Studies on Nepalese Crude Drugs. XXV.[1] Phenolic Constituents of the Leaves of *Didymocarpus leucocalyx* C. B. CLARKE (Gesneriaceae)

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Seven new phenolic compounds (8—14) including three ones having unique structure named didymocalyxins A (12), B (13) and C (14) have been isolated from the leaves of *Didymocarpus leucocalyx*, along with five known flavonoids (5-hydroxy-6,7-dimethoxyflavanone, 5,8-dihydroxy-6,7-dimethoxyflavanone, 2′,6′-dihydroxy-3′,4′-dimethoxychalcone, 3′-hydroxy-2′,4′,5′,6′-tetramethoxychalcone and 2′,5′-dihydroxy-4′-methoxy-3′,6′-dioxochalcone) and two known anthraquinoids (physcion and catenarin). The structures of 8—14 were determined to be 3′,4-dihydroxy-2′,4′,5′,6′-tetramethoxychalcone (8), 5,8-dihydroxy-6,7-dimethoxyisoflavone (9), 1,6,8-trihydroxy-4-benzoyloxy-3-methylanthraquinone (10), (2*S*)-2,3-dihydroxypropyl 1,6, 8-trihydroxy-3-methyl-9,10-dioxoanthracene-2-carboxylate (11), (±)-1,4-dihydroxy-2,3,6,7-tetramethoxy-10-phenyl-9,10-dihydrocyclohepta[2,1-*b*]4*H*-chromene-8,11-dione (12), 3-((1*E*,2*E*)-1-hydroxy-3-phenylprop-2-enylidene)-7-((2*E*)-3-phenylprop-2-enoyl)-6-hydroxy-4,5-dimethoxybenzo[*b*]furan-2-one (13) and 2((1*E*)-2-phenylvinyl)-5,6-dihydroxy-7,8-dimethoxy-4*H*-pyrano[3,2-*d*]benzo[*b*]furan-4-one (14) on the basis of chemical and spectroscopic evidence and X-ray analysis.

Key words *Didymocarpus leucocalyx*; Gesneriaceae; phenolic compound; flavonoid; anthraquinone; didymocalyxin

Didymocarpus leucocalyx C. B. CLARKE is a perenial herb of the Family Gesneriaceae, which is distributed in the central and eastern Himalayan region of Nepal.[3)] In Nepal, the young leaves of this plant are called "Kumkum" and have been used as aromatic stomachics and carminatives for diseases due to the disorder of "VATA" ("Wind" or Vital energy) in the Ayurvedic system of medicine.[4,5)] Nothing has been published about the constituents of this plant. As part of our studies on Nepalese crude drugs, the phenolic constituents of this plant were examined. As described in the experimental section, seven known compounds (**1**—**7**) were isolated from a methanol extract of the leaves of this plant together with seven new compounds (**8**—**14**) including three (**12**—**14**) having a rather unique structure, which we have named didymocalyxins A, B and C. This paper deals with their structural identification.

Compounds **1**—**7** were identified as 5-hydroxy-6,7-dimethoxyflavanone (onysilin) (**1**),[6)] 5,8-dihydroxy-6,7-dimethoxyflavanone (didymocarpin A) (**2**),[7)] 1,8-dihydroxy-6-methoxy-3-methylanthraquinone (physcion) (**3**),[8)] 1,4,6,8-tetrahydroxy-3-methylanthraquinone (catenarin) (**4**),[9)] 2′,6′-dihydroxy-3′,4′-dimethoxychalcone (pashanone) (**5**),[10)] 3′-hydroxy-2′,4′,5′,6′-tetramethoxychalcone (**6**)[11)] and 2′,5′-dihydroxy-4′-methoxy-3′,6′-dioxochalcone (pedicinin) (**7**)[12)] by comparisons of their physical and spectral data with those described in the literature.

Compound **8** was obtained as a yellow powder, and formulated as $C_{19}H_{20}O_7$ from high resolution (HR)-EI-MS. The IR spectrum gave absorption bands corresponding to hydroxyl and conjugated carbonyl groups and aromatic rings. The UV and ^{1}H-NMR spectra suggested **8** was a dihydroxy-tetramethoxychacone.[13)] The presence of a *p*-coumaroyl moiety in **8**

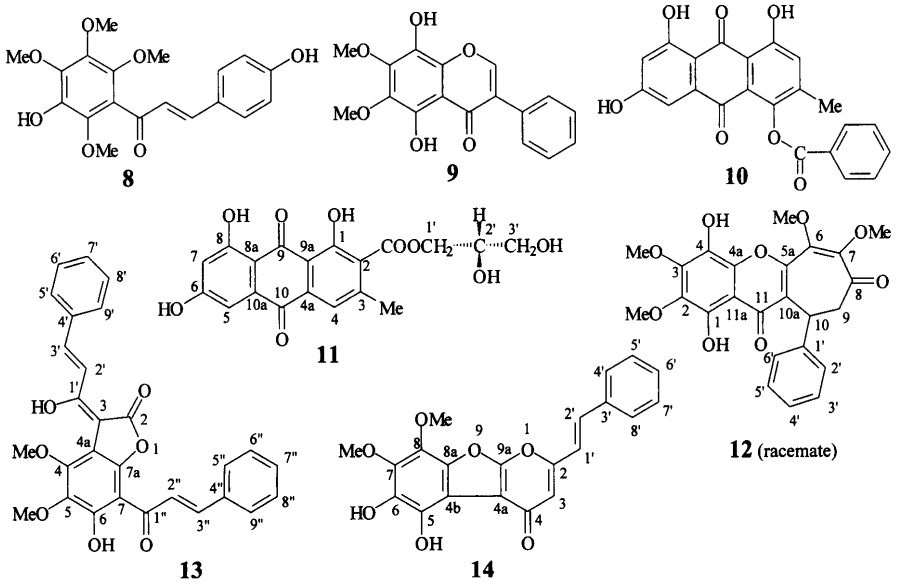

Fig. 1

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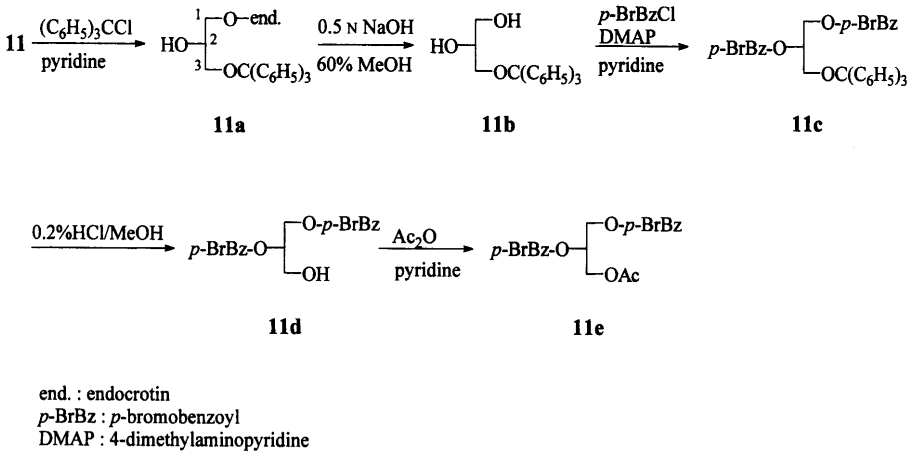

end. : endocrotin
p-BrBz : *p*-bromobenzoyl
DMAP : 4-dimethylaminopyridine

Chart 1

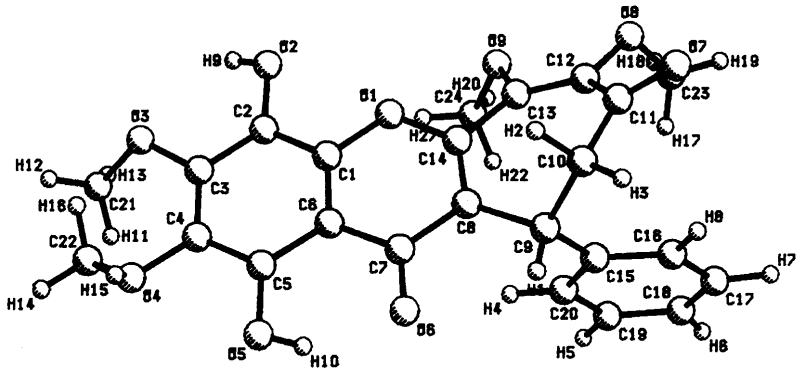

Fig. 2. ORTEP Representation of **12**

was easily deduced from the ^{1}H- and ^{13}C-NMR spectral data. In the ^{13}C-NMR spectrum of **8**, the carbon signals due to the A-ring were almost identical with those of **6**. The structure of **8** was, therefore, concluded to be 3′,4-dihydroxy-2′,4′,5′,6′-tetramethoxychalcone, which was further confirmed by the heteronuclear multiple bond connectivity (HMBC) spectrum and nuclear Overhauser effect (NOE) experiments.

