bromides were quantitatively analyzed by integration on a Varian HA-60IL nmr spectrometer. Each integration was performed at least ten times. Reactions were run with varying quantities of bromine to ensure consistent results. Relative rate constants were calculated using the standard equation[3]

$$k/k_0 = \ln\,[(A_0 - X)/A_0]/\ln\,[(T_0 - Y)/T_0]$$

where A_0 and T_0 are initial moles of hydrocarbon and toluene and X and Y are the corresponding moles of bromides obtained upon completion of the reaction. No reaction was carried beyond consumption of 30% of the methylarenes.

Registry No.—Hydrogen, 1333-74-0; bromine, 7726-95-6; 2-methylphenanthrene, 2531-84-2; 2-methylnaphthalene, 91-57-6; 3-methylphenanthrene, 832-71-3; 1-methylphenanthrene, 832-69-9; 1-methylnaphthalene, 90-12-0.

Acknowledgment.—The authors gratefully acknowledge the financial aid from the Research Corporation that made possible the purchase of some of the instrumentation used in this study.

Reductive Conversion of 1-Aryl-3-hydroxymethyl-3,4-dihydro-2-naphthoic Acid Lactones into Substituted Tetrahydro-1*H*-cyclopropa[*a*]naphthalenes[1a]

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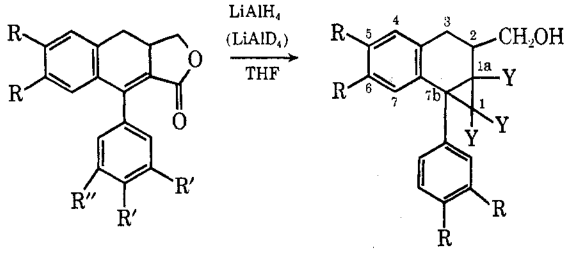
Received December 7, 1971

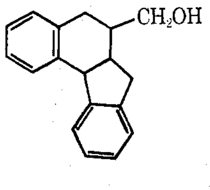
The ease of synthesis of cyclolignan lactones of the 3,4-dihydronaphthalene type **1** by means of the intramolecular Diels–Alder reaction[2,3] prompted us to investigate the formation of reduction products of **1**. Cis and trans addition of hydrogen to the α,β-unsaturated lactone system of γ-apopicropodophyllin (**1c**) by means of catalytic[4] and electrochemical[3] processes, respectively, have been described previously. We now report the chemical reduction of **1a** and **1b** by means of excess lithium aluminum hydride in tetrahydrofuran.

Isolated from the chemical reduction of **1a** was a crystalline product A, molecular formula $C_{18}H_{18}O$, in 70% yield. The infrared spectrum of A indicated the presence of an alcoholic OH group. The mass spectrum showed prominent peaks at *m/e* values of 250 $(M)\cdot^+$, 232 $(M - H_2O)\cdot^+$, and 219 $(M - CH_2OH)^+$. A was readily converted into a crystalline monoacetate and a crystalline monotosylate. The absence of an alkenic double bond in A was apparent from chemical tests on the acetate, the failure of A to absorb hydrogen in the presence of Pd/C at room temperature and pressure, and the relatively low extinction coefficient of the acetate (ϵ_{244} 1540, ϵ_{282} 160) compared to that of styrene ($\epsilon_{244}^{\max}$ 12,000, $\epsilon_{282}^{\max}$ 450)[5] in the wavelength range of 240–285 nm. A Kuhn–Roth determination on A showed no *C*-methyl group. Two structures, **2a** and **3**, seemed plausible on the basis of these data, though the former was preferred because of precedent for reduction of cinnamate esters to phenylcyclopropane[6] under conditions similar to those used on **1a**.

