Tetrahedron Letters No.14, pp. 1461-1465, 1966. Pergamon Press Ltd.
Printed in Great Britain.

THE CONSTITUTION OF DECURSIN, A NEW COUMARIN ISOLATED FROM THE ROOT OF ANGELICA DECURSIVA FR. ET SAV. (UMBELLIFERAE)

K.Hata and K.Sano
Faculty of Pharmaceutical Sciences
Kyoto University
Kyoto, Japan

(Received 27 January 1966)

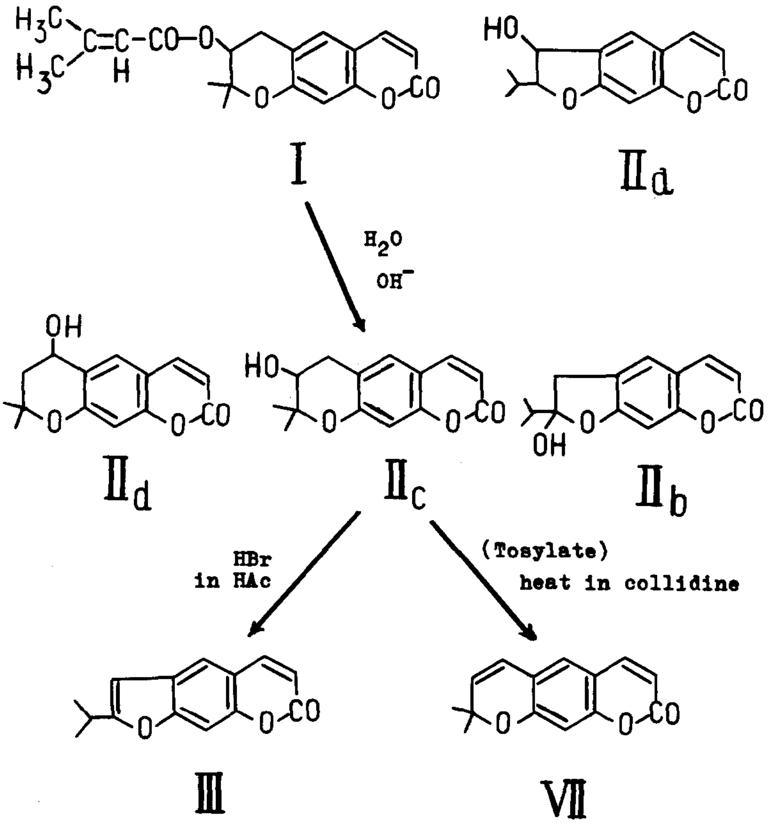
Angelica decursiva Fr. et Sav. (Japanese name "Nodake") is a stout herb widely distributing in Japan and China, and has been regarded as one of original plants of "Qianhu", Chinese Peucedanum root. Originally, the root of this species was chemically investigated by Arima, who isolated a coumarin glucoside, so called nodakenin (1). Later, the structure of its aglycon, nodakenetin, was elucidated by Späth, et al (2). Recently, the authors have isolated a new coumarin compound, named decursin (I), $C_{19}H_{20}O_5$, m.p.110-111°, $[\alpha]_D^{15}$ +172.9°($CHCl_3$), besides above nodakenetin and a known coumarin, umbelliferone, from the ethereal extract of the root after chromatography on silica gel. The present communication concerns the structure elucidation of the compound.

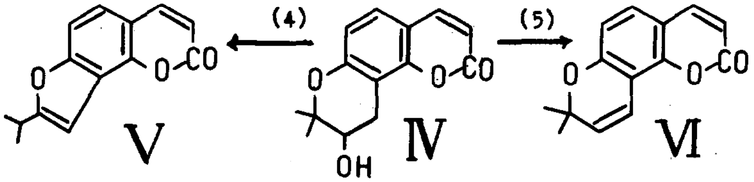
Decursin is soluble in benzene, ethyl acetate, chloroform and ethanol, and sparingly soluble in ether and n-hexane. It is crystallized from ethanol as colorless prisms, and negative towards phenol and carbonyl reagents. The ultraviolet spectrum of the compound, maxima at 330mμ and minima at 265mμ, is similar to those of umbelliferone derivatives. The infrared spectrum of decursin reveals the presence of the following functional groups, a conjugated lactone, an ester, a double bond and an aromatic ring.

