and D-glucose from **4**. All these compounds were identified by TLC comparison with authentic samples.

Detection of **3** *and* **4** *in the fresh bark.* Fresh cut bark (100 g) was soaked into 500 ml of Me_2CO and extracted in a ultrasonic bath for 30 min. The concd Me_2CO extract was extracted with *n*-BuOH. The *n*-BuOH extract was checked by TLC using silica gel F_{254} (Merck) and $CHCl_3$–MeOH–H_2O (3:1:0:0.1). R_f value of **3**; 0.19, **4**; 0.28.

Compound **5**. Amorphous pale yellow powder (5.50 mg). $[\alpha]_D^{26}$ $-38.7°$ (Me_2CO; *c*0.60). All spectral data were identical with lit. values [2].

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REFERENCES

1. Shimomura, H., Sashida, Y. and Adachi, T. (1987) *Phytochemistry* **26**, 249.
2. Shimomura, H., Sashida, Y. and Adachi, T. (1987) *Phytochemistry* **26**, 2363
3. Yoshimoto, K., Itatani, Y. and Tsuda, Y. (1980) *Chem. Pharm. Bull.* **28**, 2065.
4. Akhmedov, S. G. and Litvinenko, V. I. (1968) *Dokl. Akad. Nauk. Azerb. SSR* **24**, 89.
5. Shimonyan, A. V., Litvinenko, V. I. and Shinkarenko, A. L. (1972) *Khim. Prir. Soedin.*, 383.
6. Litvinenko, V. I., Popova, T. P., Shimonyan, A. V., Zoz, I. G. and Sokolov, V. S. (1975) *Planta Med.* **27**, 372.
7. Tanaka, N., Nagase, S., Wachi, K., Murakami, T., Saiki, Y. and Chen, C. M. (1980) *Chem. Pharm. Bull.* **28**, 2843.
8. Hase, T. and Hasegawa, K. (1982) *Phytochemistry* **21**, 1021.
9. Strack, D., Dahlbender, B., Grotjahn, L. and Wray, V. (1984) *Phytochemistry* **23**, 657.

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PHENOLIC GLUCOSIDES FROM *PARABENZOIN PRAECOX*

HIROKO SHIMOMURA, YUTAKA SASHIDA, MOTOMU OOHARA and HIROKO TENMA

Tokyo College of Pharmacy, 1432-1, Horinouchi, Hachioji, Tokyo 192-03, Japan

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Key Word Index—*Parabenzoin praecox*; Lauraceae; bark; thalictoside; thalictoside caffeoyl ester; phenolic glucoside.

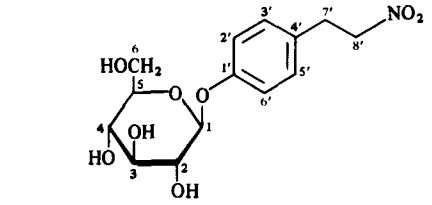
Abstract—From the methanolic extract of the bark of *Parabenzoin praecox* (Sieb. et Zucc.) Nakai, a new phenolic glucoside ester, 4-(2-nitroethyl)phenyl β-D-(6-*O*-caffeoyl)glucopyranoside, and a new phenolic glucoside, 3,4,5-trimethoxyphenyl β-D-glucopyranoside have been isolated together with a known compound, thalictoside. The structures of these compounds have been determined on the basis of spectroscopic studies and chemical evidence.

In the course of our studies on the constituents of the Lauraceae, new glucosides, 4-(2-nitroethyl)phenyl β-D-(6-*O*-caffeoyl)glucopyranoside and 3,4,5-trimethoxyphenyl β-D-glucopyranoside together with a known compound, thalictoside, have been isolated from the bark of *Parabenzoin praecox*.

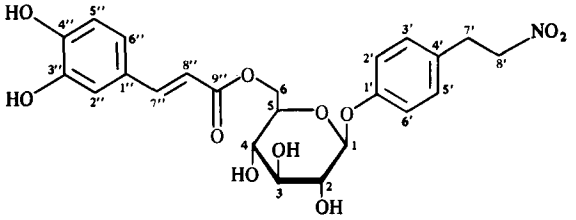
Compound **1** was identified as thalictoside, which was isolated from *Thalictrum aquilegifolium* (Ranunculaceae) [1], by its spectroscopic data and by mixed melting point test with an authentic sample.

