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A NOVEL DIHYDROCHALCONE, LINDERATIN FROM LINDERA UMBELLATA
VAR. LANCEA

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The structure of linderatin, a novel dihydrochalcone from the fresh leaves of Lindera umbellata Thunb. var. lancea Momiyama, was determined to be 1 on the basis of chemical and spectroscopic evidence.

KEYWORDS— Lauraceae; Lindera umbellata var. lancea; linderatin; dihydrochalcone; p-menthene

In a previous paper, we reported¹⁾ the isolation of two dihydrochalcones, 2',4',6'-trihydroxydihydrochalcone (3) and 2',6'-dihydroxy-4'-methoxydihydrochalcone (4), isolated from the fresh leaves of Lindera umbellata Thunb. var. lancea Momiyama. Further fractionation of n-hexane extract of the fresh leaves led to the isolation of a novel dihydrochalcone derivative, named linderatin (1). The present communication describes the structure elucidation of the compound.

Linderatin (1), oil, $[\alpha]_D^{20} +19.1^\circ$ (c=0.45, CHCl_3), gave a bluish color with ethanolic ferric chloride. The molecular formula of 1 was determined to be $\text{C}_{25}\text{H}_{30}\text{O}_4$ by the high-resolution mass spectrum (m/z 394.2116). The ^{13}C -NMR spectrum indicated the presence of twenty-five carbons (Table I). Methylation of 1 with methyl iodide and potassium carbonate gave a dimethyl ether (2)^{2),3)} [oil, M^+ , m/z 422, ^1H -NMR (acetone- d_6) δ : 3.85, 3.93 (each 3H, 2 x s, 2 x OCH_3)]. The compound (1) showed the following spectra: IR $\nu_{\text{max}}^{\text{CHCl}_3}$ cm^{-1} : 3580, 3350, 1620, 1605, 1495; UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 225 (sh, 4.11), 290 (4.15). ^1H -NMR (acetone- d_6) δ : 0.82 (6H, d, $J=7$ Hz, 2 x CH_3), 1.64 (3H, s, CH_3), 2.92 (2H, t, $J=8$ Hz, C- β), 3.37 (2H, t, $J=8$ Hz, C- α), 3.84 (1H, br d, $J=12$ Hz), 5.23 (1H, s), 5.96 (1H, s, C_5 -H), 7.20 (5H,

br s, 5 x arom. H), 13.88 (1H, s, OH). The ^1H -NMR spectrum suggested that the compound (1) is a derivative of 2',4',6'-trihydroxydihydrochalcone (3). The chemical shifts of the trihydroxydihydrochalcone moiety are as follows: δ 2.92, 3.37, 5.96, 7.20, and 13.88. This assumption was further supported by a comparative examination of the ^{13}C -NMR spectra of 1 and its dimethyl ether (2) with those of 3 and 4 (Table I). In the ^{13}C -NMR spectra of 1 and 2, the chemical shifts of the carbon atoms of the dihydrochalcone skeleton,⁴⁾ except that of the carbon atom at C-3',

Table I. ^{13}C -NMR Chemical Shifts of 1, 2, 3 and 4 in Acetone- d_6

Carbon	1	2	3	4
C-1	143.2 s	142.6 s	142.9 s	143.3 s
C-2	129.4 d	129.1 d	129.1 d	129.6 d
C-3	129.6 d	129.2 d	129.2 d	129.8 d
C-4	127.1 d	127.0 d	126.5 d	127.1 d
C-5	129.6 d	129.2 d	129.2 d	129.8 d
C-6	129.4 d	129.1 d	129.1 d	129.6 d
C-1'	105.4 s	106.1 s	105.1 s	106.2 s
C-2'	161.4*s	162.8*s	165.4 s	165.7 s
C-3'	110.5 s	113.0 s	95.8 d	94.8 d
C-4'	163.9*s	165.4*s	165.4 s	167.4 s
C-5'	95.8 d	87.8 d	95.8 d	94.8 d
C-6'	165.9*s	165.3*s	165.4 s	165.7 s
C=O	205.9 s	205.6 s	205.2 s	206.0 s
C- α	46.6 t	46.7 t	46.3 t	46.9 t
C- β	31.5 t	31.5 t	31.4 t	30.5 t
OMe	-	56.0 q	-	56.2 q
C-1''	135.4 s	131.9 s	-	-
C-2''	126.9 d	126.5 d	-	-
C-3''	36.0 [†] d	36.0 [†] d	-	-
C-4''	43.0 d	42.2 d	-	-
C-5''	23.7 t	23.9 t	-	-
C-6''	31.5 t	31.5 t	-	-
C-7''	23.7 q	23.6 q	-	-
C-8''	29.1 [†] d	29.2 [†] d	-	-
C-9''	16.9 q	16.7 q	-	-
C-10''	22.0 q	21.8 q	-	-

* , [†] Assignments may be interchanged.

were similar to those of the relevant carbon atoms of **3** and **4**. These results suggest that linderatin (**1**) is a 3'-substituted 2',4',6'-trihydroxydihydrochalcone derivative.

