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Constituents of the Herb of *Isodon excisus* var. *coreanus*

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The studies were carried out to evaluate the constituents in the aerial part of *Isodon excisus* var. *coreanus* (Labiatae). From the aqueous fraction of methanol extract, compound I (α-[[3-(3, 4-dihydroxyphenyl)-1-oxo-2-propenyl]oxy]-3,4-dihydroxy-benzenepropanoic acid), compound II (9-methyl-dihydroferulic acid-4-O-β-D-glucopyranosyl (1→2)-α-L- rhamnopyranosyl (1→4)-β-D-glucopyranoside), compound III (ent-7α, 11α, 15β-trihydroxy-kaur-16-en-1-O-β-D-glucopyranoside) and compound IV (2α, 3β, 7α, 23-tetrahydroxy-olean-12-en-28-oic acid 28-O-β-D-glucopyranoside) were isolated and identified on the basis of their physicochemical and spectroscopic evidences[IR, FAB(-)MS, ^{1}H-NMR, ^{13}C-NMR, HMQC, ^{1}H-^{1}H COSY and HMBC (Heteronuclear Multiple Bond Connectivity)]. Especially, New compounds II and III were named Isodonin A and Isodonin B respectively.

Key words : *Isodon excisus* var. *coreanus*, Labiatae, Isodonin A, Isodonin B, HMQC, ^{1}H-^{1}H COSY, HMBC, α-[[3-(3,4-dihydroxyphenyl)-1-oxo-2-propenyl]oxy]-3,4-dihydroxybenzenepropanoic acid, 9-Methyl-dihydroferulic acid-4-O-β-D-glucopyranosyl(1→2)-α-L-rhamnopyranosyl (1→4)-β-D-glucopyranoside, ent-7α, 11α, 15β-Trihydroxy-kaur-16-en-1-O-β-D-glucopyranoside, 2α, 3β, 7α, 23-tetrahydroxy-olean-12-en-28-oic acid 28-O-β-D-glucopyranoside.

INTRODUCTION

Constituents of *Isodon excisus* var. *coreanus* (Labiatae) were investigated to explore a substitute for *Isodon japonicus* which has been used for the treatment of the anorexia, indigestion, stomachache, inflammation, microbism, esophageal carcinoma in Korean Folk Medicine (Lee, 1989 and Yook,1981). In the previous paper, the isolation of about 200 diterpenoids (kaurene, enmein, spirolactone, isopimathrene and abietene derivatives) from *Isodon* species were reported (Guo *et al.*, 1992). But the studies from the aerial part of *Isodon excisus* var. *coreanus* were not concerned. Therefore, we studied for the constituents in the aerial parts of this plant. Four constituents, compounds I-IV, were isolated from the aqueous fraction of the aerial part of this plant. The structures of compounds I-IV were assigned on the basis of their physicochemical and spectral data (IR, FAB(-)MS, ^{1}H-NMR, ^{13}C-NMR, ^{1}H-^{1}H COSY, HMQC and HMBC). The structures were established as α-[[3-(3,4-dihydroxy-phenyl)-1-oxo-2-propenyl]oxy]-3,4-dihydroxy-benzenepropanoic acid, 9-methyl-dihydroferulic acid-4-O-β-D-glucopyranosyl(1→2)-α-L-rhamnopyranosyl(1→4)-β-D-glucopyranoside, ent-7α, 11α, 15β-trihydroxy-kaur-16-en-1-O-β-D-glucopyranoside and 2α, 3β, 7α, 23-tetrahydroxy-olean-12-en-28-oic acid 28-O-β-D-glucopyranoside for compound I-IV respectively.