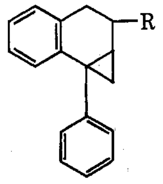


1a, R = R′ = R″ = H
b, R = R′ = CH$_3$O; R″ = H
c, R = OCH$_2$O; R′ = R″ = CH$_3$O

2a, R = H; Y = H
b, R = H; Y = D
c, R = CH$_3$O; Y = H



3



4a, R = H
b, R = CH$_2$OAc
c, R = CH$_2$OTs
d, R = CH$_3$

Careful integration of the pmr spectrum of A showed the presence of equal numbers of aromatic and aliphatic protons—a situation consistent with structure **2a** but not with **3**. However, the signal at highest field consisted of a multiplet for three protons at δ 1.1–1.7 (Figure 1), considerably downfield from the value of *ca.* 0.2 expected for protons in a cyclopropane ring magnetically unperturbed by the molecular environment.[7] The pmr spectra of A acetate and A tosylate also exhibited similar multiplets. Reduction of **1a** with lithium aluminum deuteride gave trideuterated A, a compound which showed almost exactly the same pmr spectrum as A itself, except for the absence of the high-field multiplet. Construction of a Stuart–Briegleb molecular model of **2a** indicated that protons at C-1 and C-1a should lie in the deshielding zone of the aromatic rings, and hence might be subject to the observed downfield shift.[8] On this basis the structures of A, its acetate, its tosylate, and its trideuterio derivative were assigned as **2a**, **4b**, **4c** and **2b**, respectively (where the stereochemical relationship between substituents at C-1a and C-2 remains undetermined).

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[1] (a) This investigation was supported by Research Grants No. CY-3097 from the National Cancer Institute and No. GM 12730 from the National Institute of General Medical Sciences, U. S. Public Health Service. (b) Research Assistant, 1962–1964. (c) Research Associate, 1966–1967. (d) Research Associate, 1969–1970. (e) On leave from the Department of Chemistry, Weizmann Institute of Science, Rehovoth, Israel, 1964–1969. (f) Research Assistant, 1970–1971.

[2] L. H. Klemm, K. W. Gopinath, D. H. Lee, F. W. Kelly, E. Trod, and T. M. McGuire, *Tetrahedron*, **22**, 1797 (1966); L. H. Klemm, D. H. Lee, K. W. Gopinath, and C. E. Klopfenstein, *J. Org. Chem.*, **31**, 2376 (1966); L. H. Klemm and P. S. Santhanam, *ibid.*, **33**, 1268 (1968).

[3] L. H. Klemm, D. R. Olson, and D. V. White, *ibid.*, **36**, 3740 (1971).

[4] A. W. Schrecker and J. L. Hartwell, *J. Amer. Chem. Soc.*, **75**, 5916 (1953).

[5] A. E. Gillam and E. S. Stern, "Electronic Absorption Spectroscopy," Edward Arnold, London, 1960, p 141.

[6] M. J. Jorgensen and A. W. Friend, *J. Amer. Chem. Soc.*, **87**, 1815 (1965); R. T. Uyeda and D. J. Cram, *J. Org. Chem.*, **30**, 2083 (1965); E. I. Snyder, *ibid.*, **32**, 3531 (1967).

[7] K. B. Wiberg and B. J. Nist, *J. Amer. Chem. Soc.*, **83**, 1226 (1961).

[8] *Cf.* the pmr spectrum of 1-methyl-2,2-diphenylcyclopropane [H. M. Walborsky and A. E. Young, *J. Amer. Chem. Soc.*, **86**, 3288 (1964); J. N. Pierce and H. M. Walborsky, *J. Org. Chem.*, **33**, 1962 (1968)] which shows a complexity of signals for three cyclopropane protons at δ 1.00–1.83 in CCl_4.

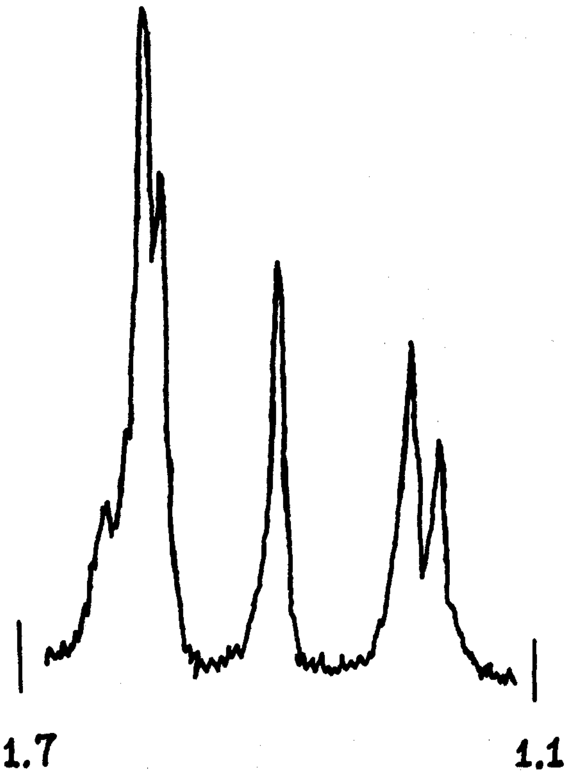

Figure 1.—Pmr spectrum for protons on the cyclopropane ring of **2a**; solvent $CDCl_3$.

