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Ferulic acid esters from *Plumeria bicolor*

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Abstract

Two new ferulic acid derivatives, 34-hydroxy tetratriacontanyl ferulate and 34-*O*-acetyl tetratriacontanyl ferulate, were isolated, along with plumericin and isoplumericin, from the stem bark of *Plumeria bicolor*. The structures of these compounds were determined on the basis of spectroscopic data. © 1999 Elsevier Science Ltd. All rights reserved.

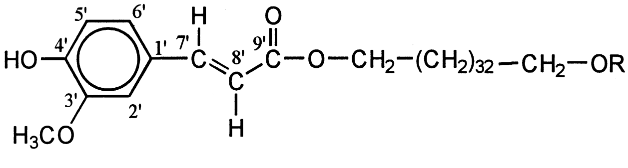
Keywords: Plumeria bicolor; Apocyanaceae; Stem bark; Ferulic acid esters; Feruloyl tetratriacontanol; 34-Hydroxy and 34-*O*-acetyl tetratriacontanyl ferulates

1. Introduction

Plants of the genus *Plumeria*, such as *P. bicolor* and *P. rubra*, are grown as ornamental plants in Rajasthan, India. Other species of this genus are widely used in the treatment of various ailments in the traditional system of medicine (Kardono, Tsauri, Padmawinata, Pezzuto, & Kinghorn, 1990). The compounds isolated from *P. rubra* were evaluated for biological activities and found useful against cell lines of murine lymphocytic leukemia (P-388) and a number of cancerous cells, i.e. breast, colon, fibrosarcoma, lung melanoma and KB in humans (Kardono et al., 1990). This paper describes the isolation and characterization of two new ferulic acid esters from the stem bark of this species, along with the two known compounds, plumericin and isoplumericin. The structures of the known compounds were confirmed by comparing their spectral data with reported values in the literature (Siddiqui, Siddiqui, Naee, & Begum, 1992; Zhao, Hui, Rupprecut, & McLaughin, 1992).

2. Result and discussion

34-Hydroxy tetratriacontanyl ferulic acid ester (**1**) was obtained as a colourless compound, m.p. 95–96°C. The molecular formula was determined as $C_{44}H_{78}O_5$ by mass spectrometry $[M]^+$ *m/z* 686. The IR spectrum of the compound indicated the presence of alcoholic and ester groups at 3440 and 1712 cm^{-1}, respectively. The presence of an absorption band and 1685 cm^{-1} confirmed the presence of a conjugated ester group, which was supported by those at 1619 and 960 cm^{-1} (conjugated double bonds) and a phenyl ring at 1595, 1590 and 1500 cm^{-1}. The ^1H NMR spectrum showed the presence of a pair of downfield doublets at δ 7.59, 7.56 and δ 6.28, 6.24 with a coupling constant 16 Hz, confirming the presence of a double bond (vinylic protons) with a *trans*-configuration. The aromatic protons were observed at δ 7.05 (dd), 7.01 (d) and 6.90 (d) as expected. In the aliphatic region, a singlet was observed at δ 5.80 and assigned to a phenolic hydroxyl group. The methoxyl protons appeared as a singlet at δ 3.90. Two triplets of equal intensity and coupling constants were observed at δ 4.17 and δ 3.67 and assigned, respectively, to a methylene group



1, R = H
2, R = COCH$_3$

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Table 1
^{1}H and ^{13}C NMR data of compounds **1** and **2**

	1		**2**	
	δH	δC	δH	δC
1′	–	127.11	–	–
2′	7.01, 1H(d)	109.44	7.01, 1H(d)	C-1′ to C-9′
3′	–	146.75	–	Values comparable with **1**
4′	–	147.90		
5′	6.90, 1H(d); $J = 8$ Hz	115.79	6.90, 1H(d)	
6′	7.05, 1H(dd); $J = 8$ Hz, 2 Hz	122.89	7.05, 1H(dd)	
7′	7.59 1H(d); $J = 16$ Hz	144.44	7.59, 1H(d)	
8′	6.28 1H(d); $J = 16$ Hz	115.79	6.28, 1H(d)	
9′	–	167.71	–	
1	4.17; 2H(t); $J = 6.5$ Hz	64.53	4.17, 2H(t)	64.53
34	3.67, 2H(t); $J = 6.5$ Hz	62.99	4.03, 2H(t)	64.47
ϕ-OH	5.80, 1H(s)	–	5.80, 1H(s)	
–OCH$_3$	3.90, 3H(s)	55.90	3.90, 3H(s)	
1″	–	–	–	171.88
2″	–	–	2.01; 3H(s)	21.11

attached to the ester linkage (Ar–OC–CH_2–R) and methylene protons attached to hydroxyl groups (–CH_2–OH). The signal for the –OH group also appeared as a triplet at δ 1.67. A broad singlet at δ 1.24 showed the presence of the remaining 64H for (CH$_2$)$_{32}$ groups. Thus, the nature and positions of all 78H were established (Govindachari, Parthasarty, Desai, & Mohane, 1971; Joshi, Sharma, & Singh, 1986). The ^{13}C NMR spectrum was also in agreement with the above values (Kuo, Chang, & Kuo, 1997) and confirmed the structure (**1**).