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MATERIALS AND METHODS

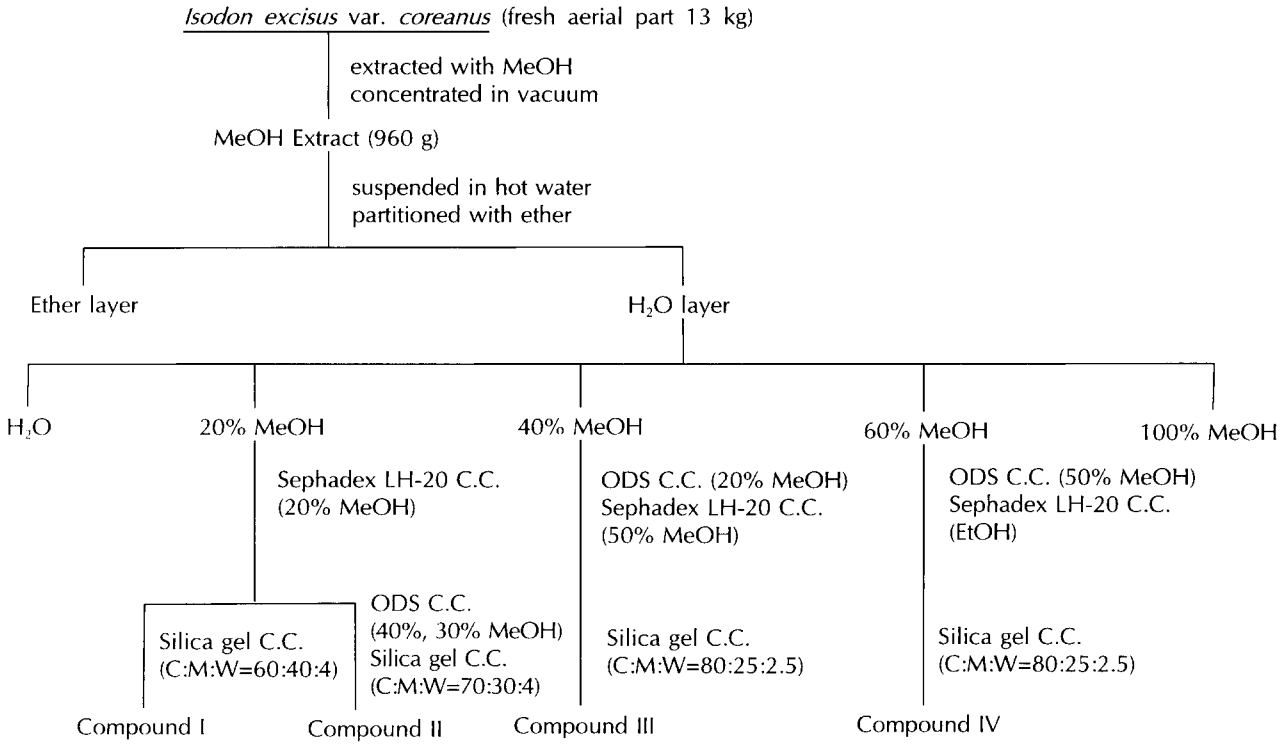
Instruments

Mps: uncorr.; NMR: TMS as internal standard; CC: nonionic polymer resin (Amberlite XAD-2, Sigma): and gel filtration (Lichroprep RP-18, Merk, Sephadex LH-20, Pharmacia and Silica gel, Merck). All solvent systems for chromatography were homogenous.

Extraction and separation

Plant material, *Isodon excisus* var. *coreanus* was collected at Mt. Chii, Korea. A voucher specimen was deposited in Department of Pharmacal Botany, College of Pharmacy, Chung-Ang University.

The fresh aerial part of *Isodon excisus* var. *coreanus* (13 kg) were extracted with MeOH under room temperature. After removal of the solvent by evaporation, the MeOH extract was suspended in hot water and extracted with ether. The water layer was concentrated and chromatographied on nonionic polymer resin with water, 20%, 40%, 60% and 100% MeOH, successively. Compound I and II were obtained from the 20% MeOH fraction by gel filtration (Sephadex LH-

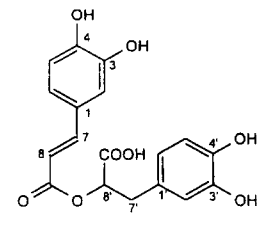


Scheme I. Extraction and isolation of compounds from the herb of *Isodon excisus* var. *coreanus*.

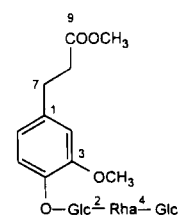
20, RP-8 and Silica gel C.C.). Compound III and IV were obtained from the 40% and 60% MeOH fraction by gel filtration (Sephadex LH-20, RP-8 and silica gel C.C.), respectively.

