

FASCIOLA-7, 18-DIEN-17-AL, A DITERPENOID WITH A NEW
TETRACYCLIC RING SYSTEM FROM THE BROWN ALGA
DILOPHUS FASCIOLA

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ABSTRACT.—From the brown alga *Dilophus fasciola* the diterpenoid **6** with a new tetracyclic ring system was isolated. The structure and relative stereochemistry of this compound were determined essentially by spectral data including two-dimensional nmr methods.

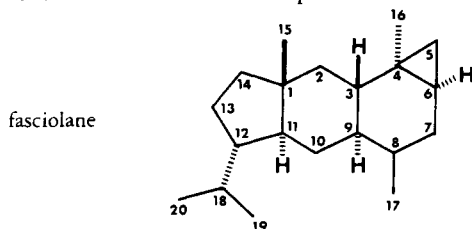
A bewildering array of mono-, di-, and tri-cyclic diterpenoids have been isolated from brown algae of the family Dictyotaceae. Representative examples of these classes are dilophol (**1**), obtained from *Dilophus ligulatus* (1), pachydictyol A (**2**) from *Pachydictyon coriaceum* (2), and amijol (**3**) isolated from *Dictyota linearis* (3).

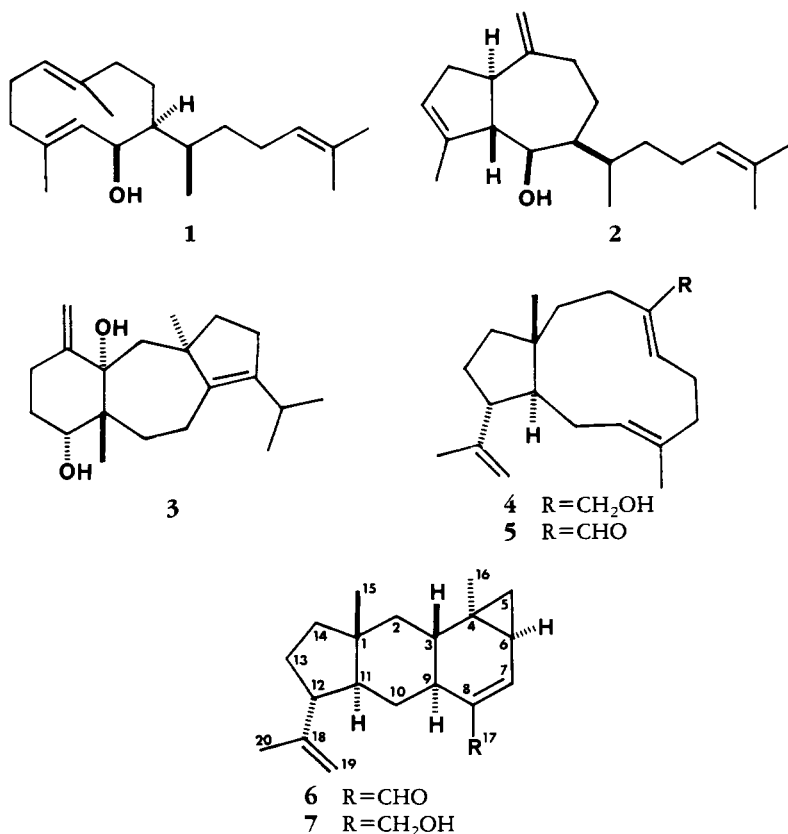
In previous papers, we described the isolation of a number of diterpenoids based on the dolabellane skeleton, for example, **4** and **5**, from a brown alga provisionally classified as *Dictyota* sp. (4-7). From this same alga, which, after a more accurate morphological examination, turned out to be a species belonging to the closely related genus *Dilophus*, namely *Dilophus fasciola* (Roth) Howe, we have now isolated a diterpenoid, fasciola-7, 18-dien-17-al¹ (**6**) with a novel 3,6,6,5-carbotetracyclic framework. We wish to describe here the structure elucidation of this new algal metabolite.

