Tetrahedron Letters No. 19, pp. 1637-1639, 1970. Pergamon Press. Printed in Great Britain.

THE STRUCTURES OF CORIOLIN B AND C

Shuji Takahashi, Hironobu Iinuma, Tomohisa Takita, Kenji Maeda & Hamao Umezawa

Institute of Microbial Chemistry, Shinagawa-ku, Tokyo, Japan

(Received in Japan 25 February 1970; received in UK for publication 23 March 1970)

In the previous paper1), we reported the structure of coriolin (I) which was isolated from a cultured broth of a Basidiomycetes, Coriolus consors. In this paper we wish to describe the structures of coriolin B and C.

Coriolin B (II) m.p. 215-6°, is obtained from the mycelium by extraction with organic solvents. The molecular formula, $C_{23}H_{36}O_6$ is shown by mass spectrometry and elemental analysis. The IR spectrum shows an ester bond at 1720 cm^{-1} and hydroxy groups at 3420 and 3450 cm^{-1}. In the NMR spectrum (Fig. 1), a hydrogen on a carbon carrying an esteric oxygen is signaled by a doublet peak at 4.95 δ (J=9.0), and two doublets at 4.43 (J=1.5) and 3.74 δ (J=6.0) suggest the presence of two secondary alcohols.

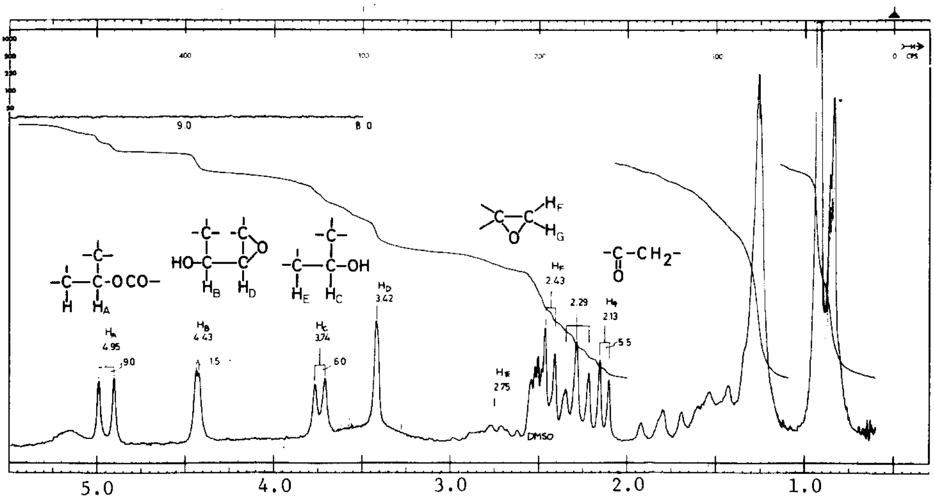
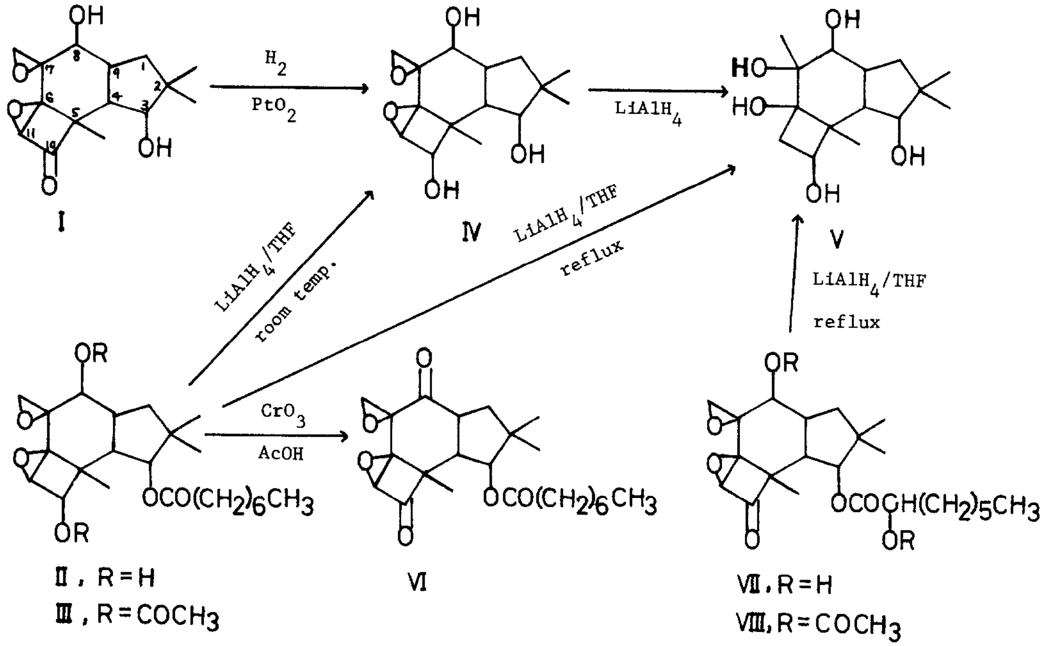


Fig. 1. NMR Spectrum of Coriolin B (100MHz;$CDCl_3$)



Acetylation of coriolin B with acetic anhydride-pyridine at room temperature gives a diacetate (III) [ν_{max}^{liquid} 1740 cm^{-1}(ester), no hydroxy band; mol. wt. 492 (mass spectroscopy)]. Two carbinol protons (4.43 and 3.74δ) of the parent compound shift to at 5.59 (J=2.5) and 5.05δ (J=6.0) in the diacetate, respectively.

