with 0.1*N* acetic acid. Recrystallization from water gave colorless prisms of I, m.p. 151~152° (decomp.).

Infrared spectrum in Nujol mull of the synthesized ibotenic acid (I) was completely superimposable on that of the natural ibotenic acid. Paper chromatography (solvent; butanol-acetic acid-water=4:1:1), thin-layer chromatography on cellulose powder (solvent; butanol-acetic acid-pyridine-water=15:3:10:12) also proved the complete identity.

This work was especially accelerated by the encouragement of Dr. Iwai of this laboratory whom the authors deeply appreciate. The authors are also very grateful to Professor T. Takemoto, Tohoku University, for supplying us with a sample of natural ibotenic acid.

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Received October 19, 1965

[Chem. Pharm. Bull. 14(1) 94~96 (1966)]

UDC 581.19 : 582.893 : 547.587.51 : 615.32

The Constitution of Anomalin, a New Coumarin Isolated from the Root of *Angelica anomala* Lall. (Umbelliferae)

Angelica anomala Lall. is a stout herb widely distributed in northeastern Asia, and it has been regarded as one of the original plants of "Pai-chi," Chinese Angelica root.

In the previous paper,[1] it was reported that two known coumarins, umbelliferone and bergapten, were isolated from the ether extract of dried root of this species collected from Aomori Prefecture. Recently, a new blue-fluorescent compound, $C_{24}H_{26}O_7$, m.p. 173~174°, $[\alpha]_D^{27}$ −78.4° (EtOH), named anomalin (I), was isolated by silica gel column chromatography from the ether extract. The present communication concerns the structure elucidation of the compound.

Anomalin is freely soluble in ethyl acetate, benzene and chloroform, and sparingly soluble in ethanol, ether and hexane. It crystallizes from ethanol in colorless needles and it gives no reaction towards phenol and carbonyl reagents.

Its ultraviolet spectrum, maxima at 323 mμ and minima at 265 μ, is very similar to those reported for a number of 7-oxygenated coumarins.[2,3]

The infrared spectrum of anomalin reveals the presence of a conjugated lactone, an ester and an aromatic group. These spectra and blue-fluorescence indicate its coumarin structure which has been subsequently confirmed from chemical evidence discussed in the sequel.

The NMR spectrum of anomalin shows two pairs of doublet with intensities corresponding to one proton each, one pair appearing at τ 2.38 and 3. 80 (J=9.5 c.p.s.) can be assigned to protons at the 4- and 3-position respectively, and the other at τ 2.60 and 3.18 (J=8.5 c.p.s.) for the *ortho*-protons in the benzene ring. Further signals are observed at τ 3.30 and 4.56 (each 1H, doublet, J=5 c.p.s.), at τ 3.92 (2H, multiplet) and

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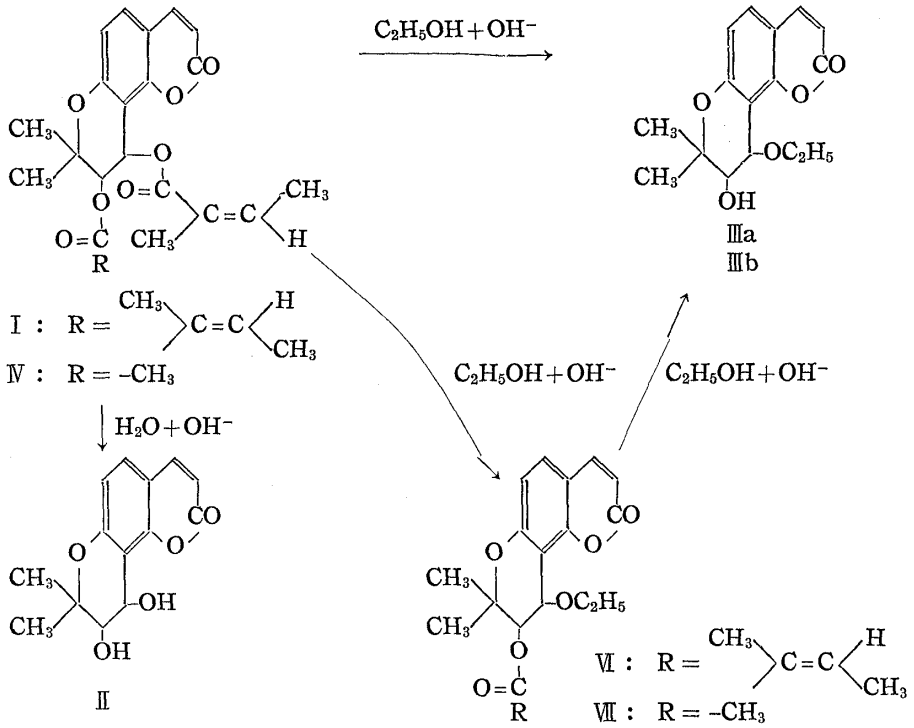
2) R.E. Willette, T.O. Soine: Journal of Pharmaceutical Sciences, **51**, 149 (1962).
3) E. Smith, N. Hosansky, W.G. Bywater, E.E. van Tamelen: J. Am. Chem. Soc., **79**, 3534 (1957).

and about 8.0 (12H, multiplet), and at τ 8.52 and 8.54 (each 3H, singlet).