Compound **9** was obtained as yellow plates, mp 166—167 °C (dec.), and formulated as $C_{17}H_{14}O_6$ from HR-EI-MS. The IR spectrum suggested the presence of hydroxyl groups, a conjugated carbonyl group and aromatic rings. The UV and ^{1}H-NMR spectra showed **9** was a dihydroxy-dimethoxy-isoflavone having no substituents in the B-ring.[13b] In the ^{13}C-NMR spectrum of **9**, the carbon signals due to the A-ring were found to be almost superimposable on those of the 5,8-dihydroxy-6,7-dimethoxyflavone series.[14] From these results, **9** was characterized as 5,8-dihydroxy-6,7-dimethoxy-isoflavone. The HMBC and NOE data also supported this structure.

Compound **10** was obtained as a yellow powder, with the molecular formula $C_{22}H_{14}O_7$ (from HR-FAB-MS). The IR spectrum suggested the presence of hydroxyl groups, conjugated carbonyl groups, ester and aromatic rings. Alkaline hydrolysis of **10** provided **4**[9] and benzoic acid. The position of the acyl group was determined from the acylation shift[15] in the ^{13}C-NMR spectrum: the signal due to C-4 was shifted upfield and the signals due to C-3, C-4a and C-1 were shifted downfield in comparison with those of **4**, showing that the benzoyl group was linked to C-4-OH. Accordingly, **10** was characterized as 1,6,8-trihydroxy-4-benzoyloxy-3-methylanthraquinone (4-*O*-benzoylcatenarin).

Compound **11** was obtained as yellow needles, mp 229—230 °C (dec.), $C_{19}H_{16}O_9$ (from HR-FAB-MS), having a negative optical rotation ($[\alpha]_D^{22}$ −30.0°). The IR spectrum suggested the presence of hydroxyl groups, conjugated carbonyl groups, ester and aromatic rings. On alkaline hydrolysis **11** afforded glycerol and endocrotin.[16] The planar structure of **11** was, therefore, determined as 2′,3′-dihydroxypropyl 1,6,8-trihydroxy-3-methylanthraquinone-2-carboxylate. The absolute configuration of the C-2′ position was established by applying a dibenzoate chirality method reported by Uzawa *et al.*[17] as follows. Compound **11** was treated as summarized in Chart 1 to obtain a 1,2-di-*O*-*p*-bromobenzoyl-3-*O*-acetylglycerol (**11e**). The CD spectrum of **11e** showed positive first (255 nm) and negative second Cotton effects (237 nm), indicating that the C-2 of **11e** was *S*. Thus, the absolute configuration of the original compound **11** was confirmed to be *S*.

Compound **12** (didymocalyxin A) was obtained as orange needles, mp 211—212 °C (dec.), $C_{24}H_{22}O_9$ (from HR-EI-MS), having no optical rotation. The IR spectrum suggested the presence of hydroxyl groups, conjugated carbonyl groups and aromatic rings. A single crystal of **12** was subjected to X-ray crystallographic analysis, and the structure was determined as (±)-1,4-dihydroxy-2,3,6,7-tetramethoxy-10-phenyl-9,10-dihydrocyclohepta[2,1-*b*]4*H*-chromene-8,11-dione, and its ORTEP representation is shown in Fig. 2. The CD spectrum also showed **12** was a racemate. Based on the established structure and two dimensional (2D)-NMR spec-

tral data (Fig. 3) of **12**, the ^{1}H- and ^{13}C-signals were assigned as shown in Table 1.

Compound **12** has a dihydrotroponochromone skeleton with a phenyl group, and is presumed to be formed biogenetically by cyclization of an intermediate derived from a cinnamoylpropenoate and four malonates as shown in Chart 2.

Compound **13** (didymocalyxin B) was obtained as brown needles, mp 188—189 °C (dec.). $C_{28}H_{22}O_7$ (from HR-EI-MS). The IR spectrum suggested the presence of hydroxyl groups, conjugated lactone and carbonyl groups and aromatic rings. The structure was elucidated by X-ray crystallographic analysis as 3-((1*E*,2*E*)-1-hydroxy-3-phenylprop-2-enylidene)-7((2*E*)-3-phenylprop-2-enoyl)-6-hydroxy-4,5-dimethoxybenzo[*b*]furan-2-one, and its ORTEP representation is shown in Fig. 4. The full NMR assignment of **13** was achieved based on the established structure and the 2D-NMR spectral data (Fig. 5) as shown in Table 1.

Compound **13** is the first example of a chalcone having a C_6–C_3–C_2 unit at the A-ring, and is presumed to be formed biogenetically by oxidative coupling of the two precursors, compound **5** and an enolic form of cinnamoylacetic acid, as shown in Chart 2.

Compound **14** (didymocalyxin C) was obtained as yellow needles, mp 256—257 °C (dec.), $C_{21}H_{16}O_7$ (from HR-EI-MS), and had absorption bands assignable to hydroxyl groups, a conjugated carbonyl group and aromatic rings in the IR spectrum. The UV spectrum (λ_{max} 323 nm) is similar to that of the pseudoyangonin series.[18] The presence of a 2-oxygenated-6-styryl-γ-pyrone moiety in **14** was confirmed from the NMR spectral data (Table 1) of **14** as follows. The ^{1}H-NMR spectrum revealed the presence of five aromatic protons (δ 7.42—7.74), a pair of *trans*-coupled olefinic protons (d, J=16.4 Hz) at δ 7.64 and 7.33 and an isolated olefinic proton at δ 6.74. Further information was obtained from 2D-NMR experiments (Fig. 6). In the HMBC spectrum of **14**, one of the *trans*-olefinic proton signals at δ 7.64 (H-2′) showed a cross-peak with the carbon signal at δ 127.8 (C-4′,8′). The isolated olefinic proton signal at δ 6.74 (H-3) showed correlations with the signals at δ 118.8 (C-1′), 159.6 (C-2), 176.4 (C-4) and 103.1 (C-4a). In addition, the other *trans*-olefinic proton signal at δ 7.33 (H-1′) showed a cross-peak with the carbon signal at δ 163.2 (C-9a), which may be attributed to W-type long-range coupling through four bonds.[19] This evidence led to the partial structure A of **14** as depicted in Fig. 6. On the other hand, the partial structure B (Fig. 6) was established as follows. The ^{1}H-NMR spectrum of **14** showed the presence of two phenolic hydroxyls and two methoxyls. The UV spectrum of **14** showed a bathochromic shift on adding $AlCl_3$, but no shift was observed on adding $AlCl_3$/HCl, indicating the presence of an *ortho*-diphenol in **14**.[13c] The presence of an *ortho*-dimethoxy system in **14** was confirmed by NOE experiments. In the HMBC spectrum of **14**, one of the hydroxyl proton signals at δ 9.21 (5-OH) showed cross-peaks with the carbon signals at δ 106.7 (C-4b) and δ 135.8 (C-6). The other hydroxyl proton signal at δ 8.82 (6-OH) showed cross-peaks with the carbon signals at δ 134.0 (C-5) and 141.2 (C-7), the second of which is correlated with the methoxyl proton signal at δ 3.80. Thus, the partial structure B (Fig. 6) of **14** was corroborated. The linkage of A to B was clarified by the HMBC