Compound **6**, C₂₀H₂₈O (hrms) was isolated by repeated chromatography of the CHCl₃ extract of the alga as an optically active, crystalline solid. Its spectral properties revealed remarkable, albeit partial, similarities with those of the dolabellane-based diterpenoids. Thus, the eims of **6** contains intense peaks at *m/z* 121 (C₉H₁₃) and 81 (C₆H₉) which are present in the mass spectrum of all the dolabellanes we have so far investigated and can be assigned to fragments I and II.

However, the molecular formula combined with the presence of a conjugated formyl group [ir: 1678 cm⁻¹; ¹H nmr: δ 9.48 (s, 17-H) and 6.94 (t, *J*=3 Hz, 7-H); ¹³C nmr: 153.7 (C-7), 148.0 (C-8), and 194.3 ppm (C-17)] and a terminal double bond [δ 4.77 and 4.82 (1H each, bs, 19-Ha and 19-Hb); ¹³C nmr: 147.4 (C-18), 111.0 (C-19), and 26.1 ppm (C-20)], which accounted for all the ¹³C-nmr resonances for sp²-hybridized carbons, required **6** to have a tetracyclic framework. A preliminary examination of the ¹H-nmr (Table 1) and ¹³C-nmr (Table 2) spectra pointed to a novel ring system, and, therefore, efforts were directed toward the preparation of a single crystal amenable to X-ray structural elucidation. Since these attempts were frustrated by the fact that **6** crystallized in a form unsuitable for X-ray analysis, we tried to solve the structure by spectroscopic methods only.

¹We have named the aldehyde (**6**) as a derivative of the hypothetical hydrocarbon "fasciolane." The numbering system follows that for the related dolabellane diterpenoids.





A close analysis of the 500-MHz ¹H-nmr spectrum, aided by a COSY-90 (8,9) spectrum and extensive decoupling experiments, allowed us to determine the complete sequence of protons in **6**. Irradiation at the C-6 methine signal (δ 1.11) converted the signal of the C-5 methylene (5-Ha: δ 0.46, dd, $J=4$ and 3.5 Hz; 5-Hb δ 0.98, dd, $J=9$ and 3.5 Hz) into an isolated AB pattern and at the same time located 7-H (δ 6.94, t, $J=3$ Hz). The high-field position of the C-5 and C-6 protons (particularly 5-Ha) and the value (3.5 Hz) of the geminal coupling constant of the protons at C-5 indicated a cyclopropane ring. The uv spectrum of **6** [λ max (cyclohexane) 195 ($\epsilon=11,000$), 247 ($\epsilon=8,500$), and 323 nm ($\epsilon=50$)] agreed with a conjugated cyclopropylenal chromophore (10) and so did the uv absorption [λ max (cyclohexane) 194 ($\epsilon=10,500$) and 320 nm ($\epsilon=48$)] of the alcohol **7**, obtained by NaBH₄ treatment of **6**, which is typical of a vinylcyclopropane chromophore (11). Reduction of the formyl group also caused an upfield shift of the resonances of the C-5 and C-6 protons in the ¹H-nmr spectrum (see Table 1), and this ruled out the possibility that their high-field position could have been caused by a shielding effect of the carbonyl group.

The rest of the protons were more easily analyzed in the spectrum in C₆D₆. The methine proton at C-7 (δ 6.33) is long-range coupled with 9-H (δ 2.02), while recip-