Compound I. amorphous powder, m.p. 204-205°, $[\alpha]_D^{22}$=+145.0° (c=0.02, EtOH), IR ν_{max}^{KBr} cm^{-1}:3440 (OH), 2960, 2924 (C-H), 1611 (COOH), 1403 (C=C), 1260 (C-C), 1160, 1117 (C-O), 820 (aromatic ring), FAB(-) Mass (*m/z*):359 $[M-H]^-$, 325 $[M-(2OH+H)]^-$, 593 $[M-(C_7H_5+2OH+H)]^-$, ^{1}H-NMR (CD_3OD, 500 MHz): 7.40 (1H, d, *J*=15.9 Hz, H-7), 6.93 (1H, d, *J*=2.1 Hz, H-2), 6.82 (1H, dd, *J*=2.1, 8.4 Hz, H-6), 6.67 (1H, d, *J*=2.0 Hz, H-2'), 6.67 (1H, d, *J*=8.1 Hz, H-5), 6.58 (1H, d, *J* =8.2 Hz, H-5), 6.53 (1H, dd, *J*=2.0, 8.1 Hz, H-6'), 6.17 (1H, d, *J*=15.9 Hz, H-8), 5.00 (1H, dd, *J*=3.4, 9.8 Hz, H-8'), 3.00 (1H, dd, *J*=3.4, 14.3 Hz, H-7'), 2.83 (2H, dd, *J*=9.8, 14.3 Hz, H-7') ^{13}C-NMR (DMSO-d_6, 125 MHz, see Table I).

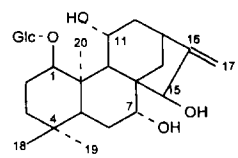
Compound II. amorphous powder, m.p. 214-217°, $[\alpha]_D^{22}$=-81.5° (c=0.02, MeOH), *Anal.* calcd. for $C_{29}H_{44}O_{18}$ $C_{29}H_{44}O_{18}$: C; 51.18%, H; 6.47%, O; 42.35%, Found: C; 51.14%, H; 6.49%, O; 42.37%, IR ν_{max}^{KBr} cm^{-1}: 3397 (OH), 2924 (C-H), 1741 (COOH), 1640, 1518 (C=C), 1396, 1260 (C-C), 1074, 1038 (glycosidic O), 800 (aromatic ring), FAB(-)Mass (*m/z*): 679 $[M-H]^-$, 371[M-(rha+glc+H)]$^-$, 209[M-(glc+rha+glc+H)]$^-$, ^{1}H-NMR (CD_3 OD, 500 MHz): 6.94 (1H, d, *J*=1.9 Hz, H-2), 6.80 (1H, d, *J*=8.3 Hz, H-5), 6.74 (1H, dd, *J*=1.9, 8.3 Hz, H-6), 4.85 (1H, d, *J*=7.6Hz, glc anomeric H), 4.69



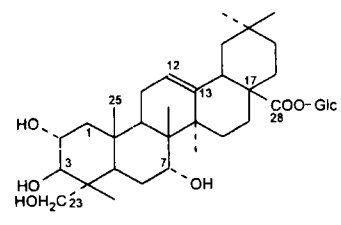
Compound I



Compound II



Compound III



Compound IV

(1H, d, *J*=1.6 Hz, rha anomeric H), 4.35 (1H, d, *J*=8.1 Hz, glc anomeric H), 3.72 (3H, s, OCH_3), 3.54 (2H, m, H-7), 2.69 (2H, m, H-8) 1.83 (3H, s, $COOCH_3$) 1.13 (3H, d, *J*=6.2 Hz, rha CH_3), ^{13}C-NMR (CD_3OD, 125 MHz, see Table I).

Compound III. needle crystal, m.p. 213-216°, $[\alpha]_D^{22}$= -59.0° (c=1, MeOH), *Anal.* calcd. for $C_{26}H_{42}O_9$: C; 62.65%, H; 8.43%, O; 28.92%, Found: C; 62.58%, H; 8.48%, O ; 28.94%, IR ν_{max}^{KBr} cm^{-1}:3426 (OH), 2938

