increase in ϵ_{max} values. Next, the A value for each substituted dibenzoate was actually computed using σ_{max}, $\Delta\sigma$, and r values estimated for the uv spectrum (Table I). In this calculation, two preferred conformations **1** and **2** (Figure 2) were considered, and the coordinates of two point dipoles were assumed to be the same for all substituted dibenzoates. The calculated A values (average value for conformations **1** and **2**)[15] in Table I are in good agreement with observed values and satisfactorily predict the substituent effect. From a practical viewpoint, the chloro- or cyanobenzoates are preferable to other chromophores because of the larger amplitude and ease of preparation.

A similar calculation was performed on a vicinal tribenzoate system, *e.g.*, α-methyl-L-arabinoside 2,3,4-tri-*p*-chlorobenzoate[7] (equatorial–equatorial–axial system). Two apparent Cotton effects are obtained in the tribenzoate system as well, and the longer wavelength Cotton effect sign is in accord with the chiralities of the benzoate chromophores ($A_{calcd} = +122$, $A_{obsd} = +107$).

The symmetrical vicinal tribenzoate (*e.g.*, equatorial–equatorial–equatorial system) does not exhibit a split Cotton effect in agreement with prediction.[7]

As exemplified above for the case of di- and tribenzoates, the aromatic chirality method rests on a sound theoretical background and provides a convenient and versatile method for determining the absolute configurations or conformations of natural products.[1]

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(15) Calculated A values are only slightly affected by conformational rotation: *e.g.*, for *p*-chlorobenzoate, conformations 1 and 2 have $A = -25.8$ and -31.6, respectively.

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Structure of the Antheridium-Inducing Factor of the Fern *Anemia phyllitidis*

Sir:

We assign structure **1** to the antheridium-inducing factor,[1] antheridiogen-An[2] (A_{An}), isolated from culture media of the fern *Anemia phyllitidis* (*Schizaiaceae*).[3] It is the first fern antheridiogen to be characterized, and induces antheridia at 10 μg/l. and also substitutes for light requirement in spore germination at 0.3 μg/l. A total of 1500 flasks, each containing 38 ml of culture medium and cultivated for 53 days, gave 18 mg of pure A_{An}, powder.[4]

The following derivatives of A_{An} [ir (KBr) 1758 (γ-lactone), 1723 cm^{-1} (hindered carboxyl)] were employed in structural studies: methyl ester **2** [(with diazomethane) mass spectrum, M$^+$ peak at 360.1584[5] (calcd for $C_{20}H_{24}O_6$, 360.1573); uv, end absorption; ir (chf), 1761 (γ-lactone), 1729 cm^{-1} (ester)], methyl ester monobenzoate **3** and dibenzoate **4** (with benzoyl chloride–pyridine), and methyl ester monoketone **5** (with chromic anhydride–pyridine). Derivatives **2–4** were submitted to extensive nmr studies (100, 220, and 300 MHz)[6] which established the presence of groups I–III.

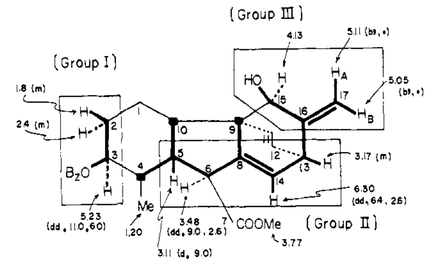

Figure 1. Nmr data of methyl ester monobenzoate **3**: ■, carbons bearing no H; the thick solid and dotted lines connect protons interrelated by nmr.

Groups I, II, and III (Figure 1). Carbinyl proton 3-H[7] (3.74 ppm in ester **2**) is axial ($J_{3,2ax}$ 11 Hz) and is coupled to two other adjacent protons. The system 5-H(ax)–6-H(ax)–14-H(olefinic)–13-H was deduced in a straightforward manner; the 13-H is further coupled to proton(s) around 1.5 ppm. Carbinyl proton 15-H (5.87 ppm in dibenzoate **4**) is weakly coupled to the two exocyclic protons (decoupling). The presence of group III is ascertained from the data of monoketone **5**: uv (EtOH) 217 nm (ε 4750); nmr ($CDCl_3$, Fourier transform) H_A at 5.78 (br, s) and H_B at 5.21 ppm (br, s).