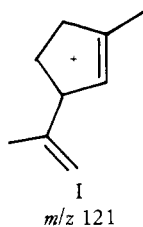


TABLE 1. ¹H-nmr Data for Compounds **6** and **7**^a

| Position | Compound | | |
|----------|---------------------------------|--|--|
| | 6 (CDCl ₃) | 6 (C ₆ D ₆) | 7 (CDCl ₃) |
| 2a | 1.25 ^b | 1.07 (1H, dd, <i>J</i> =13, 12) | 1.25 ^b |
| 2b | 1.60 ^b | 1.72 (1H, dd, <i>J</i> =12, 3.5) | 1.60 ^b |
| 3 | 1.14 ^b | 0.99 (1H, ddd, <i>J</i> =13, 11, 3.5) | 1.17 ^b |
| 5a | 0.46 (1H, dd, <i>J</i> =4, 3.5) | 0.18 (1H, bs) | 0.21 (1H, dd, <i>J</i> =4, 3.5) |
| 5b | 0.98 (1H, dd, <i>J</i> =9, 3.5) | 0.65 (2H, bs) | 0.70 (1H, dd, <i>J</i> =9, 3.5) |
| 6 | 1.11 ^b | | 0.81 (1H, ddd, <i>J</i> =4, 3, 9) |
| 7 | 6.94 | 6.33 ^c (1H, t, <i>J</i> =3) | 5.89 (1H, t, <i>J</i> =3) |
| 9 | 2.19 | 2.02 ^c (1H, dddd, <i>J</i> =12, 11, 4, 3) | 2.06 ^b |
| 10a | 1.06 ^b | 1.15 (1H, ddd, <i>J</i> =13, 12, 11) | 1.25 ^b |
| 10b | 2.89 | 3.21 (1H, ddd, <i>J</i> =11, 4, 3) | 2.06 ^b |
| 11 | 1.57 | 1.32 (1H, ddd, <i>J</i> =13, 9, 3) | 1.60 ^b |
| 12 | 2.73 | 2.63 (1H, ddd, <i>J</i> =9.5, 9, 9) | 2.73 (1H, ddd, <i>J</i> =9.5, 9, 9) |
| 13a | 1.85 ^b | 1.82 ^b m | 1.83 ^b |
| 13b | 1.89 ^b | 1.88 ^b m | 1.86 ^b |
| 14a | 1.25 ^b | 1.05 m | 1.25 ^b |
| 14b | 1.62 ^b | 1.53 m | 1.60 ^b |
| 15 | 1.03 | 0.80 (3H, s) | 1.02 (3H, s) |
| 16 | 0.78 | 0.76 (3H, s) | 0.78 (3H, s) |
| 17 | 9.48 | 9.33 (1H, s) | { 4.02 (AB syst., <i>J</i> =12) 4.19 |
| 19a | 4.77 | 4.89 (1H, bs) | 4.76 (1H, bs) |
| 19b | 4.82 | 4.94 (1H, bs) | 4.80 (1H, bs) |
| 20 | 1.77 | 1.84 (3H, s) | 1.76 (3H, s) |

^a¹H-nmr spectra were recorded at 500 MHz. Assignments were aided by spin-decoupling experiments and a COSY-90 spectrum. TMS was used as internal standard: chemical shifts are δ values. *J* values are reported in Hz.

^bOverlapped with other signals.

^cMultiplicity of these signals includes a long-range coupling.

rocal irradiation at this point simultaneously modified, in addition to the signal of 7-H, the signals of the C-10 methylene and C-3 methine groups. Irradiation at the frequency of 3-H (δ 0.99) affected the signals of a methylene [δ 1.07 (2-Ha) and 1.72 (2-Hb)] not correlated with the rest of the hydrogens. The C-10 protons were spin-coupled to a signal at δ 1.32 (11-H) which was in turn coupled to a proton at δ 2.63 (12-H). Long-range coupling between 12-H and two signals at δ 4.89 and 4.94 (19-Ha and 19-Hb) which were in turn long-range coupled with a three-proton signal at 1.84 (20-H) indicated the nature of the isopropenyl side chain and fixed its position. The methine proton at C-12 was further correlated with a methylene [1.82 (13-Ha) and 1.88 (13-Hb)] which was in turn coupled to a methylene linked to a quaternary sp³-hybridized carbon. At this point, the remaining signals in the ¹H-nmr spectrum were two three-proton singlets at δ 0.76 and 0.80 assignable to methyls bound to sp³-quaternary carbons.