Table I. ^{13}C-NMR spectrum data of Compound I-IV

No.	Compound I	No.	Compound II	No.	Compound III	No.	Compound IV
1	125.6	1	133.5	1	87.7	1	49.8
2	113.6	2	118.8	2	25.0	2	68.7
3	145.8	3	149.0	3	36.9	3	78.0
4	148.8	4	147.6	4	39.6	4	44.2
5	116.0	5	113.8	5	50.1	5	48.4
6	121.8	6	124.3	6	47.7	6	27.9
7	146.1	7	36.3	7	65.6	7	67.3
8	115.1	8	71.3	8	43.7	8	39.2
9	166.2	9	171.6	9	56.4	9	48.6
1'	127.7	glc 1'	102.6	10	57.2	10	37.9
2'	116.9	2'	82.9	11	67.1	11	23.7
3'	144.2	3'	74.9	12	42.6	12	122.9
4'	145.2	4'	77.9	13	40.5	13	143.2
5'	115.6	5'	73.7	14	37.6	14	42.5
6'	120.3	6'	62.6	15	83.4	15	29.6
7'	36.4	rha 1''	102.8	16	159.0	16	23.2
8'	73.2	2''	72.4	17	105.3	17	46.7
9'	171.2	3''	70.3	18	19.1	18	41.5
		4''	71.5	19	29.3	19	45.9
		5''	70.3	20	24.6	20	30.4
		6''	17.8	glc 1'	106.9	21	33.7
		glc 1	101.7	2'	75.3	22	32.2
		2	72.1	3'	78.4	23	65.9
		3	74.8	4'	71.7	24	15.6
		4	77.7	5'	77.9	25	18.7
		5	78.0	6'	62.9	26	18.5
		6	62.5			27	25.8
		OCH_3	56.9			28	176.1
		$COOCH_3$	20.9			29	32.7
						30	23.3
						glc 1'	95.5
						2'	73.8
						3'	78.8
						4'	70.9
						5'	78.4
						6'	61.9

(C-H), 1741 (C=O), 1647 (C=C), 1396 (C-C), 1052 glycosidic O), FAB(-)Mass (*m/z*): 497 [M-H]$^-$, 335 [M-(glc+H)]$^-$, ^{1}H-NMR (pyridine-d_5, 500 MHz): 5.18, 5.24 (each 1H, brs, H-17), 4.89 (1H, d, J=8.2 Hz, glc anomeric-H), 4.63 (1H, s, H-11α), 4.27 (1H, d, J=4.3 Hz, H-7α), 4.01 (1H, d, J=8.8 Hz, H-15β), 3.56 (1H, s, H-1), 1.74 (1H, dd, J=9.2, 13.8 Hz, H-7β), 1.49, 1.53, 1.61 (each 3H, S, angular CH_3) ^{13}C-NMR (pyridine-d_5, 125 MHz, see Table I).

Compound IV. needle crystal, m.p. 207-209°, $[\alpha]_D^{22}$ =+17.0° (c=0.25, MeOH), IR ν_{max}^{KBr} cm^{-1}: 3419 (OH), 2924, 2845 (C-H), 1733 (ester), 1647 (C=C), 1403,1260 (C-C), 1059 (glycosidic O), FAB(-)Mass (*m/z*): 665 [M-H]$^-$, 503 [M-(glc+H)]$^-$, ^{1}H-NMR (pyridine-d_5, 500 MHz): 6.27 (1H, d, J=8.0 Hz, glc anomeric H), 5.50 (1H, brs, olefinic H-12), 5.06 (1H, brs, H-7), 4.40 (1H, ddd, J=4.9, 10.4, 12.0 Hz, H-2β), 4.21 (1H, d, J=10.6 Hz, H-3α), 4.04 (2H, d, J=10.5 Hz, H-23), 3.20 (1H, dd, J=3.7, 13.5 Hz, H-18β), 2.41 (2H, J=3.1, 10.4 Hz, H-6), 2.35 (2H, J=4.2, 12.2 Hz, H-1), 1.26 (2H, J=4.4, 14.8 Hz, H-19), 0.87, 0.90, 1.26, 1.73. 1.76. 1.78 (each 3H, s, angular CH_3) ^{13}C-NMR (pyridine-d_5, 125 MHz, see Table I).

RESULTS AND DISCUSSION

The aqueous fraction of the methanol extract from the aerial part of *Isodon excisus* var. *coreanus* was chromatographed successively on Amberlite XAD-2, Sephadex LH-20 gel, RP-8 and Silica gel. Compounds I and II were isolated from the 20% MeOH fraction. Compounds III and IV were obtained from the 40% and 60% MeOH fraction respectively.

Compound I was obtained as a white amorphous powder and I.R. spectrum of compound I gave 3440 (OH), 1611 (COOH) and 820 (aromatic ring) cm^{-1}. Therefore compound I was assumed to aromatic substance.

