heated above *ca.* 265°. It is soluble in acetone and acetonitrile, but only sparingly in chloroform.[16]

An interesting property of the bis(pentalenylcobalt) molecule VI is that it is diamagnetic. Bis(*as*-indacenylcobalt) in contrast is paramagnetic.[17] The implication is that there is a cobalt–cobalt bond in the former and not in the latter, presumably because a bond of normal length (2.5 Å)[18] can be accommodated in the pentalene system,[2] but would be stretched in the *as*-indacene cystem.[19] The iron complex, III or IV, when crystalline is moderately stable in air although it begins to decompose after several hours. Air destroys solutions rapidly. The cobalt complex VI is similarly stable. The cobalticinium compound, VII or VIII, is stable in air both as a solid and in solution.[22]

Thus, at least two kinds of transition metal complexes of pentalene can be formed: those like I or VI in which two metals are sandwiched between a pair of rings, and those like bis(pentalenyl)iron (III or IV) or bis(pentalenyl)cobalticinium ion (VII or VIII), in which one of these metals is removed and the remaining free valencies[23] at carbon unite.

Acknowledgment. We are grateful to the U. S. Army Research Office-Durham for its support under Grant No. DA-ARO(D)-31-124-G1119.

(16) λ_{max} (CH_3CN) 310 nm (ε 6030), 367 (ε 3320).

(17) Unpublished experiment in this laboratory by Dr. N. Acton.

(18) M. C. Baird, *Progr. Inorg. Chem.*, **9**, 1 (1968).

(19) The distance between the two iron atoms in bis(*as*-indacenyliron) is 3.887 Å[20] and between the two nickel atoms in bis(*as*-indacenylnickel) 4.40 Å.[21]

(20) R. Gitany, I. C. Paul, N. Acton, and T. J. Katz, *Tetrahedron Lett.*, 2723 (1970).

(21) Prepared by us and X-rayed in the laboratory of Professor Iain C. Paul (unpublished experiments).

(22) Cobalticinium salts are much more resistant to oxidation than are ferrocenes. The simple salts withstand boiling nitric acid, potassium permanganate, and ozone [E. O. Fischer and G. E. Herberich, *Chem. Ber.*, **94**, 1517 (1961)].

(23) J. Thiele, *Justus Liebigs Ann. Chem.*, 306, 87 (1899).

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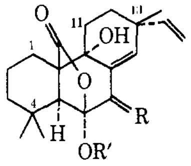
Structures of Fungal Diterpene Antibiotics LL-S491β and -γ

Sir:

We report the isolation and structural elucidation of two novel pimarane diterpenes LL-S491β (**1**) and -γ (**2**) from fermentations of the fungus *Aspergillus chevalieri* (Lederle culture S491). LL-S491β displays significant antibacterial activity against certain gram-positive organisms and LL-S491γ exhibits antiviral activity against *Herpes simplex*. Both compounds possess strong antiprotozoal activity against *Tetrahymena pyriformis*. The isolation of these metabolites is especially noteworthy in that diterpenes appear to be of limited distribution among fungi[1] and the only other pimarane examples have been the virescenols, the glycosides[2] of which also show antibacterial activity.