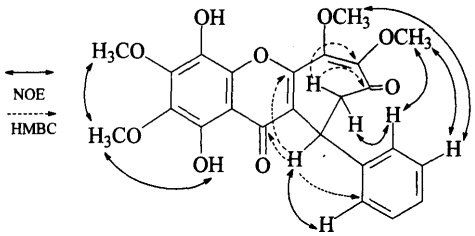

Fig. 3. Significant Correlations in the HMBC and NOE Spectra of **12**

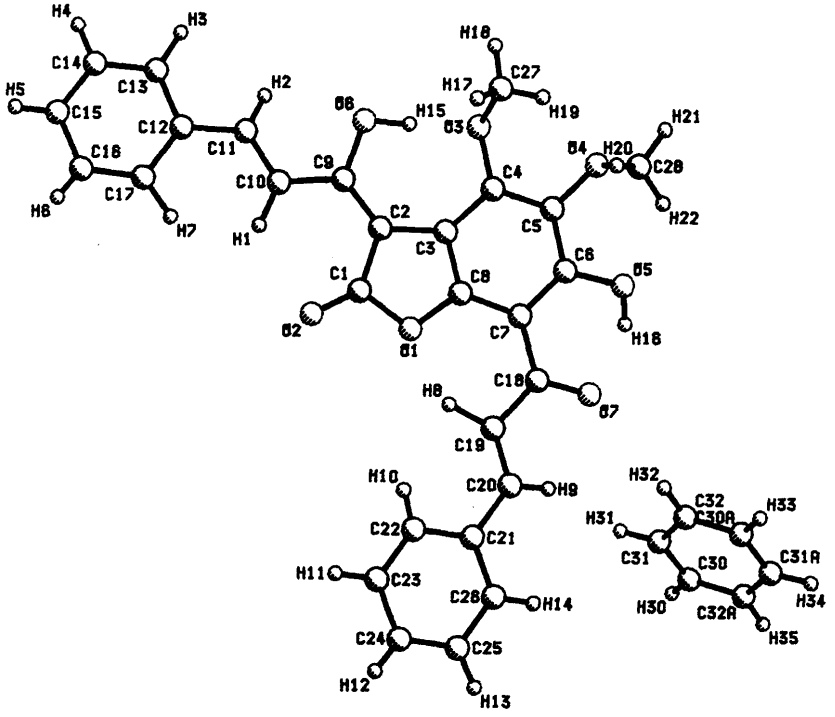

Fig. 4. ORTEP Representation of **13**

Two molecules of **13** contain one molecule of benzene.

spectrum of **14**, in which a cross-peak due to the ^4J correlation was observed between the isolated olefinic proton signal at δ 6.74 (H-3) and the carbon signal at δ 106.7 (C-4b). Therefore, the two partial structures, A and B, were linked through C-4a→C-4b and C-9a→O-9→C-8a. Accordingly, the structure of **14** was shown to be 2((1*E*)-2-phenylvinyl)-5,6-dihydroxy-7,8-dimethoxy-4*H*-pyrano[3,2-*d*]benzo[*b*]furan-4-one.

Compound **14** has a benzofurano-γ-pyrone skeleton with a styryl group, and is presumed to be formed biogenetically by oxidative coupling of the two molecules, 2-hydroxy-6-styryl-γ-pyrone and an oxygenated phenol, as shown in Chart 2.

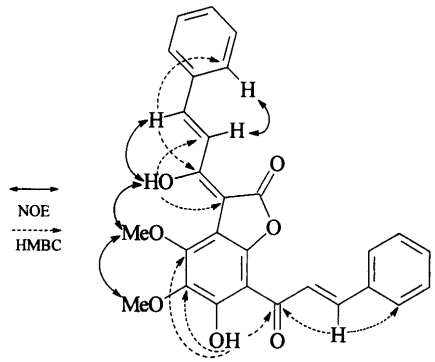

Fig. 5. Significant Correlations in the HMBC and NOE Spectra of **13**

Experimental

Unless otherwise stated, the instruments and experimental conditions were the same as in our previous paper.[20]

X-Ray Crystallographic Analysis The reflection data were collected on a Rigaku AFC-5R four-circle diffractometer with graphite-monochromated CuK_α radiation using the ω-2θ scan technique at a 2θ scan speed of 8°/min to a maximum 2θ value of 120.2°. Of the reflections collected, those above the 3σ (*I*) level were used for the calculations. The structures were solved by the direct method using MITHRIL[21] and refined by the full-matrix least-squares procedure with anisotropic temperature factors for the non-hydrogen atoms and isotropic temperature factors for the hydrogen atoms.

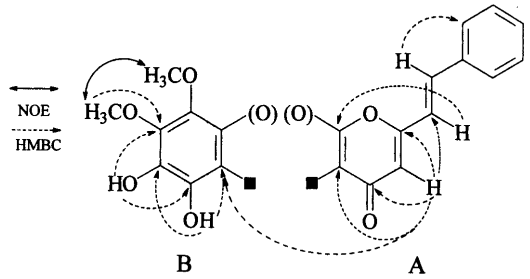

Fig. 6. Significant Correlations in the HMBC and NOE Spectra of Partial Structures A and B of **14**