Compound **2** was suggested to be a caffeoyl ester of **1** by its spectroscopic data. Acetylation of **2** with acetic anhydride–pyridine gave a pentaacetate. Alkaline hydrolysis of **2** with sodium methoxide afforded methyl caffeate and thalictoside. Comparison of the ^1H and ^{13}C NMR spectra with those of **1** (see Table 1 and Experimental) allowed the caffeoyl group to be located on the C-6 hydroxy group in the glucose moiety. Thus, the structure of **2** was determined as 4-(2-nitroethyl)phenyl β-D-(6-*O*-caffeoyl)glucopyranoside.

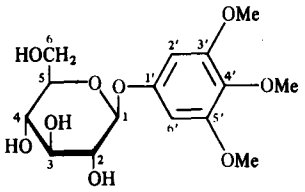
Compound **3** showed a molecular ion peak at *m/z* 346 in the EIMS. By the data of ^1H and ^{13}C NMR spectra, the existence of three methoxyl groups, an aromatic ring and a glucose were indicated. Acetylation of **3** with acetic anhydride–pyridine afforded a tetraacetate. Hydrochloric acid hydrolysis of **3** gave D-glucose and trimethoxyphenol. The data of the ^{13}C NMR spectrum of **3** suggested that three methoxyl groups were located at C-3,4,5 in phenolic moiety [2]. The mode of glucosidic linkage was determined to be β-form based on the coupling constant of the anomeric proton signal [δ4.82 (1H, *d*, $J = 7.6$ Hz)] in the ^1H NMR spectrum. Thus, the structure of **3** was established as 3,4,5-trimethoxyphenyl β-D-glucopyranoside.



1



2



3

Thalictoside (**1**) is known as a naturally occuring aliphatic nitro compound, and it has not been isolated from other natural sources. Compound **2** was obtained as a caffeoyl ester of **1**. Although the compounds containing nitro group have been isolated from the Leguminosae [3–5], these compounds are unusual in natural sources.

EXPERIMENTAL

The NMR spectra were measured at 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR. The chemical shifts were given on the δ(ppm) scale with TMS as int. standard. The voucher specimen of the plant [Y. Sashida 62001] was deposited in the herbarium of our College.

Isolation. The fresh bark of *Perabenzoin praecox* (2.5 kg) collected at Sagamiko, Kanagawa prefecture in May 1986, was extracted with hot MeOH. The MeOH soln was concd to a small vol. under red. pres. and the concd extract was suspended in H_2O. This suspension was extracted successively with $CHCl_3$ and *n*-BuOH. The *n*-BuOH soluble portion was chromatographed on silica gel and Sephadex LH-20 to afford **1**–**3**.

Compound **1**. 374.4 mg, white needles (MeOH), mp 100–101° (ref. 102–103°). Compound **1** was identified as thalictoside by mixed melting point test and comparison of its spectral data with those of the authentic sample.

Acetylation of compound **1**. Compound **1** (30.0 mg) was acetylated with Ac_2O–pyridine for 24 hr at room temp. to afford a tetraacetate. Amorphous white powder, 9.0 mg. Spectral data of the acetate were the same as those of the authentic thalictoside tetraacetate.

Compound **2**. 8.4 mg, amorphous yellow powder, $[\alpha]_D^{20}$ −25.3° (MeOH *c* 0.44), IR ν_{max}^{KBr} cm^{-1}: 3400, 2910, 1680, 1605, 1550, 1380, 1260, 1170; SIMS *m/z*: 514 $[M+23]^+$, 431, 351; ^{1}H NMR (CD_3OD): δ3.10 (2H, *t*, *J* = 7.2 Hz, H-7′), 3.38–3.51 (4H, overlapping, H-2, 3, 4, 5), 4.37 (1H, *dd*, *J* = 11.8, 7.2 Hz, H-6a), 4.50 (3H, overlapping, H-8′, 6b), 4.83 (1H, *d*, *J* = 7.5 Hz, H-1), 6.29 (1H, *d*, *J* = 15.9 Hz, H-8″), 6.81 (2H, *d*, *J* = 8.0 Hz, H-2′, 6′), 6.95–7.09 (5H, overlapping, H-3′, 5′, 2″, 5″, 6″), 7.55 (1H, *d*, *J* = 15.9 Hz, H-7″).

