[Chem. Pharm. Bull.
21(9)2095—2097(1973)]

UDC 547.587.51.02 : 581.192

Stereostructures of Decursin, Decursidin, and a New Coumarin Isolated from *Angelica decursiva*

In the previous paper,[1] we reported the isolation of two new coumarins named decursin and decursidin from the ether extract of the root of *Angelica decursiva* Fr. *et* Sav. (Japanese name: nodake, Umbelliferae), and proposed their plane structures as 3'-senecioyloxy-3',4'-dihydroxanthyletin and 3',4'-disenecioyloxy-3',4'-dihydroxanthyletin respectively (I and V without stereochemistry). The further investigation of the root ingredients has enabled us to elucidate that decursin and decursidin possess the (3'*S*)- and (3'*S*,4'*R*)-configurations as depicted by I and V and, in addition, has resulted in the isolation of a new coumarin (tentatively designated as AD-II) whose stereostructure is expressed as IX. The present communication deals with the evidences supporting the conclusions.

Decursinol (II),[1] mp 177—178°, $[\alpha]_D^{26}$ +10.8° ($CHCl_3$), $[\alpha]_D^{17}$ +103.8° (pyridine), prepared by alkaline hydrolysis of decursin (I), was treated with sodium amalgam to afford 3,4-dihydrodecursinol (III), $C_{14}H_{16}O_4$,[2] mp 140—142°, $[\alpha]_D^{20}$ +29.7° (MeOH), which was subsequently converted to a benzoate (IV), $C_{21}H_{20}O_5$, mp 54—56°, $[\alpha]_D^{10}$ +39.7° (MeOH). Since the benzoate shows a negative Cotton effect at 228 nm ($\Delta\varepsilon = -8.59$) in its cptical density (CD) spectrum, the absolute configuration of IV is determined to be 3'(*S*) on the basis of the benzoate sector rule of Nakanishi, *et al.*[3] and hence decursin is expressed as 3'(*S*)-senecioyloxy-3',4'-dihydroxanthyletin (I). The conclusion is in good agreement with the proposal by Lemmich and Nielsen[4] who elucidated, on the basis of chemical degradation, the absolute configuration of 3'(*R*)-hydroxy-3',4'-dihydroxanthyletin, mp 180.5—181.5°, $[\alpha]_D^{23}$ −11° ($CHCl_3$), $[\alpha]_D^{23}$ −102° (pyridine), an optical antipode of decursinol (II). The antipode was actually isolated as an angeloyl ester by Lemmich, *et al.*[5] from the ether extract of the root of *Seseli libanotis* (L.) Koch subsp. *eu-libanotis* (Umbelliferae).

Aqueous alkaline hydrolysis of decursidin (V) initially furnished a (−)-diol (VIa), $C_{14}H_{14}O_5$, mp 226—228°, $[\alpha]_D^{20}$ −43.8° (MeOH), which, upon the prolonged treatment, was further converted to a diastereoisomer (+)-diol (VIb), $C_{14}H_{14}O_5$, mp 229—231°, $[\alpha]_D^{20}$ +144.2° (MeOH). The only significant differences observed in the proton magnetic resonance (PMR) spectra of both diols are the coupling constants of 3'H and 4'H (J=4.2 Hz in VIa and J=9.0 Hz in VIb). As for the chemical behavior, the (−)-diol could be converted to an acetonide (VII) (colorless glassy), while the (+)-diol resisted to the acetonidation, thus demonstrating that the (−)-diol possesses a *cis* glycol moiety and the (+)-diol is a *trans* glycol. Senecioylation of the (−)-diol yielded 4'-epidecursidin (VIII), $C_{24}H_{26}O_7$ (colorless glassy), $[\alpha]_D^{15}$ +44.5° (MeOH).

Catalytic hydrogenation of the (−)-diol over Adams' catalyst in glacial acetic acid afforded 3,4-dihydrodecursinol (III) (identified by mixed mp and the comparison of specific roration). Therefore, the (3'*S*)-configuration of decursidin (V) is determined, and the (−)-diol and the (+)-diol are formulated as VIa and VIb respectively.

