(cis-exo); and (4) although the mass balance for product formation is good to moderate, the remarkably low efficiency of net chemical transformation.

Consider the last point first. One notes that the decrease in reaction efficiency may be explained in terms of the standard mechanism for aryl alkyl ketones if (1) reversible transfer hydrogen in the biradical IV is exceedingly efficient relative to closure and cleavage,[8] or (2) a new deactivation is possible for Id (and to a lesser extent Ia) which effectively degrades electronic excitation of triplets before γ hydrogen abstraction can occur.

With regard to methyl substitution in the ring, the faster rate of deactivation of Id (cis-exo) and Ic (cis-endo) *vs.* Ia suggests that the methyl groups are playing an important electronic rather than steric role in the deactivation process. On the other hand, the substantial deuterium isotope effect on $1/\tau$ for Ie (d-cis-exo) *vs.* Id (cis-exo) suggests that *degradation of electronic excitation is coupled to the electronic influence of the methyl groups via the γ-CH bond!* One can thus view the deactivation as occurring *via* coupling of the electronically excited carbonyl group to the C_2–C_3 cyclopropane bond *via* a γ-CH stretching motion.[9] This motion, of course, implies a strong coupling between the γ-CH stretching vibration and the C_2–C_3 ring stretching vibration; *i.e.*, energy degradation involves specific conversion of electronic energy into vibrational energy associated with a normal mode of the γ-HC_2C_3 unit. Significantly, we have observed that 1,1-dimethoxycyclopropane quenches acetophenone phosphorescence at a rate comparable to simple aliphatic ethers; thus, cyclopropyl ethers, *per se*, do not appear to possess special deactivation paths for standard n,π^* triplets.

In summary, we report that the introduction of remote methyl groups into α-cyclopropoxyacetophenone produces a surprising increase in the rate of chemically nonproductive radiationless decay to ground-state parent ketone. The low reaction efficiencies, compared to model compounds, point to the operation of a novel mechanism for radiationless deactivation not previously encountered in type II photoreactions.[10] The observation of a deuterium isotope effect on triplet ketone lifetime and isomerization efficiency strongly implicates the γ-H in both the novel radiationless deactivation and ring isomerization. We suggest that the fast rates of radiationless decay may result from electronic vibrational coupling in which the stretching of the C_2–C_3 bond,[11] induced by excited ketone γ-H interaction, serves as an energy sink.

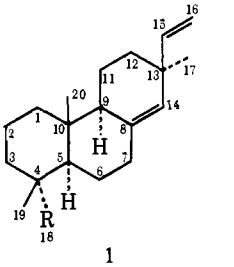
Acknowledgment. The authors wish to thank Professor Frederick D. Lewis for a preprint of his work on α-cyclopropoxyacetophenone and for productive and stimulating discussions. The authors also thank the referees for making several valuable comments on the original manuscript. They also acknowledge the Air Force Office of Scientific Research for its generous support of this work (Grant No. AFOSR-70-1848D).

Thomas R. Darling, Nicholas J. Turro*
Department of Chemistry, Columbia University
New York, New York 10027
Received October 7, 1971

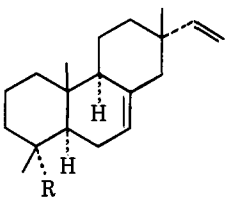
Carbon-13 Nuclear Magnetic Resonance Spectroscopy of Naturally Occurring Substances. X. Pimaradienes[1]

Sir:

In continuation of our ^{13}C nmr study of organic natural products the first systematic analysis of diterpenic compounds was undertaken. The following chemical-shift data for the pimaradienic substances **1**–**4** were utilized for the determination of the otherwise difficultly assignable ring C conformation of the $\Delta^{8(9)}$-pimaradienes (**4**) as well as for the elucidation of the biosynthesis of the virescenosides, fungal isopimaradienic glycosides.[2]