Derivation of Planar Structure. Irradiation at 3.17 ppm (13-H) in monobenzoate **3** caused a small but definite increase in the 17-H_B signal area (*ca.* +2.7%) (at 100 MHz, also at 300 MHz). Observation of this crucial NOE allows one to link group II and group III so that they comprise one continuous proton system as in Figure 1. A methyl singlet was present at 1.17–1.28 ppm in all derivatives. Evidence for attachment of this methyl at C-4 and presence of a 6–5–6 ring system was established by microselenium dehydrogenation of A_{An} to yield 1-methylfluorene (purified by sublimation), which was compared with an authentic sample by uv, tlc with several solvents, and Fourier transform nmr. Evidently the allylic alcohol moiety is lost upon selenium dehydrogenation.

The diaxial relation of 5-H and 6-H ($J_{5,6}$ = 9.0–9.6 Hz) in all derivatives **2–5** precludes involvement of C-6 in any bridged system, and hence the methoxycarbonyl group must be attached to C-6. Because C-10 bears no hydrogen, the γ-lactone then can only be connected between C-4 and C-10, with its carbonyl terminal at C-4, as deduced from the 4-Me chemical shift (1.17–1.28 ppm in **2–5**; 1.13–1.22 ppm in models **6–9**).

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(1) W. Döpp, *Ber. Deut. Bot. Ges.*, **63**, 139 (1950).

(2) U. Näf, *Nature* (*London*), 184, 798 (1959).

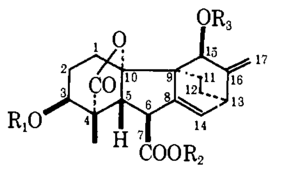
(3) M. Endo, K. Nakanishi, and U. Näf, *Science*, submitted for publication.

(4) A_{An} and derivatives were all purified by tlc and the purity was checked by nmr and mass spectral data; due to scarcity of material, no attempts were made to crystallize the compounds.

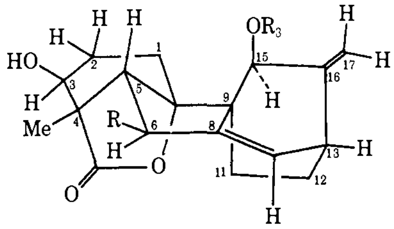
(5) We thank Dr. G. van Lear, Lederle Laboratories, for the full high-resolution mass spectrum of methyl ester 2 (measured with a MS-9 instrument).

(6) J values were verified by decoupling experiments. We thank Mr. I. Miura for the measurements carried out at Columbia University, and Mr. L. Cary for measurments taken at 300 MHz at Varian Associates.

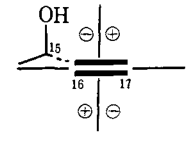
(7) In view of the close relation between gibberellins and A_{An}, the gibberellane (gibbane) nomenclature is adopted. The numbering system is based on the third revision of diterpene nomenclature as proposed to IUPAC by J. W. Rowe, USDA, Madison, Wisc.



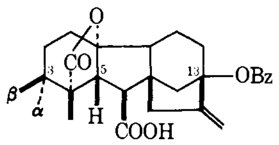
1, $R_1 = R_2 = R_3 = H$
2, $R_1 = R_3 = H; R_2 = Me$
3, $R_1 = Bz; R_2 = Me; R_3 = H$
4, $R_1 = R_3 = Bz; R_2 = Me$
5, $R_1 = H; R_2 = Me$; C=O at C-15



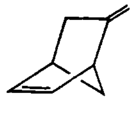
1a, R = COOH



1b



6, 3β-OH, 3α-H
7, 3β-OBz, 3α-H (5.21 ppm, t, $w_{1/2}$ 7 Hz)
8, 3α-OH, 3β-H
9, 3α-OBz, 3β-H (5.02 ppm, dd, $J = 10.4, 6.2$ Hz)