Hydrolysis of coriolin B with alkali affords n-caprylic acid which was identified by comparison of IR and mass spectra of the methyl ester with those of the authentic sample.

Reduction of coriolin B with $LiAlH_4$ in THF at room temperature gives dihydrocoriolin (IV)[1] and n-octyl alcohol (identified by mass spectrometric and gas chromatographic comparisons). With the same reagent, hexahydrocoriolin (V) is obtained under refluxing. From these observations, it is deduced that coriolin B is an ester of dihydrocoriolin and n-caprylic acid.

Oxidation of coriolin B with CrO_3 in acetic acid at room temperature gives a diketone (VI) [$C_{23}H_{32}O_6$; m.p. 148°; ν_{max}^{KBr} 1760 (α-epoxy cyclobutanone), 1755 (ester), 1721 cm^{-1} (cyclohexanone), and no hydroxy absorption; mol. wt. 404 (mass spectroscopy)]. This indicates that two secondary hydroxy groups of coriolin B are at C-8 and C-10, and a n-capryl ester at C-3. The position of the ester is confirmed further by comparison of NMR spectra of coriolin B and dihydrocoriolin; that is, C-3 hydrogen of dihydrocoriolin was at 3.4δ (d, J=9.0) and that of coriolin B shifted to at 4.95δ (d, J=9.0).

Coriolin C (VII) is another metabolite isolated from the mycelium. The molecular formula $C_{23}H_{34}O_7$ was established by mass spectrometry. The IR spectrum shows the presence of an ester bond at 1740, α-epoxy cyclobutanone function at 1760, and a hydroxy group at 3450 cm^{-1}. The NMR spectrum shows the presence of four methyl groups [0.95 (s), 1.05 (s), 1.15 (s), and 0.95δ (t, J=6.5)] and an exocylic ethylene oxide (2.49 and 3.02δ, J=6.0). A singlet peak at 3.47δ indicates the presence of α-epoxy cyclobutanone. A hydrogen on a carbon carrying the esteric oxygen is signaled by a doublet peak at 5.09δ (J=8.0), and two carbinol protons are present at 3.94 .

Reduction of coriolin C with $LiAlH_4$ in THF gives hexahydrocoriolin (V) and n-octan-1,2-diol (identified by IR, MS, and GC comparisons). These observations suggest that coriolin C is an ester of coriolin and α-hydroxy n-caprylic acid.

Acetylation of coriolin C with acetic anhydride-pyridine gives a diacetate (VIII) [$C_{27}H_{38}O_9$; mol. wt. 506 (mass spectroscopy), ν_{max}^{liquid} 1760, 1740 cm^{-1}, and no hydroxy band]. The NMR spectrum (Fig. 2) shows signals at 5.19 (1H; d, J=5.5) and 4.85δ(1H; t, J=6.0), indicating the presence of two secondary hydroxy groups in the parent compound. The position of α-hydroxyl-n-capryl ester of coriolin C was determined to be at C-3 by comparison of NMR spectra of coriolin and coriolin C; that is, C-3 hydrogen of coriolin was at 3.47δ(d, J=9.5) and that of coriolin C shifted to at 5.09δ(d, J=8.0).

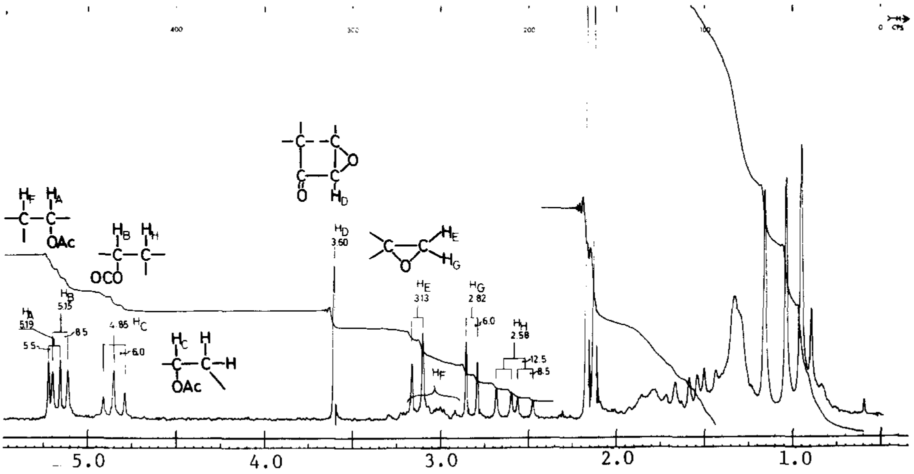


Fig. 2. NMR Spectrum of Coriolin C Diacetate (100MHz;$CDCl_3$)

References

1. S. Takahashi, H. Iinuma, T. Takita, K. Maeda and H. Umezawa, Tetrahedron Letters, No. 53 4663 (1969).