Communications to the Editor

Chem. Pharm. Bull.
34(10)4418—4421(1986)

STRUCTURE OF A NEW POLYPHENOL FROM CASSIA GARRETTIANA CRAIB.

Kimiye Baba, Yuko Tabata, Kaoru Maeda, Mitsunobu Doi
and Mitsugi Kozawa*
Osaka University of Pharmaceutical Sciences, Kawai 2-10-65, Matsubara,
Osaka 580, Japan

A new polyphenol, cassigarol A (1), has been isolated from the heartwood of Cassia garrettiana Craib.(Thai drug "Sa mae sarn", Leguminosae). The structure of 1 was established by means of chemical, spectral and X-ray analysis.

KEYWORDS —— Cassia garrettiana; Leguminosae; polyphenol; cassigarol A; stilbene dimer; X-ray analysis

In the previous paper, we reported the isolation of five anthraquinones[1)] including cassialoin, nine phenolic compounds[2)] and betulinic acid from the heartwood of Cassia garrettiana Craib. (Leguminosae, one of the Thai drugs, "Sa mae sarn"). Recently, we reinvestigated this crude drug in order to study its phenolics and isolated a new polyphenolic compound, cassigarol A (1). This communication describes the structure of cassigarol A.

Cassigarol A (1) is $C_{28}H_{24}O_8$, a pale brown viscid oil, Gibbs reagent + (grayish purple), optical inactive, UVλ_{max}^{MeOH}nm (log ε): 284(4.03). From the ^{1}H-NMR spectrum (δ, DMSO-d_6) of 1 (Table I), the presence of the following skeleton and groups in the molecule was deduced: a 4,5-disubstituted 1,3-dioxybenzene [6.09, 6.05(each 1H, d, J=2.3 Hz)], a 4,5-disubstituted 1,2-dioxybenzene [6.27, 6.15 (each 1H, s)], a 3,4-dioxyphenyl [6.70(1H, d, J=7.9 Hz), 6.62(1H, d, J=2.0 Hz), 6.52(1H, dd, J=7.9, 2.0 Hz)], a 3,5-dioxyphenyl [6.04(2H, d, J=2.3 Hz), 5.99(1H, t, J=2.3 Hz)], two pairs of adjacent benzyl methine and benzyl methylene [4.58(1H, dd, J=7.0, 9.0 Hz), 3.18(1H, dd, J=9.0, 14.0 Hz), 3.05(1H, dd, J=7.0, 14.0 Hz) and 3.78(1H, dd, J=4.0, 13.0 Hz), 3.64(1H, dd, J=13.0, 16.0 Hz), 2.52(1H, dd, J=4.0, 16.0 Hz)] and eight phenolic hydroxyls (8.98, 8.94, 8.94, 8.87, 8.79, 8.64, 8.42, 8.37). The ^{13}C-NMR spectrum(δ,DMSO-d_6)(Table I) showed signals due to twenty-four sp^2 carbons ($=\overset{|}{C}-O$ X 8, $=\overset{|}{C}-$ X 6, =CH- X 10) and four sp^3 carbons ($-CH_2-$ X 2, $-\overset{|}{C}H-$ X 2).

The methylation of 1 with dimethyl sulfate and K_2CO_3 in acetone gave octa-

Table I. NMR Data for Cassigarol A

	C	H	
	δ ppm	δ ppm	J
1	154.3		
2	100.2	6.09d	2.3
3	155.5		
4	107.6	6.05d	2.3
4a	131.7a)		
5	42.4	3.64dd	13.0, 16.0
		2.52dd	4.0, 16.0
6	48.8	3.78dd	4.0, 13.0
6a	141.0		
7	118.5b)	6.27sc)	
8	143.2		
9	143.2		
10	119.9b)	6.15sc)	
10a	141.0		
11	43.1	4.58dd	7.0, 9.0
12	45.1	3.18dd	9.0, 14.0
		3.05dd	7.0, 14.0
1'	142.2		
2'	115.5	6.62d	2.0
3'	145.1		
4'	142.9		
5'	115.6	6.70d	7.9
6'	118.7	6.52dd	2.0, 7.9
1"	132.8a)		
2"	107.1	6.04d	2.3
3"	157.7		
4"	100.2	5.99t	2.3
5"	157.7		
6"	107.1	6.04d	2.3
OH		8.98s 8.94s 8.94s 8.87s 8.79s 8.64s 8.42s 8.37s	

a)-c) Assignments may be reversed. Assignments based on C/H 2D correlations.