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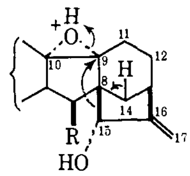

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Data presented so far define the planar structure excepting the point of attachment of one hydroxyl group (C-3 or C-1). All major peaks in the high-resolution mass spectrum of ester 2[5] were in full agreement with the deduced planar structure.[8]

Determination of 3β-Hydroxyl. If the nonallylic hydroxyl were at C-1 the two hydroxyls would be in close proximity. An exciton splitting[9] would then be expected in dibenzoate 4, and this would result in two strong ($\Delta\epsilon$ 10–15) Cotton effects of opposite signs around 233 and 219 nm.[10] As this was clearly *not* the case,[11] the hydroxyl is at C-3.

Its β nature is clear from comparisons with data of gibberellin A_1 (GA_1) 6 and pseudo-GA_1 8 (chromic anhydride–pyridine oxidation of GA_1 followed by sodium borohydride reduction at 0°). Benzoylation of 3β-OH in 6 to give 7 results in a 0.26-ppm downfield shift of the 5β-H doublet ($J = 10$ Hz), *i.e.*, from 3.21 to 3.47 ppm; in the epimeric pseudo-GA_1 series there is hardly any change, *i.e.*, 2.79 ppm in 8 and 2.80 ppm in 9 (both d, $J = 10.5$ Hz). A 0.24-ppm downfield shift is observed in going from A_{An} ester 2 (2.87 ppm, d, 9.6) to 3-monobenzoate 3 (3.11 ppm, d, 9.0). The 3-hydroxyl is therefore cis to the 5β-H.[12]

The C–D Ring Structure. Stereochemistry of the bicyclo[2.2.2] system containing the homoconjugated diene and the allylic alcohol group is considered next. The CD of ester 2 (in MeOH) has a maximum at 215 nm ($\Delta\epsilon$ +13.2), but the 200–215-nm curve shape indicates that this region is a composite curve[13] ($\Delta\epsilon$ reading at 200 nm is +11.4).

The published ORD curve of (+)-1(1*R*)-5-methylenebicyclo[2.2.1]hept-2-ene (10)[15] shows that $\Delta\epsilon$ of the chiral homoconjugated diene is at least *ca.* +40 at 220 nm (or probably at shorter wavelength). A bicyclodiene moiety with similar geometry is present in A_{An} (1a), and it is clear that the short-wavelength CD curve of ester 2 should be dominated by the strong Cotton effect arising from this chiral diene moiety. As model 10 and A_{An} ester 2 both exhibit positive CD, it follows that the exocyclic methylene is at C-16 (positive chirality) and not at C-12 (negative chirality).

The CD extrema at *ca.* 205 nm ($\Delta\epsilon$ 6–15) of bicycloallylic alcohols of the type encountered in gibberellins[14] and 15-hydroxykaur-16-enes have been analyzed on the basis of an inverse octant rule[16] (*e.g.*, see 1b). The positive but lower $\Delta\epsilon$ of ester 2 (+13.2 at 215 nm) as compared to model 10 (*ca.* +40) and the compositive shape of the 200–215-nm region CD curve (see above) indicates that the 15-OH is exerting a negative effect (1b) around 205 nm and therefore it should be β (1a). The relative stereochemistry at all chiral centers has thus been deduced.

Absolute Configuration. The CD curve of 3-monobenzoate 3 (in MeOH) has, in addition to the 215-nm maximum of 2 (see above), a shoulder at 228 nm, the differential curve leading to $\Delta\epsilon$ *ca.* +6.0. These $\Delta\epsilon$ and wavelength values, which are typical for isolated benzoates,[17] indicate that the benzoate sector method[17] can be applied to 3 unambiguously. This leads to a 3*S* configuration for A_{An} 1 (or 1a).

Significantly, a close structural relation between A_{An},

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(8) The peaks formed were those resulting from losses of elements of H_2O, HCO_2H, HCO_2CH_3, CO_2, CO, CH_3OH, and C_2H_4 in various sequences.