To confirm these assignments the model compound **4a** was synthesized by means of Simmons–Smith methylenation of the known 1-phenyl-3,4-dihydronaphthalene.[9] This compound also exhibited a three-proton multiplet at δ 1.1–1.6 and gave negative tests for alkenic unsaturation. Further structural confirmation was obtained from examination of the infrared spectra of **2a**, **4a** and **4b**, especially in the short-wavelength region. Thus, each of these three compounds showed an absorption band at 1.635 μ for cyclopropyl C–H stretching,[10] while the deuterated compound **2b** did not absorb in this region.

In extensions of these studies, tosylate **4c** was reduced by means of lithium aluminum hydride to hydrocarbon **4d** and the tetramethoxycyclolignan lactone **1b** was converted into the benzonorcarene derivative **2c**. Compound **2c** likewise showed a multiplet at δ 0.9–1.5 and an absorption band at 1.645 μ. Its mass spectrum exhibited prominent peaks at *m/e* 151 $[(CH_3O)_2C_7H_5]^+$, 339 $(M - CH_3O$ or $M - CH_2OH)^+$, and 370 $(M)\cdot^+$.

Experimental Section[11]

7b-Phenyl-1a,2,3,7b-tetrahydro-1*H*-cyclopropa[*a*]naphthalene (4a).—To the mixture which resulted from stirring 1.4 g of zinc-copper couple (Alfa Inorganics), 8 ml of ether, and a crystal of iodine[12] was added dropwise a mixture of 4 g of 1-phenyl-3,4-dihydronaphthalene,[9] 2 ml of methylene iodide, and 10 ml of ether. The reaction mixture was refluxed, with stirring, for 24 hr and filtered. The ether layer plus washings of the solid residue was dried (Na_2SO_4) and distilled to give a viscous liquid, bp 128–134° (0.8 mm), separated into nearly equal parts of starting hydrocarbon and product **4a** by means of vpc at 185° with a stationary phase of 10% silicone DC-550 on 60–80 mesh Chromosorb W. Repetitive vpc gave an analytically pure sample of **4a**: negative permanganate test, inert to a mixture of 5% Pd/C and hydrogen gas at room temperature and pressure; pmr δ 1.1–1.6 (m, 3, H-1a plus 2 H-1), 2.0–2.9 (m, 4, 2 H-2 plus 2 H-3), 6.6–7.3 (m, 9, aromatic protons, including a five-proton singlet at δ 7.25 for the phenyl group); mass spectrum *m/e* 220 (M, 100%).

Anal. Calcd for $C_{17}H_{16}$: C, 92.68; H, 7.32. Found: C, 92.55; H, 7.58.

2-Hydroxymethyl-7b-phenyl-1a,2,3,7b-tetrahydro-1*H*-cyclopropa[*a*]naphthalene (2a).—To a stirred slurry of 0.8 g (21 mmol) of lithium aluminum hydride in 30 ml of tetrahydrofuran was slowly added a solution of 1.2 g (4.6 mmol) of 1-phenyl-3-hydroxymethyl-3,4-dihydro-2-naphthoic acid lactone (**1a**)[3] in 30 ml of the same solvent. The mixture became warm and developed a red-brown color, which disappeared in 30 min. The mixture was refluxed for 3 hr, cooled, and treated first with 1:1 (v/v) ether–EtOAc and then with water. The organic layer, plus ether extracts of the aqueous phase, was dried (Na_2SO_4) and evaporated to give a liquid, which crystallized from ether–petroleum ether (bp 30–60°) as prisms: mp 97–98°; yield 0.8 g (70%); pmr δ 1.1–1.7 (m, 3, H-1a plus 2 H-1),[13] 2.17 (s, 1, disappears on shaking with D_2O, OH), 2.24–2.63 (m, 1, H-2), 2.73 (d, 2, J = 5 Hz, 2 H-3), 3.51 and 3.62 (2 overlapping d of d, 2 total, AB portion of ABX system, $J_{AB} = -10.5$ Hz, a' = 3.2 Hz, a = 2.3 Hz, CH_2OH),[14] 6.5–7.2 (m, 4, H-4 to H-7), 7.27 (s, 5, phenyl group); ir ($CHCl_3$) 3460 and 3620 cm^{-1} (OH); mass spectrum[15] *m/e* (rel intensity) 250 (M, 47), 232 (36), 231 (30), 219 (100).

Anal. Calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.25; *C*-methyl, none. Found:[16] C, 86.00; H, 7.12; *C*-methyl, none.