Acetylation of **2**. Compound **2** (2 mg) was treated with Ac_2O–pyridine for 24 hr at room temp. to afford a pentaacetate. Amorphous white powder, 2.6 mg, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2950, 1765, 1565, 1540, 1380, 1240; ^{1}H NMR ($CDCl_3$): δ2.04–2.07 (each 3H, *s*, OCOMe × 3), 2.31 (6H, *s*, OCOMe × 2), 3.16 (2H, *t*, *J* = 7.3 Hz, H-7′), 3.94 (1H, *m*, H-5), 4.36 (2H, *m*, H-6), 4.47 (2H, *t*, J = 7.3 Hz, H-8′), 5.05 (1H, *d*, *J* = 7.5 Hz, H-1), 5.17 (1H, *dd*, *J* = 9.9, 7.5 Hz, H-2), 5.27–5.31 (2H, overlapping, H-3, 4), 6.38 (1H, *d*, *J* = 16.0 Hz, H-8″), 6.92 (2H, *d*, *J* = 8.7 Hz, H-2′, 6′), 7.05 (2H, *d*, *J* = 8.7 Hz, H-3′, 5′), 7.25 (1H, *d*, *J* = 8.2 Hz, H-5″), 7.39 (1H, *d*, *J* = 1.9 Hz, H-2″), 7.42 (1H, *dd*, J = 8.2, 1.9 Hz, H-6″), 7.63 (1H, *d*, *J* = 16.0 Hz, H-7″).

Alkaline methanolysis of **2** *with* NaOMe. Compound **2** (4 mg) was treated with methanolic 3% NaOMe for 3 hr at room temp. to give methyl caffeate and thalictoside. These compounds were identified by TLC comparison with authentic samples respectively.

Compound **3**. 46.7 mg, white needles (ether–MeOH = 15:1), mp 201–203°, $[\alpha]_D^{20}$ −22.3° (MeOH; *c* 0.38), IR ν_{max}^{KBr} cm^{-1}: 3410, 2910, 1650, 1075; EIMS *m/z*: 346.1229 (calc. for $C_{15}H_{22}O_9$, 346.1264) $[M]^+$, 184, 169, 84; ^{1}H NMR (CD_3OD): δ3.32–3.47

Table 1. ^{13}C NMR chemical shifts (δ) of compounds **2** and **3**, 100 MHz (CD_3OD)

	2	3
Glucose moiety		
1	102.4	103.3
2	75.0	75.0
3	78.1	78.2*
4	72.1	71.8
5	75.6	78.5*
6	64.7	62.8
Aglycone moiety		
1′	158.7	156.0
2′	118.3	96.4
3′	130.7	154.9
4′	131.8	145.8
5′	130.7	154.9
6′	118.3	96.4
7′	33.5	
8′	77.3	
Caffeoyl moiety		
1″	127.8	
2″	115.2	
3″	147.0	
4″	145.4	
5″	116.7	
6″	123.1	
7″	147.2	
8″	115.3	
9″	169.0	
OMe		56.6 × 2
OMe		61.3

*Assignments may be interchanged.

(4H, overlapping, H-2, 3, 4, 5), 3.66 (1H, *dd*, $J = 12.3$, 2.6 Hz, H-6a), 3.69 (3H, *s*, OMe), 3.80 (6H, *s*, OMe × 2), 3.92 (1H, *dd*, $J = 12.3$, 5.3 Hz, H-6b), 4.82 (1H, *d*, $J = 7.6$ Hz, H-1), 6.48 (2H, *s*, H-2′, 6′).