1, R = O; R′ = H
2, R = β-OH, α-H; R′ = H
3, R = O; R′ = Ac

A pimarane or closely related skeleton[3] for LL-S491β (**1**), $C_{20}H_{26}O_5$, mp 180–185°, $[\alpha]_D$ +112.4° (MeOH), is suggested by the very characteristic eight-line nmr[4] pattern at δ 5.02–5.65 (2 H) and a four-line system at 5.84 (1 H) typical of vinyl protons of a C_{13} vinylidene grouping.[5] Three tertiary C-Me's are indicated by signals at δ 1.09 (3 H, s) and 1.20 (6 H, s), and a doublet in the ir at 1370 cm^{-1} in the spectrum of **1**, **2**, and many of their derivatives suggest that two C-Me's are geminal.[6] Hydroxy, γ-lactone, ketone, and double bond functionalities are indicated by ir bands at 3500, 1755, 1710, and 1620 cm^{-1}, respectively. Two 1 H exchangeable nmr signals at δ 1.90 and 5.25 resonate as sharp singlets indicative of two tertiary hydroxyl groups. Pyridine-catalyzed acetylation of **1** gave monoacetate **3**, containing a broad 1785-cm^{-1} ir band suggestive of a γ-lactol acetate system. The nmr of **3** is devoid of the C_6OH signal at δ 5.25 but the C_9OH proton signal shifts to 2.15.

A uv maximum at 241 nm (ε 5850)[7] in the spectrum of **1** supports the presence of an α,β-unsaturated ketone (1710 cm^{-1}) which is cisoid because of the strong intensity of the 1620-cm^{-1} ir absorption.[8] The H_{14} signal resonates at δ 6.86 (J ± 1 Hz)[9] consistent with this view. The unusually high ketone frequency is undoubtedly due to electronic interactions with the nearby oxygen functions and has ample precedent in certain picrotoxinin derivatives.[11]

Borohydride reduction of **1** gave LL-S491γ (**2**), mp 190–195°, $[\alpha]_D$ +69.3° (MeOH), which has only end

(1) W. B. Turner, "Fungal Metabolites," Academic Press, New York, N. Y., 1971, p 235.

(2) N. Cagnoli-Bellavita, P. Ceccherelli, R. Mariani, J. Polonsky, and Z. Baskevitch, *Eur. J. Biochem.*, **15**, 356, (1970), and references therein; N. Cagnoli-Bellavita, German Offen. 2,100,918 (1971); *Chem. Abstr.*, **75**, 130094*t* (1971).

(3) R. McCrindle and K. H. Overton in "Rodd's Chemistry of Carbon Compounds," S. Coffey, Ed., Vol. II, Part C, Elsevier, London, 1969, Chapter 14.

(4) Satisfactory analyses (high-resolution mass spectral and in some cases elemental) were obtained for all compounds reported; uv spectra were taken in methanol, ir in KBr discs, and nmr spectra in deuteriochloroform at 100 MHz. We thank W. F. Fulmor and L. Brancone and associates for the spectral and analytical data, Dr. G. Van Lear for the mass spectra, and P. Mullen of the Stamford Laboratories for the CD curves. We also wish to thank A. Shay, M. Dann, and associates for the large scale fermentations and initial processing, Dr. H. Tresner for the identification of the culture, and A. Dornbush, Dr. H. Lindsay, H. Lindh, and staffs for the biological testing.

(5) E. Wenkert and P. Beak, *J. Amer. Chem. Soc.*, **83**, 998 (1961); see also R. M. Carman, *Aust. J. Chem.*, **16**, 1104 (1963).

(6) K. Nakanishi, "Infrared Spectroscopy-Practical," Holden-Day, San Francisco, Calif., 1962, p 22.

(7) The uv spectrum in basic solution reveals a bathochromic shift of the maximum to 263 nm (ε 4600) (reversible on addition of acid) which represents the α-diketone chromophore. No evidence for the diosphenol chromophore was observed in the basic spectrum although prolonged exposure to base caused considerable degradation. The existence of the ketonic form to the apparent exclusion of the enolic structure is reminiscent of the chemistry of xanthoperol and 6,7-diketo-5-isodeoxypodocarponitrile: E. Wenkert and B. G. Jackson, *J. Amer. Chem. Soc.*, **80**, 211 (1958).

(8) R. L. Erskine and E. S. Waight, *J. Chem. Soc.*, 3425 (1960).

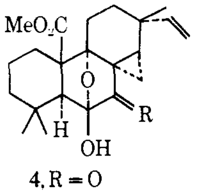
(9) Spin-decoupling experiments have shown the splitting to be due to a proton in the methylene envelope. This is most likely the C_{12} equatorial hydrogen as this would allow for W-type coupling (see ref 10).