2-Hydroxymethyl-7b-phenyl-1,1,1a-trideuterio-1a,2,3,7b-tetrahydro-1*H*-cyclopropa[*a*]naphthalene (2b).—Reaction of lithium aluminum deuteride with **1a** in the preceding manner gave a liquid, purified by evaporative distillation at 150° (0.1 mm) (single spot in tlc on silica gel with 1:1 benzene–ether) and then crystallization from ether-pentane as plates: mp 96–97.5°; pmr δ 1.99 (s, 1, OH), 2.1–2.43 (m, 1, H-2), 2.76 (split d, 2, J = 5 Hz, 2 H-3), 3.53 and 3.65 (two overlapping d of d, 2 total, AB portion of ABX system, $J_{AB} = -10.1$ Hz, a' = 3 Hz, a = 2.3 Hz, CH_2OH),[14] 6.5–7.2 (m, 4, H-4 to H-7), 7.27 (s, 5, phenyl group); ir ($CHCl_3$) 3470 and 3620 cm^{-1} (OH); mass spectrum[15] *m/e* 253 (M, 72%), 222 $(M - CH_2OH$, 100), 221 (43), 204 (38), 93 $(C_7H_5D_2$, 45).

Anal. Calcd for $C_{18}H_{15}D_3O$: 16.67 atom % excess D. Found:[17] 15.75 atom % excess D.

Acetylation of 2a.—A mixture of 0.56 g of alcohol **2a**, 5 ml of pyridine, and 3 ml of acetic anhydride was refluxed for 1 hr and then poured into ice–water. A $CHCl_3$ extract of the mixture was washed with 2% HCl and then water, dried, and evaporated. The residue crystallized from MeOH to give 0.62 g (95%) of prisms (acetate **4b**): mp 95–97°, raised to 100.5–101° on recrystallization; negative tests with Br_2–CCl_4 and $KMnO_4$ in acetone; λ_{max}^{EtOH} 253 nm (ϵ 534), 260 (595), 266 (608), 269 (600), 278 (472), plus stronger, short-wavelength end absorption; pmr δ 1.1–1.7 (m, 3, H-1a plus 2 H-1), 1.96 (s, 3, Ac), 2.3–2.9 (m, 3, H-2 plus 2 H-3), 4.05 and 4.16 (2 d of d, 2 total, AB portion of ABX system, $J_{AB} = -10.8$ Hz, a' = 8.7 Hz, a = 8.6 Hz, CH_2OAc),[14] 6.5–7.1 (m, 4, H-4 to H-7), 7.29 (s, 5, phenyl group).

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[9] R. Weiss, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 729.

[10] P. G. Gassman and F. V. Zalar, *J. Org. Chem.*, **31**, 166 (1966).

[11] Unless otherwise noted, microanalyses were performed by Micro-Tech Laboratories, Skokie, Ill., and M-H-W Laboratories, Garden City, Mich. Ultraviolet spectra were obtained by means of a Cary Model 11 spectrophotometer; pmr spectra, by means of a Varian A-60 spectrometer with $CDCl_3$ as solvent (unless otherwise noted) and tetramethylsilane as internal standard; and mass spectra, by means of a CEC Model 21-110 instrument at 70 eV.

[12] R. D. Smith and H. E. Simmons, *Org. Syn.*, **41**, 72 (1961).

[13] Thanks to Mr. Ronald Merrill of this laboratory, this multiplet was resolved (by use of a europium shift reagent) into two other multiplets for H-1a at lower field and 2 H-1 at higher field. Fuzziness in the multiplets, however, prevented clear assignment of coupling constants to these signals.

[14] See P. L. Corio, "Structure of High-Resolution NMR Spectra," Academic Press, New York, N. Y., 1966, pp 299–305. The negative sign of J_{AB} is assumed. Constant a' denotes the separation of the two central lines of the upfield d of d. Constant a gives the respective information for the downfield d of d.

[15] Only peaks of intensity ≥30% of the most abundant peaks are reported.

[16] Analyses by Clark Microanalytical Laboratory, Urbana, Ill.

[17] Analysis by Josef Nemeth, Urbana, Ill.

Anal. Calcd for $C_{20}H_{20}O_2$: C, 82.15; H, 6.89; sapon equiv, 292. Found: C, 82.04; H, 7.05; sapon equiv,[18] 292.

Basic hydrolysis of acetate **4b** gave recovery of alcohol **2a**.