These results are summarized in the open structure A from which, taking into account the fact that the multiplicities of 3-H and 11-H require that the pertinent carbons are to be linked to quaternary carbons, only three general structures (B, C, and D, exclusive of stereochemistry) can be derived. Structure B was rejected from both mass and ¹H-nmr spectral evidence since the mass spectrum of **6** displays, as noted before,

TABLE 2. ^{13}C -nmr Data for Compound 6^a

| Position | δ (CDCl ₃) | |
|----------|-------------------------------|---|
| 1 | 41.1 | s |
| 2 | 29.6 ^b | t |
| 3 | 46.0 ^c | d |
| 4 | 19.3 | s |
| 5 | 24.9 | t |
| 6 | 21.8 | d |
| 7 | 153.7 | d |
| 8 | 148.0 ^d | s |
| 9 | 44.6 ^c | d |
| 10 | 27.8 ^b | t |
| 11 | 51.1 | d |
| 12 | 38.7 ^c | d |
| 13 | 41.3 ^e | t |
| 14 | 43.6 ^e | t |
| 15 | 20.4 | q |
| 16 | 18.8 | q |
| 17 | 194.3 | d |
| 18 | 147.4 ^d | s |
| 19 | 111.0 | t |
| 20 | 26.1 | q |

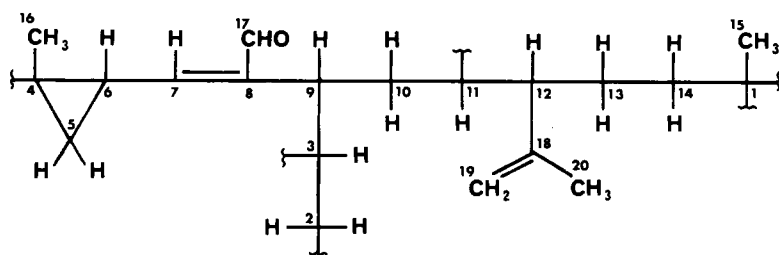
^aSpectra were recorded at 20.1 MHz in CDCl₃, and chemical shifts are reported in ppm from TMS. Multiplicities were obtained by "off-resonance" decoupling. Assignments were based on comparison to models.

^{b-c}Values with identical superscript within each column may be interchanged.

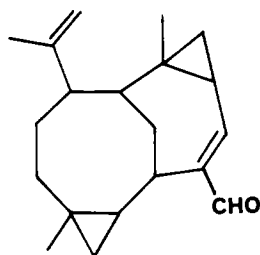
fragments which point to an isopropenylcyclopentane moiety, while the ^1H -nmr spectrum does not contain any signals expected for a second cyclopropane ring.

The subsequent choice between structures C and D was somewhat less obvious. An indication in favor of structure D came from the magnitudes of the coupling constants $J_{2a,3}$, $J_{3,9}$, $J_{9,10a}$, and $J_{10a,11}$ which are reasonable for axially oriented protons in a six-membered ring in a chair conformation, whereas they are out of the range normally encountered in a cyclopentane system (12). Further evidence supporting the correctness of structure D was obtained from the determination of the nOe and lanthanide induced shifts (LIS) for selected protons; the almost complete lack of conformational flexibility of the tetracyclic ring system facilitated these studies. Since interpretation of the nOe and LIS data required the unambiguous assignment of the methyl resonances at δ 0.76 and 0.80 ppm, solvent shifts [$\Delta(\delta_{\text{CDCl}_3} - \delta_{\text{C}_6\text{D}_6})$] were measured and found to be +0.23 for the peak at δ 0.80 and +0.02 for the 0.76 signal. The observation that in the Dreiding models of all the stereoisomers of structures C and D compatible with the above data the methyl groups of C-4 is located behind the orthogonal plane through the carbonyl carbon atom, allowed us to assign the resonance at δ 0.76 and 0.80 to C-4 Me and C-1 Me, respectively (13).

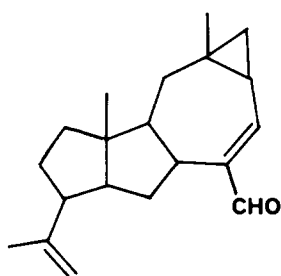
NOEDS (14) and NOESY (15) experiments (see Table 3) confirmed the relative orientation of 3-H, 9-H, and 11-H and, in addition, allowed us to establish that the C-1 Me is axial. Furthermore, the fact that 3-H and 5-H_a are within nOe proximity, in addition to the strong shielding effect experienced by 3-H (16), fixed the orientation of the cyclopropane ring. These observations settled the relative stereochemistry of all the chiral centers except C-12. Lack of enhancement of the signals for 12-H and the C-1 Me following irradiation at 11-H, and the near identity of the coupling constants for 12-H



