Acknowledgment. We are indebted to Dr. Ch. S. Mantzos of our Microanalytical Laboratory for the microanalyses. Thanks are due to Mrs. M. Kyttari and Mrs. M. Voyadji for technical assistance.

Registry No. 1, 32669-06-0; $PhCH_2Li$, 766-04-1; 2-$PyCH_2Li$, 1749-29-7; 4-$PyCH_2Li$, 26954-25-6; Ph_2CHLi, 881-42-5; 9-FlLi, 881-04-9; 2-Py(Ph)CHLi, 56501-99-6; 4-Py(Ph)CHLi, 81771-00-8; Ph_3CLi, 733-90-4; Ph(SPh)CHLi, 41979-02-6; $Ph_2C(SPh)Li$, 81771-01-9; $Ph_2(CN)CLi$, 66785-30-6; $(Ph_2CO)^{2-}Li_2^{2+}$, 34510-08-2; PhCH-$(CO_2Li)Li$, 56842-55-8; $Ph_2(CO_2Li)Li$, 60538-71-8; $Ph(CH_2)_3OCHPh_2$, 42113-39-3; 2-$Py(CH_2)_3OCHPh_2$, 81771-02-0; 4-$Py(CH_2)_3OCHPh_2$, 81771-03-1; $Ph_2CH(CH_2)_2OCHPh_2$, 81771-04-2; 9-Fl-$(CH_2CH_2OCHPh_2)_2$, 81771-05-3; 2-Py(Ph)$CH(CH_2)_2OCHPh_2$, 81771-06-4; 4-Py(Ph)$CH(CH_2)_2OCHPh_2$, 81771-07-5; Ph_3C-$(CH_2)_2OCHPh_2$, 81771-08-6; Ph(SPh)$CH(CH_2)_2OCHPh_2$, 68602-18-6; $Ph_2C(SPh)(CH_2)_2OCHPh_2$, 81771-09-7; $Ph_2C(CN)(CH_2)_2OCHPh_2$, 81771-10-0; $Ph_2C(OH)(CH_2)_2OCHPh_2$, 81771-11-1; $PhCH(CO_2H)$-$(CH_2)_2OCHPh_2$, 81771-12-2; $Ph_2C(CO_2H)(CH_2)_2OCHPh_2$, 81771-13-3; Ph_2CHOH, 91-01-0; 3-phenylpropanol, 122-97-4; 1,1′-[(phenylthio)methylene]bisbenzene, 21122-20-3; diphenylpropanol, 20017-67-8; diphenylacetic acid, 117-34-0; 3,3,3-triphenylpropanol, 15070-88-9.

Crystal Structure and Stereochemistry of Florigrandin[1]

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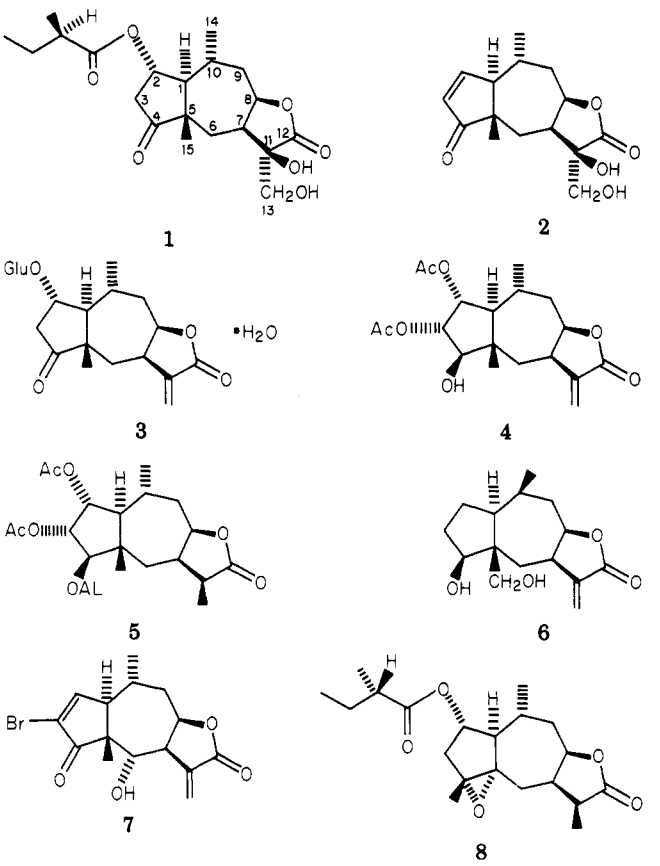
Received February 10, 1982

In a recent note[2] we discussed the problems associated with determining the C-11 stereochemistry of sesquiterpene lactones in which the α-methylene γ-lactone function is oxidized to an 11,13-diol. Two such compounds are the pseudoguaianolides florigrandin and hymenoflorin from *Hymenoxys grandiflora*.[3] The relative and absolute stereochemistry shown in formulas 1 and 2 for C-1, C-2 (for florigrandin), C-5, C-7, C-8, and C-10 has been established,[3] but attempts to use various chiroptical methods for solving the C-11 stereochemistry failed[3,4] and the configuration of the 2-methylbutyrate ester side chain of florigrandin remained unknown.