(10) S. Sternhell, *Quart. Rev., Chem. Soc.*, **23**, 236 (1969).

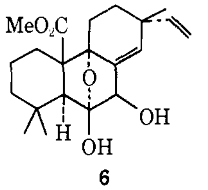
(11) R. M. Carman, G. Hassan, and R. B. Johns, *J. Chem. Soc.*, 130 (1959). See also Y. Mazur and F. Sondheimer, *Experientia*, **16**, 181 (1960), and references therein.

absorption in the uv and γ-lactol absorption at 1745 cm^{-1} in the ir. The stereochemistry of the C_7OH is assigned on mechanistic grounds[12] as well as the $J_{7,14}$ of 2.0 Hz[10] for the H_{14} signal at δ 5.83 and H_7 signal at 4.30. Oxidation of **2** with activated manganese dioxide regenerated **1**.

Esterification of **1** with diazomethane surprisingly gave the cyclopropyl derivative **4** (1730 ($C_7C{=}O$) and 1705 cm^{-1} (CO_2Me)).[13] The cyclopropyl hydrogen nmr signals are obscured by the methylene envelope in the spectrum of **4**. However, they are shifted upfield and thus are clearly visible as a 2 H multiplet at δ 0.50 in the spectrum of **5** (**5** was obtained from **4** by borohydride reduction). Treatment of **2** with diazomethane gave **6** as expected (1720 (CO_2Me), $J_{7,14}$ = 2.5 Hz).

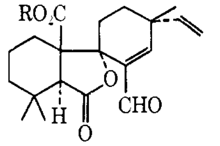


4, R = O
5, R = β-OH, α-H

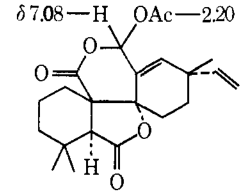


6

The vicinal relationship of the C_7 ketone and terminus of the lactol grouping in **1** is suggested by the strong positive blue tetrazolium reaction[14] given by both **1** and **2**. Periodate oxidation of **2** gave **7** [1775, 1725, and 1685 cm^{-1}; λ_{max} 233 nm (ε 8700)] confirming the color test as well as providing unequivocal evidence as to the arrangement of the C_9 and C_{10} substituents. Sharp 1 H singlets at δ 9.62 and 6.77 in the nmr of **7** are attributable to the aldehyde and C_{14} protons while the carboxyl proton resonates as a rather broad singlet at δ 8.47. Esterification of **7** with diazomethane gave **8**. The trans relationship of the C_{10} and C_9 substituents is indicated by the formation of **9** by treatment of **7** with acetic anhydride and a trace of toluenesulfonic acid.[15] The broad ir absorption at 1785 cm^{-1} is consistent with this formulation as is the lack of uv absorption at 233 nm.

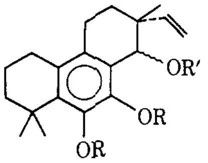


7, R = H
8, R = Me



9

Compelling evidence for the carbon skeleton and for the masked α-diketone system in **1** was obtained by methanolic hydrochloric acid treatment of **1** to give the catechols **10** [λ_{max} 289 nm (ε 2265)] and **11** [λ_{max} 280 nm (ε 2320)]. Three tertiary C–Me nmr signals appear as 3 H singlets at δ 1.25, 1.42, and 1.45 in the spectrum of **10**. A 1 H exchangeable doublet at δ 2.20 (J = 5.0 Hz) is assigned to the secondary benzylic OH proton and the corresponding H_{14} signal resonates at δ 4.72 (J = 5.0 Hz). A 4 H signal (crude triplet) at δ 2.48 in the spectrum of **10** and 2.46 in that of **11** is attributable to the H_1 and H_{11} methylene signals. The remaining six methylene protons resonate at δ 1.60 as compact multiplets in the two spectra. Acetylation of **10** and **11** gave a triacetate **12** (1770 and 1735 cm^{-1}) and a diacetate **13** (1770 cm^{-1}), respectively.