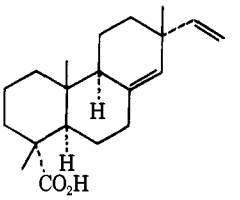


1



2

a, R = Me
b, R = CH_2OH
c, R = CO_2H



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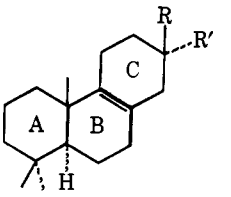


4a, R = C_2H_3; R′ = Me
b, R = Me; R′ = C_2H_3

Application of chemical-shift theory[3] to the noise decoupled and off-resonance decoupled spectra[1] of the nine compounds and inspection of cmr spectra of pimarol (**1b**) in the presence of the paramagnetic shift agent,[4] $Pr(dpm)_3$, yielded the data collated in Table I.

(8) For this situation to be the case, nearly 99% of the biradicals derived from Id, compared to only about 1% of the biradicals derived from IIa, would be required to reabstract the hydroxyl hydrogen without prior transformation.
(9) B. H. Al-Sader and R. J. Crawford, *Can. J. Chem.*, 46, 3301 (1968).
(10) Any alternative deactivation, such as charge transfer or reversible carbonyl addition to the ring, which accounts for the ring isomerization and the large inefficiency must contribute the entire deuterium dependence in $1/\tau$.
(11) The ring cleavage of conjugated cyclopropyl ketones is a well-established photochemical process. For leading references see: D. N. Marsh, J. N. Pitts, Jr., K. Schaffner, and A. Truinman, *J. Amer. Chem. Soc.*, 93, 333 (1971); H. E. Zimmerman, S. S. Hixon, and E. F. McBride, *ibid.*, 92, 2000 (1970); and W. H. Dauben, L. Schutte, and R. E. Wolf, *J. Org. Chem.*, 34, 1849 (1969).

(1) For the preceding paper see E. Wenkert, D. W. Cochran, F. M. Schell, R. A. Archer, and K. Matsumoto, *Experientia*, 28, 250 (1972).
(2) J. Polonsky, Z. Baskevitch, N. Cagnoli-Bellavita, P. Ceccherelli, B. L. Buckwalter, and E. Wenkert, *J. Amer. Chem. Soc.*, 94, 4369 (1972).
(3) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 2, Pergamon Press, New York, N. Y., 1966; D. K. Dalling and D. M. Grant, *J. Amer. Chem. Soc.*, 89, 6612 (1967); H. J. Reich, M. Jautelat, M. T. Messe, F. J. Weigert, and J. D. Roberts, *ibid.*, 91, 7445 (1969); D. W. Cochran, Ph.D. Dissertation, Indiana University, 1971.
(4) *Cf.* M. Christl, H. J. Reich, and J. D. Roberts, *J. Amer. Chem. Soc.*, 93, 3463 (1971); J. Briggs, F. A. Hart, G. P. Moss, and E. W. Randall, *Chem. Commun.*, 364 (1971); O. A. Gansow, M. R. Willcott,

Table I. Cmr Chemical Shifts[a]