In the FAB-MS (negative) spectrum of compound I,

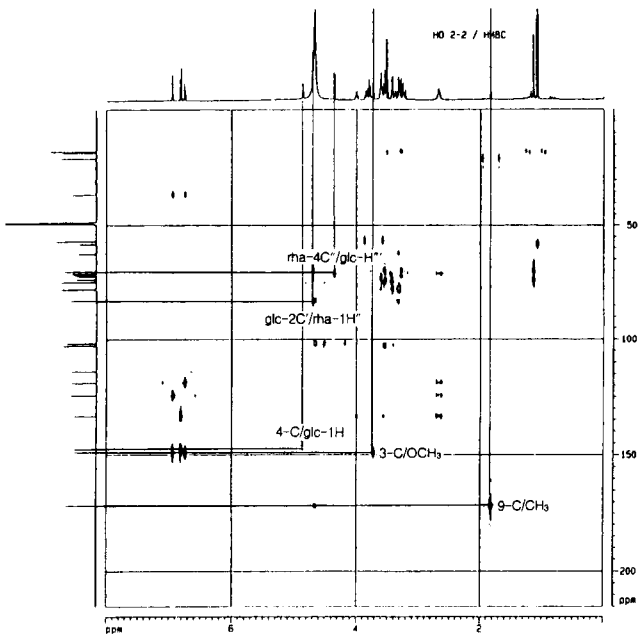


Fig. 1. HMBC spectrum of Compound II.

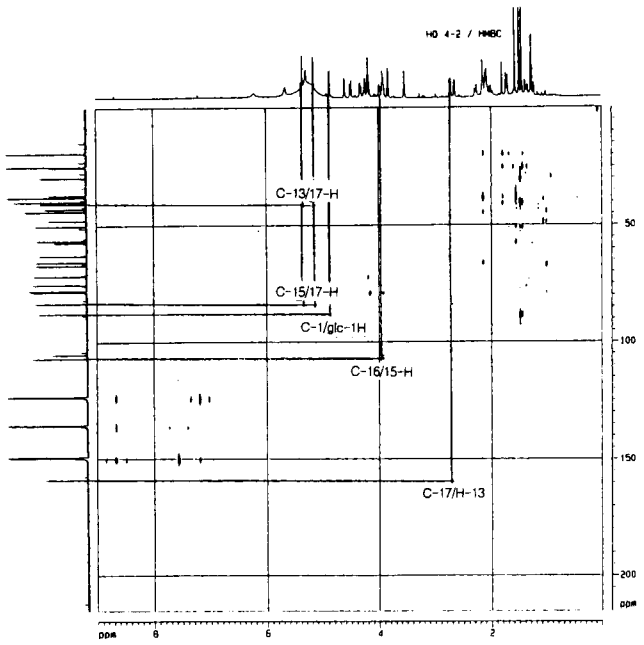


Fig. 2. HMBC spectrum of Compound III.

molecular and fragment ion peak appeared at *m/z* 359 $[M-H]^-$, 325 $[M-2H_2O]^-$ and 236 $[M-(C_7H_5+2H_2O)]^-$. In the ^{1}H-NMR spectrum two doublet signals at δ 6.17 and 7.40 ppm (each J=15.9 Hz) were assigned trans-olefinic proton of phenylpropanoid and meta coupling signals of aromatic ring proton appeared at δ 6.93, 6.82 ppm (each J=2.1 and δ 6.67, 6.53 ppm (each J= 2.0 Hz).

And also ortho coupling signals of aromatic ring proton were showed at δ 6.82, 6.67 ppm (each J=8.4 Hz) and δ 6.58, 6.53 ppm (each J=8.1 Hz) respectively.

In the ^{13}C-NMR spectrum, compound I showed a unit of caffeic acid. The signals exhibited 2 carboxyl groups at δ 166.2 and δ 171.2 ppm, trans-olefinic carbon groups at δ 115.1 at 146.1 ppm, 1 methylene at δ 36.4 ppm and 1 methine linked to oxygen at δ73.2 ppm, six aromatic methines at δ 113.6, 115.6, 116.0, 116.9, 120.3 and 121.8 ppm and six aromatic quaternary carbon at δ 125.6, 127.7, 144.2, 145.2, 145.8 and 148.8 ppm. From these spectral data, compound I was found to be phenylpropanoid of depside type.

The identification of compound I was confirmed by ^{1}H-NMR, ^{13}C-NMR, HMQC, ^{1}H-^{1}H COSY spectrum and by comparison of the reported data (Kohda *et al.*, 1989, Oh *et al.*, 1996).

