
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.

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(6) W. Theis, and C. Wehmer in G. Klein, *Handbuch der Pflanzenanalyse*. Bd. III, 2 Teil, Vienna, 1932, p. 845.

(7) R. L. Hossfeld and F. H. Kaufert, *Forest Prods. J.*, 7, 437 (1957).

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

(1) I. A. Pearl and S. F. Darling, *J. Org. Chem.*, 24, 731 (1959).

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

(3) J. Rabaté, *Bull. Soc. Chim. Biol.*, 17, 328 (1935).

(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).

the same as those recently reported by Moodie, Connor, and Stewart.¹ The ions with all rings similarly deuterated gave the following results: 3,5-*d*, two peaks, intensity 1:2, low intensity at low field; 3,4,5-*d*, one peak with weak trace at low field; 2,4,6-*d*, with traces of undeuterated material, one intense peak, with one weak triplet at low fields, and a weak doublet at high fields very close to the intense peak. We have assigned the low field peaks, in agreement with the work of Moodie, Connor, and Stewart,¹ as belonging to the *para*-protons. The group at highest fields must be due to the *ortho*-protons, and the intermediate absorption, close to the *ortho*-peak, arises from *meta*-protons.

The identity of the three rings is established as follows: The 3,5-*d* spectrum may correspond either to two kinds of rings, with essentially no chemical shift within each kind, or to two kinds of positions, with all three rings equivalent. The single strong peak in the 3,4,5-*d* species shows that the *ortho*-positions of all three rings are equivalent, and so therefore must the other positions be also.

The apparent conflict between these results, which establish ring equivalence and those of Newman and Deno² which base nonequivalence on the ultraviolet spectrum, may be resolved by reinterpretation of the origin of the ultraviolet bands. Historically, the virtual identity of the spectra of triarylcarbonium ions with those of related fuchsones has been interpreted as evidence in support of quinoid structure in one (or more) rings. Reconsideration of the nature of the trityl cation chromophore suggests that it should be attributed instead to the ion as a whole. Its ground and first excited electronic energy levels, respectively, can be characterized as the totally symmetric (A) and doubly degenerate (E) combinations of one quinoid and two benzenoid structures. The A \leftrightarrow E transition is allowed and is probably the source of the intense color in triphenylcarbonium and other di- and triarylcarbonium ions as well.³ With only one ring (phenylcarbonium), no such combinations can exist, so no low-frequency absorption takes place.

The shift of the aromatic protons relative to an external water peak is approximately -100 c.p.s., in agreement with Moodie *et al.* The chemical shifts, from audio modulation at 60 mc., give $\delta_{ortho-para} \sim 31$ c.p.s. and $\delta_{meta-para} \sim 21$ c.p.s. Tentative spin coupling values are $J_{ortho-meta} \sim 1.8$ c.p.s. and $J_{meta-para} \sim 3.0$ c.p.s. No *ortho-para* coupling was detected.

The results show that negative charge density

(1) R. B. Moodie, T. M. Connor, and Ross Stewart, *Canad. J. Chem.*, **37**, 1402 (1959).

(2) M. S. Newman and N. C. Deno, *J. Am. Chem. Soc.*, **73**, 3644 (1951).

(3) One of us (RSB) is indebted to Professor W. T. Simpson, The University of Washington, Seattle, for helpful and enlightening discussion of this problem.

is greatest on the *ortho*-positions, slightly less on the *metas*, and considerably less still on the *para*-positions. This is in excellent agreement with the predictions of self-consistent molecular orbital theory, as carried out by Pople⁴; his calculations give the following charge densities: *ortho*-, 0.95; *meta*-, 0.94, and *para*-, 0.81.⁵

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(4) J. A. Pople, *J. Phys. Chem.*, **61**, 6 (1957).

(5) Note added in proof: At the suggestion of Professor Newman, we have examined the proton resonance spectrum of tri-*O*-tolyl carbonium ion at 40 mc., under the same conditions as triphenylcarbonium ion. Steric blocking by the methyl groups effectively prohibits coplanarity of the rings. The magnetic resonance spectrum shows a single sharp methyl peak, thus indicating that even in this extreme case the three rings are equivalent on a time scale of 0.1 sec., and suggests that the molecule is propeller-shaped [cf. N. C. Deno, P. T. Groves, and G. Saines, *J. Am. Chem. Soc.*, **81**, 5790 (1959)].

16,16-Dimethylprednisone Acetate

Sir:

In view of the enhanced anti-inflammatory activity and elimination of sodium retention brought about by introduction of a 16 α -methyl¹ or 16 β -methyl² group into cortical steroids we undertook the synthesis of a suitable 16,16-dimethyl steroid. In the present communication we describe the preparation of 16,16-dimethylprednisone acetate (IV).

The conjugate addition of methylmagnesium iodide³ to 3 α -acetoxy-16-methyl-16-pregnene-11,20-dione (I)^{2a,b} in the presence of cuprous chloride

(1) (a) G. E. Arth, J. Fried, D. B. R. Johnston, D. R. Hoff, L. H. Sarett, R. H. Silber, H. C. Stoerk, and C. A. Winter, *J. Am. Chem. Soc.*, **80**, 3161 (1958). (b) E. P. Oliveto, R. Rausser, L. Weber, A. L. Nussbaum, W. Gebert, C. T. Coniglio, E. B. Hershberg, S. Tolksdorf, M. Eisler, P. L. Perlman, and M. M. Pechet, *J. Am. Chem. Soc.*, **80**, 4431 (1958).

(2) (a) D. Taub, R. D. Hoffsommer, H. L. Slaters, and N. L. Wendler, *J. Am. Chem. Soc.*, **80**, 4435 (1958). (b) E. P. Oliveto, R. Rausser, A. L. Nussbaum, W. Gebert, E. B. Hershberg, S. Tolksdorf, M. Eisler, P. L. Perlman, and M. M. Pechet, *J. Am. Chem. Soc.*, **80**, 4428 (1958). (c) E. P. Oliveto, R. Rausser, H. L. Herzog, E. B. Hershberg, S. Tolksdorf, M. Eisler, P. L. Perlman, and M. M. Pechet, *J. Am. Chem. Soc.*, **80**, 6627 (1958).

(3) M. Kharasch and P. O. Tawney, *J. Am. Chem. Soc.*, **63**, 2308 (1941); R. E. Marker and H. M. Crooks [*J. Am. Chem. Soc.*, **64**, 1280 (1942)] prepared 16 α -alkylpregnan-20-ones by conjugate addition of Grignard reagents to 16-unsubstituted-16-pregnene-20-ones.