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Synthesis of Natural Uvidin C

José LOPEZ, Jorge SIERRA, and Manuel CORTES*
Facultad de Química, Pontificia Universidad Católica de Chile,
Casilla 6177, Santiago, Chile

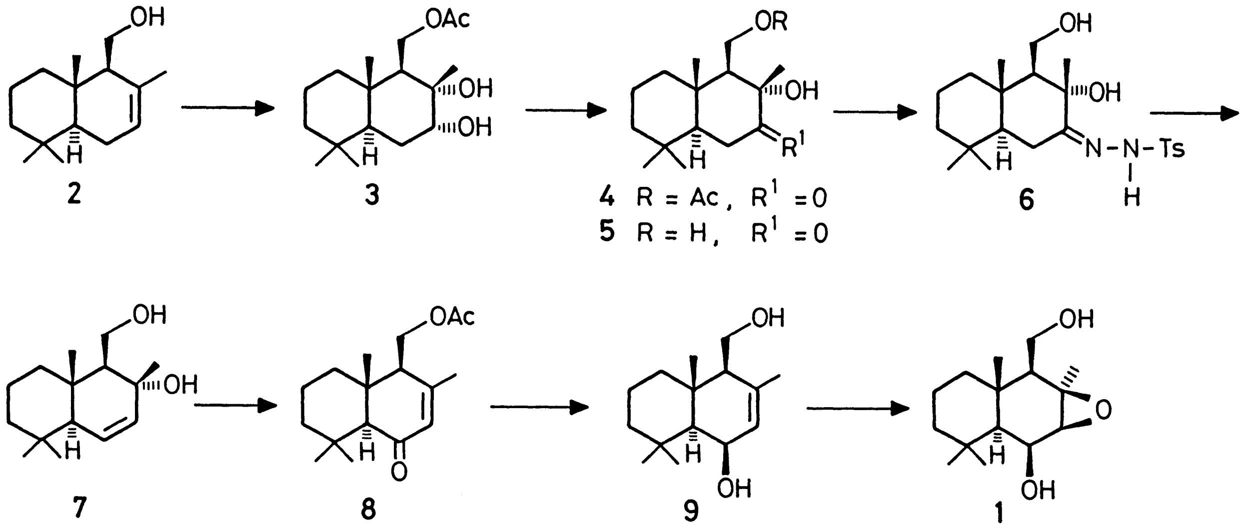
The first synthesis of (-)-Uvidin C from (-)-drimenol through the ketol is described.

Uvidin C (**1**) isolated from *Lactarius uvidus* Fries1) (Basidiomycetes) is an oxidized drimane type sesquiterpene. The presence of the adjacent oxidized functional groups of this molecule aroused interest of its synthesis. A recent communication on the racemic synthesis of this compound2) prompts us to report the first synthesis of (-)-uvidin C with natural configuration.

Drimenol (**2**) which was easily obtained from the bark of *Drimys winteri* Forst3) was chosen as the chiral starting material. By acetylation and dihydroxylation according to the known procedure,4) compound **3** was obtained with an overall yield of 56%. Although we have found in a previous work4) that oxidation of **3** with thioanisol-chlorine gave a 48% yield of ketol **4** oxidation of this compound with N-bromosuccinimide in dichloromethane5) afforded **4** in 70% yield.

Saponification of **4** (KOH,MeOH) followed by treatment of the resulting diol **5** with tosylhydrazide ($BF_3 \cdot OEt_2$, PhH, 12 h) gave compound **6** in 87% yield.6) Tosylhydrazone **6** was converted with BuLi (THF, 0 °C, 24 h)7) to the allylic alcohol **7** in 91% yield.8) Acetylation of **7** and subsequent oxidative rearrangement9) with pyridinium chlorochromate gave enone **8** in 69% yield. Reduction of **8** with DIBAL (THF, 0 °C, 1 h) afforded the allylic alcohol **9** in 98% yield.10)

Finally the synthesis of uvidin C (**1**) was achieved by treatment of **9** with m-chloroperbenzoic acid (CH_2Cl_2, room temperature, 1 h, 95% yield) mp 107-109 °C (lit1) 110-112 °C), $[\alpha]_D^{20}$ - 165°(c 1, CH_3OH)11). The IR and ^1H NMR spectra were identical with those of natural uvidin C.



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References

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8) All attempts to form the allylic alcohol 7 by the selective dehydration of secondary alcohol 3 by means of a variety of reagents resulted in only very low conversion (5-15%).
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10) The 6β configuration of the secondary alcohol is assigned on the presumption of a sterically controlled approach of the reductant to the α face of the keto group of 8.
11) The optical rotation of a natural sample could not be taken owing to a small isolation amount from *L. uvidus* (Personal communication from Prof, P. Vita-Finzi).

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