related by loss of a proton to the corresponding polynuclear carbonyl anions[17] and could, therefore, in some cases be very strong proton-releasing acids. The electron-deficient polynuclear carbonyl hydrides would also be isoelectronic with polynuclear protonated metal carbonyl species such as $(\pi\text{-}C_5H_5)(CO)_2FeHMn(CO)_5^+$ or $(\pi\text{-}C_5H_5)(CO)_3WHW(CO)_3(\pi\text{-}C_5H_5)^+$ reported by Wilkinson and co-workers.[18] The question of the placement of the hydrogen atoms is the same in these two classes of compound.

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[17] See U. Anders and W. A. G. Graham, *J. Am. Chem. Soc.*, **89**, 539 (1967), and references cited therein.

[18] A. Davison, W. McFarlane, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 3653 (1962).

[19] Work performed during the temporary residence of R. B. and sabbatical leave residence of H. D. K. at Harvard University.

H. D. Kaesz,[19] R. Bau[19]
Department of Chemistry, University of California
Los Angeles, California 90024
M. R. Churchill
Department of Chemistry, Harvard University
Cambridge, Massachusetts 02138

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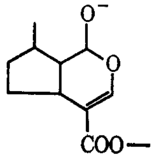
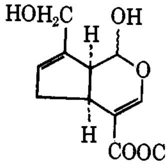
The Total Synthesis of Racemic Genipin

Sir:

Since the pioneering work of Schmid on the structure of plumieride,[1] the group of monoterpenes containing part structure **1** has rapidly expanded. The suggestion[2] that such compounds are intermediates in the biosynthesis of indole alkaloids has recently been supported by preliminary experiments[3] which, however, need confirmation with multiply labeled compounds. Until now no member of this class of natural products has been prepared from the elements, but the present communication reports on a synthesis of genipin (**2**).[4]

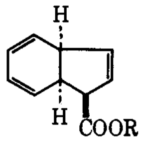


1

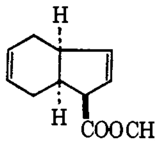


2

The bicyclic ethyl ester **3**[5–7] on base hydrolysis was transformed to the acid **4**, mp 53–55° (lit.[8] mp 51–52°). Reduction with lithium in liquid ammonia followed by esterification with methanol in the presence of *p*-toluenesulfonic acid afforded a mixture of methyl esters containing approximately 90% of **5**.

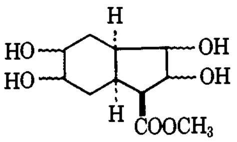


3, R=C_2H_5
4, R=H

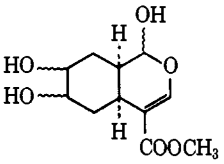


5

When the diene **5** was treated with osmium tetroxide in dimethylformamide and the resulting osmate ester cleaved with hydrogen sulfide,[9] a crystalline tetrol (**6**), mp 163–165°, was formed in 50% yield. Although this material was a mixture of two epimers it was used directly for further transformation. Taking advantage of earlier work which demonstrated that *cis*-cyclopentane-1,2-diols are cleaved much more rapidly with lead tetraacetate than *cis*-1,2-cyclohexanediols,[10] the mixture of tetrols **6** was exposed to 1 equiv of this reagent in glacial acetic acid solution. Oxidation was complete within seconds and chromatography of the resulting mixture of products gave three triols: **7a** [11%; mp 156–157°; infrared absorptions (KBr) 3550, 1700, 1640 cm^{-1}; ultraviolet absorptions in EtOH 240 mμ (ε 10,500), in 0.01 *N* NaOH 273 mμ (ε 19,000)], **7b** [12%; mp 176–177°; infrared absorptions (KBr) 3500, 3355, 1690, 1635 cm^{-1}; ultraviolet absorptions same as those of **7a**], and **7c** [22%; mp 202–208°; infrared absorptions (KBr) 3425, 3250, 1690, 1635 cm^{-1}; ultraviolet absorptions same as those of **7a**]. Investigations aimed at clarifying the configurations of the three triols **7** are incomplete but isomers **7a** and **7b** on consecutive treatments with acetone and with dicyclohexylcarbodiimide–dimethyl sulfoxide[11] yielded the same lactone, **8**, mp 109–110°, having infrared and ultraviolet absorptions identical with those of **7a**. This tentatively indicates that the two triols differ only in the configuration of the hemiacetal carbon atom. Triol **7c** did not yield an acetonide but was quantitatively cleaved by periodic acid.