Tosylation of 2a.—To a solution of 1.48 g (5.9 mmol) of alcohol **2a** in 10 ml of pyridine at 0° was added dropwise (with swirling) a solution of 2.3 g (12 mmol) of *p*-toluenesulfonyl chloride in 10 ml of pyridine. The mixture was kept at −20° for 24 hr, then poured onto ice and processed as in the preceding acetylation. The residue, 2.24 g (94%) of tosylate **4c**, mp 119–120.5°, formed prisms from benzene–hexane: mp 122–123°; pmr δ 1.1–1.7 (m, 3, H-1a plus 2 H-1), 2.43 (s, 3, tosylate CH_3), *ca.* 2.70 (broadened s, 3, H-2 plus 2 H-3), 3.8–4.2 (irregular t, 2, CH_2OTs), 6.6–7.9 (m, 13, aromatic protons); ir (KBr) 1180 and1350 cm^{-1} (sulfonate).

Anal. Calcd for $C_{25}H_{24}O_3S$: C, 74.24; H, 5.96; S, 7.93. Found: C, 74.15; H, 6.02; S, 8.00.

2-Methyl-7b-phenyl-1a,2,3,7b-tetrahydro-1*H*-cyclopropa[*a*]-naphthalene (4d).—To a stirred slurry of 0.75 g (20 mmol) of $LiAlH_4$ in 50 ml of tetrahydrofuran at 0° was added dropwise a solution of 1.57 g (3.9 mmol) of tosylate **4c** in 100 ml of the same solvent. The mixture was then stirred at 25° for 30 min, refluxed for 6 hr, treated dropwise with water, brought to pH 1, and extracted with ether. Evaporation of the water-washed, dried extract gave a liquid which formed prisms (0.91 g, 99%) from hexane–ether: mp 70–72° (raised to 72–73° on recrystallization); mass spectrum[15] *m/e* (rel intensity) 234 (M, 100), 219 (M − CH_3, 73), 205 (M − C_2H_5, 33), 192 (M − $CH_3CH{=}CH_2$, 43).

Anal. Calcd for $C_{18}H_{18}$: C, 92.26; H, 7.74. Found: C, 92.49; H, 7.50.

5,6-Dimethoxy-2-hydroxymethyl-7b-(3,4-dimethoxyphenyl)-1a,2,3,7b-tetrahydro-1*H*-cyclopropa[*a*]naphthalene (2c).—In the same manner as used for the synthesis of **2a**, tetramethoxy compound **1b**[3] was reduced to **2c**. The oily product was chromatographed by means of Florisil and (in succession) eluents of benzene and benzene–$CHCl_3$ (1:1, v/v). From the latter eluent was obtained a 36% yield of **2c** (single spot on tlc), converted to light yellow prisms on crystallization from hexane: mp 45–46°; pmr (CCl_4) δ 0.9–1.5 (m, 3, cyclopropane protons), *ca.* 2.6 (broad signal, disappears on shaking with D_2O, OH) which overlaps 2.1–3.0 (complex, 3, H-2 plus 2 H-3), 3.50 (s, 3, OCH_3 at C-6), 3.68, 3.74, 3.77 (3s, other OCH_3 groups) which obscure signals for CH_2OH, 6.30 (s, 1, H-7), 6.52 (s, 1, H-4), 6.57–6.9 (broad s plus m, 3, H-2′, H-5′, and H-6′); ir ($CHCl_3$) 3500 cm^{-1} (broad, OH); mass spectrum[15] *m/e* 370 (M, 69%), 339 (100), 151 (36), 57 (32).

Anal. Calcd for $C_{22}H_{26}O_5$: C, 71.33; H, 7.08. Found: C, 71.61; H, 7.16.

Infrared Spectra.—Spectral examination of samples in the near infrared region of the spectrum was made by means of a Cary model 14 spectrophotometer, with a concentration of *ca.* 50 mg of substrate per milliliter of solvent, CCl_4. Compounds **2a**, **2c**, **4a**, and **4b** (but not deuterated compound **2b**, nor the impure product from catalytic hydrogenolysis of **4d**) showed prominent absorption shoulders or peaks at 1.635–1.645 μ. Extinction coefficients for **2a**, **4a**, and **4b** were 0.35, 0.19, and 0.32, respectively.