The mass spectrum of (**1**) showed the [M]$^+$ at m/z 686, with a base peak at m/z 177, confirming the presence of a 4-hydroxy-3-methoxy cinnamic (ferulic) acid moiety. The spectrum was in agreement with earlier work; reported by Govindachari et al. for cluytyl ferulate isolated from *Lannea grandis* (Govindachari et al., 1971); however, Joshi et al. reported the base peak and [M]$^+$ at m/z 586 for octacosanyl ferulate isolated from *Tecomella undulata* (Joshi et al., 1986).

34-*O*-Acetyl tetratriacontanyl ferulate (**2**) was obtained as a colourless powder, m.p. 68°C. The IR spectrum showed the presence of a phenolic hydroxyl group at 3419 cm^{-1} and an alkyl acetate group at 1729 cm^{-1}. The conjugated double bonds present with an ester group showed characteristic absorption at 1687 cm^{-1} and the presence of a phenyl group was confirmed by the absorption at 1604, 1590 and 1500 cm^{-1}. The ^{1}H NMR spectrum exhibited a signal at δ 2.10 (3H, s), confirming that the alcoholic group has been changed into an acetyl group. The methylene protons attached to the acetoxyl group (–CH$_2$–O–COCH) and (Ar COOCH$_2$–R) were observed as triplets at δ 4.03 (2H, t) and δ 4.17 (2H, t), both with the same coupling constant (6.5 Hz). The protons of the (*E*)-feruloyl moiety showed a similar pattern to those in (**1**). The ^{1}H and ^{13}C NMR data were comparable with those of **1** and are summarised in Table 1.

3. Experimental

3.1. General

M.p.'s: uncorr. CC: silica gel containing 13% CaSO$_4$ as binder. ^{1}H and ^{13}C NMR: recorded at 500 and 100 MHz, respectively, in CDCl$_3$.

3.2. Plant material

Stem bark of *P. bicolor* was collected in April 1995 from Rajasthan, University Campus, Jaipur and identified by Dr. Navjyot Sarna. A voucher specimen is deposited in the Botany Department of Rajasthan University, Jaipur, India.

3.3. Extraction and isolation

Shade-dried stem bark (1.5 kg) was extracted with CHCl$_3$. The extract was concd. under red. pres. and treated with MeCN to separate fatty (insol.) and non-fatty (sol.) frs. The insol. fr. was chromatographed over silica gel and afforded **1** and **2** by eluting with CHCl$_3$ and was separated by prep. TLC using CHCl$_3$–MeOH (4:1). The non-fatty portion was also chromatographed over silica gel, elution with C$_6$H$_6$–CHCl$_3$ (1:1) giving isoplumericin and elution with CHCl$_3$ yielding plumericin.

3.4. 34-Hydroxy tetratriacontanyl ferulate (*1*)

C$_{44}$H$_{78}$O$_5$. M.p. 95–96°C. IR $\nu_{\max}^{\mathrm{KBr}}$ 3440, 2910, 2831, 1712, 1687, 1619, 1590, 1500, 1253, 1050, 1000, 960

cm^{-1}. ^{1}H and ^{13}C NMR Table 1. MS, *m*/*z* (rel. int.): 686 ($[\mathrm{M}]^+$, 8.7), 685 (14.8), 671 (18.7), 219 (16.8), 194 (49.2), 178 (15.6), 177 (100), 150 (26.1), 137 (36.4), 135 (26.3), 131 (15.6).

*3.5. 34-O-acetyl tetratriacontanyl ferulate (**2**)*

M.p. 68–69°C. IR $\nu_{\mathrm{max}}^{\mathrm{KBr}}$ 3419, 2924, 2445, 1729, 1687, 1619, 1604, 1590, 1530, 1500, 1460, 1260, 1020, 850 cm^{-1}. ^{1}H and ^{13}C NMR Table 1. MS, *m*/*z* (rel. int.) 728 (2.8), 685 (7.4), 657 (17.1), 644 (2.8), 219 (16.8), 195 (49.2), 177 (100).

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