6



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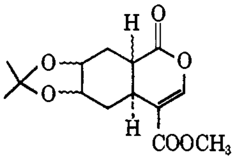

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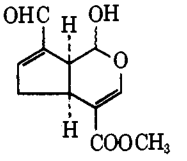

9

The resulting crude dialdehyde was cyclized by the agency of piperidine acetate,[12] and the desired bicyclic aldehyde **9** was obtained in 68% yield in the form of a liquid with infrared absorptions ($CHCl_3$) at 2800, 1700, 1670, 1630 cm^{-1}. Reduction of the aldehyde **9** with lithium tri-*t*-butoxyaluminohydride[13] in ether gave racemic genipin (**2**), mp 116–117°. Identity with natural genipin[14] was established by comparison of infrared,

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[13] H. C. Brown and R. F. McFarlin, *ibid.*, **80**, 5372 (1958).

[14] We are grateful to Professor C. Djerassi, Stanford University, for a sample of natural genipin.

ultraviolet, mass,[15] and proton spectra as well as by the ability of genipin to produce an ineffaceable blue color when applied to skin.[16] An identical series of reactions also served in the transformation of triol **7b** to racemic genipin (**2**).

Acknowledgment. The authors express their thanks for the generous support of this investigation by the National Institutes of Health (GM 09686-06). We also thank Mr. M. Kassenoff for his participation in some phases of this work.

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(15) Mass spectra were measured in the laboratory of Professor K. Biemann, Massachusetts Institute of Technology.

(16) C. Djerassi, J. D. Gray, and F. A. Kincl, *J. Org. Chem.*, **25**, 2174 (1960).

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G. Büchi, B. Gubler, Richard S. Schneider,[17] J. Wild
Department of Chemistry, Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

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Luminescence of Iridium(III) Chelates with 2,2′-Bipyridine and with 1,10-Phenanthroline

Sir:

Very few complexes of transition metal ions having a partly filled d shell are luminescent in fluid solutions. One notable exception is the tris(1,10-phenanthroline)-ruthenium(II) ion; this species and several other Ru(II) chelates with some similar ligands were first reported to luminesce by Brandt and co-workers.[1,2] Paris and Brandt[1] assigned the bands in the absorption spectrum of the tris(2,2′-bipyridine)ruthenium(II) ion and concluded that the emission accompanied a ligand-to-metal charge-transfer ($\pi^* \rightarrow d$) transition. Later, weak absorption bands at 539 mμ (18.550 kK) and at 664 mμ (15.050 kK) were reported for the latter species and led to reassignment of the luminescence as fluorescence associated with a ligand-field ($^1T_1 \rightarrow {}^1A_1$) radiative transition.[3] More recently other workers have concluded that there is no compelling reason to assign the luminescence of the tris(2,2′-bipyridine)ruthenium(II) ion to a ligand-field transition; indeed, there are several sound reasons against such an assignment.[4]

The present work describes luminescence from fluid solutions of the analogous iridium(III) chelates: tris(2,2′-bipyridine)iridium(III) ion, $[Ir(bipy)_3]^{3+}$, and tris(1,10-phenanthroline)iridium(III) ion, $[Ir(phen)_3]^{3+}$. The group theoretical classification of these chelates is D_3. The metallic ion is in an octahedral environment; moreover, these species are diamagnetic: the metallic ion has the low-spin d^6 configuration and geometry analogous to the ruthenium(II) chelates. The emission appears to accompany charge-transfer transitions from the ligand to the metal ion ($\pi^* \rightarrow d$), *i.e.*, similar in kind to that assigned by Paris and Brandt for the luminescence of the Ru(II) chelates.[1]

The ultraviolet–visible absorption spectra for the Ir(III) species are shown in Figure 1. The absorption spectrum of 2,2′-bipyridine in concentrated sulfuric acid is included in Figure 1 because the diprotonated form most nearly approximates chelated 2,2′-bipyridine with respect to the energies of the intraligand ($\pi^* \leftarrow \pi$) transitions. Assignments of the absorption bands are given in Table I.