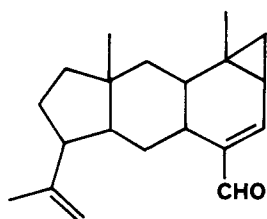
A



B



C



D

with those for the analogous atom in **5** permitted the assignment of the stereochemistry of the last center. The close similarity of the ^{13}C -nmr chemical shifts for the carbons of the cyclopentane moiety to those of the corresponding atoms in the dolabellane diterpenoids further supported this inference.

At this stage, $\text{Eu}(\text{fod})_3$ induced shifts were measured in the ^1H -nmr spectrum of **6** for selected protons (the pertinent LIS are reported in Table 4). The so-called $1/r^2$ method (17) was applied to correlate these data with r values (Table 4) measured on a

TABLE 3. Cross-relaxation Connectivities for **6** as Obtained from ^1H NOESY (14)^a

| Cross peak co-ordinates below the diagonal d(x)-d(y) | Protons correlated |
|--|--------------------|
| 0.76-0.99 | 1-Me - 3-H |
| 0.18-0.99 | 3-H - 5-Ha |
| 0.18-0.65 | 5-Ha - 5-Hb |
| 0.65-6.33 | 6-H - 7-H |
| 6.33-9.33 | 7-H - 17-H |
| 1.32-2.02 | 9-H - 11-H |
| 1.07-2.02 | 9-H - 2-Ha |
| 1.15-3.21 | 10-Ha - 10-Hb |
| 1.07-1.72 | 2-Ha - 2-Hb |

^a ^1H -NOESY spectrum was recorded at 250 MHz, in C_6D_6 .

TABLE 4. Measured LIS for Selected Protons of Compound **6** and Calculated r Values in Models C and D^a

| Position | LIS | $r(\text{C})$ | $r(\text{D})$ |
|---------------|-------|---------------|---------------|
| 5a | 2.49 | 6.10 | 5.45 |
| 7 | 4.29 | 3.85 | 3.95 |
| 9 | 7.28 | 3.60 | 3.50 |
| 10a | 13.42 | 2.10 | 2.50 |
| 10b | 20.17 | 2.55 | 2.15 |
| 12 | 3.56 | 4.35 | 4.50 |
| 15 | 3.15 | 3.50 | 4.95 |
| 16 | 1.50 | 7.50 | 6.85 |

^a r values are expressed in Å. (For details see Experimental section).

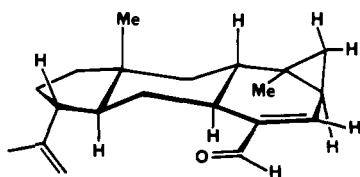


FIGURE 1. Stereostructure D.

Dreiding model of stereostructure D (Figure 1); a plot of LIS vs. $10^2 r^{-2}$ gave a straight line (correlation coefficient = 0.996, Figure 2A). An analogous plot for structure C, maintaining the same stereochemistry at the chiral centers as in D in accordance with the above reported data, gave a much less reasonable correlation (correlation coefficient = 0.809, Figure 2B). Therefore, structure **6** has been confidently assigned to the new algal metabolite, which is the first example of a tetracyclic diterpenoid isolated from a member of the family Dictyotaceae. This compound probably shares with the verrucosanes, a different type of 3,6,6,5-tetracyclic diterpenoids from liverworts (18, 19), a common biogenetic origin from a precursor with the dolabellane skeleton.