To settle these matters and to continue our study of the conformations of different types of sesquiterpene lactones, we undertook an X-ray analysis of florigrandin. Crystal data for florigrandin are listed in the Experimental Section. Figure 1a is a stereoscopic drawing of the molecule which shows that the C-11 hydroxyl group is β and that the earlier[3] stereochemical assignments for the other asymmetric centers were correct. Since β elimination of the five-carbon ester side chain results in conversion of florigrandin to hymenoflorin, the stereochemistry of the latter compound is thereby established as well. Figure 1a also represents the absolute configuration because of the negative Cotton effect due to the cyclopentenone chromophore of **2**. Hence the configuration of the 2-methylbutyrate ester side chain is *R*.



Tables I–IV listing final atomic and final anisotropic thermal parameters, bond lengths, and bond angles are available as supplementary material. Table V lists selected torsion angles. As is apparent from these and from Figure 1a and the framework model **1b**, the cycloheptane ring closely approximates a twist boat, whose C_2 axis passes through C-10 and the midpoint of the C-6,C-7 bond. Σ_2, the deviation of the ring from C_2 symmetry,[5] is only 11°. The two five-membered rings are attached to the cycloheptane ring in the C-5(e), C-1(e), and the C-7(e), C-8(e) positions, respectively. The cyclopentanone and the lactone rings are very slightly distorted envelopes with C-5 and C-7 as the respective flaps.

The conformation of the cycloheptane ring of florigrandin is very similar to the conformations found in the C-8 cis-lactonized pseudoguaianolides paucin monohydrate (**3**),[6] hymenograndin (**4**),[7] hymenolane (**5**),[8] and rudmollin (**6**)[9] but different from the conformation found in bromohelenalin (**7**), which approximates a twist chair.[10] Apparently the presence or absence of unsaturation in the cyclopentane ring is of some importance, whereas saturation of the α-methylene γ-lactone ring exercises little influence on the conformation of the seven-membered ring. For reasons that are not immediately apparent, the cyclopentanone ring of paucin monohydrate (**3**), which in all other respects very closely resembles florigrandin, is a half-chair rather than an envelope.[6] It is also noteworthy

(1) Work at the Florida State University was supported in part by a grant from the U.S. Public Health Service (CA-13121) through the National Cancer Institute.

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(4) However, the chemical shift of H-7 in hymenoflorin (2.74 ppm),[3] which indicates little or no deshielding by the C-11 hydroxyl, suggests that the latter is β orientated.

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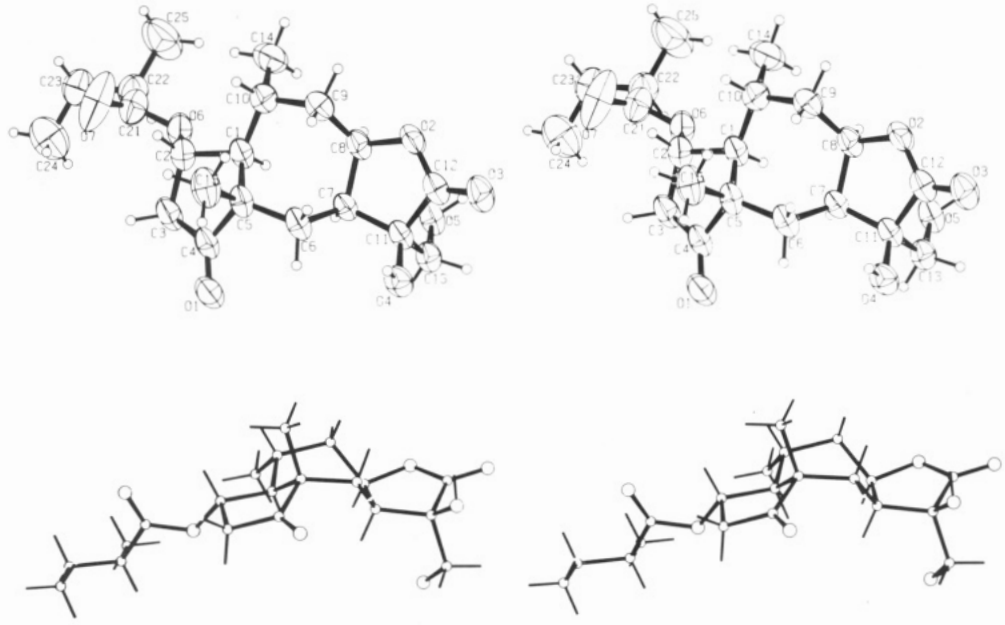