Ozone oxidation of decursidin (V) in a shorter period under ice-cooling followed by silica gel column chromatography yielded the (+)-diol as a sole product though in a low yield and the (−)-diol was not obtained thereby. Consequently, decursidin is now expressed as 3'(*S*),4'(*R*)-disenecioyloxy-3',4'-dihydroxanthyletin (V). It has been noticed[6] in the PMR spectra

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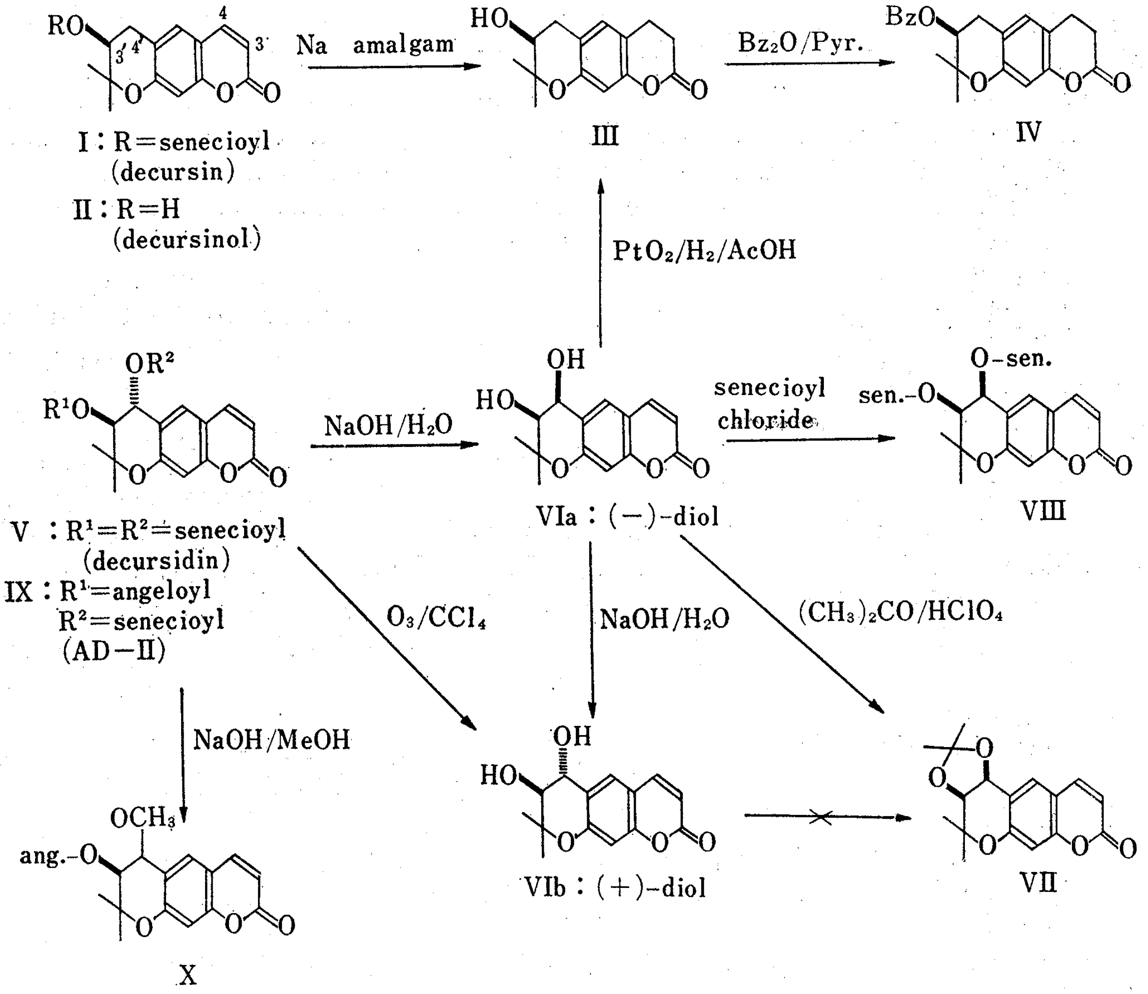
[1] K. Hata and K. Sano, *Yakugaku Zasshi*, **89**, 549 (1969).
[2] All the new compounds given with the molecular formulae gave the satisfactory analytical values.
[3] N. Harada, Mo. Ohashi, and K. Nakanishi, *J. Am. Chem. Soc.*, **90**, 7349 (1969).
[4] J. Lemmich and B.E. Nielsen, *Tetrahedron Letters*, **1969**, 3.
[5] J. Lemmich, E. Lemmich, and B.E. Nielsen, *Acta Chem. Scand.*, **20**, 2497 (1966).
[6] Private communication of Professor K. Hata, to whom the authors' thanks are due. The detailed discussion will be presented in a full paper.