Table II. NMR Data for Compound 5 and 6

	5			6		
	C	H		C	H	
	δ ppm	δ ppm	J	δ ppm	δ ppm	J
1	181.5			182.3		
2	158.9			158.4		
3	106.9	5.74d	2.3	107.9	5.90s	
4	187.1			186.5		
5	134.2	6.21d	2.3	144.0		
6	153.2			130.2	6.50d	1.0
α	31.8	3.60m		41.4	4.40ddd	1.0, 8.0, 9.0
		3.15dd	9.5, 13.5			
β	35.8	5.46dd	6.5, 9.5	32.5	3.05ddd	1.0, 9.0, 15.0
					2.97ddd	1.0, 8.0, 15.0
1'	135.2			181.7		
2'	111.4	6.66sd)		158.8		
3'	145.3a)			107.2	5.83d	2.3
4'	146.3a)			186.9		
5'	111.4	7.21sd)		134.3	6.35ddd	1.0, 1.5, 2.3
6'	131.7b)			151.1		
α'	196.0					
1"	125.9			131.4		
2"	159.2c)			111.5	6.68d	2.5
3"	104.6	6.35d	2.7	149.2		
4"	159.5c)			148.4		
5"	103.8	6.51d	2.7	111.5	6.78d	8.0
6"	136.3			120.1	6.73dd	2.5, 8.0
1‴	130.0b)					
2‴	111.3	7.14d	2.0			
3‴	149.4					
4‴	148.6					
5‴	109.6	6.64d	8.5			
6‴	125.7	6.83dd	2.0, 8.5			
CHO	191.0	9.92s				
OCH_3	56.3 56.1 56.1 55.9 55.6 55.3 55.2	3.97s 3.91s 3.86s 3.78s 3.77s 3.62s 3.59s		56.3 56.0 55.9 55.9	3.84s 3.84s 3.81s 3.80s	

a)-d) Assignments may be reversed. Assignments based on C/H 2D correlations.