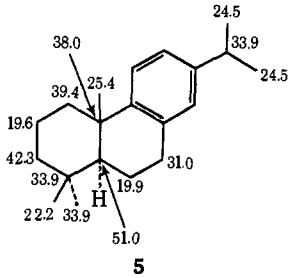
	1a[b]	1b[c]	Δ_{Pr}[d]	1c[b]	2a[c]	2b[c]	2c[b]	3[c]	4a[c]	4b[c]
C-1	39.7	38.3	9.4	38.6	40.1	39.6	39.2	38.4	37.0	36.7
C-2	19.4	18.5	11.2	18.5	19.0	18.5	17.9	18.3	19.1	19.0
C-3	42.5	35.5	20.8	37.5	42.5	35.8	37.2	37.1	42.4[e]	42.2[e]
C-4	33.5	37.9	31.8	47.6	33.1	37.6[e]	46.4	47.2	33.5	33.5
C-5	55.2	47.5	18.4	49.1	50.5	43.7	45.4	48.7	52.4	52.0
C-6	22.9	22.5	13.6	25.5	23.5	23.5	25.7	24.9	20.8	21.3
C-7	36.3	35.5	5.4	35.8	121.6	121.5	121.5	35.5	32.7	32.6
C-8	138.8	138.1	6.0	138.5	135.2	135.3	136.0	136.2	124.4	124.4
C-9	51.8	51.5	6.8	51.9	52.2	52.0	52.4	50.7	136.5	134.4
C-10	38.8	38.8	7.6	38.1	35.6	35.4	35.5	37.8[e]	37.6	37.7
C-11	19.1	19.3	4.0	19.5	20.3	20.5	20.5	18.8	19.1	19.0
C-12	36.3	36.0	3.6	36.0	36.4	36.5	36.0	34.6	34.1	35.1
C-13	38.8	39.0	2.2	39.0	37.0	36.9[e]	37.5	37.4[e]	34.9	35.1
C-14	128.1	128.1	3.0	128.2	46.3	46.4	46.5	129.3	42.0[e]	42.0[e]
C-15	147.7	147.0	1.8	147.8	149.9	150.0	150.7	149.0	148.8	146.8
C-16	112.9	113.1	1.4	113.2	109.5	109.5	109.7	110.5	109.8	111.2
C-17	29.8	29.8	2.2	29.9	21.8	21.8	21.9	26.2	23.5	28.2
C-18	34.5	71.7	80.2	185.7	33.9	71.9	183.9	185.3	33.5	33.5
C-19	22.5	18.3	21.2	17.6	22.6	18.5	17.5	16.8	22.0	22.5
C-20	14.9	15.6	7.0	15.4	15.2	15.9	15.7	15.3	19.7	19.7

[a] Spectra taken at 15.077 MHz on a Fourier transform spectrometer; chemical shifts in parts per million downfield from TMS. [b] In chloroform solution; $\delta^{TMS} = \delta^{CHCl_3} + 77.6$ ppm. [c] In carbon tetrachloride solution; $\delta^{TMS} = \delta^{CCl_4} + 96.3$ ppm. [d] $\Delta_{Pr} = \delta_0 - \delta_{complex}$, where complex = 1:1 Pr(dpm)$_3$/**1b**. [e] Values in any vertical column may be reversed.

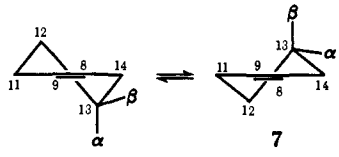
The Δ_{Pr} values resolved all chemical shifts of pimarol and hence also those of pimaradiene (**1a**) and pimaric (**1c**) and sandaracopimaric (**3**) acids,[5] while the following arguments delineated all shifts of isopimaradiene (**2a**), isopimarol (**2b**), and isopimaric acid (**2c**). The similarity of the environment of the ring A and olefinic carbons in isopimarol with that in pimarol allowed signal assignment of the isopimarol carbons at positions 1, 2, 3, 4, 7, 8, 15, 16, 18, 19, and 20. Comparison of spectra within the isopimaric series yielded δ values for the environmentally invariant carbons 9, 11, 12, and 14 and for C-6 in view of the identical effect thereon by variation of substituent R in either the pimaric or isopimaric series. Qualitative Pr(dpm)$_3$ shift data on isopimarol distinguished its C-10 from C-13. This leaves C-5 and C-17 the remaining methine and methyl groups, respectively.

Analysis of the $\Delta^{8(9)}$ compounds **4** was aided by dehydroabietane (**5**) serving as a model for rings A and B.[6] Shift assignment of C-13, -15, and -16 came from off-resonance data, C-8 and -9 from shift differences expected for olefinic carbons of dissimilar environment,[7] and C-11 and -12 from comparison with δ values of **2a** leaving C-14 as the remaining methylene group.[8] The methyl functions C-17 and C-20 were differentiated by a constancy of shift of the angular methyl group in **4a** *vs.* **4b** in the face of invariancy of the shifts of its neighbors, C-1, C-10, and C-11.

