contamination. The severe distortions of line shapes observed for these compounds as a result of inhomogeneous sample charging was effectively eliminated by scraping small quantities of the powdered materials into partially roughened surfaces of the gold covered sample holders.

In Figure 1 we present the X-ray photoemission spectra of ruthenium 3d and carbon 1s electrons in both pentaammine and bipyridine systems. As shown, the electron binding energies of the C 1s peak in the *p*-toluenesulfonate (= tosyl) anion for the former system and the same peak as observed in bipyridine for the latter have been arbitrarily assigned a value of 284.4 eV for purposes of comparison (absolute binding energies are not meaningful quantities for irradiated insulators[10,11]). Superposed on the raw data we have indicated the $Ru3d_{5/2}$–$Ru3d_{3/2}$ spin-orbit components split by 4.1 ± 0.1 eV, as determined from analysis of $Ru(NH_3)_5Cl_3$ in which C 1s obstruction is not a problem.

Inspection of Figure 1 reveals conclusively that the valences of ruthenium in the [II, III] salts in both systems are, in spite of their molecular symmetry, inequivalent.[12] This, then, is the necessary (but not sufficient) evidence required for the assignment of the charge-transfer band in the pentaammine system. We should mention that this statement, although inferred from solid-state measurements, is applicable to those measurements made in solution for the pentaammine compounds since the spectral properties in both phases for that system are observed to be virtually identical.[7,13] For the bipyridine system, on the other hand, there is as yet no such firm evidence. It is therefore not inconceivable that the [II, III] bipyridine salt is simply a 50–50 mixture of the constituent [II, II] and [III, III] complexes in the solid phase. We may assume, however, that this is probably not the case based on its similarity to the pentaammine system and on the observation of no significant spectral changes concurrent with different phases for other, similar bridged mixed-valence ruthenium systems we have studied.[14] With this assumption, then, the possibility of not observing the charge-transfer band in solution as a result of electron delocalization is immediately ruled out. This, in turn, implies that the absence of a charge-transfer band in this class II mixed-valence salt[15] stems not from the Franck–Condon energy barrier being too low to observe the transition in the near-ir region but rather from the resonance stabilization in the individual ruthenium sites simply being too large. This resonance stabilization may be understood to result from the additional electron on the Ru(II) site being delocalized over the rather extended bipyridine π system. That we observe Ru(II) and Ru(III) 3d electron binding energies in the [II, III] salts that are slightly converged with respect to those in the [II, II] and [III, III] salts for the pentaammine case and not so converged for the bipyridine case may be interpreted as a reflection of the relative magnitudes of the square of the mixing coefficients coupling the ground and vibrationally excited states[4] and is thus supporting evidence for this explanation. Further discussion of these and other systems will be published in a separate work.

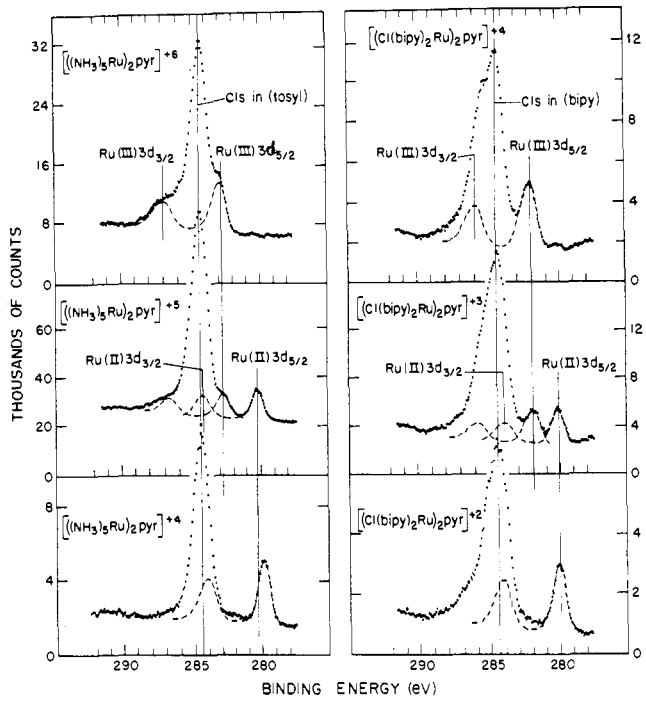

Figure 1. X-Ray photoemission spectra of $[(NH_3)_5Ru(pyr)Ru(NH_3)_5]^{4+,5+,6+}$ and $[Cl(bipy)_2Ru(pyr)Ru(bipy)_2Cl]^{2+,3+,4+}$ salts. The C 1s electron binding energies in both systems have been arbitrarily assigned as 284.4 eV for purposes of comparison.