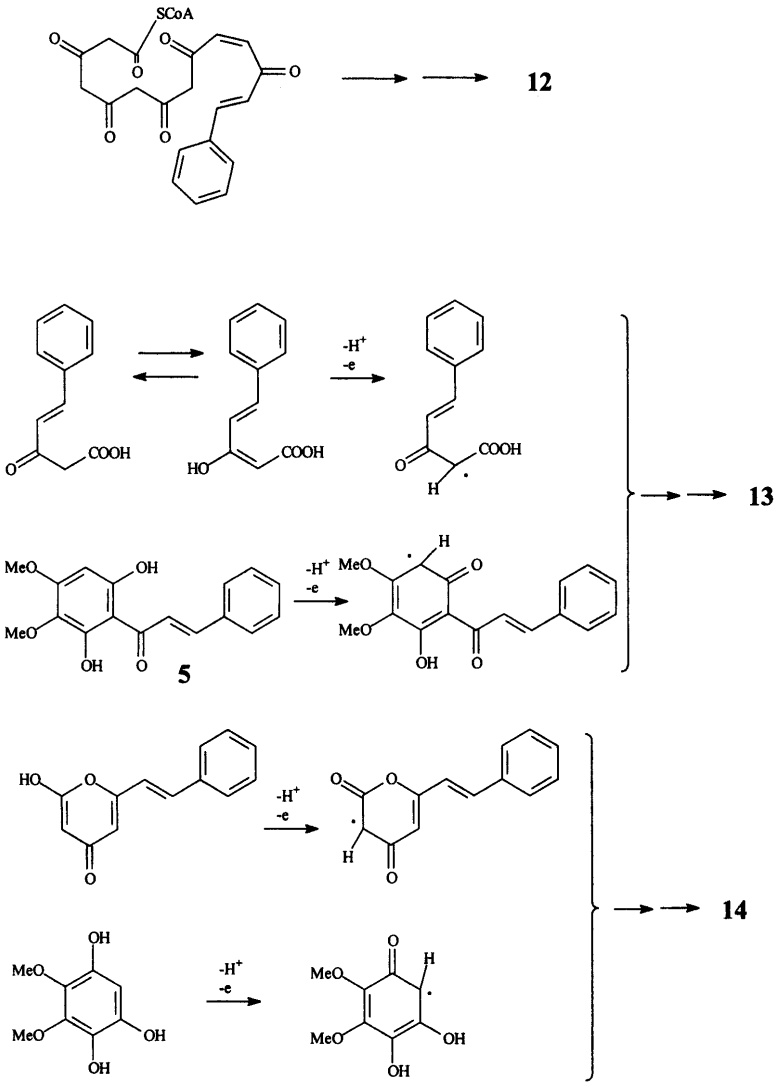

Chart 2. Possible Biogenetic Precursors of **12**, **13** and **14**

Table 1. ^{1}H- and ^{13}C-NMR Data of **12**, **13** and **14**

12			**13**			**14**		
Position	δ_H (J Hz) DMSO-d_6	δ_C	Position	δ_H (J Hz) $CDCl_3$	δ_C	Position	δ_H (J Hz) DMSO-d_6	δ_C
1		144.4	2		166.9	2		159.6
2		136.2	3		96.4	3	6.74 s	111.4
3		148.4	4a		107.8	4		176.4
4		130.7	4		148.6	4a		103.1
4a		141.4	5		135.7	4b		106.7
5a		155.9	6		158.7	5		134.0
6		148.1	7		105.2	6		135.8
7		148.9	7a		146.8	7		141.2
8		193.9	1′		164.0	8		131.6
9	3.21 dd (2.4, 18.4)	46.6	2′	8.35 dd (1.6, 16.0)	118.5	8a		133.3
	3.56 dd (6.0, 18.4)							
10	4.95 m	29.1	3′	7.67 d (16.0)	140.0	9a		163.2
11		180.8						
11a		106.2						
1′		138.0	4′		136.0	1′	7.33 d (16.4)	118.8
2′,6′	7.20 m	126.9	5′,9′	7.66 m	128.3	2′	7.64 d (16.4)	136.2
3′,5′	7.27 m	128.3	6′,8′	7.39 m	128.9	3′		134.8
4′	7.21 m	126.5	7′	7.37 m	130.0	4′,8′	7.44 m	127.8
1-OH	12.07 s		1″		191.9	5′,7′	7.46 m	129.0
4-OH	9.31 s		2″	8.10 d (16.0)	124.6	6′	7.42 m	129.9
2-OMe	3.85 s	60.6	3″	7.98 d (16.0)	146.3	5-OH	9.21 s	
3-OMe	3.95 s	61.3	4″		134.7	6-OH	8.82 s	
6-OMe	3.64 s	60.5	5″,9″	7.72 m	129.2	7-OMe	3.80 s	
7-OMe	3.20 s	59.6	6″,8″	7.44 m	129.1	8-OMe	3.98 s	
			7″	7.44 m	131.2			
			6-OH	13.87 s				
			1′-OH	10.95 d (1.6)				
			4-OMe	4.31 s	63.5			
			5-OMe	3.94 s	61.2			

Table 2. Positional Parameters and B(eq) for **12**

Atom	x	y	z	B(eq)	Atom	x	y	z	B(eq)
O(1)	0.9416 (1)	0.4340 (3)	0.0091 (2)	3.0 (1)	C(20)	0.8505 (2)	0.0669 (6)	0.0487 (3)	4.1 (2)
O(2)	0.9838 (1)	0.7058 (4)	0.0670 (2)	3.9 (1)	C(21)	1.0781 (2)	0.7697 (6)	0.2995 (3)	5.9 (3)
O(3)	1.0642 (1)	0.7221 (3)	0.2144 (2)	3.6 (1)	C(22)	1.1453 (2)	0.4147 (8)	0.2980 (3)	6.5 (3)
O(4)	1.1037 (1)	0.4421 (3)	0.3084 (2)	3.7 (1)	C(23)	0.7625 (2)	0.272 (1)	−0.2034 (5)	12.0 (5)
O(5)	1.0588 (1)	0.1653 (4)	0.2499 (2)	3.5 (1)	C(24)	0.8491 (2)	0.5216 (8)	−0.0144 (4)	7.7 (4)
O(6)	0.9911 (1)	0.0154 (3)	0.1267 (2)	3.6 (1)	H(1)	0.923 (1)	−0.075 (5)	0.007 (2)	4 (1)
O(7)	0.8353 (2)	0.0380 (5)	−0.2489 (2)	7.5 (2)	H(2)	0.932 (2)	0.035 (6)	−0.116 (3)	8 (1)
O(8)	0.8018 (1)	0.3012 (5)	−0.2164 (2)	6.0 (2)	H(3)	0.893 (2)	−0.111 (6)	−0.135 (3)	6 (1)
O(9)	0.8532 (1)	0.4834 (4)	−0.0892 (2)	4.3 (1)	H(4)	0.876 (1)	0.129 (5)	0.092 (2)	3 (1)
C(1)	0.9820 (1)	0.4315 (5)	0.0837 (2)	2.6 (2)	H(5)	0.807 (2)	0.099 (6)	0.104 (3)	6 (1)
C(2)	1.0032 (1)	0.5748 (5)	0.1137 (3)	2.7 (2)	H(6)	0.746 (2)	−0.043 (7)	0.009 (4)	9 (2)
C(3)	1.0439 (1)	0.5780 (5)	0.1900 (2)	2.8 (2)	H(7)	0.749 (2)	−0.167 (7)	−0.114 (3)	7 (2)
C(4)	1.0630 (1)	0.4384 (5)	0.2340 (3)	3.0 (2)	H(8)	0.821 (2)	−0.138 (5)	−0.120 (3)	4 (1)
C(5)	1.0405 (1)	0.2975 (5)	0.2043 (2)	2.7 (2)	H(9)	0.995 (2)	0.781 (6)	0.094 (3)	5 (1)
C(6)	0.9994 (1)	0.2908 (5)	0.1271 (2)	2.5 (2)	H(10)	1.041 (2)	0.090 (6)	0.225 (3)	6 (2)
C(7)	0.9754 (1)	0.1455 (5)	0.0918 (3)	2.8 (2)	H(11)	1.0769	0.6811	0.3315	7.2
C(8)	0.9311 (1)	0.1570 (5)	0.0155 (3)	2.8 (2)	H(12)	1.1094	0.8103	0.3224	7.2
C(9)	0.9032 (2)	0.0099 (6)	−0.0241 (3)	3.3 (2)	H(13)	1.0568	0.8482	0.3009	7.2
C(10)	0.8975 (2)	−0.0059 (7)	−0.1145 (3)	4.6 (2)	H(14)	1.1720	0.4233	0.3512	7.9
C(11)	0.8581 (2)	0.0887 (7)	−0.1785 (3)	4.7 (2)	H(15)	1.1439	0.3124	0.2759	7.9
C(12)	0.8444 (2)	0.2445 (6)	−0.1578 (3)	4.0 (2)	H(16)	1.1473	0.4907	0.2606	7.9
C(13)	0.8703 (2)	0.3369 (6)	−0.09116 (3)	3.5 (2)	H(17)	0.7709	0.2064	−0.1557	14.8
C(14)	0.9162 (1)	0.2994 (5)	−0.0205 (2)	2.9 (2)	H(18)	0.7503	0.3691	−0.1941	14.8
C(15)	0.8564 (1)	−0.0036 (5)	−0.0171 (3)	3.2 (2)	H(19)	0.7390	0.2220	−0.2516	14.8
C(16)	0.8189 (2)	−0.0907 (6)	−0.0743 (3)	4.1 (2)	H(20)	0.8226	0.5903	−0.0279	9.4
C(17)	0.7769 (2)	−0.1073 (8)	−0.0687 (4)	5.5 (3)	H(22)	0.8442	0.4285	0.0104	9.4
C(18)	0.7717 (2)	−0.0357 (9)	−0.0043 (4)	6.1 (3)	H(27)	0.8772	0.5728	0.0238	9.4
C(19)	0.8084 (2)	0.0497 (8)	0.0550 (4)	5.9 (3)					

