ISSN 0371-4845

Showa
Pharmaceutical
University

紀　　要

（人文・社会・自然）

第 48 号

昭和薬科大学

２０１４

昭和薬科大学紀要
Vol.48 ; 1-11, 2014

原 著

A New Interesting Phenolic Compound from the Resin of *Dracaena draco*

Takeshi KOIKE*

*Education Center for Fundamental Pharmaceutical Sciences
(Laboratory of Pharmaceutical Education Chemistry),
Department of Pharmacy,
Showa Pharmaceutical University

Dracaena draco 樹脂から単離された興味深い新規フェノール性化合物

小池　猛*

*昭和薬科大学　薬学部

Summary

The dark red resinous substance obtained from the plant (*Dracaena draco*) has been used as the interesting drug [including new phenolic compound **(1)**] (hemostatic agent, external injury medicine etc.) in the world (Canary Islands, South East Asia, and Japan etc.).

A new hydroxyphenylic compound **(1)** [natural product (chemical constituent)] was isolated from the resin of *Dracaena draco*. The chemical structure was established using a combination of different NMR spectroscopy techniques (^{1}H-^{1}H COSY, NOESY, HMBC), high resolution EI-MS and chemical method (transformation). Fascinating biological activity (acceleration activity of granuloma formation etc.) would be expected from this compound **(1)**.

Key words
hydroxyphenylic compound, natural product, chemical structure, *Dracaena draco*, expected biological activity

Summary（和文）

リュウケツジュの植物が生産する赤色の樹脂物質は、古くから日本を含む世界各地で創傷治療薬等として用いられて来た。今回この樹脂（肉芽形成促進作用を示した成分分画部分）から、この興味深い化学成分の探索を行った結果、新規化合物を単離し、その化学構造がヒドロキシフェニル化合物（**1**）であることを種々の核磁気共鳴分光法、質量分析法、アセチル化（化学的変換法）等により解明した。この化合物は医薬としての新しい用途も期待される。

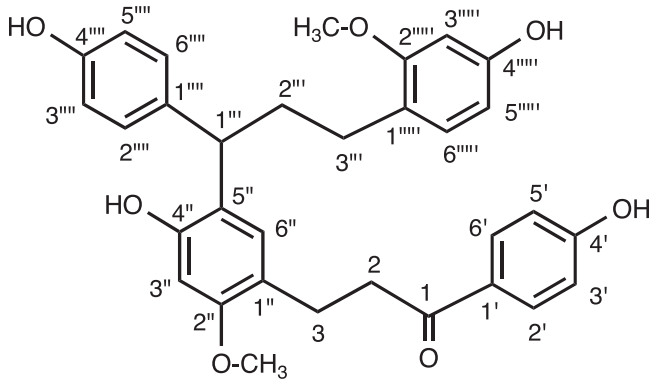
Key words（和文）
ヒドロキシフェニル化合物、天然産物、化学構造、リュウケツジュ、期待される生理活性

Ⅰ. Introduction

The dark-red colored resin obtained from various plants, so-called "Dragon's Blood", has been used as the interesting drug (for instance, antidiarrheic, hemostatic agent, and external injury medicine etc.) in the world (Indian Ocean island of Socotra, Canary Islands, Madeira, Indonesia, South East Asia, and Japan etc.).[1-9)]

Previously,[1)] we reported that the crude divided part substance by solubility from ether extract of the resin (*Dracaena draco* L) drug, mixture of ingredients including new phenolic compound **(1)**, had a potent activity to promote the granuloma formation action etc. in rats. Therefore we made investigation into the chemical constituent of the crude divided part substance.

This paper focuses on the isolation and structural elucidation of new hydroxyphenylic compound **(1)**[1)] (Fig. 1), purifying by silica gel column chromatography, ordinary-phase silica gel medium pressure liquid chromatography (MPLC) and NH-silica gel column chromatography from ether extract of the resin, which is expected to be potentially useful and biological activity (acceleration activity of granuloma formation etc.[1)]).