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(12) Spectra of Ru 3p electrons also clearly show inequivalent ruthenium sites split by 2.7 ± 0.1 eV, consistent with that shown in Figure 1 for Ru 3d electrons. In both spectra the Ru(III) peak heights are smaller than those for Ru(II) but, because the Ru(III) line widths are also slightly larger (owing to multiplet splitting from the unfilled valence 4d band), the relative integrated intensities are 1 :1.
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Structure of Two Triterpenes. Application of Partially Relaxed Fourier Transform ^{13}C Nuclear Magnetic Resonance

Sir:

In the following we describe structural studies with extensive usage of partially relaxed Fourier transform[1] (PRFT) ^{13}C nmr on two triterpenes closely related to

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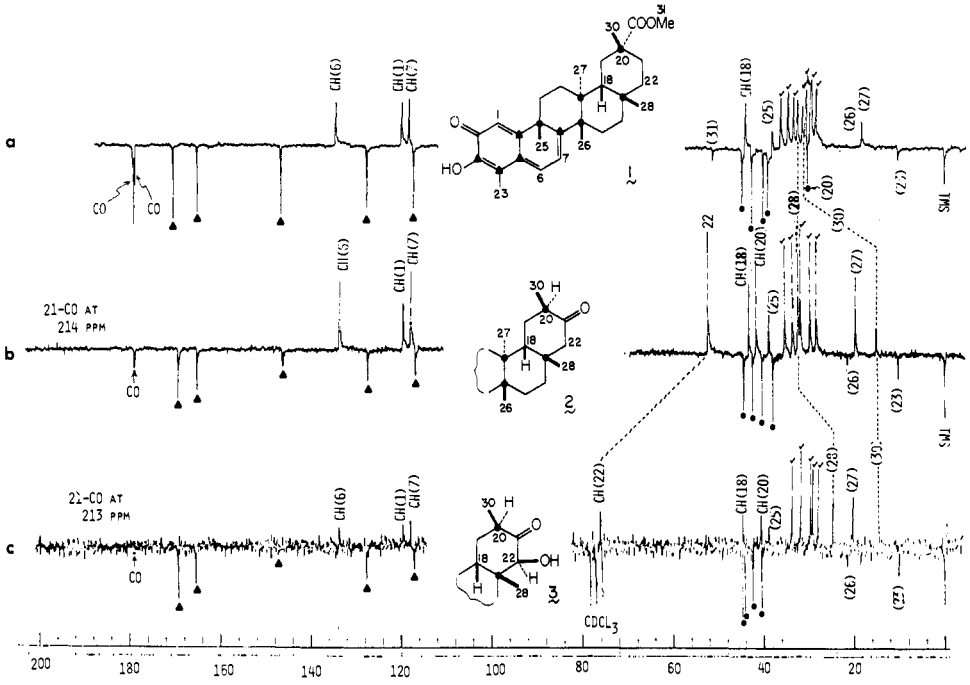
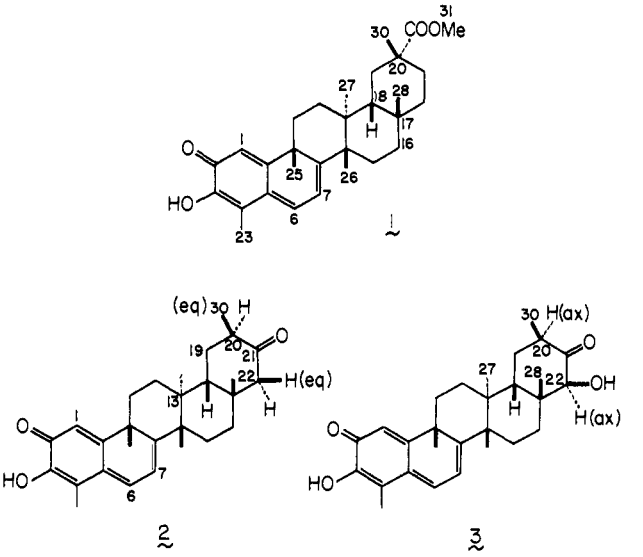


Figure 1. Proton decoupled natural abundance ^{13}C partially relaxed Fourier transform nmr spectra[6] of pristimerin **1** (400 mg), tingenin A **2** (137 mg), and tingenin B **3** (60 mg) in $CDCl_3$ at 25.149 MHz. The number of scans were 512, 9943, and 14,419, respectively. The interval time, τ, between the 180° pulse and 90° pulse was 0.6 sec and the recycle time was 6 sec. The ▲ and ● indicate carbons with no protons, and √ indicates methylene carbons.

