symmetry plane passes through C(1) (ΔC_s—C=69.0°) indicates that the ring conformation lies closer to the more frequently encountered, lower energy twist-chair form.[5]

Acknowledgement Crystallographic calculations, performed on an IBM 370/165 computer located at the Triangle Universities Computation Centre, Research Triangle Park, North Carolina, were supported by a grant of computer time from Duke University.

Faculty of Pharmacy
Meijo University
Yagoto, Tempaku,
Nagoya

HIROSHI FURUKAWA
MASATAKA ITOIGAWA
NOBUKO KUMAGAI
KAZUO ITO

Paul M. Gross Chemical Laboratory
Duke University
Durham, North Carolina 27706,
U.S.A.

ANDREW T. MCPHAIL
KAY D. ONAN

Received January 17, 1978

5) A.T. McPhail and G.A. Sim, *Tetrahedron*, **29**, 1751 (1973).

[Chem. Pharm. Bull. 26(4)1337—1338(1978)]

UDC 547.914.02 : 581.192

Structure of Anthriscusin, a New Phenylpropanoid Ester from the Roots of *Anthriscus sylvestris* HOFFM.

A new phenylpropanoid ester, anthriscusin was isolated from the roots of *Anthriscus sylvestris* HOFFM. (Umbelliferae), and was elucidated as O-[(*Z*)-2-angeloyloxymethyl-2-butenoyl]-3-methoxy-4,5-methylenedioxycinnamyl alcohol on the basis of the spectral data and the chemical evidence.

Keywords——anthriscusin; O-[(*Z*)-2-angeloyloxymethyl-2-butenoyl]-3-methoxy-4,5-methylenedioxycinnamyl alcohol; phenylpropanoid ester; (*Z*)-2-angeloyloxymethyl-2-butenoic acid; 3-methoxy-4,5-methylenedioxycinnamyl alcohol; crocatone; *Anthriscus sylvestris* HOFFM.

Anthriscus sylvestris HOFFM. (Umbelliferae) is a perennial herb growing in Eurasia and eastern North America. The roots of this plants had been used once as one of the chinese drug "qianhu (前胡)" and had been demonstrated to afford a lignan, anthricin(desoxypodophyllotoxin).[1] In order to examine the constituents of this plants more closely, the authors have reinvestigated this roots and have obtained a new phenylpropanoid ester(I), named anthriscusin, besides several lignans and carboxylic acid from the hexane extract. The structure of I was established as O-[(*Z*)-2-angeloyloxymethyl-2-butenoyl]-3-methoxy-4,5-methylenedioxycinnamyl alcohol on the basis of the spectral data and the chemical evidence. This paper deals with the structure elucidation of I.

I, viscous liquid, yield 0.05%, $bp_{0.25}$ 205—210°, $C_{21}H_{24}O_7$, gives a violet coloration with chromotropic acid and sulfuric acid and shows the infrared absorption bands (cm^{-1}, $CHCl_3$) at 1720, 1700 (C=O); 1643, 1625 (C=C); 1605, 1500 (aromatic ring). The proton magnetic resonance (PMR) spectrum of I exhibits the signals (δ ppm, $CDCl_3$) at 1.89 (3H, m), 1.94 (3H

1) T. Noguchi and M. Kawanami, *Yakugaku Zasshi*, **60**, 629 (1940).

m) and 6.05 (1H, m) which can be assigned to angeloyl group, and the signals at 2.12 (3H, br. d, J=7 Hz), 4.83 (2H, br. s) and 6.58 (1H, br. q, J=7 Hz) being attributable to O-acylated sarracinoyl group. These signals are almost superimposable with those of (*Z*)-2-angeloyloxymethyl-2-butenoic acid(II), which has been isolated from this plant material besides I, suggesting the presence of the moiety of this acid in I, and this was confirmed by the identification of angelic and sarracinic acids on alkaline hydrolysis of I.