On the basis of the above results, compound I was identified as α-[[3-(3,4-dihydroxyp-henyl)-1-oxo-2-propenyl]oxy]-3,4-dihydroxy-benzenepropanoic acid.

Compound II was obtained as an white amorphous power and I.R. spectrum of compound II gave 3397 (OH), 1074, 1038 (glycosidic CO) and 800 (aromatic ring) cm^{-1}. Therefore compound II was assumed to phenolic glycoside.

In the FAB-MS (negative) spectrum of compound II, molecular and fragment ion peak appeared at *m/z* 679$[M-H]^-$, 517$[M-(glc+H)]^-$, 371$[M-(glc+rha+H)]^-$ and 209 $[M-(glc+rha+glc+H)]^-$.

The ^{1}H-NMR spectrum exhibited three aromatic methine protons (δ 6.94, d, J=1.9 Hz, 6.80, d, J=8.3 Hz and 6.74,,dd, J=1.9, J=8.3 Hz)ppm, ester methyl proton (δ 1.83 ppm, s), angular methyl of rhamnose (δ 1.13, d, J=6.2 Hz)) and three anomeric proton signals (δ 4.69, d, J=1.6 Hz, δ 4.35, d, J=8.1 Hz and δ 4.85, d, J=7.6 Hz)ppm which were consistant with the configuration α for L-rhamnose, β for D-glucose and β for D-glucose respectively. Furthermore, a three proton singlet at δ 3.72 was attributed to an aromatic methoxy group on the aglycone moiety. Therefore compound I was assumed to phenolic glucoside substance.

In the ^{13}C-NMR, DEPT 135°spectrum, the signals were identified three aromatic quaternary carbons (δ 133.5, 147.6 and 149.0 ppm), carboxyl carbon (δ 171.6 ppm), four methylenes (δ 36.3, 62.5, 62.6 and 71.3 ppm), methoxyl carbon (δ 56.9 ppm), aromatic methines (δ 113.8, 118.8 and 124.3 ppm), and ester methyl carbon (δ 20.9 ppm).

In the HMQC, ^{1}H-^{1}H COSY, HMBC spectrum, the linkage between C-4 (δ 147.6 ppm) of aglycone and glucose, C'-2 and rhamnose as an inner sugar and C''-4 and glucose as an terminal sugar was determined. the signal methoxyl proton was linked to C-3 (δ 149.0 ppm) of aglycone and the ester methyl proton was linked to C-9 (δ 171.6 ppm) of aglycone. From these spectral data, compound II was found to containe a D-glucose (1→2)-L-rhamnose (1→4) and a D-glucose moiety attached to 9-methyl dihydroferulic acid (Shoya-

ma *et al.*, 1987, Calis *et al.*, 1988 and Saijo *et al.*, 1996).

Especially, the HMBC spectrum of compound II exhibited signals which can be ascribed to the dihydroferulic acid moieties along with those of three anomeric protons of glucose (2 mol) or rhamnose (1 mol) linked to C-4, C-4'' and C-2', at δ 4.35, 4.85 ppm and δ 4.69 ppm respectively.

On the basis of the above results, compound II was established 9-methyl-dihydroferulic acid-4-O-β-D-glucopyranosyl (1→2)-α-L-rhamnopyranosyl (1→4)-β-D-glucopyranoside.

Compound III was obtained as an colourless needle crystal and I.R. spectrum of compound III gave 3426 (OH), 1647 (C=C) and 1052 (glycosidic CO) cm^{-1}. In the FAB-MS (negative) spectrum of compound III, molecular and fragment ion peak appeared at *m/z* 497 $[M-H]^-$ and 335 $[M-(glc+H)]^-$.

The ^{1}H-NMR spectrum contained signals for three angular methyl groups (δ 1.49, 1.53 and 1.61 ppm), an exocyclic methylene group (δ 5.18 and 5.42 ppm) as well as four secondary hydroxyl groups (α 3.56, 4.63, 4.01 and 4.27 ppm). Therefore compound III was assumed to terpene glycoside.

In the ^{13}C-NMR, DEPT 135° spectrum, the signals were identified three angular methyls (δ 19.1, 24.6 and 29.3), five methylenes below 60 ppm (δ 25.0, 36.9, 37.6, 42.6 and 47.7 ppm), three methines below 60 ppm (δ 40.5, 50.1 and 56.4 ppm), three quaternary carbons (δ 39.6, 43.7 and 57.2 ppm), four secondary hydroxyl groups (δ 65.6, 67.1, 83.4 and 87.7 ppm) as well as two olefinic carbons (δ 159.0 and 105.3 ppm) composing an exocyclic methylene moiety. These spectral features disclosed a diterpenoid nature of the kaurene type glycoside bearing four hydroxy substituents.