Compound (1)

Fig. 1. Structure of Compound **(1)**

Ⅱ. Results and Discussion

Compound **(1)** was obtained as colorless solid {mp 76-78°C, $[\alpha]_D^{25}$ +9.61° (c = 0.113, MeOH)}. The molecular formula was deduced to be $C_{32}H_{32}O_7$ by high-resolution EI-MS spectroscopy, with a [M^+] mass ion observed at m/z calcd for 528.2148, (Found: 528.2156).

The IR (infrared spectroscopy) spectrum showed the presence of hydroxyl (3400cm^{-1}), conjugated carbonyl (1665cm^{-1}), and aromatic (1600cm^{-1}) groups. On the basis of these NMR experiment, the basic carbon connectivity of structure of compound **(1)** was deduced to be that as shown Fig. 1. The ^{1}H- and ^{13}C-NMR spectra data of together with the heteronuclear multiple-bond connectivity (HMBC) spectra relationships showed in Table 1. Except for two methoxy methyl carbon, compound **(1)** consisted of

thirty carbons, hydrogen and oxygen.

In the ^{1}H-NMR spectrum of compound **(1)**, the chemical shifts and the coupling constants of H-(C-2') [δ_H 7.81, d, J=8.9Hz]/H-(C-3') [δ_H 6.79, d, J=8.9Hz], H-(C-5') [δ_H 6.79, d, J=8.9Hz]/H-(C-6') [δ_H 7.81, d, J=8.9Hz], and H-(C-2''') [δ_H 7.04, d, J=8.5Hz]/H-(C-3''') [δ_H 6.70, d, J=8.5Hz], H-(C-5''') [δ_H 6.70, d, J=8.5Hz]/H-(C-6''') [δ_H 7.04, d, J=8.5Hz] indicated the presence of two *para*-disubstituted benzene system, which also supported by the ^{1}H-^{1}H correlation spectroscopy (COSY) correlations (Fig. 2).

Also the chemical shifts and the coupling constants of H-(C-3'''') [δ_H 6.37, d, J=2.4Hz], H-(C-5'''') [δ_H 6.31, dd, J=8.2, 2.4Hz], H-(C-6'''') [δ_H 6.84, d, J=8.2Hz] indicated the presence of the C-1'''', C-2'''', C-4''''- trisubstituted benzene system. Similarly, H-(C-3'') [δ_H 6.34, s] and H-(C-6'') [δ_H 6.96, s] indicated the presence of the C-1'', C-2'', C-4'', C-5''-tetrasubstituted benzene system, which was also supported by the HMBC spectrum correlations (Table 1).

The ^{13}C-NMR and HMBC spectra showed 32 carbon signals that were attributed to two methoxy methyl, four methylene, one methine, one carbonyl carbon, and four aromatic carbons on the basis of their chemical shifts. The ^{13}C chemical shifts of C-4', C-4'', C-4''', and C-4'''' indicated that they were directly connected with their own hydroxy group. This result was confirmed by deuterium oxide additive in the ^{1}H-NMR spectrum, which was also supported from acetylated derivative compound **(2)** (Fig. 4) by chemical transformation.

In the HMBC spectrum of compound **(1)**, the resonance at δ_H 4.04 corresponding to the methine proton on the C-1''' correlated with the signals at C-4'' (δ_C 153.19), C-5'' (δ_C 123.06), C-6'' (δ_C 129.13), C-2''' (δ_C 35.66), C-3''' (δ_C 28.29), and C-1'''' (δ_C 136.44). These correlations indicated the presence of a propyl moiety in the structure of compound **(1)**.

Table 1. ^{1}H- and ^{13}C-NMR Spectral Data of together with the HMBC Relationships for Compound **(1)**[a)]