Acetylation of **3**. Compound **3** (10 mg) was treated with Ac_2O–pyridine for 24 hr at room temp. to afford a tetraacetate. Amorphous yellow powder, 5.9 mg, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3054, 1760, 1600, 1510, 1220; EIMS *m/z*: 514 $[M]^+$, 331, 184, 169; ^1H NMR ($CDCl_3$): δ 2.03–2.08 (each 3H, *s*, OCOMe × 4), 3.79 (3H, *s*, OMe), 3.83 (6H, *s*, OMe × 2), 3.85 (1H, *m*, H-5), 4.25 (1H, *dd*, $J = 12.3$, 5.3 Hz, H-6a), 4.29 (1H, *dd*, $J = 12.3$, 2.6 Hz, H-6b), 5.04 (1H, *d*, $J = 7.6$ Hz, H-1), 5.15 (1H, *dd*, $J = 9.3$, 7.6 Hz, H-2), (1H, *dd*, $J = 9.3$, 9.3 Hz, H-4), 5.30 (1H, *dd*, $J = 9.3$, 9.3 Hz, H-3), 6.27 (2H, *s*, H-2′, 6′).

Acid hydrolysis of compound **3**. Compound **3** (20 mg) was treated with 3% HCl for 1.5 hr at 80–90° to afford D-glucose and 3,4,5-trimethoxyphenol. D-Glucose was identified by TLC comparison with an authentic sample. 3,4,5-Trimethoxyphenol, amorphous white powder, 5.4 mg, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3610, 3320, 1605, 1515, 1480, 1210, 1138; EIMS *m/z*: 184 $[M]^+$, 169, 141; ^1H NMR ($CDCl_3$): δ 3.78 (3H, *s*, OMe), 3.82 (6H, *s*, OMe × 2), 6.09 (2H, *s*, H-2, 6).

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REFERENCES

1. Ina, H. and Iida, H. (1986) *Chem. Pharm. Bull.* **34**, 726.
2. Nonaka, G., Nishimura, H. and Nishioka, I. (1982) *Chem. Pharm. Bull.* **30**, 2061.
3. Stermitz, F. R., Norris, F. A. and Williamsons, M. C. (1969) *J. Am. Chem. Soc.* **91**, 4599.
4. Finnegan, R. A. and Muller, W. H. (1965) *J. Pharm. Sci.* **54**, 1136.
5. Finnegan, R. A. and Muller, W. H. (1968) *J. Pharm. Sci.* **57**, 353.

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ANTHAXANTHONE, A 1,3,7,8-TETRAOXYGENATED XANTHONE FROM *HAPLOCLATHRA LEIANTHA*

TANUS J. NAGEM and JOSÉ C. DA SILVEIRA

Departamento de Química do Instituto de Ciências Exatas and Faculdade de Farmacia, Universidade Federal de Minas Gerais, Belo Horizonte, 30.000 Brasil

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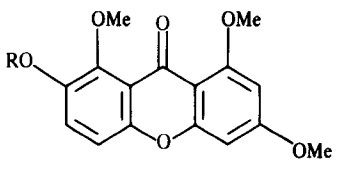
Key Word Index—*Haploclathra leiantha*; Guttiferae; trunk wood; 7-hydroxy-1,3,8-trimethoxyxanthone; anthaxanthone.

Abstract—A new xanthone was isolated from the trunk wood of *Haploclatha leiantha* and its structure determined by UV, IR, NMR and mass spectrometry as 7-hydroxy-1,3,8-trimethoxyxanthone.

INTRODUCTION

In connection with our work in trunk wood of *Haploclathra leiantha* (Benth) Benth, we undertook investigation of other fractions from this species. Previously, the isolation of 'Leiaxanthone' was reported from this Laboratory, besides several known xanthones (see Experimental part of ref [1]). Now we are describing the isolation and characterization of a new 1,3,7,8-tetraoxygenated xanthone, for which we give the trivial name 'anthaxanthone'. In this communication we report its structure as **1** which to our knowledge is the first report of the occurrence of a tetraoxygenated xanthone from this source.



	R
1	H
2	Me
3	Ac