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2008 10 07

(71)

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(72)

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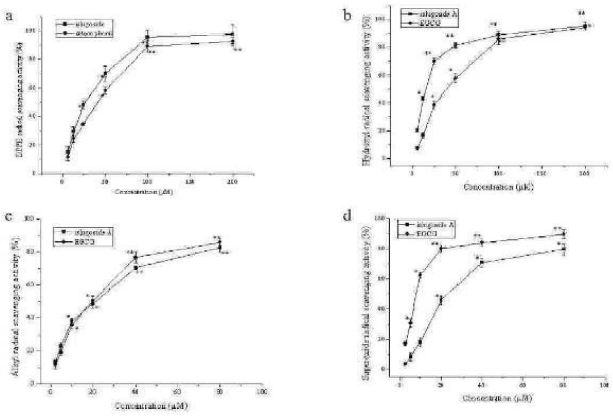
(74)

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(54)

(57)

, ,
, 1 DPPH, ,
, .
- 1



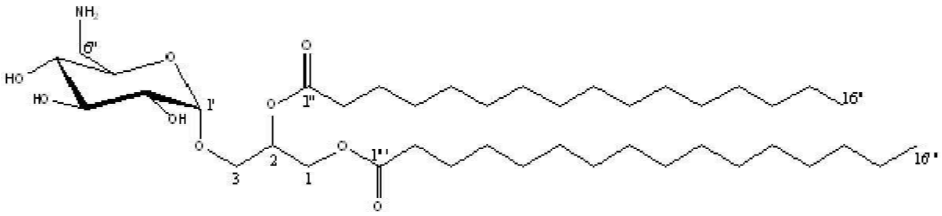
(72)

2

3 599-1 125-1402

1

1 (ishigoside) .



2

1 .

[0001] , .

[0002] ($O_2^{\cdot -}$), (HO·), (ROO·), (RO·), , - . , , , , , , , . , , , .

[0003] (Ishige okamurae) , , (Ishigeaceae) , . (phytochemical) , , , (pheophytins), .

[0004] , A2 .

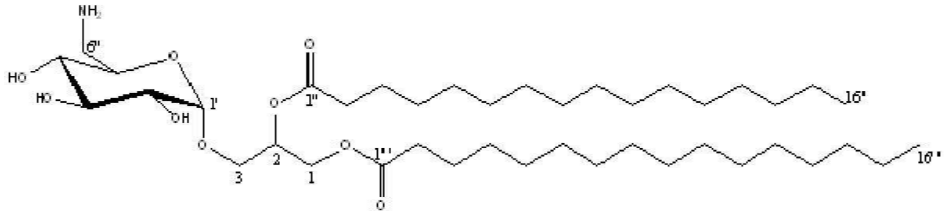
[0005] , .

[0006] .

[0007] .

[0008] , ,
, DPPH, ,
.

[0009] 1 .



[0010]

[0011] , 1D 2D NMR, MS
1, 2- -O- -3-O-(6- -6-)-a-D-
- , (ishigoside) .

[0012] ,
, .
1 , , .
, ,
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[0013] , , E Z
. 1 .
1 .

[0014] , ,
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[0015] 1 . ,
, , ( ) (
, HCl) . ,
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(,),
(,) ,
(, ,) (,)
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[0016] , 1 ,
, , , , , , ,
, , , p- .
, , , ,
.

[0017] 1 DPPH, ,

ESR , .

[0018] 1 .

[0019] , “ ” . ( ) .

[0020] 1 DPPH, , , .

[0021] . .

[0022] **1 :**

[0023] ^{1}H-NMR, ^{13}C-NMR, 2D-NMR JEOL JNM-ECP 400 , (δ) TMS ppm . IR (Bucker) FT-IR model IFS-88 . MS JEOL JMX-700 . - (Perkin-Elmer)-341 . GC-MS (Shimadzu) GC-MS-QP5050A .

[0024] JESFA ESR (JEOL, Tokyo, Japan) . 2,2- -1- (DPPH), 5,5- -1- -N- (DMPO), $FeSO_4$, H_2O_2, 2,2- -(2-)- (AAPH), a-(4- -1-)-N-t- (4-POBN) (Sigma Chemical Co.; St. Louis, MO, USA) . 60 (0.036-0.2 mm, Merck), LH-20(Sephadex LH-20; Pharmacia Biotech AB, Uppsala, Sweden), ODS-A (DAISO CO., LTD., Japan) . 60 F_{254} (Kieselgel 60 F_{254} 5715, Merck) . TLC , 10% , H_2SO_4 5% , 105 4

[0025] 2007 10 . (voucher specimen)(No. 20071003) . 3 , . , , -20 .

[0026] ± , t . $p < 0.05$.