Carbon	^{13}C (ppm)	^{1}H (ppm)	HMBC (H→C)[d)]
1	200.23	-	-
2	39.06	3.17-3.06 (m)	C-1, C-3, C-1"
3	26.12	2.93 (t, 7.9)	C-1, C-2, C-1", C-2", C-6"
1'	129.36	-	-
2'	130.85	7.81 (d, 8.9)	C-1, C-4', C-6'
3'	115.28[b)]	6.79 (d, 8.9)	C-1', C-4', C-5'
4'	161.49	-	-
5'	115.28[b)]	6.79 (d, 8.9)	C-1', C-3', C-4'
6'	130.85	7.81 (d, 8.9)	C-1, C-2', C-4'
1"	120.74	-	-
2"	156.33	-	-
3"	99.47	6.34 (s)	C-1", C-2", C-4"
4"	153.19	-	-
5"	123.06[c)]	-	-
6"	129.13	6.96 (s)	C-3, C-2", C-4", C-1"'
1"'	42.51	4.04 (t, 7.6)	C-4", C-5", C-6", C-2"', C-3"', C-1""
2"'	35.66	2.18-2.09 (m)	C-5"
3"'	28.29	2.51-2.40 (m)	C-2"', C-1""', C-2""'
1""	136.44	-	-
2""	128.99	7.04 (d, 8.5)	C-1"', C-4"", C-6""
3""	115.24[b)]	6.70 (d, 8.5)	C-1"", C-4"", C-5""
4""	154.58	-	-
5""	115.24[b)]	6.70 (d, 8.5)	C-1"", C-3"", C-4""
6""	128.99	7.04 (d, 8.5)	C-1"', C-2"", C-4""
1""'	122.29[c)]	-	-
2""'	158.44	-	-
3""'	98.99	6.37 (d, 2.4)	C-1""', C-2""', C-4""', C-5""'
4""'	155.83	-	-
5""'	106.53	6.31 (dd, 8.2, 2.4)	C-1""', C-3""'
6""'	130.20	6.84 (d, 8.2)	C-3"', C-2""', C-4""'
2"-O$\underline{C}$H$_3$	55.32	3.74 (s)	C-2"
2""'-O$\underline{C}$H$_3$	55.25	3.73 (s)	C-2""'

a) ^{1}H-NMR (500 MHz) and ^{13}C-NMR (125 MHz) in $CDCl_3$ + CD_3OD.
b-c) Assigments may be interchangeable.
d) HMBC corresponded to two or three bonds connectivities.

Table 2. ^{1}H- and ^{13}C-NMR Spectral Data of together with the HMBC Relationships for Compound **(2)**[a)]

Carbon	^{13}C (ppm)	^{1}H (ppm)	HMBC (H→C)[d)]
1	198.63	-	-
2	38.92	3.20 (t, 7.3)	C-1, C-3, C-1"
3	25.71	2.98 (t, 7.3)	C-1, C-2, C-1", C-2", C-6"
1'	134.58	-	-
2'	129.73	7.98 (d, 8.6)	C-1, C-4', C-6'
3'	121.71	7.17 (d, 8.6)	C-1', C-4', C-5'
4'	154.20	-	-
5'	121.71	7.17 (d, 8.6)	C-1', C-3', C-4'
6'	129.73	7.98 (d, 8.6)	C-1, C-2', C-4'
1"	127.27	-	-
2"	156.17	-	-
3"	105.23	6.51 (s)	C-1", C-2", C-4", C-5"
4"	147.51	-	-
5"	127.80[b)]	-	-
6"	129.39	7.12 (s)	C-3, C-2", C-4", C-1"'
1"'	42.79	3.97 (t, 7.6)	C-4", C-5", C-6", C-2"', C-3"', C-1""
2"'	34.77	2.24-2.19 (m)	C-5", C-1""'
3"'	28.38	2.52 (t, 7.6)	C-1"', C-2"', C-1"", C-2""', C-6""'
1""	141.69	-	-
2""	128.75	7.18 (d, 8.9)	C-1"', C-4"", C-6""
3""	121.30	6.98 (d, 8.9)	C-1"", C-4"", C-5""
4""	148.89	-	-
5""	121.30	6.98 (d, 8.9)	C-1"", C-3"", C-4""
6""	128.75	7.18 (d, 8.9)	C-1"', C-2"", C-4""
1""'	127.84[b)]	-	-
2""'	158.03	-	-
3""'	104.37	6.55 (d, 2.1)	C-1""', C-2""', C-4""', C-5""'
4""'	149.84	-	-
5""'	112.88	6.58 (dd, 8.2, 2.1)	C-1""', C-3""'
6""'	130.05	7.00 (d, 8.2)	C-3"', C-2""', C-4""'
2"-O$\underline{C}$H$_3$	55.42	3.76 (s)	C-2"
2""'-O$\underline{C}$H$_3$	55.35	3.75 (s)	C-2""'
4'-$\underline{C}$OCH$_3$	168.85	-	-
4'-CO$\underline{C}$H$_3$	21.17	2.32 (s)	C-4'-$\underline{C}$OCH$_3$
4"-$\underline{C}$OCH$_3$	169.57	-	-
4"-CO$\underline{C}$H$_3$	20.87	2.17 (s)	C-4"-$\underline{C}$OCH$_3$
4""-$\underline{C}$OCH$_3$	169.41[c)]	-	-
4""-CO$\underline{C}$H$_3$	21.15	2.27 (s)	C-4""-$\underline{C}$OCH$_3$
4""'-$\underline{C}$OCH$_3$	169.46[c)]	-	-
4""'-CO$\underline{C}$H$_3$	21.15	2.28 (s)	C-4""'-$\underline{C}$OCH$_3$

