Structures of Cinnzeylanine and Cinnzeylanol, Polyhydroxylated Pentacyclic Diterpenes from *Cinnamomum zeylanicum* Nees

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In continuation of our screening search for insect-growth regulators among drug plants, we isolated two active components, named cinnzeylanine (**1**) and cinnzeylanol (**2**), from dried barks of *Cinnamomum zeylanicum* Nees. Because of the scarcity of the samples and of the complexity of the molecules, the structures were determined by X-ray crystal analysis.

Cinnzeylanine (**1**), $C_{22}H_{34}O_8$, mp 265~267°C, $[\alpha]_D^{27} +45$ (MeOH, $c=2.0$) was recrystallized from ethyl acetate-benzene to yield well formed crystals: space group $P2_12_12_1$; $a=12.195$ (2), $b=13.476$ (2), $c=12.891$ (1) Å; $Z=4$; $D_x=1.35$ g/cm³; $D_m=1.34$ g/cm³ (flotation). Intensity data were collected on a Rigaku automatic four circle diffractometer

with Mo K α radiation, and a total of 2445 independent reflections with non-zero intensity was obtained. The structure of **1** was solved by the direct method with the refinement by block-diagonal least-squares method. The

FIG. 1. Stereoscopic View of **1** with Thermal Ellipsoids at 30% Probability.

final R value was 0.067. The molecular shape of **1** is shown in Fig. 1.

The chemical and spectrometric data are rationalized by the structure. The signals of six methyl groups observed in the PMR spectrum* of **1** in methanol- d_4 are assigned as follows: C-19 and C-20 isopropyl methyls at 0.94 (d, $J=6.5$) and 0.98 (d, $J=6.5$); C-15 at 0.84 (d, $J=6.6$); C-16 at 0.87 (s), C-17 at 1.32 (s), and an acetyl methyl at 2.14 (s). A C-1 methine proton and one of C-14 methylene protons were clearly observed at 5.22 (d) and 2.36 (d, $J=15.0$), respectively. The absorption band at 1686 cm^{-1} due to carbonyl in the IR spectrum of **1** (nujol) is well interpreted by intermolecular hydrogen-bondings.

Compound **1** consumed one mole of periodic acid to afford a dioxo derivative (**3**), $\text{C}_{22}\text{H}_{32}\text{O}_8$, mp $257\sim 259^\circ\text{C}$, ν_{max} 1757, 1730, 1670 cm^{-1} . Two AB-type signals in the PMR spectrum of **3** in pyridine- d_5 were ascribed to C-10 and C-14 methylene protons: 2.57 (1H, d, $J=15.0$) and 2.94 (1H, d, $J=15.0$); 2.70 (1H, d, $J=13.5$) and 3.80 (1H, d, $J=13.5$).

On treatment of **1** with hydrogen chloride-methanol, the following reactions occurred simultaneously resulting in the formation of an anhydro derivative (**4**): bond fission between C-11 and C-12, dehydration, and formations of a six membered lactone and a double bond between C-12 and C-13.¹⁾ Compound **4**, $\text{C}_{22}\text{H}_{32}\text{O}_7$, ν_{max} 1724, 1745 cm^{-1} , PMR 1.60 (C-12 allylic methyl), 2.34 (2H, s, C-14 me-

thylene), 2.75 (1H, m, C-18 methine) consumed one mole of periodic acid to afford an anhydrodioxo derivative (**5**), $\text{C}_{22}\text{H}_{30}\text{O}_7$, mp $204\sim 206^\circ\text{C}$, ν_{max} 1760, 1715, 1675 cm^{-1} .

The PMR spectrum of cinnzeylanol (**2**), $\text{C}_{20}\text{H}_{32}\text{O}_7$, mp $125\sim 127^\circ\text{C}$, $[\alpha]_{\text{D}}^{15} + 18.4$ (MeOH, $c=2.5$) is quite similar to that of **1**, except for that a signal due to a methine proton bearing oxygen function shifted to 3.76 (d, $J=10.0$). The IR spectrum of **2** also showed the absence of carbonyl function.

Treatment of **1** with NaOH in aq. methanol gave a compound which is completely identical with **2** isolated from barks of the cinnamon. Thus the structure of **2** was established.

The pentacyclic skeleton in **1** and **2** is quite similar to that of ryanodine,¹⁾ a diterpene derivative isolated from *Ryania speciosa* Vahl. To our knowledge, **1** and **2** are the second compounds having such a unique structure. Since $[\alpha]_{\text{D}}$ of ryanodol (+18),²⁾ a diterpene moiety of ryanodine, is almost the same as that of **2**, the latter might possess the same absolute configuration as in the case of ryanodol.³⁾ The confirmation is in progress by the use of anomalous X-ray scattering.

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* Chemical shifts in PMR spectra are indicated as δ value (ppm) from TMS and J values are recorded as Hz.