pristimerin **1**,[2] a potent but toxic antitumor agent.[3] The leaves of *Euonymus tingens* Wall. (*Celastraceae*), a common Himalayan tree, had previously given[4] epifriedelinol, taraxerol, and dulcitol; in a reinvestigation of a pristimerin-like compound $C_{28}H_{36}O_3$ (tingenone[5]) from its inner stem bark, a 16-oxo-17-desmethyl-20-*gem*-dimethyl structure has been proposed.[5]

Extraction of 5 kg of stem bark with hexane followed by silica gel chromatography gave 1 g of orange crystals, mp 155–165°, from the fraction eluted with $CHCl_3$–MeOH (98:2). Although the crystals gave a single spot on tlc, it was found that they were a mixture of at least 11 components by high pressure liquid chromatography, Waters ALC-100, 3 × 3 ft Corasil II, hexane–$CHCl_3$–CH_3CN (10:1:0.5). From 560 mg of original "crystals," there were obtained two major compounds, tingenin A (137 mg) and tingenin B (36 mg).

The following spectroscopic data show that tingenins A and B are closely related to pristimerin **1**: *tingenin A*, **2** (mp 203–204°), M^+ 420.262 (calcd for $C_{28}H_{36}O_3$, 420.266); uv (MeOH) 253 (sh, ε 7400), 290 (sh, ε 2200), 420 nm(ε 9600); ir ($CHCl_3$) 3600–3300, 1715, 1650 (w), 1595 cm^{-1}; pmr ($CDCl_3$) 2.22 (3 H, s, 4-Me), 6.54 (1 H, d, J = 1.6 Hz, 1-H), 7.05 (1 H, dd, J = 8.0 and 1.6 Hz, 6-H), 6.37 (1 H, d, J = 8.0 Hz, 7-H); *tingenin B*, **3** (mp 210–211°), M^+ 436.260 (calcd for $C_{28}H_{36}O_4$, 436.261); uv (MeOH) 255 (sh, ε 6700), 287 (ε 1300), 420 nm (ε 9900); ir ($CHCl_3$) 3700–3300, 1705, 1650 (w), 1590 cm^{-1}; pmr ($CDCl_3$) 2.22 (3 H, s, 4-Me), 6.53 (1 H, d, J = 1.6 Hz, 1-H), 7.05 (1 H, dd, J = 8.0 and 1.6 Hz, 6-H), 6.38 (1 H, d, J = 8.0 Hz, 7-H). The close similarity with the spectroscopic data of pristimerin **1** [uv (MeOH) 254 (sh, ε 7600), 288 (sh, ε 1900), 424 nm (ε 10,400); ir ($CHCl_3$) 3600–3200, 1725, 1650 (w), 1590 cm^{-1}; pmr ($CDCl_3$) 2.21 (3 H, s, 4-Me), 6.53 (1 H, d, J = 1.6 Hz, 1-H), 7.02 (1 H, dd, J = 8.0 and 1.6 Hz, 6-H), 6.34 (1 H, d, J = 8.0 Hz, 7-H)] clearly showed that the chromophore was identical in all three. This is corroborated by the great similarity in the cmr peaks of carbons C-1 to C-9 which appear at fields lower than 110 ppm (Figure 1).



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The following techniques were employed for analyzing the cmr spectrum[6] of pristimerin: (i) proton noise decoupling, (ii) off-resonance ^1H decoupling, (iii) single frequency decoupling of previously assigned ^1H peaks, (iv) partially relaxed Fourier transform (PRFT) (Figure 1).

The T_1 relaxation times of ^{13}C contained in alicyclic molecules, *e.g.*, cholesteryl chloride[7] or gibberellins,[8] usually increase in the sequence of CH_2, CH, CH_3, and C with no protons.[7] As shown in Figure 1a for pristimerin at an interval time, τ, of 0.6 sec, PRFT is especially useful for assigning ^{13}C peaks in congested spectra. As τ is increased the negative peaks invert to positive peaks in the general sequence shown above; thus, in Figure 1a, quaternary and carbonyl carbons are still negative, all methylene and methine peaks are positive, while the methyl ^{13}C peaks are weakly negative, nulled, or weakly positive. A typical simplification is seen in the 40–50 ppm region of Figure 1b.

The peaks thus assigned to pristimerin were as follows: seven Me groups, 10.2 (C-23), 18.3 (C-27), 21.5 (C-26), 30.8 (C-30)[9] and 31.5 (C-28),[9] 38.2 (C-25), 51.4 (C-31); seven CH_2 groups, 28.6, 29.6, 29.8, 30.4, 33.5, 34.8, 36.3; four CH groups 44.2 (C-18), 118.0 (C-7), 119.5 (C-1), 133.8 (C-6); ten quaternary carbons, 30.5 (C-20), 38.3, 39.3, 40.3, 44.9, 117.1, 127.2, 146.0, 164.0, 169.8; two carbonyl groups, 178.1, 178.4 ppm (Figure 1a).