a) ^{1}H-NMR (500 MHz) and ^{13}C-NMR (125 MHz) in $CDCl_3$.
b-c) Assigments may be interchangeable.
d) HMBC corresponded to two or three bonds connectivities.

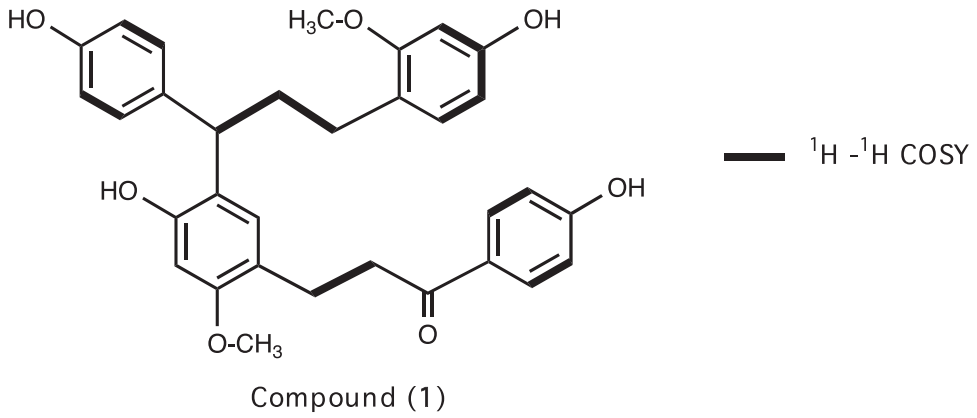


Fig. 2. ^{1}H-^{1}H COSY Correlations for Compound **(1)**

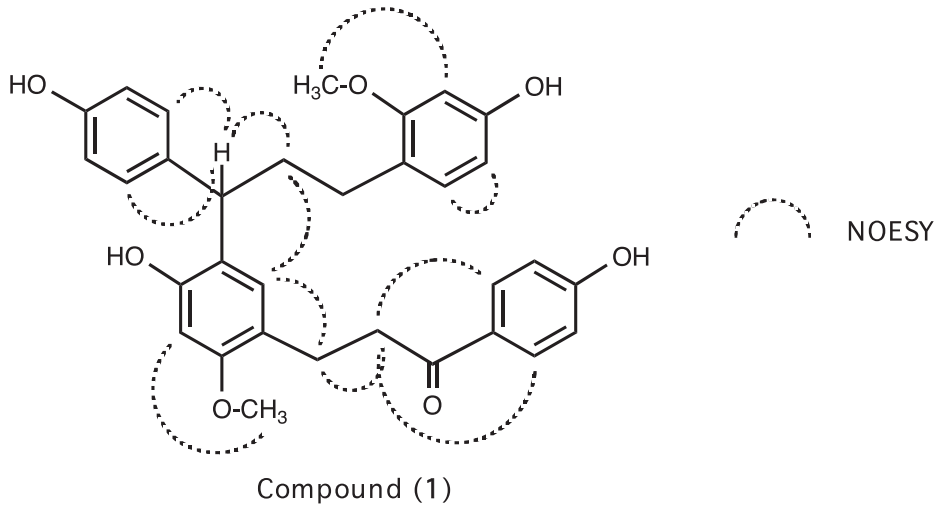


Fig. 3. Selected NOESY Correlations for Compound **(1)**

The HMBC spectrum of compound **(1)** also revealed that the methylene proton signals of H-3 (δ_H 2.93) correlated with C-1 carbonyl carbon (δ_C 200.23), C-2 (δ_C 39.06), C-1" (δ_C 120.74), C-2" (δ_C 156.33), and C-6" (δ_C 129.13).

