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SUITABILITY OF SULPHUROUS ACID FOR HYDROLYSIS OF CONDENSED TANNINS

V.C. Quesnel

Regional Research Centre, University of the West Indies,

St. Augustine, Trinidad.

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Although condensed tannins are hydrolysed by dilute acids, concommittant acid-catalysed polymerization occurs so that the main products of acid treatment are not simple phenols but complex polymers. Alkaline hydrolysis is complicated by oxidative condensation. In an attempt to overcome these difficulties, Forsyth and Roberts[1] used sulphurous acid, a weak acid and a reducing agent, to hydrolyse a dimeric leucocyanidin isolated from unfermented cacao beans. The work briefly reported here shows the suitability of their procedure for investigations on the structure of condensed tannins.

The following polymers have been examined: (-)-epicatechin polymerized by acid and by oxidation; a mixture of cacao leucocyanidins 1 and 2 (L_1 and L_2) similarly polymerized; naturally

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[1] W.G.C. Forsyth and J.B. Roberts, Biochem. J. 74, 374 (1960).

occurring polymeric leucocyanidin from cacao (cacao tannin) and mangrove tannin. Acid-catalysed polymers were prepared by the method of Goldstein and Swain[2]. The polymers were precipitated during the course of the reaction and were collected by filtration. Oxidation polymers were prepared by overnight oxidation at room temperature of 100 mg. amounts of the compounds in 50 ml. of water with 75 mg. of sodium iodate. The polymers were precipitated by saturation of the solutions with salt (acid-precipitated polymers are insoluble) and collected on sintered glass funnels. Cacao and mangrove tannins were extracted with methanol from cacao polyphenol storage cells[3] and mangrove bark respectively and precipitated with two volumes of ether. They were purified by repetition of the procedure twice.

The acid-catalysed polymers were practically insoluble in water but the polymer from epicatechin was partly soluble in ethanol and the polymer from the leucocyanidin mixture wholly soluble; the others were all soluble in water. None of these polymers on 2-way chromatography in 2% aqueous acetic acid and the butanol phase of butanol-acetic acid-water (4:1:5) showed any discrete spot mobile in both solvents.

The polymers were refluxed with aqueous or aqueous ethanolic sulphurous acid for 2 hr.[1] and again examined chromatographically.

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[2] J.L. Goldstein and T. Swain, *Phytochemistry* **2**, 371 (1963).

[3] H.B. Brown, *Nature, Lond.* **173**, 492 (1954).

No spot mobile in both solvents was produced from the acid polymers or the oxidation polymer of the mixture of L_1 and L_2 but mobile spots were produced from the other polymers.

The oxidation polymer of epicatechin was partially split to give a conspicuous spot with Rf's of 0.02 (water) and 0.5 (butanol) and another spot with Rf's of 0.95 and 0.5. Cacao tannin was almost completely split to give substances with the chromatographic properties of (-)-epicatechin and the substance A of Forsyth and Roberts[1] and a new spot, substance B, near to substance A. Small quantities of L_1 and another compound were also produced. Longer treatment of the cacao tannin gave complete hydrolysis to substance A, (-)-epicatechin and (+)-catechin (produced from (-)-epicatechin by epimerization). Substance B and the traces of other mobile compounds disappeared.

Chromatograms of hydrolysates of mangrove tannin were very similar to those of the cacao tannin though the products were more numerous. Hydrolysis, though not complete, was extensive: in one experiment the addition of 2N HCl to the sulphurous acid hydrolysate after 2 hr. produced a precipitate only one eighth the weight of a precipitate obtained by similar means from the unhydrolysed solution. Longer treatment lead to a simplification of the chromatogram, the main product being chromatographically identical with substance A from cacao and two of the minor products being chromatographically identical with (-)-epicatechin and (+)-catechin.

The products of sulphurous acid treatment are at least partly specific to this acid: substance A is known to contain sulphur[1] and the pattern of spots on the chromatogram is not duplicated with hydrolysates obtained with dilute hydrochloric acid.

It is clear that in their response to sulphurous acid treatment the naturally occurring polymers resemble one another and are different from the acid-catalysed and oxidation polymers. Although its lesser degree of hydrolysis, its greater variety of products and the dark brown colour indicate that mangrove tannin may contain some oxidation-type polymer, it seems that the bulk of the tannin is closely similar to that of cacao. This raises the possibility that other condensed tannins are similar to cacao tannin and suggests the use of sulphurous acid in investigations of their structure. Quebracho tannin is already known to be extensively altered by bisulphite treatment[4].

An account of the chemistry of cacao tannin will be presented elsewhere.

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[4] D.E. Hathway, in Wood Extractives, Ed. W.E. Hillis, Academic New York, p.191 (1962).