PHENOLATION OF (+)-CATECHIN WITH MINERAL ACIDS. IDENTIFICATION OF NEW REACTION PRODUCTS

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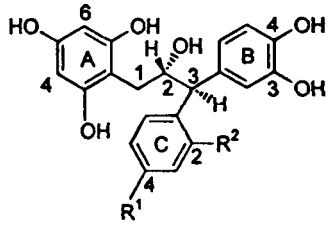
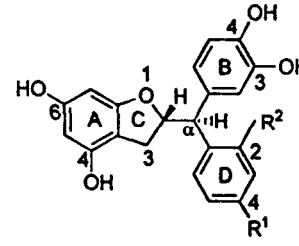
Condensed tannins (polyflavanoids) and, importantly, even whole bark, can be "liquefied" in phenol with an acid catalyst. This process is refered to as phenolysis or phenolation because the phenol acts not only as the solvent but as a reactant. The product can be used directly, without isolating the tannin by extraction from the bark, to partially replace phenol in the formulation of wood adhesives.[1-4] Better understanding of the reactions that take place between phenol and tannin is needed to assess the use of the phenolation of bark tannins in adhesives to bond wood.

(+)-Catechin serves as a model compound for reactions because it is representative of the repeating units in tannins isolated from most conifer tree barks. Mitsunaga and his coworkers[5-7] conducted pioneering studies on the reactions of catechin with phenol in benzene and xylene solvents using BF_3 as the catalyst. They isolated and determined, using NMR and mass spectral techniques, the structures of several reaction products including Compounds 1 and 3.



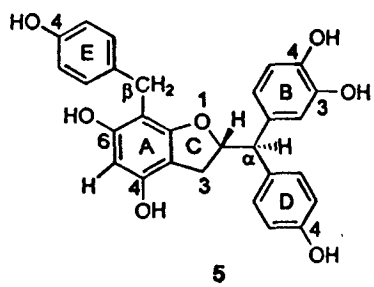
1 R^1 = OH; R^2 = H
2 R^1 = H; R^2 = OH



3 R^1 = OH; R^2 = H
4 R^1 = H; R^2 = OH

Our experiments were primarily directed to phenol both as a reactant and as the solvent in reactions catalyzed with mineral acids. During the course of our investigation, we isolated eight additional reaction products, four of which (2, 4, 5, 6) were compounds that have not been described previously. The structures of these compounds were determined using a combination of mass spectral and NMR techniques. The structures of these compounds are consistent with opening of the pyran ring of catechin and reaction at

C-2 by either the *para* or the *ortho* position of phenol. Additional products resulting from reaction between pyran ring cleavage products and catechin and from reaction of cleavage products were found. Similar reactions would be expected to take place during the phenolysis of condensed tannins.



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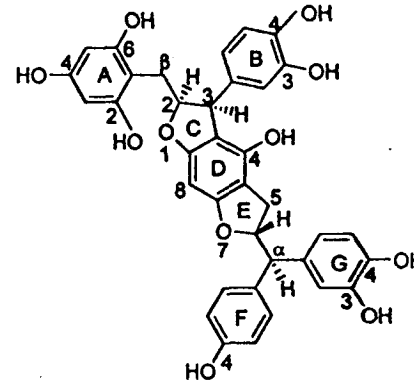

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REFERENCES

1. Santana, M. A. E.; Baumann, M. G. D.; Conner, A. H. *Holzforschung*, 49:146-152, 1995.

2. Santana, M. A. E.; Baumann, M. G. D.; Conner, A. H. In: Leao, A. L.; Carvalho, F. X.; Frollini, E. (eds.) *Lignocellulosic-Plastics Composites*, Universidade de Sao Paulo, Sao Paulo, Brazil, pp. 325-341, 1997.

3. Ono, H. K.; Inoue, A. In: Hse, C. Y.; Tomita, B.; Branham, S. J. (eds.) *Adhesives and Bonded Wood Products*, Proceedings No. 4735, Forest Products Society, Madison, WI, pp. 330-343, 1994.

4. Pu, S.; Yoshioka, M.; Tanihara, Y.; Shiraishi, N. In: Hse, C. Y.; Tomita, B.; Branham, S. J. (eds.) *Adhesives and Bonded Wood Products*, Proceedings No. 4735, Forest Products Society, Madison, WI, pp. 344-355, 1994.

5. Mitsunaga, T.; Abe, I. *Mokuzai Gakkaishi*, 38:585-592, 1992.

6. Mitsunaga, T.; Abe, I.; Nogami, T. *Mokuzai Gakkaishi*, 39:328-332, 1993.

7. Mitsunaga, T.; Abe, I.; Ohara, S. *Mokuzai Gakkaishi*, 38:100-106, 1994.

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