The remaining part of the C-3' substituent, consisting of the C₁₀H₁₇ portion in the structure of **1**, was indicated by the ¹H-NMR spectrum to contain an isopropyl group, an olefinic proton, and a methyl group on a double bond. Comparisons of the ¹³C-NMR spectrum of the substituent with those of the menthane type derivatives reported in the literature⁵⁾ revealed that the chemical shifts of the carbon atoms are similar to chemical shifts of the relevant carbon atoms of *p*-menthene skeleton. Therefore, the deduced structure of the C-3' substituent of the C₁₀H₁₇ is shown to be *p*-menthene. Further supporting data for the structure were obtained by the following mass spectrum of **1**. The mass spectrum exhibited the characteristic of fragment ion at *m/z* 324 (a, M⁺-C₅H₁₀, 75.3 %), the formation of which occurred by the retro Diels-Alder reaction⁶⁾ of *p*-menthene portion and this result furthermore suggested that the trihydroxydihydrochalcone moiety in **1** was linked at the C-3" carbon atom of *p*-menthene structure.

In order to confirm the linking position of the trihydroxydihydrochalcone moiety to the *p*-menthene group, we next synthesized the following two compounds (**6** and **7**). Condensation of phloroglucinol with a readily available *p*-menth-1-ene-6-ol⁷⁾ in 5 % citric acid solution for 2 days produced the compound (**6**)⁸⁾ [oil, M⁺, *m/z* 262, ¹H-NMR (acetone-d₆) δ: 0.86 (3H, d, J=7 Hz, CH₃), 0.88 (3H, d, J=7 Hz, CH₃), 1.67 (3H, br s, CH₃), 3.83 (1H, br s, benzylic H), 5.76 (1H, m, olefinic H), 5.90 (2H, s, 2 x arom. H)]. On a similar treatment of phloroglucinol with piperitol,⁹⁾ the expected compound (**7**) was obtained [oil, M⁺, *m/z* 262, ¹H-NMR (acetone-d₆) δ: 0.83 (6H, d, J=7 Hz, 2 x CH₃), 1.69 (3H, br s, CH₃), 3.80 (1H, br d, J=10 Hz, benzylic H), 5.34 (1H, br s, olefinic H), 5.91 (2H, s, 2 x arom. H)]. The chemical shifts and coupling constants in the ¹H-NMR spectra of **6** and **7** were in close agreement except for those of the hydrocinnamoyl group in **1**. Treatment of **1** with saturated hydrogen chloride gas in chloroform afforded the compound (**5**)³⁾ whose spectral data showed the presence of a benzopyran structure¹⁰⁾ and a *tert*-methyl group [mp 128-130°C, M⁺, *m/z* 394; ¹H-NMR (CDCl₃) δ: 0.94 (3H, d, J=7 Hz, CH₃), 1.05 (3H, d, J=7 Hz, CH₃), 1.33 (3H, s, CH₃), 3.00 (2H, t, J=8 Hz, C-β), 3.40 (2H, t, J=8 Hz, C-α), 5.83 (1H, s, C₃-H), 7.18 (5H, br s, 5 x arom. H)]. These data suggest that the double bond in the *p*-menthene portion located at C-1" and linderatin **1** contains the partial structure (**7**) in the molecule. Thus, the alternative structure (**8**) was eliminated and linderatin was represented by the formula (**1**).

As to the stereochemistry of the *p*-menthene portion, we examined the ^1H -NMR spectrum of **1**. Namely, the olefinic proton ascribed to C-2" position was observed as a singlet at δ 5.23 and the coupling constant between the $\text{C}_3''\text{-H}$ and $\text{C}_4''\text{-H}$ was 12 Hz, demonstrating that the hydrogens are trans-oriented. The relative stereostructure of (**1**) was thus deduced for linderatin.

This is the second example¹¹⁾ of a new class of compound in which a $\text{C}_6\text{-C}_3\text{-C}_6$ unit (flavonoid) is linked with a cyclic monoterpene.

REFERENCES AND NOTES

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- 8) This compound exhibited one spot on TLC. in various solvents and was not diastereomeric mixture.
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