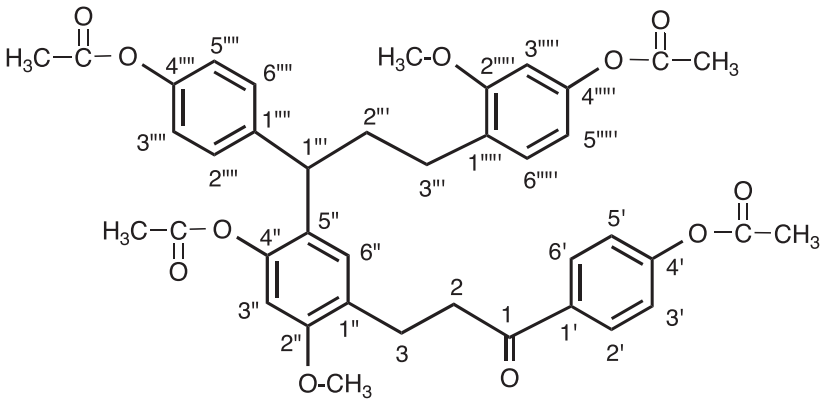
Moreover, the presence of the (*p*-hydroxyphenyl) moiety at C-1 was suggested by the correlation of the aromatic proton at C-2' (δ_H 7.81) to C-1 (δ_C 200.23), C-4' (δ_C 161.49), C-6' (δ_C 130.85), and also aromatic proton C-6' (δ_H 7.81) to C-1 (δ_C 200.23), C-2' (δ_C 130.85), C-4' (δ_C 161.49). Similarly, the presence of the (*p*-hydroxyphenyl) moiety at C-1''' was suggested by the correlation of the aromatic proton at C-2'''' (δ_H 7.04) to C-1''' (δ_C 42.51), C-4'''' (δ_C 154.58), C-6'''' (δ_C 128.99), and also aromatic proton C-6'''' (δ_H 7.04) to C-1''' (δ_C 42.51), C-2'''' (δ_C 128.99), C-4'''' (δ_C 154.58).

The presence of the (*p*-hydroxy-2-methoxyphenyl) moiety at C-3''' was suggested by the correlation of the methylene proton at C-3''' (δ_H 2.51-2.40) to C-2''' (δ_C 35.66), C-1'''' (δ_C 122.29), C-2'''' (δ_C 158.44). The HMBC correlation between the protons of the methoxy group at C-2'' (δ_H 3.74) and C-6'' (δ_C 129.13) revealed that the methoxy group was located at C-2''. Similarly, the HMBC correlation between the protons of the methoxy group at C-2'''' (δ_H 3.73) and C-6'''' (δ_C 130.20) revealed that the methoxy group was located at C-2''''.

As shown in Fig. 2, the ^{1}H-^{1}H correlation spectroscopy (COSY) spectrum of compound **(1)** revealed the successive connectivity of δ_H 4.04 (t, *J*=7.6 Hz) [C-1'''], δ_H 2.18-2.09 (m) [C-2'''], and δ_H 2.51-2.40 (m) [C-3'''].

In the ^{1}H-^{1}H COSY spectrum, the methylene proton signal at δ_H 3.17-3.06 (m, H-2) correlated with the methylene proton at δ_H 2.93 (t, *J*=7.9 Hz, H-3).

Based on the HMBC correlation data, and the ^{1}H-^{1}H COSY correlations of H-(C-2')/H-(C-3'), H-(C-5')/H-(C-6'), and H-(C-2'''')/H-(C-3''''), H-(C-5'''')/H-(C-6''''), the presence of two 1,4-disubstitution aromatic units were confirmed. Also, the ^{1}H-^{1}H COSY correlations of H-(C-3''''')/H-(C-5''''') and H-(C-5''''')/H-(C-6''''') revealed that the presence of 1'''',2'''',4''''-trisubstituted aromatic unit were confirmed.



