
Communications TO THE EDITOR

Studies on the Barks of the Family Salicaceae. II. Salireposide from the Bark of *Populus tremuloides*

Sir:

In our recent paper¹ on the structure of the new glucoside, tremuloidin, the presence of the glucoside, populin, in the extract of the bark of *Populus tremuloides* was confirmed. Further investigation of the glucosides of *P. tremuloides* bark with diazotized *p*-nitroaniline spray reagent on paper chromatograms indicated that the glucoside mistakenly identified as populin was in fact salireposide, a glucoside first isolated from the bark of *Salix repens* by Wattiez² in 1931. At that time Wattiez showed salireposide to be the benzoate of a phenolic glucoside. Later, Rabaté³ isolated the aglucone and inferred from its empirical formula that it could be gentisyl alcohol. Sakai, Tsurumi, Eno, and Inukai⁴ isolated the same salireposide from a Japanese willow, *Salix purpurea* L. subsp. *angustifolia* Koidz. Still later Fujikawa and Tokuoka⁵ obtained salireposide from another willow, *S. koriyanagi* Kimura, proved the aglucone to be gentisyl alcohol and the glucoside linkage to involve the 2-hydroxyl group of the gentisyl alcohol, and assumed the structure of salireposide to be hydroxypopulin.

Re-examination of several crystalline fractions isolated from the bark of *P. tremuloides*¹ by means of paper chromatography indicated that the glucoside originally reported to be populin gave an intense bluish violet spot when sprayed with diazotized *p*-nitroaniline whereas populin and tremuloidin gave no spots whatsoever. One fraction was recrystallized first from water and then from methanol to give colorless crystals shrinking at 154–156° and melting at 205–206°, $[\alpha]_D^{25} - 35.6^\circ$ (c, 5 in 80% acetone). Acetylation with acetic anhydride in pyridine yielded the penta-acetate melting at 124–126°. These properties are identical with those reported for salireposide.^{2–5} Hydrolysis yielded benzoic acid, glucose, and gentisyl alcohol.

A re-investigation of all glucoside fractions obtained from the bark of *P. tremuloides* by means of paper chromatography and the diazotized *p*-nitroaniline spray indicated substantial amounts of salicin, tremuloidin, and salireposide, but no popu-

lin. This is the first reported instance of the presence of salireposide in a *Populus* species.

Although populin is not present in the bark of *P. tremuloides*, it is definitely present in the bark and leaves of the two European species *P. tremula* and *P. alba*. Earlier indications of the presence of populin in the bark of *P. tremuloides*^{6,7} on the basis of indirect evidence confirm the need for more absolute identification of these glucosides when reporting their presence in plant materials.

Work in our laboratory on the isolation, characterization, and determination of the complete structure of salireposide will be published in future papers.

THE INSTITUTE OF PAPER CHEMISTRY IRWIN A. PEARL
APPLETON, WIS. STEPHEN F. DARLING

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Ring Equivalence and Charge Distribution in Triphenylcarbonium Ion from NMR Spectra

Sir:

We have examined the proton magnetic resonance spectra of triphenylcarbonium and several deuterated and methoxy-substituted triphenylcarbonium ions in order (a) to establish the equivalence or nonequivalence of the three rings, and (b) to ascertain the relative electron densities of the various sites on the phenyl rings. The ions were prepared *via* Grignard reactions from bromobenzene, and subsequent solution of the carbinol in SO₂, sometimes with SnCl₄ added. The specifically deuterated bromobenzenes were prepared as follows: 3,5-*d*, from *p*-bromoaniline with D₃PO₄ in D₂O, and reduction with H₃PO₂; 3,4,5-*d*, as with 3,5-*d*, but reduction with D₃PO₂; 2,4,6-*d*, by heating *p*-bromobenzenesulfonic acid with D₃PO₄ in a sealed tube; and 4-*d*, from *p*-bromoaniline with D₃PO₂ reduction. The identity and purity of the deuterated bromobenzenes were readily ascertained from their NMR spectra. An analysis of the bromobenzene NMR spectrum based on these observations will be forthcoming. The NMR spectra were measured on a Varian 4300B spectrometer at 40 mc. and also on a Varian 4300C spectrometer at 60 mc. No measurable concentration dependence was observed for the aromatic ring protons.

The spectra of undeuterated triphenylcarbonium and tri-*p*-methoxyphenylcarbonium were essentially

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(2) M. N. Wattiez, *Bull. Soc. Chim. Biol.*, 13, 658 (1931).

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(4) S. Sakai, M. Tsurumi, Y. Eno, and F. Inukai, *Bull. Inst. Phys. Chem. Research (Tokyo)*, 22, 868 (1943).

(5) F. Fujikawa and A. Tokuoka, *J. Pharm. Soc. Japan*, 67, 121 (1947).