

# ISOLATION AND IDENTIFICATION OF 6,7-SECO-AGROCLAVINE FROM *CLAVICEPS PURPUREA*

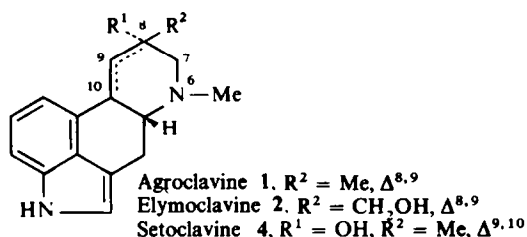
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(Received 10 July 1978)

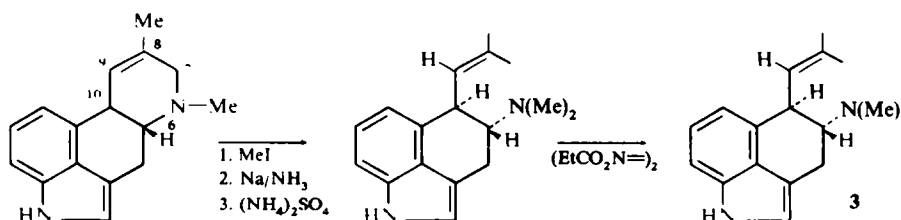
**Key Word Index**—*Claviceps purpurea*, strain AA-218; fungus; clavines; 6,7-seco-agroclavine; ergot alkaloids.

Agroclavine 1 and elymoclavine 2 are the major clavine alkaloids from *Claviceps purpurea*, strain AA-218 [1]. Analysis of the crude fermentation product by TLC (Si gel, 1% conc. ammonia, 5% MeOH, 94% CHCl<sub>3</sub>) has shown 5 additional minor components positive to spraying with Allport and Cocking's reagent. The *R<sub>f</sub>*s are: 0.14 (elymoclavine) (2); 0.39 (3), 0.41 (4); 0.53 (agroclavine) (1); 0.63–0.77 (3 very minor components, not analysed further).



The two most prominent of the minor alkaloids, 3 and 4, have been purified by HPLC followed by PLC, using the above solvent system. Compound 4 has been identified as setoclavine, mp 215–217° dec., (lit. [2], 229–234° dec.) by comparison of the PMR [3] and IR spectra [2] with that published. The UV spectrum has confirmed the presence of the  $\Delta^{9,10}$  double bond [2] and, in addition, the compound gives a green colour with Allport and Cocking's reagent rather than the blue colour seen with the  $\Delta^{8,9}$  clavines [2, 4]. The mass ion of 254 has confirmed the MW.

Compound (3) mp 126–129° subl., gives a blue colour with Allport and Cocking's reagent and has been identified as 6,7-seco-agroclavine by the following spectral data; IR  $\nu_{\text{max}}$  (CHCl<sub>3</sub>); 3480 (indole NH), 3320 (aliphatic NH), 1605, 1445 (C=C) cm<sup>-1</sup>; UV  $\lambda_{\text{max}}$  (EtOH): 225, 283 and 293 nm, PMR (60 Hz),  $\delta$  (CDCl<sub>3</sub>): 1.85 (s, 6H); 2.53 (s, with hyperfine splitting, 3H); 2.4 (br s, 1H); 2.6–3.5 (m, 4H); 3.75–4.15 (m, 1H); 5.0–5.3 (d, 1H (C-10-H)); 6.6–7.3 (m, 4H); 8.1–8.5 (br s, 1H (indole)); and MS *m/e*: 240, 225, 208, 197, 184, 168, 155. Furthermore, the compound is identical in the above respects to a sample synthesized from agroclavine as outlined below [5]:



It is interesting to speculate on the biosynthetic origin of (3) as the occurrence of the discrete dimethylvinyl moiety in ergot alkaloids is unusual. It is found only in clavicipitic acid and in the free isoprenyl unit of dimethylallyltryptophan, the biosynthetic precursor of ergot alkaloids [6]. The accepted oxidative biosynthetic route to clavines from dimethylallyltryptophan through chano-clavine I involves hydroxylation of the *gem*-dimethyl group *before* closure to ring D [6]. Clearly, if 3 is involved in an oxidative sequence to clavines, as previously suggested [7], then it may indeed be a precursor of chano-clavine I. However, its incorporation into agroclavine, elymoclavine or paspalic acid by such a scheme has been excluded by feeding experiments with the radiolabelled material [5, 6]. Although these data do not rule out a role for (3) in the biosynthesis of clavines, it appears more likely that it is a reductive metabolite of agroclavine. The ease at which cleavage of the 6,7-bond of quaternized elymoclavine [8] and agroclavine [5] occurs by chemical methods (for example, with sodium in liquid ammonia, as outlined above) may support this contention.

**Acknowledgements**—We thank Dr. E. Kornfield and Dr. H. Higgins, Eli Lilly and Co., Indianapolis, for supplying the crude agroclavine and Dr. D. Rackham and Mrs. S. Morgan for addition PMR spectra (90 Hz). We also thank Professor J. E. Baldwin and Mr. D. E. Tupper for valuable discussions.

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