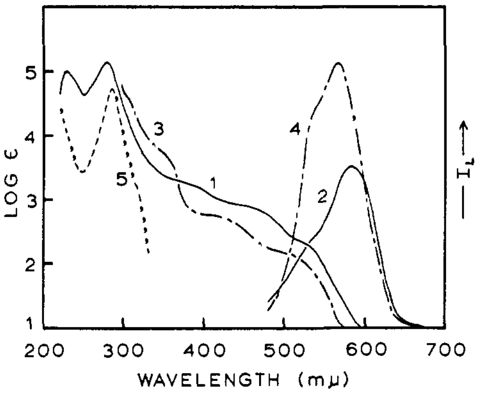

Figure 1. Absorption and luminescence spectra: (1) $[Ir(bipy)_3]^{3+}$ absorption spectrum in DMF; (2) $[Ir(bipy)_3]^{3+}$ luminescence spectrum in DMF, 370-mμ excitation; (3) $[Ir(phen)_3]^{3+}$ absorption spectrum in DMF; (4) $Ir(phen)_3{}^{3+}$ luminescence spectrum in DMF, 475-mμ excitation; (5) 2,2′-bipyridine absorption spectrum in concentrated H_2SO_4. I_L = luminescence intensity (in arbitrary units and corrected for variation of detector response with wavelength).

Table I. Absorption Band Assignments for 2,2′-Bipyridine and 1,10-Phenanthroline Chelates of Ir(III)

Compound	λ_{max}, mμ[a]	Log ε[b]	Assignment
2,2′-Bipyridine[c]	285	4.83	$\pi^* \leftarrow \pi$
$[Ir(bipy)_3]^{3+}$ [d]	235	4.89	$\pi^* \leftarrow d$
	284	5.08	$\pi^* \leftarrow \pi$
	370 (s)	3.2	$\pi^* \leftarrow d$
	480 (s)	2.8	$\pi^* \leftarrow d$
	515 (s)	2.3	$\pi^* \leftarrow d$
$[Ir(phen)_3]^{3+}$ [d]	<300	>4.7	$\pi^* \leftarrow \pi$
	310 (s)	4.4	$\pi^* \leftarrow \pi$
	350 (s)	3.7	$\pi^* \leftarrow d$
	430 (s)	2.7	$\pi^* \leftarrow d$
	520 (s)	2.1	$\pi^* \leftarrow d$

[a] s = shoulder. [b] ε is molar absorptivity. [c] Solvent, concentrated H_2SO_4. [d] Solvent, dimethylformamide.

Jørgensen attributed bands in the range 285–345 mμ in the absorption spectra of 20 Ir(III)–pyridine complexes to ($\pi^* \leftarrow d$) charge-transfer transitions.[5] Spectral studies of the tris(ethylenediamine)iridium(III) ion, $[Ir(en)_3]^{3+}$, in solution show the lowest energy singlet $d^* \leftarrow d$ ($^1T_1 \leftarrow {}^1A_1$) transition at 249 mμ and the lowest energy triplet ($^3T_1 \leftarrow {}^1A_1$) transition at 302 mμ.[6] Both 2,2′-bipyridine and 1,10-phenanthroline are placed above ethylenediamine in the spectrochemical series.[7] Therefore, in $[Ir(bipy)_3]^{3+}$ and $[Ir(phen)_3]^{3+}$ the splitting of the several ligand field states will be larger than in $[Ir(en)_3]^{3+}$, and more energy will be required to effect the $^1T_1 \leftarrow {}^1A_1$ and $^3T_1 \leftarrow {}^1A_1$ transitions. The energy required for a ligand-field transition in the 2,2′-bipyridine and 1,10-phenanthroline chelates of Ir(III) is estimated as approximately equal to the energy necessary for an intraligand ($\pi^* \leftarrow \pi$) transition and thus is greater than that for a charge-transfer ($\pi^* \leftarrow d$) transition. The luminescence of these Ir(III) chelates is therefore assigned to a $\pi^* \rightarrow d$ transition.

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(7) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, Oxford, 1962, p 109.