Unsophisticated conformational analysis of compounds **4** suggested ring C conformations **7a** and **6b** for dienes **4a** and **4b**, respectively, on the basis of lowest 1,3-diaxial interactions between C-11 hydrogens and C-13 substituents.[9] However, the C-15 and C-17 shifts (Table I) showed the dienes to possess ring C conformations **6a** and **6b**, respectively. Hence, nonbonded 1β–11β or 1β-11α hydrogen interactions and a similar C-20–11β hydrogen involvement contribute to the conformational preference.[10,11]



5



6 **7**

a, α = Me; β = C_2H_3
b, α = C_2H_3; β = Me

and R. E. Lenkinski, *J. Amer. Chem. Soc.*, **93**, 4295 (1971); E. Wenkert, D. W. Cochran, E. W. Hagaman, R. B. Lewis, and F. M. Schell, *ibid.*, **93**, 6271 (1971); J. Duggan, W. H. Urry, and J. Schaeffer, *Tetrahedron Lett.*, 4197 (1971).

(5) It is noteworthy that the C-13 stereochemistry, a feature assessed only with difficulty during the early days of structure determination of the resin acids [R. McCrindle and K. H. Overton, *Advan. Org. Chem.*, **5**, 47 (1965)], is portrayed clearly by cmr spectroscopy.

(6) The δ values of carbons at position 1, 2, 3, 4, 5, 18, and 19 denoted on **5** emanated from chemical-shift data of **1a** and related diterpenes. The isopropyl methine and C-10 were the only remaining methine and quaternary carbon, respectively. C-6 experienced an upfield shift as in **1a**, making C-7 the remaining methylene group. The isopropyl methyl groups could be distinguished from C-20 by their greater peak intensity.

(7) G. B. Savitsky and K. Namikawa, *J. Phys. Chem.*, **68**, 1956 (1964); E. Wenkert and E. W. Hagaman, unpublished observations; D. E. Dorman, M. Jautelat, and J. D. Roberts, *J. Org. Chem.*, **36**, 2757 (1971).

(8) In view of the anomalous C-1 shift in compounds **4** it might have been confused with that of C-14. However, the latter feeling the extra deshielding effect exerted by C-7 was expected to possess a signal at lower field than C-1.

(9) J. A. Hirsch, *Top. Stereochem.*, **1**, 199 (1967).

(10) *Cf.* S. G. Levine and N. H. Eudy, *J. Org. Chem.*, **35**, 549 (1970); S. G. Levine, I. Y. Chen, A. T. McPhail, and P. Coggon, *Tetrahedron Lett.*, 3459 (1971); R. R. Sobti, J. Bordner, and S. G. Levine, *J. Amer. Chem. Soc.*, **93**, 5588 (1971), and references therein; A. W. Burgstahler, J. Gawronski, T. F. Niemann, and B. A. Feinberg, *Chem. Commun.*,

Acknowledgment. This investigation was supported by Eli Lilly and Co.

121 (1971); U. Weiss, W. B. Whalley, and I. L. Karle, *ibid.*, 16 (1962). and references therein.

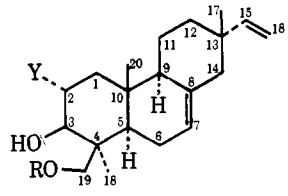
(11) Subtle differences of energy content of the two dienes **4** are noted also from a study of equilibration of their nuclear double bonds [E. Wenkert and Z. Kumazawa, *ibid.*, 140 (1968)]. While **4a** remained unfazed, acid-induced isomerization of **4b** led to an equilibrium mixture of **2a**, **4b**, and sandaracopimaradiene.