[0027] (500 g) 2 L 3 . , (96 g) H_2O , , , EtOAc n-BuOH . EtOAC- (22 g) (4L), (20:1, 10:1, 5:1, 1:1, v/v, 5L), (3L), (10:1, 5:1, 1:1, v/v, 5L) TLC 29 (1 29). 5 LH-20 3(7 mg) . 7 - (10:1 v/v) 6 (7A 7F) . 7D LH-20 **2**(16 mg) . 22

- -H_2O (5:1:0.1 v/v/v) 4 (22A 22D)
. 22C LH-20 , ODS (-H_2O /40:60)
1 1(22 mg) , (ishigoside) .

[0028] (1) NMR ,
m/z 729.5775 HREIMS $C_{41}H_{79}NO_9$. 3430 1737 cm^{-1} IR
. ^1H, ^{13}C NMR, ^1H-^1H COSY, HMQC, HMBC
1 1, 2- -O- -3-O-(6- -6-)-a-D- -
.

[0029] 1 ^1H NMR (1). 1
, d_H 0.85 (6H, t, J = 6.6 Hz) , d_H 1.23 (48H, br s)
, d_H 1.49 (4H, br s) d_H 2.28 (4H, m)
. .
2 [d_H 3.39 (1H, dd, J = 10.4, 5.8 Hz), 3.88 (1H, dd, J = 10.8, 5.8 Hz), 4.14 (1H, dd, J = 12.0, 7.5 Hz), 4.33 (1H, dd, J = 12.0, 2.9 Hz), 5.13 (1H, m)] . 3
, d_H 2.94-3.77 (m)
, d_H 4.57 (1H, d, J = 3.3 Hz) , d_H 2.56 (1H, dd, J = 13.7, 6.7 Hz), 2.88 (1H, dd, J = 13.7, 4.6 Hz) . ^{13}C NMR (1) d_C 172.5 172.4
, d_C 13.9 , d_C 22.1-33.5 28
, d_C 62.6, 64.6, 69.7 , d_C 54.7, 68.5, 71.6, 72.9, 74.3, 98.3 .

[0030] (upfield) H-6' (d_H 2.56 and 2.88) ^1H NMR C-6' (d_C 54.7) ^{13}C-NMR
, C-6' . C-1'
(J = 3.3 Hz) α .
, 1 6- -6- -a-D- ^{13}C-NMR
. 1 NaOMe/MeOH ,
GC-MS ,
. H-1' C-3, H-2 C-1'', H-1 C-1''' HMBC - C-2 ,
C-1 C-2 .

[0031] (1): . [a]22D = + 34.2 (c 0.305, MeOH). IR (neat) g_{max}: 3430, 2914, 1737 cm^{-1}. HREIMS m/z 729.5775 $[M]^+$, Calc. for $C_{41}H_{79}NO_9$, 729.5755. ^1H NMR (DMSO-d_6, 400 MHz), ^{13}C NMR (DMSO-d_6, 100MHz), COSY HMBC(1).

[0032] < 1>

[0033] DMSO-d_6* NMR

	δ_H (mult, J in Hz)	δ_C	DEPT	HMBC (H → C)	COSY
1a	4.33 (dd, 12.0, 2.9)	62.6	CH_2	2, 3, 1'''	1b
1b	4.14 (dd, 12.0,7.5)			2, 3, 1'''	1a, 2
2	5.13 (m)	69.7	CH	1, 3, 1''	1b, 3b
3a	3.88 (dd, 10.8, 5.8)	64.6	CH_2	1, 2, 1'	3b
3b	3.39 (dd, 10.4, 5.8)			1, 2, 1'	2, 3a
1'	4.57 (d, 3.3)	98.3	CH	3, 2', 3', 5'	2'
2'	3.18 (m)	71.6	CH	1', 3'	1', 3'
3'	3.37 (m)	72.9	CH	2', 4'	2', 4'
4'	2.93 (m)	74.3	CH	3', 5', 6'	3', 5'
5'	3.76 (m)	68.5	CH	1', 4', 6'	4', 6'a, 6'b
6'a	2.56 (dd, 13.7, 6.7)	54.7	CH_2	4', 5'	5', 6'b
6'b	2.88 (dd, 13.7, 4.6)			4', 5'	5', 6'a
1''		172.5	C		
2''	2.28 (m)	33.4	CH_2	1'', 3''	3''
3''	1.49 (br s)	24.5	CH_2	2''	2''
4''-13''	1.23 (br s)	28.5-29.1	CH_2		
14''	1.23 (br s)	31.3	CH_2	15'', 16''	15''
15''	1.23 (br s)	22.1	CH_2	14'', 16''	14'', 16''
16''	0.85 (t, 6.6)	13.9	CH_3	14'', 15''	15''
1'''		172.4	C		
2'''	2.28 (m)	33.5	CH_2	1'', 3'''	3'''
3'''	1.49 (br s)	24.5	CH_2	2''	2'''
4'''-13'''	1.23 (br s)	28.5-29.1	CH_2		
14'''	1.23 (br s)	31.3	CH_2	15''', 16'''	15'''
15'''	1.23 (br s)	22.1	CH_2	14''', 16'''	14''', 16'''
16'''	0.85 (t, 6.6)	13.9	CH_3	14''', 15'''	15''

[0034]

[0035] * : ^{1}H ^{13}C NMR 400 100 MHz .