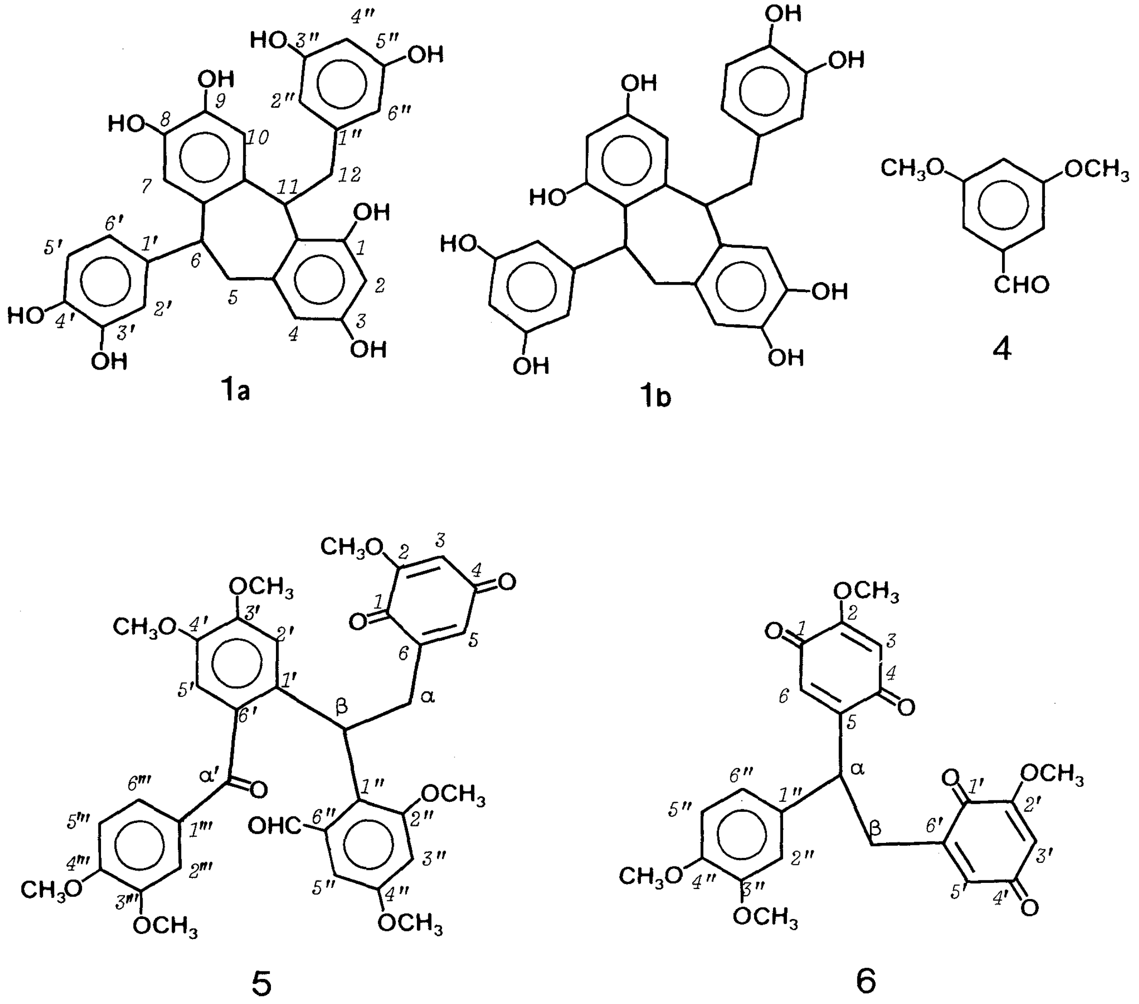

Fig.1

Crystal Data

Chemical formular	$C_{44}H_{40}O_{16}\cdot CHCl_3$
Molecular weight	944.17
Crystal system	monoclinic
Space group	$P2_1/c$
Cell constant	
a(Å)	12.518(3)
b(Å)	8.385(2)
c(Å)	44.239(21)
(°)	90.0
(°)	93.80(6)
(°)	90.0
Volume(A^3)	4633(3)
Z	4
Dm($g.cm^{-3}$)	1.348(1)
Dx($g.cm^{-3}$)	1.354
R-value	0.110
Number of reflections	5372

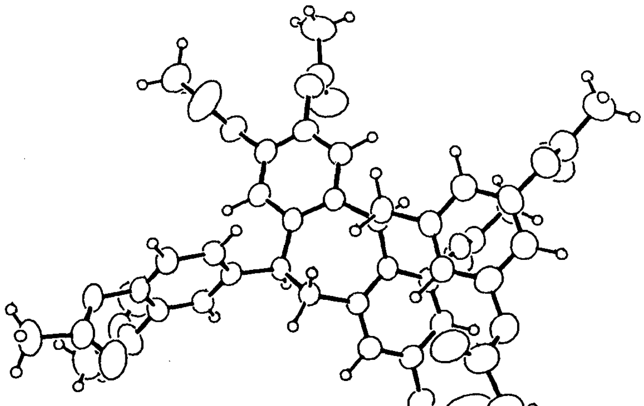

Fig.2

methyl ether (2), a viscid oil. The acetylation of 1 with Ac_2O and AcONa afforded octaacetate (3), a colorless crystal, mp 189-190°C. From these results and the finding that this plant has piceatannol (3,4,3',5'-tetrahydroxystilbene) and its dihydroderivative in large quantities, it was assumed that 1 is either 1a or 1b (Fig. 1). The degradation of 2 with CrO_3 in $AcOH/H_2O$ afforded 3,5-dimethoxybenzaldehyde (4) and two benzoquinone derivatives (5 and 6) corresponding to the formulas 5 and 6 (Fig. 1). Compound 5, brownish red crystalline powders, a $C_{35}H_{34}O_{11}$, mp 163-165°C, UVλ_{max}^{MeOH}nm (log ε): 208.5(4.77), 227.0(4.55), 272.0(4.32), 304.0(4.08), 397.0(2.80). IR$\nu_{max}^{CHCl_3}$cm^{-1}: 1700, 1670, 1640, 1600, 1500. MS m/z: 630(M^+), 329, 314, 165, 151. NMR (Table II). Compound 6, orange needles, is $C_{24}H_{22}O_8$, mp 116-118°C, UVλ_{max}^{MeOH}nm (log ε): 206.5(4.69), 237.0(4.32), 265.0(4.54), 404.0(3.24). IR$\nu_{max}^{CHCl_3}$cm^{-1}: 1670, 1640, 1600, 1510. MS m/z: 438(M^+), 300, 289, 287, 151, 69. NMR (Table II). From the above results, it was decided that 1 is 1a. This structure was also supported from the X ray analysis of 3 (Fig. 2).

Oligomers of stilbene have been isolated from Vitaceae$^{3)}$ and Dipterocarpaceae.$^{4)}$ Now an analogous compound, cassigarol A (1) has been isolated from the heartwood of Cassia garrettiana Craib. (Leguminosae). Further investigations are required to make clear whether this compound originated in the plant or was formed by oxidative condensation during the the preparation of the crude drug.

ACKNOWLEDGEMENT We are grateful to Miss M. Nabae and Miss M. Danjo of this University for the measurments of the NMR and Mass spectra.

REFERENCES AND NOTES

1) K. Hata, K. Baba and M. Kozawa, Chem. Pharm. Bull., 26, 3792 (1978).

2) K. Hata, K. Baba and M. Kozawa, Chem. Pharm. Bull., 27, 984 (1979).

3) R. J. Pryce and P. Langcake, Phytochemistry, 16, 1452 (1977).

4) a) R. Madhav, T. R. Sechadri and G. B. V. Subramaniam, Phytochemistry, 6, 1155 (1967); b) S. Sotheeswaran, M. U. S. Sultanbawa, S. Surendrakumar and P. Bladon, J. Chem. Soc. Perkin Trans. 1, 699 (1983); c) M. N. C. Diyasena, S. Sotheeswaran, S. Surendrakumar, S. Balasubramanian, M. Bokel and W. Kraus, J. Chem. Soc. Perkin Trans. 1, 1807 (1985); d) Y. A. G. P. Gunawardena, S. Sotheeswaran, M. U. S. Sultanbawa, S. Surendrakumar and P. Bladon, Phytochemistry, 25, 1498 (1986).

(Received July 28, 1986)