of 3′,4′-dihydroxy-pyranocoumarin derivatives that the chemical shift of benzylic 4′H in the *trans* isomer is generally observed at the higher field than that of the corresponding *cis* isomer, since the 4′H in the *trans* isomer seems to hold more axial character than that in the *cis* isomer and to be more markedly affected by the shielding effect of the adjacent benzene ring current. Examination of the chemical shift of 4′H of decursidin (V) in comparison with that of 4′-epidecursidin (VIII) reveals the same tendency: 4.08 τ in V and 3.86 τ in X.



abbreviation: sen.=senecioyl, ang.=angeloyl

Chart 1

A newly isolated coumarin derivative AD-II (IX), $C_{24}H_{26}O_7$, $[\alpha]_D^{12}$ −24.2° (EtOH), UV λ_{max}^{EtOH} nm (log ε): 221 (4.66), 255 (3.75), 325 (4.29); IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1750—1730 (br), 1630, 1565, 1500, 1450, 1390, 1140; PMR (τ, CCl_4, 60 MHz): 2.50, 3.91 (1H each, d, J=9.5 Hz, -C$\underline{H}$=C$\underline{H}$-), 2.75, 3.31 (1H each, s, 2×aromatic H), 3.7—4.2 (1H, m, CH_3-C$\underline{H}$=C<), 4.02, 4.76 (1$\underline{H}$ each, d, J=6.3 Hz, O-ĊH-ĊH-O), 4.35 (1H, m, -C$\underline{H}$=C$(CH_3)_2$), 7.80, 8.08, 8.14 (totally 12H, $(C\underline{H}_3)_2C$=CH-, $C\underline{H}_3CH$=$CC\underline{H}_3$-), 8.56, 8.62 (3H each, s, >C$(C\underline{H}_3)_2$), is a colorless glassy substance, whose physical properties and chemical behaviors resemble those of decursidin (V).[1] On alkaline hydrolysis, AD-II afforded the (−)-diol (VIa), angelic acid and senecioic acid, whereas methanolysis accomplished with 1% methanolic sodium hydroxide furnished senecioic acid and a methoxyl angeloyl derivative (X),[7] $C_{20}H_{22}O_6$ (colorless glassy), $[\alpha]_D^{20}$ +79.4° (MeOH). Mild ozone oxidation of AD-II as for decursidin again yielded the (+)-diol (VIb) as a sole product.

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7) The PMR spectrum of X shows uniformity of the substance ($J_{3'4'}$=4.8 Hz), however, the absolute configuration at 4′ has not yet been confirmed.

Consequently, AD-II is now formulated as 3′(*S*)-angeloyloxy-4′(*R*)-senecioyloxy-3′,4′-dihydroxanthyletin (IX). Although the physico-chemical properties of AD-II (IX) are quite alike to those reported for andelin, $[\alpha]_D^{20}$ −28.0° ($CHCl_3$), which was isolated from the root of white flowering form of *A. decursiva* and proposed to be 3′-senecioyloxy-4′-angeloyloxy-3′,4′-dihydroxanthyletin (without stereochemistry) by Avramenko, *et al.*,[8] the identity of both compounds is still uncertain due to the lack of direct comparison, and the matter should be a subject of further investigation.

It is noted that decursidin (V) and AD-II (IX) are the unprecedented examples possessing the *trans* glycol system among the naturally occurring pyranocoumarin derivatives.

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Received May 8, 1973

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[8] L.G. Avramenko, G.K. Nikonov, and M.G. Pimenov, *Khiv. Priv. Soedin*, **6**, 190 (1970) (*Chem. Abstr.*, **73**, 87814x (1970)).