Ernest Wenkert,* Brian L. Buckwalter
Department of Chemistry, Indiana University
Bloomington, Indiana 47401
Received February 11, 1972

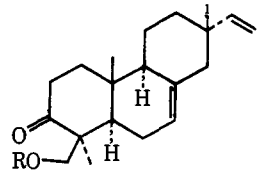
Carbon-13 Nuclear Magnetic Resonance Spectroscopy of Naturally Occurring Substances. XI. Biosynthesis of the Virescenosides[1]

Sir:

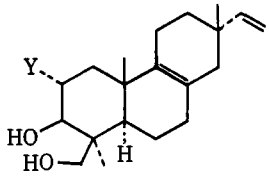
Structure analysis of the metabolites of the mushroom *Oospora Virescens* (Link) Wallr. has shown them to be diterpenic glycosides and the first altrose derivatives in nature.[2] Each metabolite contains one of three isopimaradienic aglycone units [*e.g.*, the virescenosides A, B, and C (**1c**, **1d**, and **2b**, respectively)], the biosynthesis of two of which (**1a** and **1b**) now has been uncovered. This study constitutes the first analysis of terpene biosynthesis by cmr spectroscopy.[3]



1a, R = H; Y = OH
b, R = Y = H
c, R = β-D-altropyranosyl; Y = OH
d, R = β-D-altropyranosyl; Y = H



2a, R = H
b, R = β-D-altropyranosyl



3a, Y = OH
b, Y = H

(1) For the preceding paper see E. Wenkert and B. L. Buckwalter, *J. Amer. Chem. Soc.*, **94**, 4367 (1972).

(2) N. Cagnoli-Bellavita, P. Ceccherelli, M. Ribaldi, Z. Baskevitch, and J. Polonsky, *Gazz. Chim. Ital.*, **97**, 1344, 1625 (1967); J. Polonsky, Z. Baskevitch, N. Cagnoli-Bellavita, and P. Ceccherelli, *Chem. Commun.*, 1404 (1968); J. Polonsky, Z. Baskevitch, N. Cagnoli-Bellavita, and P. Ceccherelli, *Bull. Soc. Chim. Fr.*, 1912 (1970); N. Cagnoli-Bellavita, P. Ceccherelli, M. Ribaldi, J. Polonsky, and Z. Baskevitch, *Gazz. Chim. Ital.*, **99**, 1354 (1969); N. Cagnoli-Bellavita, P. Ceccherelli, R. Mariani, J. Polonsky, and Z. Basekvitch, *Eur. J. Biochem.*, **15**, 356 (1970).

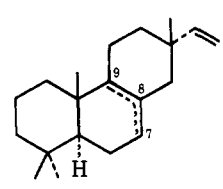
(3) For previous cmr-aided biosynthesis studies see M. Tanabe, H. Seto, and L. F. Johnson, *J. Amer. Chem. Soc.*, **92**, 2157 (1970); M. Tanabe, T. Hamasaki, H. Seto, and L. F. Johnson, *Chem. Commun.*, 1539 (1970); M. Tanabe, T. Hamasaki, D. Thomas, and L. F. Johnson, *J. Amer. Chem. Soc.*, **93**, 273 (1971); A. G. McInnes, D. G. Smith, L. C. Vining, and L. F. Johnson, *Chem. Commun.*, 325 (1971); R. Neuss, C. H. Nash, P. A. Lembe, and J. B. Grutzner, *J. Amer. Chem. Soc.*, **93**, 2337 (1971); R. J. Cushley, D. R. Anderson, S. R. Lipsky, R. J. Sykes, and H. H. Wasserman, *ibid.*, **93**, 6284 (1971). For previous studies of the biosynthesis of diterpenes by other means see B. E. Cross, *Progr. Phytochem.*, **1**, 195 (1968); J. R. Hanson, "The Tetracyclic Diterpenes," Pergamon Press, New York, N. Y., 1968, Chapter 8.