(9) A. S. Davydov, "Theory of Molecular Excitons," M. Kasha and M. Oppenheimer, Jr., Transl., McGraw-Hill, New York, N. Y., 1962; J. A. Schellman, *Accounts Chem. Res.*, 1, 144 (1968).

(10) N. Harada and K. Nakanishi, *J. Amer. Chem. Soc.*, 90, 7349 (1968).

(11) CD of dibenzoate 4 (in MeOH): $\Delta\epsilon$ + 8.0 (229 nm), $\Delta\epsilon$ +23.0 (205 nm).

(12) The difference in the coupling pattern of 3α-H in GA_1 benzoate 7 (t, see 7) and A_{An} benzoate 3 (dd, Figure 1) shows that rings A adopt, respectively, a chair form and twist boat form (see 1a). This variance is probably due to the different C–D ring structures.

(13) The γ-lactone CD need not be considered in the present discussion because of its position and small intensity (see ref 14).

(14) *E.g.*, CD of GA (6, 13-OH) (in MeOH): $\Delta\epsilon$ −0.80 (227 nm, γ-lactone), $\Delta\epsilon$ +6.1 (207 nm, allylic OH). For CD of gibberellins around 230 nm (γ-lactone), see: H. Meguro, K. Tuzimura, and N. Takahashi, *Tetrahedron Lett.*, 6305 (1968).

(15) L. S. Forster, A. Moscowitz, J. G. Berger, and K. Mislow, *J. Amer. Chem. Soc.*, 84, 4353 (1962); the recorded ORD is a plain curve measured and calculated only to 220 nm ([Φ] +8000). See also B. Bosnich, A. De Renzi, G. Paiaro, J. Himmelreich, and G. Snatzke, *Inorg. Chim. Acta*, 3, 175 (1969).

(16) The olefin symmetry rule [A. I. Scott and A. D. Wrixon, *Tetrahedron*, 26, 3695 (1970)] has successfully been extended to allylic alcohols to predict their configurations: A. I. Scott and A. D. Wrixon, *ibid.*, in press. We thank Professor Scott for furnishing us a copy of their paper prior to publication.

(17) N. Harada and K. Nakanishi, *J. Amer. Chem. Soc.*, 90, 7351 (1968); N. Harada, M. Ohashi, and K. Nakanishi, *ibid.*, 90, 7349 (1968).

the first member of a new class of diterpenes, and the gibberellins is immediately obvious; *i.e.*, an intermediate such as **11**, readily derivable from a gibberellin, could undergo facile rearrangement leading to the A_{An} skeleton with the correct absolute configuration and C–D configuration. Antheridium-inducing properties of gibberellins have indeed been previously noted, although at a much lower threshold activity, *i.e.*, 1 mg/l. for GA_3[18] and 0.3 μg/l. for A_{An}.[19,20]

[18] H. Schraudolf, *Nature* (*London*), 201, 98 (1964).

[19] Physiological activity tests are being carried out by Dr. G. W. Keitt, Jr., Brooklyn Botanical Gardens, as well as by one of us (U. N.).

[20] The study was supported by Public Health Service Grant No. CA-11572 and the Hoffmann-La Roche Co.

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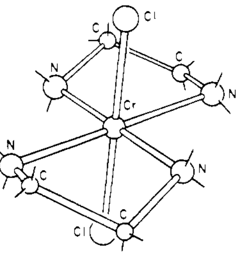
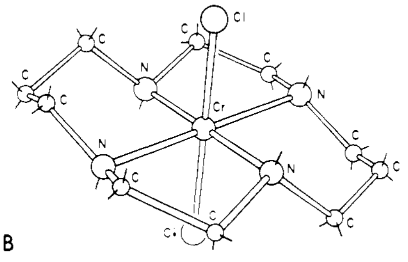
trans-Dichloro-1,4,8,11-tetraazacyclotetradecanechromium(III). A Photoinert Chromium(III)–Ammine Complex

Sir:

