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Cinncassiol C₁, a Novel Type of Diterpene from Cinnamomi Cortex¹⁾

A new and highly functionalized diterpene, which had been isolated from the water extractive exhibiting anti-allergic activity of Cinnamomi Cortex and named cinncassiol C₁, was assigned the full structure VII by chemical, spectral and X-ray crystallographic study.

Keywords—diterpene; cinncassiol C₁; Cinnamomi Cortex; *Cinnamomum cassia*; Lauraceae; anti-allergic activity; X-ray

The isolation of a series of diterpenes (compounds I—X) from the water extractive exhibiting anti-allergic activity²⁾ of Cinnamomi Cortex ("Kannan Keihi," the dried bark of *Cinnamomum cassia* BLUME (Lauraceae); one of the most widely used crude drugs), identifications of compounds I and II respectively with cinnzeylanine and cinnzeylanol³⁾ and structure elucidations of compounds III—VI were reported in the preceding paper.⁴⁾ This report provides an account of the structure determination of compound VII (named cinncassiol C₁), a novel and highly oxygenated tetracyclic diterpene, on the basis of chemical and spectroscopic evidence and by X-ray crystallographic analysis.

Cinncassiol C₁, colorless plates (MeOH), mp 204—207°, $[\alpha]_D -3.6^\circ$ (MeOH), C₂₀H₂₈O₇ (M⁺ *m/z* 380), showed in its IR spectrum the absorptions due to hydroxyl (3440 cm⁻¹), carbonyl (1740 cm⁻¹), and α,β -unsaturated ketone (1650 cm⁻¹) functions. The UV spectrum ($\lambda_{\max}^{\text{EtOH}}$ 242 nm, $\epsilon=6400$) also suggested the presence of an enone system. Its ¹³C-NMR spectrum (in CD₃OD) exhibited the signals of twenty carbons including those of two carbonyls (δ 173.3 and 212.6), one hemiacetal (δ 104.7), one tri-substituted double bond (δ 127.9 and 159.3), and four carbons (δ 66.6, 71.7, 79.2 and 91.9) each bearing a hydroxyl or an ether oxygen atom. Supposing that cinncassiol C₁ is closely related in structure with the coexisting compounds I and II, the signals in the ¹H-NMR spectrum (in CD₃OD) were respectively assigned by comparison with those of compound II (cinnzeylanol) as follows; δ 0.98, 1.32 (3H each, both singlet, 9- and 12-*tert*-methyls, respectively), 0.97, 1.14 (3H each, both doublet(d) of $J=6$ Hz, 2- and 18-*sec*-methyls, respectively), 2.16, 2.43 (2H, AB quartet, $J=13$ Hz, 10-methylene), 3.36, 3.72 (1H each, doublet of doublet (d d), $J=8, 11$ Hz and d d, $J=6, 11$ Hz, respectively, 19-hydroxymethyl) and 3.65 (1H, d, $J=10$ Hz, 1-H). In addition, the signals due to an allylic proton (multiplet) around δ 2.65 and an olefinic proton at δ 5.80 are ascribable to 18-H (by spin decoupling experiment) and 14-H, respectively. Therefore, the double bond should be located between C-13 and -14, to which one of two carbonyls is adjacent to form α,β -unsaturated ketone. When the oxidative cleavage of glycol at C-7 and -8 in II is assumed to take place, all the above data could be reasonably interpreted by the speculative structural formula VII for cinncassiol C₁. In order to prove this tentative structure, X-ray crystallographic analysis was subsequently undertaken.

The crystal of cinncassiol C₁ employed was obtained by recrystallization from dil. MeOH and its data were as follows; C₂₀H₂₈O₇·H₂O; size, 0.15×0.2×0.3 mm; monoclinic, space group $P2_1(Z=2)$; lattice constants $a=17.034(4)$, $b=8.191(2)$, $c=7.148(1)$ Å, $\beta=100.73(2)^\circ$, $V=979.91$ Å³; $D_{\text{calcd.}}=1.350$, $D_{\text{obsd.}}=1.350$ g·cm⁻³. The intensity data of 1976 ($2\theta \leq$

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Fig. 1

50°) were measured with a Syntex P_1 full automated four-circle diffractometer using $2\theta-\theta$ scan technique and monochromated $\text{Mo}(K\alpha)$ radiation ($\lambda=0.71069 \text{ \AA}$). The structure was solved *via* MULTAN program.⁵⁾ Block diagonal least-squares refinements with anisotropic nonhydrogen atoms and isotropic hydrogens have currently converged to a standard residual of 0.041 for the 1649 observed reflections ($I > 2.3\sigma(I)$). A computer-generated perspective drawing thus obtained is shown in Fig. 1. Therefore, the molecular structure is represented by the formula VII as tentatively assigned or its enantiomer, the latter of which could be, however, excluded because the configurations, at C-2, -9 and -12 for example, are most likely identical with those of II. Cinnassiol C_1 is a novel and highly oxygenated tetracyclic diterpene, which possesses an eight-membered ring carrying two ketone functions in the molecule.

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