Tingenin A **2** has a secondary methyl (pmr, 1.00 ppm, br, d 6), which was assigned to C-20, and a carbonyl group (ir, 1715 cm^{-1}) at C-19 or C-21, both assignments based on biogenetic arguments. The cmr spectrum (Figure 1b) fully supports this and, moreover, places the carbonyl at C-21. Namely, the 30.5 ppm quat-C signal (C-20) in pristimerin (Figure 1a) is replaced by a 41.8 ppm methine, a methyl (C-30) is shifted upfield to 15.1 ppm (because it is attached to sec-C),[10] and a *methylene* (C-22) is shifted downfield to 52.4 ppm. Finally, the 20-Me at 1.00 ppm (pmr) is equatorial because of its W-type coupling between the 2.9 ppm 22-eq-H signal (br d, J = 14 Hz) and the large $W_{1/2}$ (18 Hz) of the 20-H (ax) at 2.4 ppm; the 20-Me is also β from the observation of an NOE between 20-H and 13-Me.

In tingenin B **3** (Figure 1c) containing a *sec*-hydroxyl group (3.67 ppm; d, in pmr; disappears with D_2O addition), a new methine (C-22) appears in the cmr at 76.4 ppm instead of the C-22 methylene in tingenin A. Hence the hydroxyl is attached to C-22. In addition, there is seen a high-field shift of a methyl group, which is either 27 or 28. In the pmr spectrum, there was observed a W-type coupling between the 4.55 ppm carbinyl proton (22-H) and a methyl at 0.86 (hence 28), and a 19% NOE between 22-H and a 0.99 ppm methyl (hence 27). It follows that the 22-OH is equatorial (β) and that the methyl which moves upfield from 32.5 to 25.0 ppm in the cmr is C-28. Finally, the 20-H is α and axial because a small (3%) but distinct NOE was observed on 22-H upon irradiation of 20-H.[11,12]

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(11) Support from National Institutes of Health Grant No. CA 11572 is gratefully acknowledged.
(12) NOTE ADDED IN PROOF. Structure **2** with the carbonyl position undetermined has been proposed for the antitumor agent maitenin isolated from *Maytenus* sp. (Celastraceae): F. Delle Monache, G. B. Marini-Bettolo, O. Goncalves de Lima, I. Leoncio D'Albuquerque, and J. de B. Coelho, *Gazz. Chem. Ital.*, **102**, 317 (1972).

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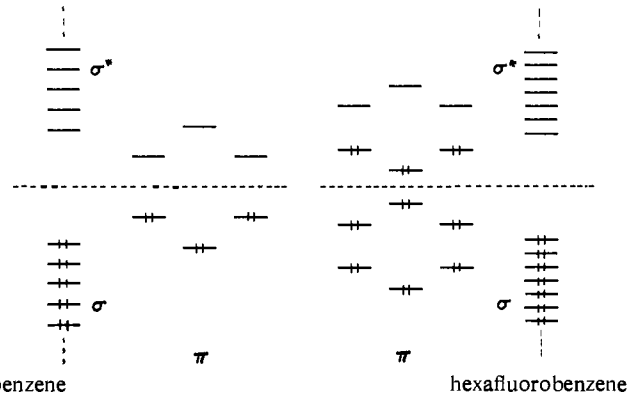
Electron Paramagnetic Resonance of Free Radicals in an Adamantane Matrix. VI.[1] The Hexafluorobenzene Anion Radical

Sir:

The epr spectrum of hexafluorobenzene anion radical in an adamantane matrix at 218°K is shown in Figure 1. It was prepared by 50 kV X-irradiation at 77°K of an adamantane matrix containing ~0.5% hexafluorobenzene and a somewhat larger amount of trimethylamine–borane (TMAB). The smaller lines in the center of the spectrum are due to the anisotropically broadened epr spectrum of a cyclohexadienyl type of radical caused by hydrogen atom addition to hexafluorobenzene. Data on this type of radical together with information on the use of TMAB to stabilize anion radicals will be published later. The $C_6F_6^-$ radical has six equivalent fluorine nuclei with a_F = 137 G and g = 2.0015 as can be seen from the placement of the second-order components[2] in the stick diagram. These fluorine hyperfine splitting constants (hfs) are about ten times larger than would be expected for a π radical based upon all previous results for fluorinated benzyl radicals, fluorinated aromatic cation radicals, and fluorinated aromatic anion radicals.[3] This strongly suggests that the electronic structure of $C_6F_6^-$ is better described as a σ radical than as a π radical. This novel suggestion can be easily understood by consideration of the LCAO–MO diagrams for the valence-electron orbitals of benzene and hexafluorobenzene schematically shown below.



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