The NMR spectrum of the compound shows a pair of doublets at τ3.98 and 2.55 with coupling constance 9.5cps, which are identical with the signals of 3 and 4 protons of the coumarin system, respectively. Two singlets at τ3.39 and 2.93 can be assigned to the para protons of the benzene ring. These signals are suggestive of the presence of 6,7-disubstituted coumarin nucleus in decursin. Further signals are observed at τ8.65(6H) for gem-dimethyl, at τ8.12, 7.87(3H each) and 4.41 (1H) for senecioyl group. ABX pattern centering at τ6.81, 7.27(1H each) and 5.00(1H) suggests the presence of $>CH-CH_2-$ grouping.

Hydrolysis of I with hot aqueous or ethanolic alkali led to the formation of senecioic acid, identified by its p-phenyl phenacyl ester, and a neutral substance (II), $C_{14}H_{14}O_4$, m.p.176-177°, which gave monoacetate, $C_{16}H_{16}O_5$, m.p.138-139°. The NMR spectrum of II shows a signal of a hydroxyl proton, which was eliminated by exchange with D_2O. The X-portion of ABX pattern in the NMR spectrum of II appears at τ6.11, which is about 70cps higher than those of I and the monoacetate, indicating the presence of a secondary hydroxyl group which is senecioylated in I (3).

Acid catalyzed dehydration of II afforded a known compound, anhydronodakenetin (III) which was originally derived from nodakenetin by Späth, et al (4). This result indicated that decursin possesses the coumarin nucleus which contains


I
IIa
H2O
OH⁻
IId
IIc
IIb
HBr
in HAc
(Tosylate)
heat in collidine
III
VII


(4)
(5)
V
IV
VI

a ring system attached through an ethereal oxygen at the position 7 to position 6.

Based on the formation of III as a dehydrated product of II, possible structure of II as the furanocoumarin type would be presented by the alternative formulae, IIa or IIb. These, however, must be ruled out by nonconformity to the NMR spectrum of II. The remaining structural possibilities were IIc or IId, assuming that a ring contraction could occur under the conditions of dehydration to yield III. Similar ring contraction has been known to occur on acid catalyzed dehydration of lomatin (IV) resulting the formation of dihydroöroselone (V) (5), while it has been reported that jatamansinol, established to have the same plane structure as IV, was dehydrated accompanying no ring contraction to yield seselin (VI), when its tosylate was heated in collidine (6). When the tosylate of II was treated under the same condition as that above mentioned, xanthyletin (VII) was formed. This result confirmed that the compound (II) possesses the structure of pyranocoumarin type, IIc or IId.

The compound (II) was fairly stable towards chromic acid - pyridine, revealing the absence of benzylic hydroxyl group. This observation conducted the view that the structure of II is preferably presented by IIc. Further evidence for this assignment was obtained by investigating the NMR spectrum of II. The signals at τ6.84 and 7.22, AB-portion of ABX pattern being similar to those reported for the 4'-protons of lomatin (at τ6.89 and 7.07) (5), are in conformity with the presence of the methylene protons on the benzylic carbon (7). Morever, the signal at τ6.11, X-portion of ABX pattern, is at the right position for the methine proton attached to a carbon bearing secondary hydroxyl group (3), while it has been reported that such a proton on the benzylic carbon in costatolide exhibits a signal at τ4.98 (8).

Thus, the compound (II) was confirmed to be 3'-hydroxy-3',4'-dihydroxanthyletin (IIc), elaborating the structure of decursin as 3'-senecioyloxy-3',4'-dihydroxanthyletin (I).

The stereochemical studies are presently under investigation.

Acknowledgment

The authors are gratefully indebted to Professor (Mrs.) A.Chatterjee, Department of Chemistry, University College of Science, Calcutta, India, for supplying an authentic sample of xanthyletin, to Dr.T.Shingu of this Faculty for the measurement of NMR spectra, and to the members of the Institute of Elemental Analyses of Kyoto University for Microanalyses.

REFERENCES

1. J.Arima, Jour.Chem.Soc.Japan **48**,457 (1927); **49**,530 (1928)
2. E.Späth and E.Tyray, Ber.dtsch.Chem.Ges. **72**,2089 (1939)
3. L.M.Jackman, "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry",Pergamon Press, p.55 (1959)
4. E.Späth and P.Kainrath, Ber.dtsch.Chem.Ges. **69**,2062 (1936)
5. T.O.Soine and F.H.Jawad, Jour.Pharm.Sci. **53**,990 (1964)
6. S.N.Shanbhag, C.K.Mesta, M.L.Maheshwari, S.K.Paknikar and S.C.Bhattacharyya, Tetrahedron **20**,2605 (1964)
7. L.M.Jackman, "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry",Pergamon Press, p.58 (1959)
8. G.H.Stout and K.L.Stevens, Jour.Org.Chem. **29**,3604 (1964)