cyanophenylsulfonyl chloride. mp 62–63°C(lit[9]. mp 69–69.5°C)IR(nujol) 3090(aromatic C–H), 2215(CN), 1340, 1178 cm^{-1} (SO_2); ^{1}H-NMR($CDCl_3$)δ7.8 – 8.2 ppm(m, 4H); MS, m/e(relative intensity) 203(4, M+2), 202(2, M+1), 201 (11, M^+), 166(50), 102(100), 75(40).

Synthesis of N-chlorosaccharin. A mixture of saccharin (0.05 mole, 9.15g) or its sodium salt (0.05 mole, 20.5g) and $POCl_3$ (0.3 mole, 30m*l*) was refluxed for 2 – 3 h. After distillation of excess $POCl_3$, the residue was poured into 400 m*l* of cold water with stirring, filtered and dried to give 7.6g (75%) of N-chlorosaccharin. mp 216 – 217°C(lit[8,9]. mp 215 – 216°C); IR(nujol) 1680(C=O), 1565(aromatic C=C), 1305, 1150 cm^{-1} (SO_2); ^{1}H-NMR ($CDCl_3$)δ8.1 ppm(s, 4H).

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A Short Synthesis of Dendrolasin

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(Received October 6, 1984)

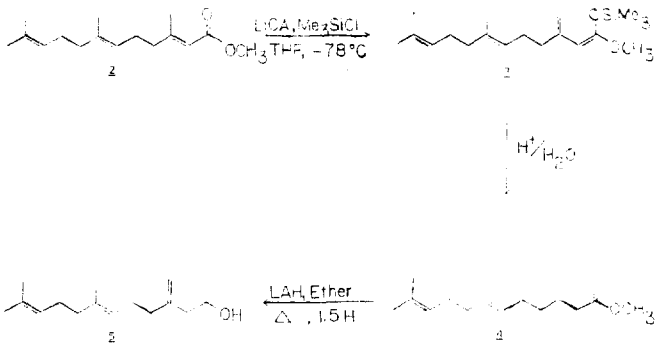
Dendrolasin(**1**) is a representative furanoid sesquiterpene isolated from insects and other sources[1]. Some syntheses of dendrolasin[2] start with 3–substituted furans as starting materials and involve classical problems of forming trans trisubstituted double bond common to many acyclic terpenes. Lithium di (3–furyl) cuprate was used to synthesize 3–substituted furans in general[3]. Geranylacetone[4] and myrcene[5] were also used in the synthesis of dendrolasin: in these cases, furan ring formation is the key step.

A biogenetic–type synthesis was accomplished in this laboratory using farnesol as the starting material[6]. The scheme involves Sharpless epoxidations of allylic and homoallylic alcohols and a crucial 3,4–epoxyaldehyde–furan conversion on a silica gel column. This report describes a new short synthesis of dendrolasin from methyl farnesoate(**2**) in which the homoallylic alcohol intermediate(**5**) is synthesized in three steps from **2**.

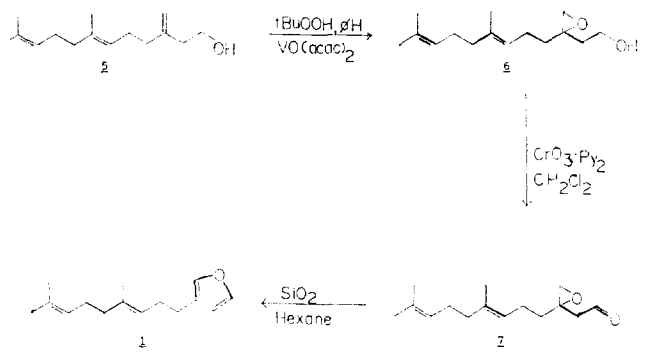
Methyl farnesoate(**2**) was dissolved in THF and added to 1.05 eq. of lithium cyclohexylisopropylamide in THF at −78°. The THF solution was stirred 20 minutes and 2.0 eq. of trimethylsilyl chloride was added to quench the enolate anion. After stirring 30 minutes, standard work-up provided almost quantitative yield of the silyl enol ether(**3**). The H–2 singlet at δ5.60 in the nmr spectrum of methyl farnesoate disappeared completely suggesting facile enolate and subsequent silyl enol ether formation. Under the reaction conditions employed, kinetically favored enolate anion should be predominantly produced and the structural assignment of **3** with an exo methylene unit is supported by the disappearance of the H–15 methyl singlet at δ2.15. Stereochemistry at C–1 involving $-OSiMe_3$ and –OMe is more difficult to define and no effort was made to distinguish E-Z isomers of **3** since both should give rise to the same product at the next step.

Regeneration of methyl ester functionality resulted in the formation of varying ratios of α,β– and β,γ –unsaturated esters depending on the desilylation conditions used. When the silyl enol ether(**3**) was treated with tetra–n–butylammonium fluoride in THF at room temperature, methyl farnesoate was the major component of the product mixture. In the nmr spectrum, the characteristic peaks at δ5.60 and δ2.15 decreased relative to other signals, but the signals for the desired β,γ–unsaturated ester(**4**) were not clearly seen. The ratio of α,β– and β,γ–unsaturated esters was roughly calculated to be 7:3 from the nmr integration experiment.

Simple elution of **3** through a silica gel column with hexane-ethyl acetate(50:1 and 20:1) produced 85% yield of a product which turned out to be 35:65 mixture in favor of the deconjugated ester (**4**). New signals at δ3.04 for H–2 and at δ4.88



Scheme 1.



Scheme 2.

for H-15 were clearly seen in the nmr spectrum.

The best result was obtained when **3** was dissolved in ethyl acetate and the solution was equilibrated briefly with aqueous 2N HCl solution. This procedure produced almost quantitative yield of a crude product consisted of 1:3 mixture in favor of the desired β,γ-unsaturated ester(**4**).

In earlier trial experiments, methyl geraneate was almost totally regenerated upon lithium diisopropylamide treatment and subsequent quenching with aqueous acid. This result, together with that of fluoride desilylation experiment of **3**, indicates that direct acid quenching of the enolate anion involved here results in the predominant formation of α,β-unsaturated esters rather than the desired deconjugated products.

Since the separation of α,β- and β,γ-unsaturated esters was tedious and resulted in the loss of material, subsequent reactions were performed using the mixture of esters as they were obtained from desilylation procedure. Thus the ester **4** was reduced with lithium aluminum hydride in boiling ether to yield crude homoallylic alcohol (**5**) (Scheme 1) and the alcohol **5** was converted to the epoxyalcohol (**6**) using Sharpless epoxidation procedure[7] with an overall yield of 54 %. The epoxyalcohol **6** was cleanly oxidized to the epoxyaldehyde (**7**) upon treatment with chromium trioxide and pyridine in dichloromethane[8]. The crude aldehyde **7** was eluted through a silica gel column in hexane to produce dendrolasin(**1**) in 34 % overall yield. (Scheme 2) The reaction conditions in the conversion of **5** to 1 were already outlined in the previous report[6].

The sequence reported here involves six steps from methyl farnesoate to dendrolasin and the total yield of 18 %.

Acknowledgements. This research was supported by a grant (1982) of the Ministry of Education.

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