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A Novel Fortunate A from Cryptomerica fortunei

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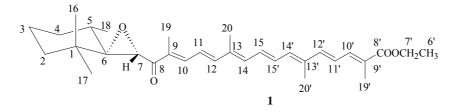
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Abstract: A novel compound, named fortunate **A**, was isolated from the ethanol extract of the stem bark of *Cryptomerica fortunei*. Its structure was established on the basis of the spectral evidences including 1D and 2D NMR spectrum.

Keywords: Cryptomerica fortunei, carotenoids.

Chinese cedar, *Cryptomeria fortunei*, is a large fast growing tree. Many authorities consider *C. fortunei* to be a variety of *C. japonica* (*fortunei* = *japonica var. sinensis*). The Chinese cedar grows to a height of 240 ft. and is probably the tallest tree native to China. The root barks and stem barks are used in traditional Chinese medicine as antidote, insecticide, and antipruritic. Chemical ingredients of *C. japonica* has already been intensively studied. Lots of biflavonoids, sesquiterpenoids, diterpenoids, and triterpenoids ¹⁻⁵ were isolated from the leaves, cones, woods of *C. japonica*. But chemical study on *C. fortunei* had not been reported yet. We investigated the chemical ingredients of the stem barks of *C. fortunei* and led to isolation of a new compound, named fortunate **A**. In the present paper, the isolation and structural elucidation of this compound was presented.

Figure 1 The structure of fortunate A



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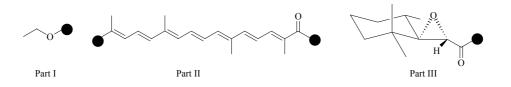
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The ethanol extract of the stem barks of *Cryptomerica fortunei*, which were collected in Nanchuan county, Sichuan Province, was chromatographed on silica gel column with different solvent system, then was chromatographed on ODS to yield fortunate A.

Fortunate A (1) was obtained as a red gum. According to its ESI-MS $(m/z 493 [M+H]^+)$ 515 [M+Na]⁺), ¹H NMR and ¹³C NMR spectral data, its molecular formula was determined to be $C_{32}H_{44}O_4$, which was further confirmed by its HR-ESI-MS (found: m/z 493.3340 $[M+H]^+$, calcd. $C_{32}H_{44}O_4$ for 493.3318). In the ¹H NMR spectrum of **1** (Table1), four characteristic methyl groups at $\delta_{\rm H}$ 2.02, 2.00 (two methyl verlapped), 1.97 and eight olefinic protons (from $\delta_{\rm H}$ 6.36 to 7.40) were observed. The ¹³C and DEPT NMR spectral (**Table1**) of 1 indicated 32 distinct signals including eight methyls, four methylenes (including an oxymethylene at δ_c 60.8), twelve methines (including an oxymethine to δ_c 62.9, ten olefinic carbons), eight quaternary carbons [incuding four olefinic carbons, a ketone carbonyl carbon $(\delta_{c} 196.3)$, a ester carbonyl carbon $(\delta_{c} 168.6)$]. The spectral data of 1 indicated that its structure was similar to an azafrin methyl ester 5-O-monomethyl ether⁶. Cross peaks oberserved in its ¹H-¹H COSY spectrum, between $\delta_{\rm H}$ 7.38/6.67, 7.29/6.52, 6.74/6.38, 6.74/ 6.46, 6.67/6.65, 6.57/6.52, 4.32/1.32, established 1 contained two fragments OCH₂CH₃ (part I) and -C(CH₃)=CH-CH=CH-C(CH₃)=CH-CH=CH-CH=C(CH₃)-CH=CH-CH=C(CH₃)-(part II). In the HMBC spectrum, the two methyl protons at $\delta_{\rm H}$ 1.01 and 1.11 (1,1-dimethyl) were correlated with carbon signals at δ_c 39.7 (C-2), 35.9 (C-1), and 71.1 (C-6); the 5-methyl protons at $\delta_{\rm H}$ 0.80 were correlated with carbon signals at $\delta_{\rm c}$ 33.2 (C-4), 31.4 (C-5), 71.1 (C-6); the oxymethine at $\delta_{\rm H}$ 3.94 (H-7) was correlated with carbon signals at $\delta_{\rm c}$ 71.1 (C-6), 196.3 (C-8). Therefore, the third structural fragment was deduced as shown in Figure 2 (part III). The methylene protons at $\delta_{\rm H}$ 4.24 (H-7') were correlated with the carbonyl carbon signal at δ_c 168.6 (C-8'), the methyl protons at δ_H 1.97 (9-Me) were correlated with the carbonyl carbon signal at δ_c 196.3 (C-8). Thus, the three parts were connected into the planar structure of compound 1 as showed in Figure 3. In its NOESY spectrum, $\delta_{\rm H}$ 1.01 (H-16) and 1.11 (H-17) were correlated with $\delta_{\rm H}$ 3.79 (H-7), $\delta_{\rm H}$ 3.79 (H-7) were correlated with $\delta_{\rm H}$ 7.38 (H-10), its key NOESY correlations were showed in **Figure 4**. The full assignment of protons and carbons of compound 1 was made by means of ¹H NMR, ¹³C NMR, HMQC, and HMBC spectra.

Figure 2 The structures of the fragments of compound 1



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Figure 3 The key HMBC correlations of compound 1

ÇH3 CH₂ -H ĊH2 °CH₂

Figure 4 The key NOESY correlations of compound 1

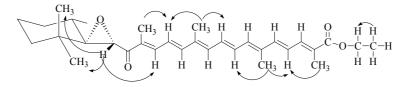


Table 1 NMR data of compound 1^* (δ ppm)

Position	$\delta_{\rm H}(J \text{ in Hz})$	$\delta_{ m c}$	Position	$\delta_{\rm H}(J \text{ in Hz})$	$\delta_{\rm c}$
1		35.9	17	1.11 (s, 3H)	26.7
2	1.54 (2H, overlapped)	39.0	18	0.80 (d, 3H, 7.2)	17.7
3	1.62 (2H, overlapped)	19.7	19	1.97 (s, 3H)	11.7
4	1.46 (2H, overlapped)	33.2	20	2.02 (s, 3H)	13.0
5	1.85 (1H, overlapped)	31.4	6'	1.32 (t, 3H, 6.9)	14.6
6		71.1	7 '	4.24 (q, 2H, 6.9)	60.8
7	3.79 (s, 1H)	62.9	8 '		168.6
8		196.3	9'		127.2
9		134.8	10 '	7.29 (d, 1H, 11.7)	138.7
10	7.38 (d, 1H, 9)	141.4	11'	6.52 (1H, overlapped)	143.6
11	6.67 (1H, overlapped)	145.3	12 '	6.57 (1H, overlapped)	124.4
12	6.65 (1H,overlapped)	124.1	13 '		136.7
13		137.5	14 '	6.38 (d, 1H, 9.9)	135.3
14	6.46 (d, 1H, 9.6)	136.8	15 '	6.74 (1H, overlapped)	132.3
15	6.74 (1H, overlapped)	131.3	19 '	1.97 (s, 3H)	13.1
16	1.01 (s, 3H)	25.0	20 '	2.00 (s, 3H)	13.0

* (Spectra taken at 300 and 75 MHz for proton and carbon in CDCl₃, respectively)

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