Figure 1. Top: stereoscopic view of florigrandin molecule with ellipsoids of thermal motion. Bottom: side view of molecular framework.

Table V. Torsion Angles (in Degrees) in 1 with Standard Deviations in Parentheses

C(5)-C(1)-C(2)-C(3)	−39.3 (4)
C(1)-C(2)-C(3)-C(4)	22.9 (5)
C(2)-C(3)-C(4)-C(5)	2.9 (5)
C(3)-C(4)-C(5)-C(1)	−26.8 (4)
C(4)-C(5)-C(1)-C(2)	39.7 (4)
C(1)-C(5)-C(6)-C(7)	−15.8 (5)
C(5)-C(6)-C(7)-C(8)	66.8 (5)
C(6)-C(7)-C(8)-C(9)	−10.2 (6)
C(7)-C(8)-C(9)-C(10)	−71.3 (5)
C(8)-C(9)-C(10)-C(1)	44.4 (5)
C(9)-C(10)-C(1)-C(5)	47.6 (5)
C(10)-C(1)-C(5)-C(6)	−68.7 (5)
C(11)-C(7)-C(8)-O(2)	−15.6 (4)
C(7)-C(8)-O(2)-C(12)	8.5 (5)
C(8)-O(2)-C(12)-C(11)	2.8 (5)
O(2)-C(12)-C(11)-C(7)	−12.9 (5)
C(12)-C(11)-C(7)-C(8)	16.9 (4)

that the absolute configurations of the 2-methylbutyrate ester side chains of florigrandin (**1**) and hymenosignin (**9**),[7] the latter isolated from the closely related *Hymenoxys insignis*, differ.

Experimental Section

Single crystals of florigrandin were prepared by slow crystallization from benzene–ethyl acetate. The crystals were monoclinic, space group $P2_1$, with a = 8.528 (6) Å, b = 10.421 (7) Å, c = 11.530 (7) Å, β = 92.76 (6)°, and d_{calcd} = 1.241 g cm^{-3} for Z = 2 ($C_{20}H_{30}O_7$, M_r = 382.45). The intensity data were measured on a Hilger-Watts diffractometer (Ni-filtered Cu Kα radiation, θ–2θ scans, pulse-height discrimination). The size of the crystal used for data collection was approximately 0.04 × 0.5 × 1.0 mm. A total of 1476 independent reflections were measured for $\theta < 57°$, of which 1344 were considered to be observed [$I > 2.5\sigma(I)$]. The structure was solved by a multiple-solution procedure[11] and was refined by full-matrix least-squares methods. Two reflections which were strongly affected by extinction were excluded from the final refinement and difference map. In the final refinement, anisotropic thermal parameters were used for the non-hydrogen atoms and isotropic temperature factors were used for the hydrogen atoms. The hydrogen atoms were included in the structure factor calculations but their parameters were not refined. The final discrepancy indices are R = 0.036 and R_w = 0.041 for the remaining 1342 observed reflections. The final difference map has no peaks greater than ±0.2 e Å^{-3}.

Registry No. 1, 51292-61-6.

Supplementary Material Available: Tables I–IV listing final atomic parameters, final anisotropic thermal parameters, bond lengths, and bond angles for compound 1 (5 pages). Ordering information is given on any current masthead page.

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(*N*-Alkylthiocarbamoyl)phosphonic Acid Esters. 1. Preparation and Spectral Properties

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Received August 25, 1981

(*N*-Alkylthiocarbamoyl)phosphonic acid esters **1** have been prepared and explored only occasionally.[1-3,8] Recently, the increasing interest in the biological effects of α-subsituted methyl phosphonate derivatives (carboxy-[4] and carboxamido phosphonate[5] as antiviral agents, aminomethyl phosphonate as substitutes for amino acids,[6] methylene diphosphonate compounds in treating calcium metabolism disorders,[7] and compounds containing the amidinophosphonate group as antihistaminics[8]) led us to

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