Table 3. Positional Parameters and B(eq) for **13**

Atom	x	y	z	B(eq)	Atom	x	y	z	B(eq)
O(1)	0.9919 (3)	0.3702 (3)	0.7074 (6)	3.7 (2)	C(26)	0.7969 (6)	−0.0499 (6)	0.477 (1)	6.4 (4)
O(2)	1.1539 (3)	0.3911 (3)	0.6000 (7)	4.7 (2)	C(27)	0.8106 (6)	0.7622 (5)	0.799 (1)	5.6 (4)
O(3)	0.8818 (3)	0.7002 (3)	0.8848 (6)	4.2 (2)	C(28)	0.5881 (6)	0.6451 (5)	0.919 (1)	5.2 (4)
O(4)	0.6918 (3)	0.6430 (3)	1.0105 (6)	4.3 (2)	C(30)	0.573 (1)	−0.0518 (9)	1.084 (2)	8.3 (6)
O(5)	0.6495 (4)	0.4478 (4)	0.9913 (7)	4.6 (2)	C(31)	0.6054 (8)	0.019 (1)	0.993 (2)	8.8 (7)
O(6)	1.0792 (3)	0.7063 (3)	0.7913 (7)	4.9 (2)	C(32)	0.533 (1)	0.0721 (7)	0.913 (2)	8.5 (6)
O(7)	0.7005 (4)	0.2686 (3)	0.8893 (7)	5.3 (2)	H(1)	1.240 (4)	0.534 (4)	0.585 (7)	2 (1)
C(1)	1.0760 (5)	0.4312 (5)	0.6694 (9)	3.7 (3)	H(2)	1.255 (4)	0.743 (4)	0.725 (8)	3 (1)
C(2)	1.0435 (5)	0.5344 (4)	0.7285 (8)	3.2 (3)	H(3)	1.402 (5)	0.843 (5)	0.677 (8)	4 (1)
C(3)	0.9357 (4)	0.5312 (4)	0.7996 (8)	3.2 (3)	H(4)	1.5649	0.8525	0.5409	7.1
C(4)	0.8576 (4)	0.6016 (4)	0.8684 (8)	3.1 (3)	H(5)	1.6418	0.7175	0.3561	7.4
C(5)	0.7621 (5)	0.5715 (4)	0.9288 (8)	3.5 (3)	H(6)	1.554 (6)	0.575 (6)	0.31 (1)	7 (2)
C(6)	0.7414 (5)	0.4711 (5)	0.9196 (8)	3.6 (3)	H(7)	1.373 (5)	0.547 (4)	0.447 (8)	4 (1)
C(7)	0.8122 (5)	0.3959 (4)	0.8365 (8)	3.3 (3)	H(8)	0.905 (5)	0.252 (5)	0.638 (9)	6 (2)
C(8)	0.9101 (5)	0.4311 (4)	0.7829 (8)	3.3 (3)	H(9)	0.740 (6)	0.118 (6)	0.70 (1)	7 (2)
C(9)	1.1085 (5)	0.6117 (5)	0.7234 (9)	3.6 (3)	H(10)	0.922 (6)	0.126 (6)	0.36 (1)	7 (2)
C(10)	1.2130 (5)	0.6047 (5)	0.644 (1)	3.7 (3)	H(11)	1.0012	−0.0019	0.1584	8.1
C(11)	1.2761 (5)	0.6855 (5)	0.653 (1)	4.0 (3)	H(12)	0.934 (6)	−0.157 (6)	0.14 (1)	6 (2)
C(12)	1.3799 (5)	0.6899 (5)	0.5705 (9)	3.8 (3)	H(13)	0.811 (6)	−0.193 (6)	0.36 (1)	7 (2)
C(13)	1.4322 (6)	0.7812 (5)	0.599 (1)	4.8 (4)	H(14)	0.7430	−0.0626	0.5566	7.7
C(14)	1.5297 (6)	0.7902 (6)	0.520 (1)	6.0 (4)	H(15)	1.0056	0.7025	0.8422	5.8
C(15)	1.5756 (6)	0.7103 (8)	0.412 (1)	6.2 (4)	H(16)	0.647 (7)	0.384 (6)	0.98 (1)	8 (3)
C(16)	1.5258 (7)	0.6209 (7)	0.384 (1)	5.4 (4)	H(17)	0.8184	0.7474	0.6711	6.7
C(17)	1.4283 (5)	0.6087 (5)	0.461 (1)	4.5 (3)	H(18)	0.8269	0.8301	0.8417	6.7
C(18)	0.7787 (6)	0.2915 (5)	0.808 (1)	4.1 (3)	H(19)	0.7385	0.7503	0.8270	6.7
C(19)	0.8331 (5)	0.2148 (5)	0.676 (1)	4.0 (3)	H(20)	0.5982	0.6473	0.7939	6.3
C(20)	0.7936 (6)	0.1259 (5)	0.626 (1)	4.7 (4)	H(21)	0.5491	0.7024	0.9724	6.3
C(21)	0.8326 (6)	0.0463 (5)	0.488 (1)	4.6 (3)	H(22)	0.5497	0.5871	0.9289	6.3
C(22)	0.9092 (7)	0.0629 (6)	0.365 (1)	5.7 (4)	H(30)	0.6269	−0.0878	1.1478	9.9
C(23)	0.9489 (8)	−0.0139 (7)	0.241 (1)	6.8 (5)	H(31)	0.6797	0.0320	0.9865	10.5
C(24)	0.913 (1)	−0.1091 (7)	0.237 (2)	7.5 (6)	H(32)	0.5550	0.1264	0.8495	10.0
C(25)	0.8369 (9)	−0.1276 (7)	0.354 (2)	7.6 (6)					

Some hydrogen atoms were located at calculated positions.[22]

Extraction and Isolation "Kumkum", the leaves of *Didymocarpus leucocalyx*,[5] was purchased in Kathmandu, Nepal in 1996. The botanical identification was made by Dr. N. P. Manandhar, Royal Botanical Garden, Ministry of Forests, His Majesty's Government of Nepal. A voucher specimen has been deposited at the Herbarium of the Faculty of Pharmaceutical Sciences, Hokuriku University, Kanazawa, Japan. The dried leaves (2 kg) were extracted with boiling MeOH and the MeOH extract was concentrated to dryness to give a residue (400 g), which was defatted with *n*-hexane and partitioned between H_2O and Et_2O. The Et_2O extract (220 g) was chromatographed on silica gel with a gradient of *n*-hexane–acetone (50 : 1→1 : 1) to give **13** (68 mg), **3** (26 mg), **1** (92 mg), **2** (80 mg) and six fractions (frs. 1—6), in order of elution. Fractions 1 and 2 were subjected to silica gel column chromatography using $CHCl_3$–MeOH–H_2O (10 : 0.1 : 0.01→5 : 1 : 0.01) and benzene–EtOAc (20 : 1→1 : 1) to give **4** (40 mg) and **5** (120 mg), respectively. Fraction 3 was chromatographed on an ODS column (solv., 50→90% MeOH) to give **10** (26 mg), **9** (28 mg), and **6** (472 mg). Fraction 4 was subjected to silica gel column chromatography using benzene–EtOAc (20 : 1→2 : 1) to give **14** (42 mg), **12** (74 mg) and **7** (45 mg). Fractions 5 and 6 were chromatographed on an ODS column using 50→75% MeOH and 33→66% MeOH to give **8** (14 mg) and **11** (32 mg), respectively.

Identification of 1—7 The structures of **1**—**7** were identified by comparison of their physical and spectral data with those described in the literature.[6—12]

3′,4-Dihydroxy-2′,4′,5′,6′-tetramethoxychalcone (8) A yellow amorphous powder. EI-MS *m/z* (%): 360 $[M]^+$ (100), 255 (43). HR-EI-MS *m/z*: Found 360.1208, Calcd for $C_{19}H_{20}O_7$ $[M]^+$ 360.1209. IR ν_{max} (KBr) cm^{-1}: 3400 (OH), 1636 (conjugated CO), 1582 (arom.C=C). UV λ_{max} (MeOH) nm (log ε): 332 (4.43); λ_{max} (MeOH–NaOMe) nm (log ε): 248 (4.11), 299 (3.80), 313 (3.71), 381 (4.51); λ_{max} (MeOH–$AlCl_3$) nm (log ε): 333 (4.44); λ_{max} (MeOH–$AlCl_3$–HCl) nm (log ε): 333(4.44); λ_{max} (MeOH–NaOAc) nm (log ε): 337sh (4.16), 385 (4.31); λ_{max} (MeOH–NaOAc–H_3BO_3) nm (log ε): 335 (4.40). ^{1}H-NMR (DMSO-d_6): 7.19 (1H, d, J=15.6 Hz, H-α), 6.84 (1H, d, J=15.6 Hz, H-β), 7.56 (2H, d, J=8.8 Hz, H-2,6), 6.79 (1H, d, J=8.8 Hz, H-3, 5), 3.61 (3H, s, 2′-OMe), 3.82 (3H, s, 4′-OMe), 3.81 (3H, s, 5′-OMe), 3.63 (3H, s, 6′-OMe), 8.97 (1H, s, 3′-OH), 10.09 (1H, s, 4-OH). ^{13}C-NMR (DMSO-d_6): 124.1 (C-1′), 140.2 (C-2′), 140.0 (C-3′), 142.9 (C-4′), 142.6 (C-5′), 141.2 (C-6′), 192.8 (CO), 125.3 (C-α), 145.9 (C-β), 125.0 (C-1), 130.7 (C-2, 6), 115,9 (C-3, 5), 160.2 (C-4), 60.7 (2′,6′-OMe), 61.4 (4′-OMe), 60.8 (5′-OMe).