[0036] ,

.

[0037] (**1**, 6.0 mg) 2 mL , 3 2% NaOMe-MeOH (1.5 mL) . (Dowex 50 W × 8) , . , (4.0 mg) .

[0038] GC-MS . MeOH , (SiO_2, $CHCl_3$/MeOH/H_2O, 4:1:0.1) (1.5 mg) .

[0039] , , , , 1 2 . 2- -2- , , . 6- -6- . , (*Avrainvillea nigricans*) .

[0040] **2 :**

[0041] (Nanjo et al.) DPPH . , 30 mL ( ) DPPH (60 mM) 30 mL . 10 , 100 mL , DPPH JESFA ESR (JEOL, Tokyo, Japan) . 2 ESR . : , 336.5 ±5 mT; , 5 mW; , 9.41 GHz; , 1 × 1000; , 30 s. DPPH .

[0042] DPPH (%) = (1-A/A_0) × 100,

[0043] , A ,

[0044] A_0 .

[0045] % EC_{50} .

[0046] - (Fenton HaberWeiss reaction) , DMPO . DMPO-OH ESR . (20 mL) (pH 7.4) DMPO (0.3 M, 20 mL), FeSO4 (10 mM, 20 mL) H_2O_2 (10 mM, 20 mL) , 100 L . 2.5 , ESR ESR . : , 336.5 ± 5 mT; , 1 mW; , 9.41 GHz; , 1 × 200; , 4 min. .

[0047] (%) = (1-A/A_0) × 100,

[0048] , A ,

[0049] A_0 .

[0050] (Hiramoto et al) 2,2'- (2-) (AAPH) . , 40 mM AAPH 20 mL (PBS) 20 mL, 40mM (4- -1-)-N-tert- (4-POBN) 20 mL 20 mL . , 37 30 . , , : , 100 KHz; , 10 mW; , 9441 MHz; , 336.5 ± 5 mT , 30 s. .

[0051] (%) = (1-A/A_0) × 100,

[0052] , A ,

[0053] A_0 .

[0054] UV /EDTA . 0.3 mM , 1.6 mM EDTA, 800 mM DMPO 365 nm UV 1 . ESR 100 mL . : , 336.5 ± 5 mT; , 10 mW; , 9.41 GHz; , 1 × 1000; , 1 min. .

[0055] (%) = (1-A/A_0) × 100,

[0056] , A ,

[0057] A_0 .

[0058] , ESR .
ESR ,
. , ESR DPPH, , ,
, 1
.

[0059] DPPH , - ,
DPPH . ,
. DPPH 1a . -
DPPH . 6.25 mM 100 mM , DPPH
15.4% 95.4% ; DPPH 12.5 mM
($p < 0.05$). 100 mM DPPH .
50% EC_{50} α-
($p > 0.05$), DPPH α- .

[0060] (HO·) ROS , ,
. DMPO
(Fenton system) , HO·
. - .
DMPO-OH ESR , ESR .
, 1b .
- EGCG . EGCG
, EC50(16.7 mM) ECGC EC50(41.0 mM)
. 12.5 mM , 43.2%
($p < 0.05$) , EGCG 16.7% ,
($p > 0.05$).

[0061] ESR .
AAPH , 4-POBN , ESR
. - (1C).
10 mM , , 80 mM
82.8% . EGCG EC_{50} 22.7 mM 21.6 mM ,
EGCG EC_{50} ($p > 0.05$),
EGCG .

[0062] , .
, ,
, ROS-
. /EDTA UV . ,
ESR . 1D
EGCG . -
, EGCG
. EGCG , EC_{50}(26.8 mM)
EGCG EC_{50}(0.05 mM) ($p < 0.05$). 20 mM
, 80 mM
79.4% , EGCG 89.7% ($p < 0.01$).

[0063] , , ,
. . ,
DPPH, ,
. DPPH, ,
EC_{50} 31.2 mM, 16.7 mM, 22.7 mM, 26.8 mM . EC_{50} ,
, DPPH
, - .
.

[0064] ,
, 1D 2d NMR, MS
. ECR DPPH, , -
. , 16.7 mM
EC_{50} .
.

[0065] 1 ESR , (a) DPPH
, (b) , (c) , (d)
, 3 ± SD .

1

