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## SYNTHESIS OF DIHYDROACTINIOLIDE AND A TRIMETHYLOCTALENEDIONE

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Dihydroactiniolide is isolated from leaves of <u>Actinidia polugama</u><sup>la)</sup> and essential oils of tea leaves<sup>lb)</sup> and tobacco<sup>lc)</sup> and has been shown to have the structure (I) by Sakan<sup>la)</sup> Mousseron-Canet has reported the formation of this lactone by photosensitized oxygenation of  $\beta$ -ionone<sup>2)</sup>

In the course of our studies on syntheses of terpenes from a pyran (II), autoxidation of this compound was found to produce dihydroactiniolide (I) and a hemiketal (V), which showed novel reaction to afford a hydroindenone derivative (VII).

Photoirradiation on  $\beta$ -ionone was known to produce a mixture of the pyran (II) and a diene (III).<sup>3)</sup> We devise the selective preparation of these compounds: short time irradiation of  $\beta$ -ionone by a high pressure mercury lamp with a Pyrex filter quantitavely affords the pyran (II), whereas the photolysis without the filter gives diene (III).

The exposure of pyran (II) to an atomospheric oxygene resulted in the formation of three oxygenated compounds. They were purified by recrystallization or chromatography on silisic acid. The structure of the first product obtained in 4.5% yield (mp 39°) was assigned as (I) from its spectral properties;  $\lambda_{max}$  212nm ( $\varepsilon$  13800),  $\nu$  1750, 1621cm<sup>-1</sup>, and  $\delta$ (CCl<sub>4</sub>), 1.22(3H,s), 1.28(3H,s), 1.51

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(3H,s), 5.50(1H,s). These physical properties were coincident with those of authentic dihydroactiniolide (I)<sup>1a)</sup> The spectra of the second product (2.2% yield): v 1740, 1660, 1597cm<sup>-1</sup>;  $\delta$  1.18, 1.29, 1.75, 1.92(each 3H,s), 5.77(1H, d,J=8), 10.21(1H,d,J=8Hz), suggested the structure (IV). The nmr spectrum of the third product obtained in 28% yield shows the presence of four methyl as three singlets at 1.15, 1.48 and 1.62, a carbinyl proton at 4.0(1H,m), and a vinyl proton at 5.47(1H,d,J=3Hz). The ir spectrum shows the presence of hydroxyl group(3460cm<sup>-1</sup>) and hemiketal group(1220cm<sup>-1</sup>). These properties and elemental analysis assigned the structure (V) for the third product.

The hemiketal (V) was also converted into dihydroactiniolide (I). The periodate oxidation of (V) afforded the same acetoxyaldehyde (IV) as described above. Base hydrolysis of this aldehyde to an acetal (VI) and subsequent oxidation with chromic acid gave the dihydroactiniolide (I) in 57% over all yield from (V).

The hemiketal (V) was converted into an octalendione (XI) which would be useful for synthesis of various terpenoids. The hydroxyhemiketal (V) was refluxed in benzene to yield a dehydration product(VII), $C_{13}H_{20}O_2$ , mp 110°,  $\lambda_{max}$ 237nm( $\varepsilon$  12400),  $\nu$  3450, 1700, 1590cm<sup>-1</sup>. The nmr spectrum showed three singlets at 1.21, 1.25, 1.30 assignable to four methyl groups, and a singlet at 5.90(1H) assignable to  $\alpha$ -proton in an  $\alpha\beta$ -unsaturated ketone. These spectral properties were in accord with structure (VII). The possible mechanism for the formation of (VII) is suggested by the following equation.



Cleavage of the ketol bond of (VII) by periodic acid afforded a lactol (VIII) in quantitative yield: mp 156°,  $\lambda_{max}$  227nm( $\epsilon$  11600),  $\nu$  3310, 1680, 1595cm<sup>-1</sup>,  $\delta$  1.23(6H,s), 1.30(3H,s), 1.55(3H,s), 5.92(1H,s). This lactol was converted into an enol lactone (IX) and a lactol acetate (X) by refluxing with



acetic anhydride: (IX), mp 51°,  $\lambda_{max}$  226nm( $\varepsilon$  11200), v 1725, 1645cm<sup>-1</sup>,  $\delta$  1.22, 1.28, 1.45(each 3H,s), 4.31, 4.61(two d, J=2Hz), 5.71(1H,s); (X), mp 107°, v 1760, 1750, 1715cm<sup>-1</sup>,  $\delta$  1.22, 1.28, 2.30(each 3H,s), 1.81(3H,s), 1.91(3H,s), 5.80(1H,s). The  $\beta$ -diketone (XI) was obtained in 80% yield by simple treatment of the enol-lactone (IX) with methanolic potassium hydroxide, mp 160°,  $\lambda_{max}$ 242( $\varepsilon$  10000), 291nm(5100), v 2520, 1640, 1620, 1560cm<sup>-1</sup>,  $\delta$  1.22, 1.32, 1.57 (each 3H,s), 3.50(2H,q,J=18Hz), 6.25(1H,s). Transformation of the diketone to terpenoids is now under investigation. <u>Acknowledgments</u> We are grateful for partial financial support from the Iyaku Shigen Kenkyu Shinkokai, and thank Dr. T.Kusumi, this Department, and Dr.K.Iguchi, Tokyo College of Pharmacy, for helpful discussions.

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