5,8-Dihydroxy-6,7-dimethoxyisoflavone (9) Yellow plates (MeOH), mp166—167 °C (dec.). EI-MS *m/z* (%): 314 $[M]^+$ (100), 299 (93). HR-EI-MS *m/z*: Found 314.0788, Calcd for $C_{17}H_{14}O_6$ $[M]^+$ 314.0791. IR ν_{max} (KBr) cm^{-1}: 3352 (OH), 1620 (conjugated CO), 1586 (arom. C=C). UV λ_{max} (MeOH) nm (log ε): 268 (4.53); λ_{max} (MeOH–NaOMe) nm (log ε): dec.; λ_{max} (MeOH–$AlCl_3$) nm (log ε): 287 (4.54); λ_{max} (MeOH–$AlCl_3$–HCl) nm (log ε): 286 (4.56); λ_{max} (MeOH–NaOAc) nm (log ε): dec.; λ_{max} (MeOH–NaOAc–H_3BO_3) nm (log ε): 268 (4.50). ^{1}H-NMR (DMSO-d_6): 8.56 (1H, s, H-2), 7.58 (2H, m, H-2′, 6′), 7.42—7.49 (3H, m, H-3′, 4′, 5′), 3.83 (3H, s, 6-OMe), 3.94 (3H, s, 7-OMe), 12.31 (1H, s, 5-OH), 9.39 (1H, s, 8-OH). ^{13}C-NMR (DMSO-d_6): 155.6 (C-2), 121.9 (C-3), 181.0 (C-4), 145.1 (C-5), 136.3 (C-6), 148.0 (C-7), 130.6 (C-8), 141.7 (C-9), 107.2 (C-10), 130.8 (C-1′), 129.1 (C-2′, 6′), 128.3 (C-3′, 5′), 128.1 (C-4′), 60.5 (6-OMe), 61.3 (7-OMe).

1,6,8-Trihydroxy-4-benzoyloxy-3-methylanthraquinone (4-*O*-Benzoylcatenarin) (10) A yellow amorphous powder. EI-MS *m/z* (%): 157 (22), 141 (18), 78 (95). FAB-MS (negative) (magic bullet) *m/z* (%): 389 $[M-1]^-$ (24). HR-FAB-MS *m/z*: Found: 389.0671, Calcd for $C_{22}H_{13}O_7$ $[M-1]^-$ 389.0662. IR ν_{max} (KBr) cm^{-1}: 3464 (OH), 1696 (COO), 1630 (conjugated CO), 1610 (arom. C=C). UV λ_{max} (MeOH) nm (log ε): 248 (4.30), 267 (4.27), 287 (4.24), 327 sh (3.69), 443 (4.00), 467 sh (3.94); λ_{max} (MeOH–NaOMe) nm (log ε): 254 (4.31) 308 (4.23), 387 sh (3.50), 500 (3.94); λ_{max} (MeOH–$AlCl_3$) nm (log ε): 254 (4.36), 268 (4.35), 303 (4.18), 367 sh (3.45), 487 (4.14); λ_{max} (MeOH–$AlCl_3$–HCl) nm (log ε): 250 (4.35), 267 (4.35), 298 (4.18), 315 sh (3.80), 364 sh (3.50), 487 (4.08); λ_{max} (MeOH–NaOAc) nm (log ε): 254 (4.39), 315 (4.26), 397 sh (3.63), 495 (3.99); λ_{max} (MeOH–NaOAc–H_3BO_3) nm (log ε): 253 (4.29), 300 (4.13), 322 sh (4.05), 470 (3.85). ^{1}H-NMR (DMSO-d_6): 7.44 (1H, s, H-2), 6.94 (1H, d, J=2.2 Hz, H-5), 6.59 (1H, d, J=2.2 Hz, H-7), 8.18 (2H, m, H-2′, 6′), 7.66 (2H, m, H-3′, 5′), 7.80 (1H, m, H-4′), 2.25 (3H, s, 3-Me), 12.50 (1H, s, 1-OH), 11.10

(1H, br s, 6-OH), 12.00 (1H, s, 8-OH). ^{13}C-NMR (DMSO-d_6): 159.4 (C-1), 126.5 (C-2), 143.1 (C-3), 142.0 (C-4), 123.1 (C-4a), 108.8 (C-5), 165.9 (C-6), 107.8 (C-7), 164.2 (C-8), 108.6 (C-8a), 189.1 (C-9), 113.8 (C-9a), 180.4 (C-10), 135.6 (C-10a), 128.9 (C-1′), 130.0 (C-2′, 6′), 129.0 (C-3′, 5′), 134.1 (C-4′), 16.4 (3-Me), 164.2 (COO).

Alkaline Hydrolysis of 10 A solution of **10** (5 mg) in 0.5 N NaOH/60% MeOH (1 ml) was heated at 80 °C for 2 h. The reaction mixture was poured into cold H_2O, acidified with HCOOH, and extracted with Et_2O. The organic layer was washed with H_2O and concentrated to dryness, then the residue was subjected to silica gel chromatography eluting with $CHCl_3$–MeOH–H_2O (50 : 1 : 0.1→30 : 1 : 0.1) to afford benzoic acid (1.3 mg) and catenarin (**4**) (1.8 mg), both of which were identified by direct comparison (IR and ^{1}H-NMR).

(2′*S*)-2′,3′-Dihydroxypropyl 1,6,8-Trihydroxy-3-methylanthraquinone-2-carboxylate (11) Yellow needles (MeOH), mp 229—230 °C (dec.). $[\alpha]_D^{22}$ −30.0° (c=0.05, MeOH). EI-MS m/z (%): 314 (10), 296 (35), 270 (100). FAB-MS (negative) (glycerol) m/z (%): 387 $[M-1]^-$ (1). HR-FAB-MS m/z: Found 387.0719, Calcd for $C_{19}H_{15}O_9$ $[M-1]^-$ 387.0716. IR ν_{max} (KBr) cm^{-1}: 3400 (OH), 1730 (COO), 1628 (conjugated CO), 1610 (arom. C=C). UV λ_{max} (MeOH) nm (log ε): 252 (4.20), 288 (4.23), 327 sh (3.67), 440 (3.92); λ_{max} (MeOH–NaOMe) nm (log ε): 307 (4.28), 393 sh (3.28), 500 (3.76); λ_{max} (MeOH–$AlCl_3$) nm (log ε): 266 (4.28), 304 (4.12), 482 (4.03); λ_{max} (MeOH–$AlCl_3$–HCl) nm (log ε): 254 sh (4.23), 267 (4.25), 300 (4.14), 368 sh (3.32), 487 (4.06); λ_{max} (MeOH–NaOAc) nm (log ε): 253 (4.20), 313 (4.26), 377 sh (3.16), 500 (3.74); λ_{max} (MeOH–NaOAc–H_3BO_3) nm (log ε): 254 (4.21), 305 (4.19), 482(3.67). ^{1}H-NMR (DMSO-d_6;*, D_2O added): 7.54 (1H, s, H-4), 7.11 (1H, d, J=2.8 Hz, H-5), 6.60 (1H, d, J=2.8 Hz, H-7), 4.22 (1H, dd, J=6.0, 10.8 Hz, H-1′), 4.38 (1H, dd, J=4.0, 10.8 Hz, H-1′), 3.77 (1H, m, H-2′), 3.39* (1H, dd, J=6.4, 10.8 Hz, H-3′), 3.42* (1H, dd, J=5.2, 10.8 Hz, H-3′), 12.35 (1H, s, 1-OH), 11.50 (1H, br s, 6-OH), 11.92 (1H, s, 8-OH), 5.04 (1H, br s, 2′-OH), 4.75 (1H, br s, 3′-OH), 2.38 (3H, s, 3-Me). ^{13}C-NMR (DMSO-d_6): 158.0 (C-1), 128.9 (C-2), 144.4 (C-3), 120.5 (C-4), 133.0 (C-4a), 109.1 (C-5), 165.8 (C-6), 108.1 (C-7), 165.6 (C-8), 109.1 (C-8a), 189.4 (C-9), 114.0 (C-9a), 181.0 (C-10), 135.1 (C-10a), 67.0 (C-1′), 69.3 (C-2′), 62.6 (C-3′), 19.6 (3-Me), 164.5 (2-COO).