Table I. Cmr Chemical Shifts[a]

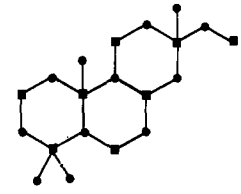
	1a	1b	2a	3a	3b
C-1	43.3	38.0	36.8[b]	42.6	35.4
C-2	69.1	28.0	35.5[b]	69.6	29.2
C-3	85.8	81.3	217.6	85.4	81.0
C-4	43.3	42.1	52.9	43.2	43.0
C-5	51.8[b]	51.4[b]	53.3[c]	51.9	52.1
C-6	23.6	23.2	24.2	21.6	21.6
C-7	121.8	121.7	121.7	32.8	33.1
C-8	135.9	136.0	136.2	125.0	125.1
C-9	52.5[b]	52.1[b]	50.8[c]	134.9	136.7
C-10	37.4[c]	35.2	35.5	38.4	37.4
C-11	21.2	20.6	21.1	19.6	19.1
C-12	36.7	36.3	36.5	35.0	34.9
C-13	37.0[c]	37.0	37.2	35.3	35.1
C-14	46.4	46.1	46.3	42.0	42.0
C-15	150.6	150.6	150.3	146.1	146.2
C-16	110.2	109.7	109.9	111.3	111.1
C-17	22.2	21.7	21.9	28.1	28.3
C-18	24.0	23.0	22.5	23.3	22.9
C-19	66.0	64.8	66.4	65.5	64.7
C-20	17.8	16.4	16.0	21.6	20.6

[a] Chloroform spectra taken at 15.077 MHz on a Fourier transform spectrometer; chemical shifts in parts per million downfield from TMS; $\delta^{TMS} = \delta^{CHCl_3} + 77.6$ ppm. [b,c] Values within any vertical column may be reversed.

The ^{13}C natural abundance nmr spectra of the aglycone alcohols **1a**, **1b**, and **2a** and their double bond isomers **3a** and **3b**, obtained by acid hydrolysis of the glycosides,[2] were recorded and their chemical shifts collated (Table I). Assignment of the δ values was based on chemical-shift theory,[4] the cmr data on the models isopimaradiene (**4a**) and $\Delta^{8(9)}$-isopimaradiene (**4b**)[1] and chemical-shift changes expected on introduction of hydroxy and keto groups into cyclic hydrocarbon skeletons.[5]



4a, $\Delta^{7(8)}$
b, $\Delta^{8(9)}$



5a, ■[1-^{13}C]acetate
b, ●[2-^{13}C]acetate

Addition of sodium [1-^{13}C]acetate to the mushroom culture medium, isolation of virescenoside A (**1c**), hydrolysis to isovirescenol A (**3a**), and inspection of the cmr spectrum of the latter revealed strong signal enhancement of the carbons depicted in **5a**. Similar treatment of the culture with sodium [2-^{13}C]acetate, isolation of virescenosides A (**1c**) and B (**1d**), conversion into isovirescenols A (**3a**) and B (**3b**), and perusal of the cmr spectra of the ^{13}C-enriched alcohols showed intense signal enlargement of the carbons portrayed in **5b**.[6] These results fit the present theory of terpene biosynthesis.[7]

(4) J. B. Stothers, *Quart. Rev., Chem. Soc.*, **19**, 144 (1965); E. F. Mooney and P. H. Winson, *Annu. Rev. Nucl. Magn. Resonance Spectrosc.*, 2, 153 (1969).

(5) J. D. Roberts, F. J. Weigert, J. I. Kroschwitz, and H. J. Reich, *J. Amer. Chem. Soc.*, **92**, 1338 (1970); F. J. Weigert and J. D. Roberts, *ibid.*, **92**, 1347 (1970).

(6) Quantitative data on the ^{13}C incorporation will be reported in connection with a parallel ^{14}C incorporation study (J. Polonsky, Z. Baskevitch, N. Cagnoli-Bellavita, and P. Ceccherelli, unpublished observations).

(7) H. J. Nicholas in "Biogenesis of Natural Compounds," P. Bernfeld, Ed., Pergamon Press, New York, N. Y., 1967.