensed tannins may provide a route to the production of valuable phenols from this abundant renewable resource.

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