Compound (2)

Fig. 4. Structure of Compound **(2)**

Selected nuclear Overhauser effect spectroscopy (NOESY) correlations are shown in Fig. 3. The methine proton on the H-(C-1''') [δ_H 4.04] had NOESY correlations with H-(C-2''') [δ_H 2.18-2.09], H-(C-2'''') [δ_H 7.04], and H-(C-6'''') [δ_H 7.04]. Moreover, the methyl protons of the methoxy group at C-2'' (δ_H 3.74) had NOESY correlations with aromatic proton on the H-(C-3'') [δ_H 6.34], another methyl protons of the methoxy group at C-2'''' (δ_H 3.73) had NOESY correlations with aromatic proton on the H-(C-3'''') [δ_H 6.37].

Also, in the NOESY spectrum, the aromatic proton on the H-(C-6'') [δ_H 6.96]

correlated with the two methylene protons at H-3 (δ_H 2.93), and H-(C-2''') [δ_H 2.18-2.09]. Other methylene proton at H-2 (δ_H 3.17-3.06) correlated with the methylene proton at H-3 (δ_H 2.93), the aromatic protons on the H-(C-2') [δ_H 7.81], and H-(C-6') [δ_H 7.81].

The structure of acetylated derivative compound **(2)** by chemical transformation of natural product compound **(1)** was shown in Fig. 4. Compound **(2)** was obtained as colorless solid {mp 57-59°C, $[\alpha]_D^{25}$ +10.98° (c = 0.080, MeOH)}. The molecular formula was deduced to be $C_{40}H_{40}O_{11}$ by high-resolution EI-MS spectroscopy, with a [M^+] mass ion observed at *m/z* calcd for 696.2608, (Found: 696.2570). The IR spectrum showed the presence of acetoxyphenyl carbonyl (1770cm^{-1}), conjugated carbonyl (1690cm^{-1}), and aromatic (1600cm^{-1}) groups, which was confirmed by the disappearance of hydroxyl groups (3400cm^{-1}). ^{1}H-NMR (500 MHz, $CDCl_3$) data, ^{13}C-NMR (125 MHz, $CDCl_3$) data, and HMBC spectrum correlations were shown in Table 2.

In the ^{1}H-NMR spectrum of compound **(2)** exhibited the signals for four methyl protons by acetylation at COMe-(C-4') [δ_H 2.32, s], COMe-(C-4'') [δ_H 2.17, s], COMe-(C-4'''') [δ_H 2.27, s], and COMe-(C-4''''') [δ_H 2.28, s]. Upon this investigation of acetylation, the presence of four hydroxyl groups into compound **(1)** was brought to light. The chemical shifts and the coupling constants of H-(C-2') [δ_H 7.98, d, J=8.6Hz]/H-(C-3') [δ_H 7.17, d, J=8.6Hz], H-(C-5') [δ_H 7.17, d, J=8.6Hz]/H-(C-6') [δ_H 7.98, d, J=8.6Hz], and H-(C-2'''') [δ_H 7.18, d, J=8.9Hz]/H-(C-3'''') [δ_H 6.98, d, J=8.9Hz], H-(C-5'''') [δ_H 6.98 , d, J=8.9Hz]/H-(C-6'''') [δ_H 7.18, d, J=8.9Hz] indicated the presence of two *para*-disubstituted benzene system, which also supported by the ^{1}H-^{1}H correlation spectroscopy (COSY) spectrum.

The chemical shifts and the coupling constants of H-(C-3''''') [δ_H 6.55, d, J=2.1Hz], H-(C-5''''') [δ_H 6.58, dd, J=8.2, 2.1Hz], H-(C-6''''') [δ_H 7.00, d, J=8.2Hz] indicated the presence of the C-1''''', C-2''''', C-4'''''- trisubstituted benzene system. Similarly, H-(C-3'') [δ_H 6.51, s] and H-(C-6'') [δ_H 7.12, s] indicated the presence of the C-1'', C-2'', C-4'', C-5''- tetrasubstituted benzene system, which was also supported by the HMBC spectrum correlations (Table 2).