10, R = R' = H
11, R = H; R' = Me (δ 3.50)
12, R = R' = Ac (δ 2.24, 2.30, and 1.92)
13, R = Ac; R' = Me (δ 2.30, 2.41, and 3.34)

Evidence for the nature of the A/B ring fusion in **1** was obtained by the downfield shift of 50 Hz of the H_5 signal (1 H, s) from δ 2.74 to 3.30 when the nmr spectrum of **1** was taken in pyridine as opposed to deuteriochloroform.[16] This result necessitates a 1–3 cis diaxial relation between the C_9 OH and H_5 and in turn a trans A/B fusion. As the γ-lactol defines the spatial arrangement between C_{10} and C_6, the relative stereochemistry at C_5, C_6, C_9, and C_{10} is defined.

The negative Cotton effect at 245 nm of Δε 3.7 (π–π^* of 8(14)-en-7-one) in the CD curve of **1** is in agreement with the corresponding transition for a known 5α,8(14)-en-7-one steroid.[17] This indicates the absolute stereochemistry at the above mentioned centers to be as shown. Supporting evidence was obtained by examination of the CD curve of the 6,7-di-*p*-methoxybenzoate of **2**. Two strong Cotton effects of opposite signs at 280 (Δε −13.2) and 253 nm (Δε +11.0) (exciton splitting)[18] are observed which, on the basis of the dibenzoate chirality rule,[19] indicate a left-handed helix for the C_6–C_7 glycol moiety in **2**.

The CD spectrum of **2** shows a positive Cotton effect at 209 nm with a Δε of 8.3. This is certainly a composite effect being dominated by the strong positive contribution of the C_9 HOCC=C (π–π^*) right-handed helix and to a lesser extent by the right-handed exocyclic C_7 allylic alcohol helix.[20] Included, however, must be the weakly negative effect of the homoconjugated 8(14),15-diene ($C_{13\alpha}$ equatorial vinylidene)

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[12] E. Wenkert, A. Fuchs, and J. D. McChesney, *J. Org. Chem.*, 30, 2931 (1965).

[13] The cyclopropyl group is designated α on the basis that the diazomethane would attack from the least hindered α side of the molecule.

[14] W. J. Nader and R. R. Buck, *Anal. Chem.*, **24**, 666 (1952).

[15] Dreiding models clearly show that a C_{10}–C_9 cis arrangement would not allow closure between the C_{10} carboxyl and C_7 aldehyde functions.

[16] A similar downfield shift is observed with the acetate **3**: P. V. Demarco, E. Farkas, D. Doddrell, B. L. Mylari, and E. Wenkert, *J. Amer. Chem. Soc.*, 90, 5480 (1968).

[17] H. Ziffer and C. H. Robinson, *Tetrahedron*, 24, 5803 (1968); see also A. W. Burgstahler and R. C. Barkhurst, *J. Amer. Chem. Soc.*, **92**, 7601 (1970).

[18] 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).

[19] N. Harada and K. Nakanishi, *J. Amer. Chem. Soc.*, **91**, 3991 (1969).

[20] Δε values of 4.5–11.5 are reported for relevant endocyclic allylic alcohols as opposed to Δε values of 0.25–2.5 for relevant exocyclic systems: A. I. Scott and A. D. Wrixon, *Tetrahedron*, **27**, 4787 (1971); A. F. Beecham, *ibid.*, 27, 5207 (1971). The CD of the γ-lactone is not considered as this transition is usually at longer wavelengths (220–230 nm) and the Δε < 1; see K. Nakanishi, M. Endo, U. Naf, and L. F. Johnson, *J. Amer. Chem. Soc.*, **93**, 5579 (1971).

moiety.[21] The 8(14),15-pimaradiene diterpenes (β axial vinylidene) have strongly positive contributions[21] and if present in **2**, in conjunction with the above mentioned positive allylic alcohol effects, would presumably result in a $\Delta\epsilon$ considerably higher (20–25) than the one observed. Thus we assign the stereochemistry at C_{13} in **1** and **2** as shown.