Alkaline Hydrolysis of 11 A solution of **11** (7.8 mg) was hydrolyzed with 0.5 N NaOH/60% MeOH (1 ml) and worked up in the same way as described for **10**. The hydrolysate obtained was chromatographed on silica gel [benzene–EtOAc (8 : 1→2 : 1)] to give glycerol and endocrotin,[16] both of which were confirmed by direct comparison (TLC, ^{1}H-NMR).

Tritylation of 11 (Formation of 11a) A solution of **11** (16 mg) and trityl chloride (12 mg) in pyridine (5 ml) was heated at 100 °C for 1 h. After cooling, the reaction mixture was poured into ice H_2O with stirring and extracted with benzene. The organic layer was washed with H_2O and concentrated to dryness, then the residue was subjected to silica gel chromatography [benzene–EtOAc (10 : 1→7 : 1)] to give **11a** (16 mg), a yellow amorphous powder, $[\alpha]_D^{24}$ −10.5° (c=0.04, MeOH). EI-MS m/z (%): 390 (15), 243 (100). FAB-MS (positive) (magic bullet) m/z (%): 653 $[M+Na]^+$ (3). HR-FAB-MS m/z: Found 653.1778, Calcd for $C_{38}H_{30}O_9Na$ $[M+Na]^+$ 653.1788. IR ν_{max} (KBr) cm^{-1}: 3500 (OH), 1630 (conjugated CO), 1610 (arom. C=C). ^{1}H-NMR (DMSO-d_6): 7.57 (1H, s, H-4), 7.16 (1H, d, J=2.5 Hz, H-5), 6.64 (1H, d, J=2.5 Hz, H-7), 4.33 (1H, dd, J=5.7, 11.2 Hz, H-1′), 4.40 (1H, dd, J=4.5, 11.2 Hz, H-1′), 3.98 (1H, m, H-2′), 3.01 (1H, dd, J=5.7, 10.5 Hz, H-3′), 3.07 (1H, dd, J=5.5, 10.5 Hz, H-3′), 12.32 (1H, s, 1-OH), 11.50 (1H, br s, 6-OH), 11.96 (1H, s, 8-OH), 5.31 (1H, d, J=5.7 Hz, 2′-OH), 2.29 (3H, s, 3-Me), 7.25—7.41 (15H, m, Ph×3). ^{13}C-NMR (DMSO-d_6): 157.9 (C-1), 128.6 (C-2), 144.3 (C-3), 120.4 (C-4), 133.1 (C-4a), 109.1 (C-5), 166.0 (C-6), 108.1 (C-7), 165.5 (C-8), 109.1 (C-8a), 189.3 (C-9), 114.0 (C-9a), 181.1 (C-10), 135.1 (C-10a), 66.8 (C-1′), 67.3 (C-2′), 64.8 (C-3′), 19.6 (3-Me), 164.5 (2-COO), 143.7 (×3), 127.8 (×6), 128.3 (×6), 127.0 (×3) (Ph×3), 85.9 (C-(Ph_3)).

Alkaline Hydrolysis of 11a (Formation of 11b) **11a** (14 mg) was treated in the same way as described for **10** and **11**. The hydrolysate obtained was chromatographed on silica gel using benzene–EtOAc (8 : 1→4 : 1) to afford endocrotin and **11b** (5 mg), colorless needles (MeOH), mp 111—112 °C. $[\alpha]_D^{24}$ −3.6° (c=0.10, MeOH). EI-MS m/z (%): 334 $[M]^+$ (7). HR-EI-MS m/z: Found 334.1567, Calcd for $C_{22}H_{22}O_3$ $[M]^+$ 334.1569. IR ν_{max} (KBr) cm^{-1}: 3416 (OH), 1600 (arom. C=C). ^{1}H-NMR (DMSO-d_6): 3.40 (2H, m, H_2-1), 3.67 (1H, m, H-2), 2.94 (1H, dd, J=4.5, 8.2 Hz, H-3), 2.96 (1H, dd, J=4.0, 8.2 Hz, H-3), 4.45 (1H, t, J=5.6 Hz, 1-OH), 4.77 (1H, d, J=5.2 Hz, 2-OH), 7.25—7.41 (15H, m, Ph×3). ^{13}C-NMR (DMSO-d_6): 63.3 (C-1), 70.7 (C-2), 65.4 (C-3), 144.0 (×3), 127.8 (×6), 128.3 (×6), 126.9 (×3) (Ph×3), 85.7 (C-Ph_3).

Di-*O*-*p*-bromobenzoate (11c) of 11b To a solution of **11b** (4.5 mg) in pyridine (2 ml) was added *p*-bromobenzoyl chloride (20 mg) and DMAP (32 mg) and the mixture was heated at 90 °C for 6 h. The reaction mixture was poured into ice H_2O slightly acidified with dil. HCl and extracted with benzene. The organic layer was washed with H_2O and evaporated. The residue was purified by silica gel column chromatography [benzene–EtOAc (25 : 1→20 : 1)] to give **11c** (4.5 mg), colorless needles (MeOH), mp 147—148 °C. $[\alpha]_D^{24}$ +8.5° (c=0.1, MeOH). EI-MS m/z (%): 441 (50), 243 (100). FAB-MS (positive) (magic bullet) m/z (%): 723 $[M+Na]^+$ (2). HR-FAB-MS m/z: Found 723.0172, Calcd for $C_{36}H_{28}Br_2O_5$ Na $[M+Na]^+$ 723.0181. IR ν_{max} (KBr) cm^{-1}: 1724 (COO), 1592 (arom. C=C). CD (c=0.004, MeOH) $[\theta]^{23}$ (nm): +18710 (254) (positive maximum), −13130 (237) (negative maximum). ^{1}H-NMR (DMSO-d_6): 4.62 (1H, dd, J=5.0, 10.0 Hz, H-1), 4.65 (1H, dd, J=5.0, 10.0 Hz, H-1), 5.58 (1H, m, H-2), 3.35 (1H, dd, J=5.0, 10.0 Hz, H-3), 3.38 (1H, dd, J=5.0, 10.0 Hz, H-3), 7.22—7.37 (15H, m, Ph×3), 7.79, 7.90 (each 4H, each d, J=8.4 Hz, *p*-Br-Ph-CO×2). ^{13}C-NMR (DMSO-d_6): 63.1 (C-1), 71.3 (C-2), 61.7 (C-3), 143.2 (×3), 127.9 (×6), 128.1 (×6), 127.1 (×3)(Ph×3), 86.1 (C-Ph_3), 164.4, 164.6 (*p*-Br-Ph-CO×2), 127.6, 127.7, 131.0 (×2), 131.1 (×2), 131.9 (×2), 132.0 (×2), 128.4, 128.5 (*p*-Br-Ph-CO×2).