The ^{1}H-NMR spectrum, ^{13}C-NMR spectrum, HMBC spectrum, ^{1}H-^{1}H COSY spectrum, and NOESY spectrum data supported the presence of the framework moiety (four methylene parts, one methine part, one carbonyl part, and four aromatic parts) of compound **(2)**, which was possessed with the same framework moiety of compound **(1)** as shown in Fig. 1.

Ⅲ. Conclusion

The natural product (chemical constituent) obtained from the dark-red colored resin drug of *Dracaena draco* was investigated to isolate the interesting new hydroxyphenylic compound **(1)**, which would be able to expect fascinating biological activity (acceleration activity of granuloma formation etc.). This chemical structure was also supported from acetylated derivative compound **(2)** by chemical transformation.

Experimental

All melting points were determined on a Yanagimoto melting point apparatus and are uncorrected. IR spectra were recorded with a JASCO FT/IR-200 spectrometer, and ^{1}H-NMR and ^{13}C-NMR, 2D NMR spectra with a JEOL JNM-α 500 spectrometer, with tetramethylsilane as an internal standard. MS were recorded with a JEOL JMS-D 300 spectrometer. Optical rotations were measured with JASCO DIP-140 Digital Polarimeter.

Ordinary-phase silica gel column chromatography (Silica gel 60 [Merck]) was used for column chromatography, and thin layer chromatography (TLC) was carried out on precoated Silica gel 60 F_{254} (0.2mm; Merck, Darmstadt, Germany). NH-silica gel (basic 100 Å type silica gel, NH-DM 1020, Fuji Silysia Chemical, Ltd.) was used for column chromatography and NH-TLC. Ordinary-phase medium pressure liquid chromatography (MPLC) [packed SiO_2 column, 21×310mm, C.I.G. I.D.-15, Kusano Kagakukikai Co., Japan] was used for column chromatography. TLC spots were detected by UV radiation (254nm).

1. Extraction and Isolation

The resins of *Dracaena draco* L (producing Hebei Province in China) were extracted with ether, and hexane of equivalent volume was added into its extracted ether soluble solution. The precipitated insoluble matter was washed by ether-hexane (1:1) solution, and remaining insoluble residue was obtained. This residue (5.5g) was separated by ordinary-phase silica gel column chromatography [EtOAc-hexane (1:1, v/v) → EtOAc-hexane (25:20, v/v)] to give three fractions of A portion (500mg), B portion (350mg), and C portion (300mg).

Next, the sample of B portion (30mg) was purified by ordinary-phase (SiO_2) medium pressure liquid chromatography (MPLC) [$CHCl_3$-MeOH (6:1)] to afford product (7mg), and further this product was purified by NH-silica gel column chromatography [$CHCl_3$-MeOH (2:1)] to provide pure natural product, compound **(1)** [5mg].

Compound (1):[1)]

1-(4-Hydroxyphenyl)-3-{4-hydroxy-5-[1-(4-hydroxyphenyl)-3-(4-hydroxy-2-methoxyphenyl)propyl]-2-methoxyphenyl}-1-propanone.

Colorless solid: mp 76-78°C. $[\alpha]_D^{25}$ +9.61° (c = 0.113, MeOH). IR (KBr) cm^{-1}: 3400, 1665, 1660, 1600, 1510, 1460, 1450. High-resolution EI-MS m/z : Calcd for $C_{32}H_{32}O_7$ (M^+): 528.2148. Found: 528.2156. ^{1}H-NMR (500 MHz, $CDCl_3$ + CD_3OD) and ^{13}C-NMR (125 MHz, $CDCl_3$ + CD_3OD) data are shown in Table 1.

2. Acetylation

Ac_2O (0.6 ml) was added to a solution of B portion (6 mg) in dry pyridine (0.3 ml) and the mixture was allowed to stir overnight (19 h) at room temperature. The reaction mixture was poured into ice-water and then extracted with ethyl acetate. The ethyl acetate layer was washed with sat. $NaHCO_3$ and sat. NaCl, then dried ($MgSO_4$) and

concentrated. This residue was separated by ordinary-phase silica gel column chromatography [EtOAc-hexane (1:1)] and ordinary-phase (SiO_2) medium pressure liquid chromatography (MPLC) [$CHCl_3$-EtOAc (10:1)] to afford 3.5 mg of compound **(2)** as a colorless solid.