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[21] C. R. Enzell and S. R. Wallis, *Tetrahedron Lett.*, 243 (1966); the reported ORD values are plain curves measured and calculated to *ca.* 225 nm with $\phi \sim 5000$ for 8(14),15-isopimaradienes and $\sim +29{,}000$ for the epimeric 8(14),15-pimaradienes.

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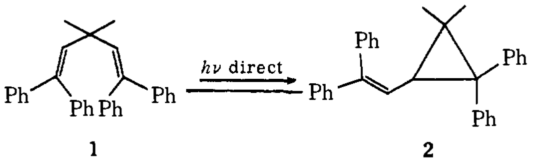
An Unexpected σ + π Rearrangement of a Di-π-methane Reactant. Inhibition of the Di-π-methane Rearrangement. Mechanistic and Exploratory Organic Photochemistry. LXX[1]

Sir:

In previous reports we have noted the ubiquity and mechanism of the di-π-methane rearrangement.[2] Typifying acyclic examples is the very facile rearrangement of dimethyltetraphenyldiene **1**.[2b,c] In contrast, pre-



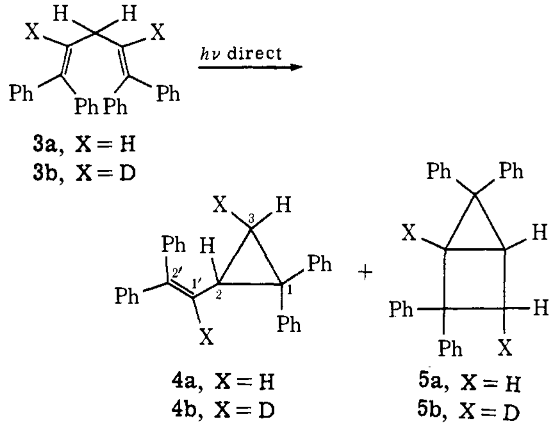
(1)

1 **2**

liminary evidence suggested that analogs lacking central methyl and terminal phenyl substitution rearrange at best with reluctance.[3] To determine the role of central methyl substitution we investigated the photochemistry of 1,1,5,5-tetraphenyl-1,4-pentadiene[4] (**3**).

Presently, we report: (a) a requirement of central methyl substitution for facile di-π-methane rearrangement; (b) the observation of the expected di-π-methane product **4**, however *via* an alternative C–H σ + π mechanism; (c) demonstration that the low reactivity of tetraphenyldiene **3** derives from an inherently low excited state reactivity and not just from rapid competitive decay; (d) formation of a housane product arising not from simple 2 + 2 addition but rather from diversion of a diradical species of the σ + π route; (e) singlet reaction multiplicity.

Preparative photolysis of tetraphenyldiene **3**[5] for 24 hr in *tert*-butyl alcohol gave 12% of 1,1-diphenyl-2-(2,2-diphenylvinyl)cyclopropane (**4a**), mp 101–102°, 11% of 2,2,5,5-tetraphenylbicyclo[2.1.0]pentane (**5a**), mp



3a, X = H
3b, X = D

4a, X = H
4b, X = D

5a, X = H
5b, X = D

(2)