The regular infrared spectra (obtained in CS_2 as solvent, by means of a Beckman IR-7 spectrophotometer) of **2a**, **4a**, and **4b** also showed a medium band at 1016–1021 cm^{-1} (ascribed to cyclopropane ring deformation)[19,20] and a weak band at 820–844 cm^{-1} (ascribed to cyclopropane ring CH_2 rocking).[20,21] The latter band was clearly resolved in all compounds, though the former band was sharp only in hydrocarbon **4a**. For **2a** it occurred only as a shoulder on the strong C–O stretching band at 1035 cm^{-1}, but some better resolution was found in the spectrum of **4b**.

Registry No.—**2a,** 34599-28-5; **2b,** 34566-27-3; **2c,** 34566-28-4; **4a,** 34566-29-5; **4b,** 34566-30-8; **4c,** 34566-31-9; **4d,** 34566-32-0.

Acknowledgment.—The authors are grateful to Professor H. M. Walborsky of Florida State University for providing us with a pmr comparison spectrum of 1-methyl-2,2-diphenylcyclopropane and to Dr. T. M. McGuire (formerly of this laboratory) for obtaining definitive pmr spectra on some of our products.

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[18] Analysis by Geller Laboratories, Charleston, W. Va.

[19] J. M. Derfer, E. E. Pickett, and C. E. Boord, *J. Amer. Chem. Soc.*, **71**, 2482 (1949); C. N. R. Rao, "Chemical Applications of Infrared Spectroscopy," Academic Press, New York, N. Y., 1963, p 146, and references cited therein.

[20] S. A. Liebman and B. J. Gudzinowicz, *Anal. Chem.*, **33**, 931 (1961); M. Hanack, H. Eggensperger, and S. Kang, *Chem. Ber.*, **96**, 2532 (1963).

[21] H. A. Szymanski, "Interpreted Infrared Spectra," Vol. 1, Plenum Press, New York, N. Y., 1964, pp 143–162.

Structure of a New Fungal Lactone, LL-P880α, from an Unidentified *Penicillium* sp.

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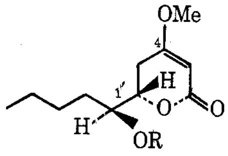
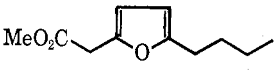
In a continuing program seeking useful pharmacologically active compounds from microorganisms, we had occasion to examine the fermentations of culture P880, an unidentified *Penicillium* species. This report describes the structure, stereochemistry, and some rearrangements of the metabolite LL-P880α.[1] This metabolite, $C_{11}H_{18}O_4$, is characterized by a uv maximum at 235 nm (ϵ 12,000) and strong ir absorption at 1710 and 1625 cm^{-1} which suggests the presence of the 4-alkoxy-5,6-dihydro-α-pyrone moiety.[2] The nmr spectrum supports this conclusion with a methoxy signal at δ 3.80, the C_3 vinyl proton signal at δ 5.16 ($J_{3,5a}$ = 2 Hz), a 1 H multiplet at δ 4.33 due to the proton of C_6, an eight-line pattern at δ 2.67 (J_{gem} = 18, $J_{3,5a}$ = 2, $J_{5a,6}$ = 11 Hz), and a four-line system at δ 2.23 (J_{gem} = 18, $J_{5e,6}$ = 4 Hz) due to the geminal C_5 protons. In addition, a primary C–Me signal at δ 0.92 as a characteristic 3 H triplet and a 1 H multiplet due to a second proton on a carbon bearing an oxygen atom at δ 3.70 are observed. The hydroxy nature of this remaining oxygen is indicated by the formation of acetate II, $C_{13}H_{20}O_5$.



I, R = H
II, R = Ac



III

The major fragmentation in the mass spectrum of I results from the loss of the five-carbon side chain, giving the base peak at *m/e* 127. The ion at *m/e* 157 is consistent with cleavage between $C_{1'}$ and $C_{2'}$ and expulsion of the *n*-butyl unit. This evidence, in conjunction with the foregoing, unequivocally indicates I as the structure of the metabolite.

The chemistry of I under acidic or basic conditions is characterized by a marked propensity to rearrange to the furanoid system or derivatives thereof. Thus hydrolysis of I in methanolic hydrochloric acid gave the furan ester III, $C_{11}H_{16}O_3$. Its nmr spectrum shows the two ring-proton signals at δ 6.08 and 5.90 as two dou-

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[1] After this work was completed, a note by Y. Kimura, K. Katagiri, and S. Tamura appeared in *Tetrahedron Lett.*, **No. 33**, 3137 (1971), which describes the same compound from *Pestalotia cryptomeriaecola.*

[2] H. B. Henbest and E. R. H. Jones, *J. Chem. Soc.*, 3628 (1950).