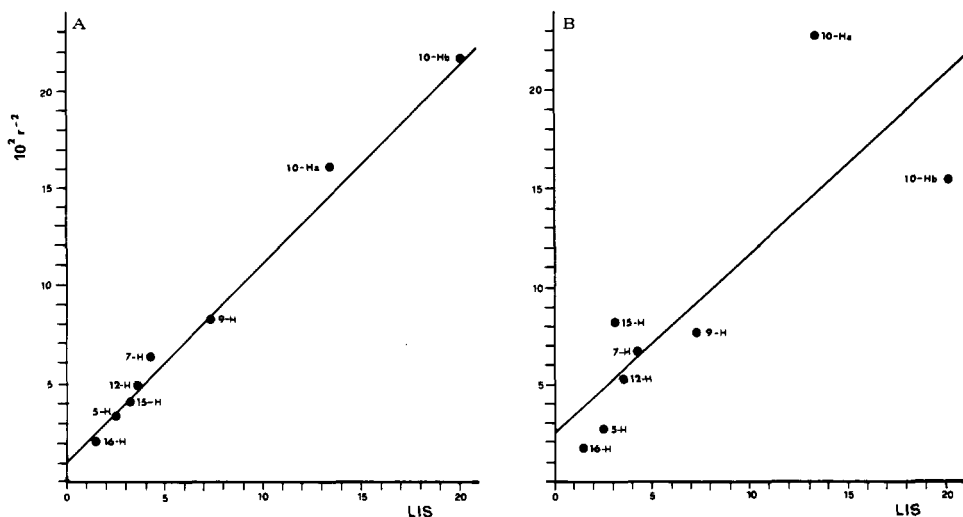


FIGURE 2. Plots of LIS vs. $10^2 r^{-2}$ for: (A) stereomodel based on D framework; (B) stereomodel based on C framework. See Experimental section for details.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—The melting point was determined using a Kofler apparatus and is uncorrected. Optical rotation was determined with a Perkin-Elmer Model 141 instrument (1 dm tube). Ir spectra were run in CHCl_3 solutions on a Perkin-Elmer Model 684 spectrophotometer. Uv spectra were obtained on a Perkin-Elmer Model 330 spectrophotometer, in degassed cyclohexane solutions. Mass spectra were recorded on a KRATOS MS-50S instrument at 70 eV. ^1H -nmr spectra were run on Bruker AM-500 (500 MHz) and AM-250 (250 MHz) FT spectrometers; CDCl_3 and C_6D_6 were used as solvents. The COSY-90 (proton-proton correlated) spectrum was obtained on a Bruker AM-200 (200 MHz) instrument. ^1H -NOEDS (nuclear Overhauser enhancement difference spectrum) and NOESY (two dimensional exchange) spectra were obtained at 250 MHz, in degassed C_6D_6 solutions. A Bruker WP-80 (20.1 MHz) was used to record the ^{13}C -nmr spectrum, in CDCl_3 solution. For both ^1H -nmr and ^{13}C -nmr spectra, TMS was used as internal standard; chemical shifts are measured in δ (ppm). Tlc was carried out using glass-backed, pre-coated silica gel F254 plates (Merck). Spot detection was obtained by spraying with 10% solution of $\text{Ce}(\text{SO}_4)_2$ in 2N H_2SO_4 , or by uv light (254 nm). Preparative liquid chromatography (plc) was effected on Jobin-Yvon Prep-10 and Miniprep liquid chromatographs. All solvents were spectral grade or distilled prior to use.

PLANT MATERIAL.—*D. fasciola* was collected by SCUBA at a depth of 4-5 m near Portopalo (south-

east coast of Sicily) in July, 1983. A specimen was deposited in the Herbarium of the Institute of Botany, Catania.

EXTRACTION AND ISOLATION OF 6.—Air-dried and ground alga (300 g) was extracted with CHCl_3 (3×1 liter) under continuous stirring. Evaporation afforded 11 g residue which was taken up in hexane- Et_2O (1:4). The solution was passed through a column of Florisil and the eluate evaporated. The residue (7 g) was subjected to plc on Si gel using 25% Et_2O in hexane as eluent. Fractions of 50 ml were collected, and those exhibiting similar tlc profiles were combined. Compound **6** was eluted in fractions 5-7 and subjected to repeated careful plc (Lichroprep Si 60) with the following solvent systems: 4% Me_2CO in hexane and 20% CH_2Cl_2 in hexane.

