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Synthesis of Natural Uvidin C

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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 2 with m-chloroperbenzoic acid (CH₂Cl₂, room temperature, 1 h, 95% yield) mp 107-109 °C (lit¹) 110-112 °C), $[\alpha]_D^{20}$ - 165° (c 1, CH₃OH)¹¹). The IR and ¹H NMR spectra were identical with those of natural uvidin C.



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References

- 1) M. De Bernardi, G. Mellerio, G. Vidari , and P. Vita-Finzi, J. Chem. Soc., Perkin Trans. 1, <u>1983</u>, 2739.
- 2) F.E. Ziegler and B.H. Jaynes, Tetrahedron Lett., <u>26</u>, 5875 (1985).
- 3) H.H. Appel, C.J.V. Brooks, and K.H. Overton, J. Chem. Soc., 1959, 3322.
- 4) H. Maturana, J. Sierra, J. López, and M. Cortés, Synth. Commun., <u>14</u>, 661 (1984).
- 5) L.F. Fieser and S. Rajapopalan, J. Am. Chem. Soc., 71, 3938 (1949).
- 6) Attempts to obtain the tosylhydrazone § from the ketol 4 were unsuccessful.
- 7) R.H. Shapiro, "Organic Reactions," ed by W.G. Dauben, John Wiley & Sons, Inc. (1976), Vol. 23, Chap. 3.
- 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%).
- 9) J.M. Luteijn and A. de Groot, J. Org. Chem., <u>46</u>, 3348 (1981).
- 10) The $\delta\beta$ 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 §.
- 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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