Some 25 Cr(III) complexes of the type MA_5X, MA_4X_2, and $M(en)_2X_2$ (X denotes a halogen, pseudohalogen, or water; A is NH_3; and en is ethylenediamine) have been investigated photochemically in various laboratories.[1–3] The general observation has been one of photosubstitution, with solvent (usually water) replacing selectively either the X or the ammine ligand with a quantum yield, ϕ, of 0.1–0.5. So consistent has been the pattern that a set of rules[4] ("Adamson's empirical rules"[2,5]) reliably predicts the course of the net photoreaction on irradiation of the L_1 (first) or L_2 (second) ligand-field band. Thus compound A, *trans*-$Cr(en)_2Cl_2^+$, is correctly predicted to show primarily chloride aquation; the observed ϕ_{Cl^-} value is 0.32–0.35.[6] Compound B, *trans*-$Cr(cyclam)Cl_2^+$ (cyclam = 1,4,8,11-tetraazacyclotetradecane), should show essentially the same photochemistry as A, since the geometric and ligand-field environment is about the same. We consider it newsworthy and potentially very significant that B is in fact photoinert.



A



B

Adamson's rules are referenced to a pseudooctahedral framework of three mutually perpendicular axes, and designate the weak ligand axis as the one photolabilized; if this axis bears two different ligands, the stronger field one of the two is preferentially labilized. It has been inferred that the rules imply the stereochemical course of the photosubstitution;[2,5,7–9] this would follow *if* the octahedral framework remains rigid during the process. This inference need not be correct. If, for example, the mechanism is one of dissociation of the labilized ligand, the pentacoordinated residue need only collapse to a trigonal-bipyramidal geometry for stereospecificity to be lost on coordination of a solvent molecule. While retention of configuration may occur,[10] it now appears that stereomobility is more common.[2,5–9,11] An especially clear demonstration of stereomobility is that in the case of A the axial ligand aquates, yet the photoproduct is *cis*- rather than *trans*-$Cr(en)_2(OH_2)Cl^{2+}$;[6] there is experimental uncertainty in the $Cr(NH_3)_5X^{2+}$ series as to which ammonia is in fact replaced. It thus appears that the photoproduced reactive state is not usually stereorigid, and the present investigation was undertaken to test whether the *imposition* of such rigidity, as in B, leads to behavior differing from that of the nonrigid analog A.

Compound B was prepared as the perchlorate salt[12] and converted to the nitrate by ion exchange. We observe a spectrum showing absorption maxima at 568 nm (22) and 366 nm (37), with a shoulder at 407 nm (33) (numbers in parentheses are the extinction coefficients in M^{-1} cm^{-1}), in good agreement with the published values.[12] The chloride analysis showed 25.44% Cl (calculated, 25.16%); also, on prolonged heating, thermal aquation yielded two chlorides per chromium.

Solutions 1.1×10^{-3} *M* in B and acidified with nitric acid to a pH of 2.40 were irradiated at 22° either at 546 or at 408 nm, using a PEK lamp with suitable interference and blocking filters. Reineckate[13] and ferrioxalate actinometry[14] were used for the two wavelengths,

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[1] A. W. Adamson, W. L. Waltz, E. Zinato, D. W. Watts, P. D. Fleischauer, and R. D. Lindholm, *Chem. Rev.*, 68, 541 (1968).

[2] V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds," Academic Press, New York, N. Y., 1970.

[3] A. D. Kirk, K. C. Moss, and J. G. Valentin, *Can. J. Chem.*, **49**, 375 (1971).

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[6] A. D. Kirk, K. C. Moss, and J. G. Valentin, *Can. J. Chem.*, **49**, 1524 (1971).

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[9] P. Riccieri and H. L. Schläfer, *ibid.*, **9**, 727 (1970).

[10] E. Zinato, R. D. Lindholm, and A. W. Adamson, *J. Amer. Chem. Soc.*, 91, 1076 (1969).

[11] E. Zinato, private communication regarding $Cr(NH_3)_5X^{2+}$, where X denotes acetato or substituted acetato.

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[14] C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc. Ser. A*, **235**, 518 (1956).