In addition to angelic and sarracinic acids, I gave an alcoholic compound(III), mp 79°, $C_{11}H_{12}O_4$, on the hydrolysis, whose PMR spectrum shows the signals (δ ppm, $CDCl_3$) due to the protons of methoxyl group at 3.89 (3H, s), methylenedioxyl group at 5.96 (2H, s) and 3-hydroxy-1-propenyl group at 1.75 (1H, s); 4.27 (2H, d, J=6 Hz); 6.17 (1H, d-t, J=15 and 6 Hz); 6.52 (1H, d, J=15 Hz) as well as a pair of doublets at 6.55 and 6.62 with the coupling constant of 1.5 Hz arising from two aromatic protons. These spectral data reveal that III must be the alternative of 3-methoxy-4,5-methylenedioxycinnamyl alcohol (III-a) or 3-methoxy-5,6-methylenedioxycinnamyl alcohol (III-b).

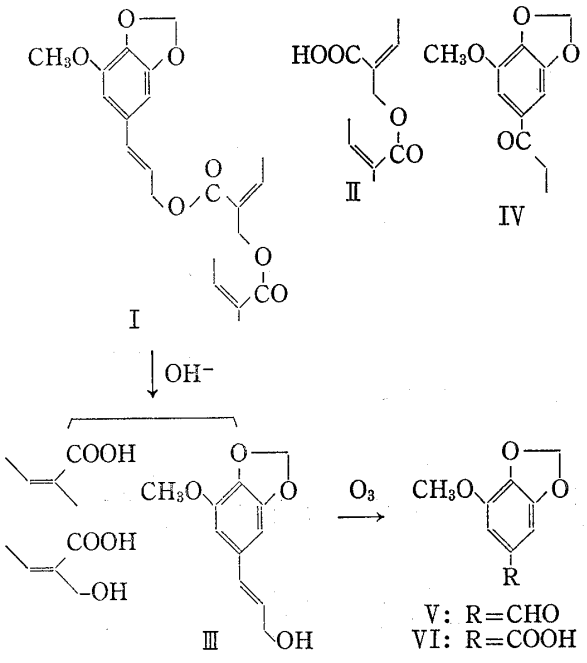

Chart 1

Taking into consideration the facts that 3-methoxy-4,5-methylenedioxypropiophenone(latifolone or crocatone[2]) (IV) was isolated from this plant material besides I and that tri-alkoxylated phenylpropanoids occurring in the Umbelliferous plants were known to have 3,4,5- and 2,4,5-trialkoxylated patterns,[3] III-a might be preferred for the structure of III. The chemical evidence for this assignment was given from the fact that III gave 3-methoxy-4,5-methylenedioxybenzaldehyde (myristicinaldehyde) (V) and 3-methoxy-4,5-methylenedioxybenzoic acid (VI) on ozonolysis.

Consequently, the structure of I is established as O-[(*Z*)-2-angeloyloxymethyl-2-butenoyl]-3-methoxy-4,5-methylenedioxycinnamyl alcohol. It is interesting that this phenylpropanoid ester, anthriscusin, consists of the rare carboxylic acid which is the ester of a carboxylic acid and a hydroxycarboxylic acid.

Acknowledgement The authors are indebted to Dr. A. Numata and Miss J. Shimada of this college for measuring the NMR spectra and to Mrs. Y. Tsujibo of this college for micro analysis. They are also grateful to Mr. S. Nishizawa of the principal of Kumogahata junior highschool for affording the convenience for collecting the plants.

Osaka College of Pharmacy
Kawai-2-Chome, Matsubara,
Osaka Pref., Japan

Mitsugi Kozawa
Nobuko Morita
Kiyoshi Hata

Received January 23, 1978

2) M. Plat, J.L. Men, and M.M. Janot, *Bull. Soc. Chem. Biol.*, **45**, 1119 (1963); K. Hata, M. Kozawa, K. Baba, and M. Mitsui, *Yakugaku Zasshi*, **93**, 248 (1973).
3) V.H. Heywood(ed.) "The Biology and Chemistry of the Umbelliferae," Linnean Society of London by Academic Press, 1971, pp. 301—303.