180–181°, and 71% of recovered reactant **3**. The structure of **4a** is that expected for simple di-π-methane rearrangement, and the nmr was consistent with this formulation. Thus on-line graphic computer simulation[7]—choosing chemical shifts as τ_2 7.64, τ_{3c} 8.50 (note subscript 3c refers to cis configuration relative to H at C-2), τ_{3t} 8.46, and $\tau_{1'}$ 4.84, and selecting coupling constants as $J_{23c} = 9$, $J_{23t} = 5.5$, $J_{33} = -6$, and $J_{21'} = 10$ Hz—gave perfect agreement with observation. Absolute structural confirmation derived from the synthesis of **4a** from the reaction of diphenyldiazomethane with 1,1-diphenyl-1,3-butadiene. The gross structure of housane **5a** was initially suggested by the lack of vinyl proton absorption in the nmr (two multiplets at τ 7.50 (3 H) and 6.97 (1 H) plus an aromatic multiplet (20 H) at 3.0) and the ultraviolet spectrum with weak peaks at 263 (1080) and 273 (760) nm characteristic of an unconjugated phenyl-substituted product. That the actual structure was that of **5a** and not the simple 2 + 2 adduct of tetraphenyldiene **3** was established by Pd/C hydrogenation to give the known 1,1,3,3-tetraphenylcyclopentane.[8]

The quantum yield of formation of **4a** on direct irradiation was found to be $\phi = 0.0024$ and that for **5a** was 0.0020. In contrast, acetophenone sensitization gave no detectible reaction (*i.e.*, $\phi < 0.00002$).

The low efficiency in the formation of **4a** on direct irradiation contrasts with the 0.082 efficiency[2b] of the dimethyltetraphenyldiene **1**. That this is an inherent difference in reactivity and not just due to differences in rates of excited state decay was ascertained by assessment of the reaction rates using the method described by us previously[2c] and also by Dalton and Turro.[9] Thus, k_r for singlet excited state formation of vinylcyclopropane **4a** is 1.2×10^{10} sec^{-1} contrasting with $k_r = 7.8 \times 10^{11}$ sec^{-1} [2c] for dimethyltetraphenyldiene **1**.[10]

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[1] For the previous paper in this series see H. E. Zimmerman, P. Baeckstrom, T. Johnson, and D. Kurtz, *J. Amer. Chem. Soc.*, **94**, 5504 (1972).

[2] (a) H. E. Zimmerman, R. W. Binkley, R. S. Givens, and M. A. Sherwin, *ibid.*, **89**, 3932 (1967); (b) H. E. Zimmerman and P. S. Mariano, *ibid.*, **91**, 1718 (1969); (c) H. E. Zimmerman and A. A. Baum, *ibid.*, **93**, 3646 (1971); (d) H. E. Zimmerman and A. C. Pratt, *ibid.*, **92**, 6259, 6267 (1970).

[3] In the gas phase with 112 kcal/mol of mercury sensitization simple di-π-methane systems lacking central substitution do rearrange. For example note: J. Meinwald and G. W. Smith, *ibid.*, **89**, 4923 (1967); R. Srinivasan and K. H. Carlough, *ibid.*, **89**, 4932 (1967).

[4] G. Wittig and B. Obermann, *Chem. Ber.*, **67**, 2053 (1934); **68**, 2214 (1935).

[5] All compounds analyzed properly. Full experimental details will appear in our full paper. Photolyses were run preparatively with a 450-Watt apparatus and quantitative runs were on our Black Box apparatus.[6]

[6] H. E. Zimmerman, *Mol. Photochem.*, **3**, 281 (1971).

[7] (a) D. Juers, R. Boettcher, V. J. Hull, and H. E. Zimmerman, Digital Equipment Users Society Program No. 8-194; (b) D. Juers, Ph.D. Thesis, University of Wisconsin, 1971.

[8] D. H. Richards and N. F. Scilly, *J. Chem. Soc. C*, 2661 (1969).

[9] J. C. Dalton and N. J. Turro, *J. Amer. Chem. Soc.*, **93**, 3569 (1971).

[10] These rates as determined by the indirect method described[2c,9] are best considered as relative to one another. Unpublished results from our laboratories obviate dependence on literature fluorescence quantum yields used for reference and give directly measured values. However, for consistency and comparison with reported values the indirect method is preferable here.