Saponification of anomalin with hot aqueous base led to the formation of angelic acid, identified as its *p*-phenylphenacyl ester, and a compound (Ⅱ), m.p. 182~183°, $C_{14}H_{14}O_5$, which yielded diacetate, $C_{18}H_{18}O_7$, m.p. 157~158°. Since any other acid could not be detected upon saponification, anomalin might be diangelate of the product (Ⅱ).

When a solution of anomalin in ethanolic sodium hydroxide was refluxed, two optically active substances, m.p. 157~158°, $[\alpha]_D^{27}$ −62.6°(EtOH) (Ⅲa) and m.p. 127~128°, $[\alpha]_D^{28}$ +138.5°(EtOH) (Ⅲb), both having the composition $C_{16}H_{18}O_5$, were formed. These compounds were confirmed to be identical with (−)-*trans*- and (+)-*cis*-ethylkhellactone respectively by the mixture melting point determination with the authentic samples of these compounds obtained from pteryxin by Soine *et al.*[2] It is well recognized that pteryxin (Ⅳ) and the allied coumarins bearing benzyl ester at the position 4′ undergo solvolysis with O-alkyl cleavage upon the treatment with ethanolic alkali forming the same ethylkhellactones.[2,3]

Accordingly, this evidence coupled with the NMR spectra elaborates the structure of anomalin as formula I, 3′,4′-diangeloyloxy-3′,4′-dihydroseselin. Further support for this assignment was obtained by the partial hydrolysis as follows.



When anomalin was treated with 1*N* ethanolic alkali for 15 minutes at a room temperature, a viscid oil besides angelic acid was obtained, which was purified chromatographically over silica gel until it gave single spot on the thin-layer chromatography. It gave an analysis corresponding to the composition $C_{21}H_{24}O_6$, and yielded angelic acid and (−)-*trans*-ethylkhellactone (Ⅲa) upon further saponification. The NMR spectrum of this product shows the signals for the protons attached to an ethoxyl and an angeloyl group.

It is known that pteryxin and the allied coumarins upon controlled hydrolysis with ethanolic alkali yield products in which an acyl group remains at the 3′-position,[2] *e. g.* 3′-acetyloxy-4′-ethoxy-3′,4′-dihydroseselin (Ⅶ) from pteryxin. These observations indicate that structure of the product must be represented as formula Ⅵ, and provide support for the proposal assigning structure I for anomalin.

The stereochemical studies are presently under investigation.

The authors are gratefully indebted to Professor T.O. Soine, the Department of Pharmaceutical Chemistry, College of Pharmacy, University of Minnesota, Minneapolis, U.S.A., for his kind making the mixture melting point determination. They are also grateful to Dr. T. Shingu, this Faculty, for the measurement of NMR spectra and to the members of the Institute of Elemental Analyses of Kyoto University for microanalyses.

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Received November 11, 1965

[Chem. Pharm. Bull. 14(1) 96~97 (1966)]

UDC 581.13 : 547.982

Biosynthesis of Lichen Substances. II. Participation of C_1-Unit to the Formation of β-Orcinol Type Lichen Depside

Previously, we reported[1] that the lichen depsides, lecanoric acid and atranorin were formed by "head to tail" condensation of acetate, while formate took part as a source of methyl and aldehyde groups of atranorin type depsides.

In the present study, tritium labeled orsellinic and β-orcinolcarboxylic acids which were obtained by the hydrolysis of lecanoric acid and atranorin, respectively with tritiated acid, were administered to fresh *Parmelia tinctorum* DESPR. by the same technique as previously reported. From the result as shown in Table I, it was recognized that orsellinic acid and β-orcinolcarboxylic acid afforded smoothly lecanoric acid and atranorin, respectively. However, the incorporation of tritiated orsellinic acid into atranorin or tritiated β-orcinolcarboxylic acid into lecanoric acid was not observed. These results showed that the participation of formate (or C_1-unit) to form β-orcinolcarboxylic acid should occur before the formation of the aromatic ring of orsellinic acid.

TABLE I. Incorporation of ^3H-Phenolcarboxylic Acids into the Depsides in *Parmelia tinctorum*

Precursor / Compound	Specific radioactivity (d.p.m./mM)	
	Orsellinic acid-^3H	β-Orcinolcarboxylic acid-^3H
Lecanoric acid	5.0×10^5	0
Atranorin	0	1.2×10^5
Chloroatranorin	0	4.2×10^4

The authors wish to thank Dr. Y. Kashida, National Institute of Radiological Sciences, and Dr. S. Kurokawa of National Science Museum of Tokyo for their kind advices.

1) M. Yamazaki, M. Matsuo, S. Shibata : This Bulletin, **13**, 1015 (1965).