Phytochemistry, 1977, Vol. 16, p. 1613. Pergamon Press. Printed in England.

STRUCTURE OF SIBIRINONE, A NEW α-PYRONE FROM *HYPOMYCES*[*]

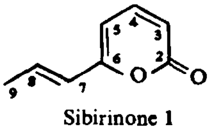
M. S. R. Nair and Susan T. Carey
The New York Botanical Garden, Bronx, NY 10458, U.S.A.

(*Received* 22 *April* 1977)

Key Word Index—*Hypomyces semitranslucens*; *Sibirina fungicola*; fungal metabolite; Pyrenomycete; α-pyrone.

A new α-pyrone, sibirinone, was isolated from a culture of *Hypomyces semitranslucens* G. Arnold, the imperfect state of which is *Sibirina fungicola* G. Arnold. Sibirinone, $C_8H_8O_2$, MW 136.0531, has λ_{max} 333 (4.15) and 226 nm (4.25) and ν_{max} at 1740, 1715 and 1653, 1605, 1550 cm^{-1}. The UV and IR spectra were very similar to those of other extended α-pyrones, [1, 2] suggesting structure **1** for sibirinone. The NMR spectrum showed signals at 1.87 (3H, *dd*, $J = 7.0, 1.2$) for the methyl protons, 5.97 (1H, *d*, $J = 6.5$) for the C_5 protons, 6.03 (1H, *dq*, $J = 15, 1.2$) for the C_7 proton, 6.12 (1H, *d*, $J = 9.5$) for the C_3 proton, 6.67 (1H, *dq*, $J = 15, 7$) for the C_8 proton, and 7.28 (1H, *dd*, $J = 6.5, 9.5$) for the C_4 proton. Signals for the C_3, C_7 and C_5 protons were crowded together and the doublet of the quartet for the C_7 proton was partially obscured. However, on adding Eu $(DPM)_3$, as expected, the signals for the C_3, and to a lesser extent that for the C_5 proton, shifted down field and the C_7 proton signals, which did not shift, were clearly visible. The coupling pattern and constants of the side chain are comparable to those of the *trans*-2-pentenyl A_3XY system of *trans*-crotonic acid and similar compounds [3]. The ring proton shifts show that the substitution is on carbon six and the coupling constants this should be corrected to read $J_{3,4} = 9.5$; $J_{4,5} = 6.5$ ($J_{3,4} = 6.5$, $J_{4,5} = 9.5$) are characteristic of α-pyrones [4].

The mass spectral fragmentation pattern of sibirinone was in complete agreement with this structure: [5]: peaks at 136 (M, 50 %), 108 (M—CO, 95 %), 95 (M—C_3H_5, 40 %) and 89 (M—CO—CHO, 100 %). Sibirinone was hydrogenated in ethanol over platinum catalyst. The main product separated by preparative TLC, had MS peaks at 144 (M), 99, 73 and 60 (base peak). This compound was identified as *n*-octanoic acid by comparison of its IR spectrum with that of an authentic sample. Formation of the octanoic acid on hydrogenation, further confirms the structure of sibirinone as **1**. Sibirinone was not active against the strain of *Staphylococcus aureus* (ATCC 9144) used in our serial dilution tests.



Sibirinone **1**

EXPERIMENTAL

General procedures. Mps are uncorr. PMR spectra were taken in $CDCl_3$ with TMS as internal standard and are expressed in the δ scale.

Isolation of sibirinone. H. semitranslucens was grown in still culture in a dextrose–yeast medium in Fernbach flasks in the dark at 25°. The culture was harvested after four weeks. The culture liquid was extracted with EtOAc and the extract was taken to dryness *in vacuo*. The residue was then chromatographed on a Si gel column (50 times the weight) and sibirinone was eluted with petrol–EtOAc (1 : 1) and was crystallised from Et_2O–petrol (1 : 1), mp 58–59°.

Hydrogenation of sibirinone. Sibirinone (10 mg) was hydrogenated in the presence of reduced PtO (15 mg) in EtOH. The products were separated by preparative TLC. The main component was *n*-octanoic acid.

Acknowledgements—This work was supported by grants RO1-AI13074 and RO1-AI13247 from the Institute of Allergy and Infectious Disease, National Institutes of Health. Authors are grateful to Dr. C. T. Rogerson who identified the fungus and provided the culture, and Mr. F. Manginelli and Mr. T. Amoto for technical assistance.

REFERENCES

1. Nair, M. S. R. and Carey, S. T. (1975) *Tetrahedron Letters* **19**, 1655.
2. Scott, A. I. (1964) *Interpretation of Ultraviolet Spectra of Natural Products* p. 141. Pergamon Press, New York.
3. Kowalewski, V. J. and De Kowalewski, D. G. (1960) *J. Chem. Phys.* **33**, 1794.
4. Batterham, T. J. (1973) *NMR Spectra of Simple Heterocycles*, p. 392. John Wiley, New York.
5. Budzikiewicz, H., Djerassi, C. and Williams, D. H. (1967) *Mass Spectrometry of Organic Compounds*, pp. 208–210. Holden-Day, San Francisco.

---

[*] Part 7 of the series, 'Metabolites of Pyrenomycetes'; for Part 6 see Nair, M. S. R. (1976) *Phytochemistry* **15**, 1090.