Compound (2):

1-(4-Acetoxyphenyl)-3-{4-acetoxy-5-[1-(4-acetoxyphenyl)-3-(4-acetoxy-2-methoxyphenyl)propyl]-2-methoxyphenyl}-1-propanone.

Colorless solid: mp 57-59°C. $[\alpha]_D^{25}$ +10.98° (c = 0.080, MeOH). IR (KBr) cm^{-1}: 1770, 1690, 1600, 1505, 1470, 1460. High-resolution EI-MS m/z : Calcd for $C_{40}H_{40}O_{11}$ (M^+): 696.2608. Found: 696.2570. ^{1}H-NMR (500 MHz, $CDCl_3$) and ^{13}C-NMR (125 MHz, $CDCl_3$) data are shown in Table 2.

^{1}H-^{1}H COSY: H-2⇔H-3. H-2'⇔H-3'. H-5'⇔H-6'. H-2'''⇔H-1''', H-3'''. H-2''''⇔H-3''''. H-5''''⇔H-6''''. H-5''''⇔H-3'''', H-6''''. Selected NOESY: H-2⇔H-3, H-2', H-6', H-6''. H-3''⇔C-2''-OMe, C-4''-OCOMe. H-6''⇔H-3, H-1''', H-2'''. H-1'''⇔H-2''', H-2'''', H-6''''. H-3''''⇔C-2''''-OMe, C-4''''- OCOMe. H-6''''⇔H-3''', H-5''''.

Memories

This paper is dedicated to the honorary Professor Seisho Tobinaga of Showa Pharmaceutical University on the second anniversary of his death. The extracted sample was brought by him, and the investigation (chemical constituent research) was performed in response to his request. We pray his soul may rest in peace.

References

1) Seisho Tobinaga, Satoshi Onodera, Takeshi Koike, and Akito Takano, *Jpn. Kokai Tokkyo Koho (A)*, JP 2006-241078 A (2006.9.14). / (Contribution: chemical constituent research, T. Koike)
2) Yingdong Zhu, Ping Zhang, Haiping Yu, Jia Li, Ming-Wei Wang, and Weimin Zhao, *J. Nat. Prod.* Vol. **70**, 1570-1577 (2007).
3) I. Juránek, V. Suchý, D. Stará, I. Mašterová, and Z. Grančaiová, *Pharmazie*, Vol. **48**, 310-311 (1993).
4) Howell G. M. Edwards, Luiz F. C. de Oliveira and Hew D. V. Prendergast, *Analyst*, Vol. **129**, 134-138 (2004).
5) Y. Seto, S. Motoyoshi, H. Nakamura, J. Imuta, T. Ishitoku, and S. Isayama, *Yakugaku Zasshi*, Vol. **112**, 259-271 (1992).
6) Abraham J. Vaisberg, Marcos Milla, Maria del Carmen Planas, Jose L. Cordova, Elva Rosas de Agusti, Ramon Ferreyra, Maria del Carmen Mustiga, Lily Carlin, and Gerald B. Hammond, *Planta Medica*, Vol. **55**, 140-143 (1989).

7) Antonio G. González, Francisco León, Lázaro Sánchez-Pinto, Juan I. Padrón, and Jaime Bermejo, *J. Nat. Prod*. Vol. **63**, 1297-1299 (2000).
8) Y. Mimaki, M. Kuroda, A. Ide, A. Kameyama, A. Yokosuka, Y. Sashida, *Phytochemistry*, Vol. **50**, 805-813 (1999).
9) A. Kanamaru, A. Tada, K. Nishikawa, *Jpn. Kokai Tokkyo Koho*, JP 2002-29985 (4392114).

紀　　要　　第４８号

2014年２月25日発行

発行者　昭和薬科大学　西　島　正　弘
東京都町田市東玉川学園3-3165
TEL　０４２－７２１－１５１１
FAX　０４２－７２１－１５８８

印刷所　コムネッツ株式会社
東京都町田市根岸2-2-3
TEL　０４２－７９４－１６００
FAX　０４２－７９４－１６５１

BULLETIN
of
Showa Pharmaceutical University

Vol.48

Showa Pharmaceutical University
2014