1(R*), 11(S*), 12(R*)-FASCIOLA-7, 18-DIEN-17-AL (6).—The natural diterpenoid **6** was obtained on recrystallization from EtOH as white needles (100 mg), mp 103-104°, $[\alpha]^{25}_{\text{D}} = -150.9$ ($c = 1$ in EtOH); ir ν_{max} (CHCl_3) 1678, 1450, 1000, 860 cm^{-1} ; uv λ_{max} (cyclohexane) 195 ($\epsilon = 11,000$), 247 ($\epsilon = 8,500$), 323 nm ($\epsilon = 50$); hrms 284.2131 (M^+ , 89%) obsd ($\text{C}_{20}\text{H}_{28}\text{O}$ requires 284.2140); ms m/z 284, 268 ($\text{M}^+ - \text{CH}_3$, 30%), 255 ($\text{M}^+ - \text{CHO}$, 25%), 241 (81%), 215 (29%), 187 (32%), 173 (34%), 159 (36%), 145 (52%), 131 (56%), 121 (60%), 119 (74%), 105 (98%), 91 (90%), 81 (80%). For ^1H and ^{13}C nmr, see Tables 1 and 2, respectively.

SODIUM BOROHYDRIDE REDUCTION OF 6 TO PRODUCE 7.—To a solution of 30 mg of **6** in EtOH (10 ml), 30 mg of NaBH_4 was added, and the mixture was stirred for 1 h. After addition of H_2O (10 ml), excess reagent was destroyed by addition of 0.2 N HCl, and the organic material was extracted three times with Et_2O . The combined extracts were dried over Na_2SO_4 and evaporated in vacuo to yield an oil (25 mg). Chromatography of the oil on Si gel (hexane- Et_2O , 80:20) gave 15 mg of **7**; ir (CHCl_3) ν_{max} 3600, 1000, and 860 cm^{-1} ; uv λ_{max} (cyclohexane), 194 ($\epsilon = 10,500$) and 320 nm ($\epsilon = 48$); ms m/z 286 (M^+ , 40%), 271 ($\text{M}^+ - \text{CH}_3$, 20%), 268 ($\text{M}^+ - \text{H}_2\text{O}$, 25%), 256 ($\text{M}^+ - \text{H}_2\text{O} - \text{CH}_3$, 40%), 121 (70%), 105 (100%), 81 (80%). For ^1H nmr see Table 1.

LANTHANIDE SHIFT STUDY OF 6.— $\text{Eu}(\text{fod})_3$ 0.274M in CDCl_3 was added in progressive aliquots to compound **6** in CDCl_3 , and the 250 ^1H -nmr spectrum was recorded. LIS values were calculated for selected protons by linear extrapolation to equimolar $[\text{Eu}(\text{fod})_3]: [\text{substrate}]$ ratio and are reported in Table 4. The so-called $1/r^2$ method (16) was used to correlate LIS with distances of the protons from the lone pair periphery of the oxygen atom, as measured on Dreiding models of stereostructures C and D, assuming a "transoid" conformation for the formyl group on the basis of an intense nOe observed between H-7 and H-17. For the methyl protons, a mean position was considered along the Me-C bond at 1.94 Å from the ring carbons. Plots of LIS vs. $10^2 r^{-2}$ (r values for models C and D are reported in Table 4) were constructed for both cases, and the best fits obtained with least-square analysis are showed in Figure 2. Correlation coefficients of 0.809 and 0.996 were calculated for models C and D, respectively.

ACKNOWLEDGMENTS

This work was financially supported by the Consiglio Nazionale delle Ricerche, Rome, under the scheme "Progetto Finalizzato per la Chimica Fine e Secondaria." The authors gratefully acknowledge Ing. H. Holenweger of Bruker Spectrospin AG, Zürich, for the determination of two-dimensional nmr spectra (COSY-90 and NOESY) and Prof. L. Mayol of Centro di Metodologie Chimico-fisiche University of Naples, for the determination of NOEDS. Thanks are due to Prof. G. Giaccone of the Istituto di Botanica e Orto Botanico dell'Università di Palermo for the classification of plant material. The authors also thank Mrs. Concetta Rocco for skillful technical assistance.

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Received 1 July 1985