Detritylation of 11c (Formation of 11d) **11c** (2.5 mg) was dissolved in hot 0.2% HCl/MeOH (2 ml) and allowed to stand for 3 min. After being poured into ice H_2O, the reaction mixture was extracted with benzene. The organic layer was washed with H_2O and concentrated to dryness, then the residue was purified by silica gel chromatography [benzene–EtOAc (15 : 1→10 : 1)] to give **11d** (1.5 mg), a white amorphous powder, $[\alpha]_D^{24}$ +43.1° (c=0.07, MeOH). EI-MS m/z (%): 458 $[M]^+$ (1), 385 (10), 243 (43). FAB-MS (positive) (magic bullet) m/z (%): 459 $[M+1]^+$ (2). HR-EI-MS m/z: Found 457.9215, Calcd for $C_{17}H_{14}Br_2O_5$ $[M]^+$ 457.9188. IR: ν_{max} (KBr) cm^{-1}: 3444 (OH), 1726 (COO), 1592 (arom. C=C). CD (c=0.003, MeOH) $[\theta]^{23}$ (nm): +29241 (253) (positive maximum), −12318 (237) (negative maximum). ^{1}H-NMR (DMSO-d_6): 4.51 (1H, dd, J=6.8, 12.0 Hz, H-1), 4.63 (1H, dd, J=3.2, 12.0 Hz, H-1), 5.34 (1H, m, H-2), 3.74 (2H, m, H_2-3), 5.15 (1H, t, J=6.0 Hz, 3-OH), 7.82, 7.88, 7.73, 7.74 (each 2H, each d, J=8.8 Hz, *p*-Br-Ph-CO×2). ^{13}C-NMR (DMSO-d_6): 63.5 (C-1), 73.3 (C-2), 59.5 (C-3), 164.7, 164.8 (*p*-Br-Ph-CO×2), 127.5 (×2), 131.0 (×2), 131.2 (×2), 131.8 (×2), 131.9 (×2), 128.5, 128.8 (*p*-Br-Ph-CO).

Acetate (11e) of 11d Ac_2O-pyridine treatment of **11d** (1.0 mg) yielded a monoacetate (**11e**) as colorless syrup (1.0 mg), $[\alpha]_D^{24}$ +15.8° (c=0.05, MeOH). EI-MS m/z (%): 500 $[M]^+$ (8), 300 (10), 298 (10), 185 (100), 183 (100), 157 (13), 155 (13). HR-EI-MS m/z: Found 499.9295, Calcd for $C_{19}H_{16}Br_2O_6$ $[M]^+$ 499.9293. IR: ν_{max} (KBr) cm^{-1}: 1728 (COO), 1591 (arom. C=C). CD (c=0.002, MeOH) $[\theta]^{23}$ (nm): +26330 (255) (positive maximum), −19460 (237) (negative maximum). ^{1}H-NMR ($CDCl_3$): 2.08 (3H, s, CH_3CO), 4.56 (1H, dd, J=6.0, 12.0 Hz, H-1), 4.64 (1H, dd, J=4.0, 12.0 Hz, H-1), 5.64 (1H, m, H-2), 4.40 (1H, dd, J=6.0, 12.0 Hz, H-3), 4.48 (1H, dd, J=4.0, 12.0 Hz, H-3), 7.86, 7.88, 7.58, 7.60 (each 2H, each d, J=8.8 Hz, *p*-Br-Ph-CO×2). ^{13}C-NMR ($CDCl_3$): 63.0 (C-1), 70.0 (C-2), 62.3 (C-3), 20.7 (CH_3CO), 170.5 (CH_3CO), 165.0, 165.3 (p-Br-Ph-CO×2), 128.3, 128.4, 131.2 (×2), 131.3 (×2), 131.9 (×4), 128.6, 128.7 (*p*-Br-Ph-CO).

Didymocalyxin A (12) Orange needles (MeOH), mp 211—212 °C (dec.). EI-MS m/z (%): 454 $[M]^+$ (100), 395 (56), 349 (28). FAB-MS (positive) (magic bullet) m/z (%): 455 $[M+1]^+$ (100), 395 (35), 351 (43). HR-EI-MS m/z: Found 454.1269, Calcd for $C_{24}H_{22}O_9$ $[M]^+$ 454.1264. HR-FAB-MS m/z: Found 455.1340, Calcd for $C_{24}H_{23}O_9$ $[M+1]^+$ 455.1342. IR ν_{max} (KBr) cm^{-1}: 3400 (OH), 1658 (conjugated CO), 1578 (arom. C=C). UV λ_{max} (MeOH) nm (log ε): 241 (4.05), 288 sh (4.18), 310 (4.23); λ_{max} (MeOH–NaOMe) nm (log ε): dec.; λ_{max} (MeOH–$AlCl_3$) nm (log ε): 250 sh (4.17), 333 (4.27), 381 sh (3.97); λ_{max} (MeOH–$AlCl_3$–HCl) nm (log ε): 245 (4.16), 333 (4.30); λ_{max} (MeOH–NaOAc) nm (log ε): 264 (4.11), 298 (4.13), 371 (3.74); λ_{max} (MeOH–NaOAc–H_3BO_3) nm (log ε): 287 sh (4.22), 308 (4.32), 331sh (4.18). ^{1}H- and ^{13}C-NMR: Table 1. Crystal data for **12**: $C_{24}H_{22}O_9$, monoclinic, a=31.284 (3), b=8.5005 (5), c=17.657 (2) Å, β=115.915 (8)°, V=4223.3 (7) Å^3, D_c=1.43 g/cm^3. Space group $C2/c$, Z=8. Number of pieces of data collected: 3466; number used for the calculation: 1703, R=0.045. Positional parameters are given in Table 2.

Didymocalyxin B (13) Brown needles (benzene), mp 188—189 °C (dec.). EI-MS m/z (%): 470 $[M]^+$ (100), 366 (50), 262 (35), 131 (92). FAB-MS (negative) (magic bullet) m/z (%): 469 $[M-1]^-$ (8). HR-EI-MS m/z: Found 470.1367, Calcd for $C_{28}H_{22}O_7$ $[M]^+$ 470.1365. IR ν_{max} (KBr) cm^{-1}: 3490 (OH), 1770 (COO), 1640 (conjugated CO), 1590, 1570 (arom. C=C). UV λ_{max} (MeOH) nm (log ε): 317 (4.15), 408 (3.96), 435 sh (3.86); λ_{max} (MeOH–NaOMe) nm (log ε): 266 sh (4.05), 301 (4.16), 414 (3.80); λ_{max} (MeOH–$AlCl_3$) nm (log ε): 332 (4.27), 382 (4.20), 442 sh (4.03); λ_{max}

(MeOH–$AlCl_3$–HCl) nm (log ε): 330 (4.27), 375 (4.26), 444 sh (4.02); λ_{max} (MeOH–NaOAc) nm (log ε): 303 (4.23), 403 sh (3.98); λ_{max} (MeOH–NaOAc–H_3BO_3) nm (log ε): 265 sh (4.05), 303 (4.22), 398 sh (3.98). ^{1}H- and ^{13}C-NMR: Table 1. Crystal data for **13**: $C_{28}H_{22}O_7 \cdot 1/2C_6H_6$, triclinic, a=12.4753 (6), b=13.659 (2), c=7.4842 (6) Å, α=100.163 (9), β=91.653 (6), γ=89.077 (7)°, V=1254.8 (2) Å^3, D_c= 1.245 g/cm^3. Space group *P1*, Z=2. Number of pieces of data collected: 3945; number used for the calculation: 2357, R=0.081. Positional parameters are given in Table 3.

Didymocalyxin C (14) Yellow needles (MeOH), mp 256—257 °C (dec.). EI-MS *m/z* (%): 380 $[M]^+$ (100), 365 (86), 237 (42). FAB-MS (positive) (magic bullet) *m/z* (%): 381 $[M+1]^+$ (100), 403 $[M+Na]^+$ (33). HR-EI-MS *m/z*: Found 380.0899, Calcd for $C_{21}H_{16}O_7$ $[M]^+$ 380.0896. IR ν_{max} (KBr) cm^{-1}: 3410 (OH), 1622 (conjugated CO), 1594 (arom. C=C). UV λ_{max} (MeOH) nm (log ε): 323 (4.57); λ_{max} (MeOH–NaOMe) nm (log ε): dec.; λ_{max} (MeOH–$AlCl_3$) nm (log ε): 293 sh (4.30), 338 (4.48), 352 sh (4.47), 393 sh (4.29); λ_{max} (MeOH–$AlCl_3$–HCl) nm (log ε): 324 (4.58); λ_{max} (MeOH–NaOAc) nm (log ε): 316 (4.54); λ_{max} (MeOH–NaOAc–H_3BO_3) nm (log ε): 305 sh (4.57), 316 (4.59). ^{1}H- and ^{13}C-NMR: Table 1.

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