The location of these hydroxy groups were deduced as follows. Besides the five oxygen atoms of a glucosyl group and C-15 hydroxyl group (totally six oxygen atoms), four oxygen atoms remained to be characterized in compound III. The presence of hydroxyl group in the 7α, 11α, 15β position was indicated.

In the HMQC, ^{1}H-^{1}H COSY, HMBC spectrum, the signal at δ 4.01 ppm (1H, d, J=8.8 Hz) was assigned to H-15, the signal at d 4.63 ppm (1H, s) was assigned 11α-H. Thus one secondary hydroxyl group should be located at C-7 and the signal at δ 4.27 ppm (1H, d, J=4.3 Hz) was assigned to the proton attached to a carbon linked to a C-6 hydroxyl group. Compound III showed that glucose anomeric proton (δ 4.89 ppm) was conjugated C-1 (δ 87.7 ppm) of aglycone, H-7 (δ 4.27 ppm) was coupled with C-8, C-9 and C-14, H-15 (δ 4.01 ppm) was coupled with C-13, C-16 and C-17, C-7α hydroxyl group could form hydrogen bond with C-15β hydroxyl group and H-11 (δ 4.63 ppm) singlet signal was coupled with C-9 and C-12. On the result, C-11, C-7 and C-15 should be oxygenated.

On the basis of the above results, the structure of compound III was established ent-7α, 11α, 15β-trihydroxy-kaur-16-en-1-O-β-D-glucopyranoside (Tanaka *et al.*, 1978, Yoshiyasu *et al.*, 1988, Yoshio *et al.*, 1989, Nagashima *et al.*, 1995).

Compound IV was obtained as an colourless needle crystal and detected by Libermann-Burchard positive reaction and I.R. spectrum of compound IV gave 3419 (OH), 1733 (ester), 1647 (C=C) and 1059 (glycosidic CO) cm^{-1}.

In the FAB-MS (negative) spectrum of compound IV, molecular and fragment ion peak appeared at *m/z* 665 $[M-H]^-$ and 503 $[M-(glc+H)]^-$.

The ^{1}H-NMR spectrum showed six angular methyl group (δ 0.87, 0.90, 1.26, 1.73, 1.76 and 1.78 ppm), anomeric proton signal (δ 6.27 ppm) and secondary hydroxyl group (δ 4.04, 4.21, 4.40 and 5.06 ppm). Therefore compound IV was assumed to be triterpene glycoside.

In the ^{13}C-NMR and DEPT 135° spectrum, these signals showed six angular methyls (δ 15.6, 18.5, 18.7, 23.3, 25.8 and 32.7 ppm), six quaternary carbons below 60 ppm (δ 30.4, 37.9, 39.2, 42.5, 44.2 and 46.7 ppm), eight methylenes below 60 ppm (δ 23.2, 23.7, 27.9, 29.6, 32.2, 33.7, 45.9 and 49.8 ppm), three methines (δ 41.5, 48.4 and 48.6 ppm), four secondary hydroxyl groups (δ 65.9, 67.3, 68.7 and 78.0 ppm), olean-12-en carbon (δ 122.9 and 143.2 ppm) and ester carbonyl carbon (δ 176.1 ppm), C-28 of the glucose unit (d 95.5 ppm). These spectral features disclosed oleanone type glucoside bearing four hydroxy substituents.

Because ester carbonyl carbon due to C-28 was shifted 4ppm downfield than free carbonyl carbon and glucose anomer carbon was 5ppm upfield than O-glycosylation anomer carbon, compound IV was assumed to oleanone-28-oic acid glycoside.

The presence of hydroxyl group in the 6β, 7α or 11β position was indicated. however the unchanged chemical shifts of C-12, C-13 olefinic carbons ruled out the possibility of the occurrence of this hydroxyl group in the 11β position.

In the HMQC, ^{1}H-^{1}H COSY spectrum, compound IV exhibited that C-2, C-3, C-7 was oxygenated because H-2, H-3 methine was axial-equatorial coupled and H-6 doublet signal was coupled with H-7 singlet.

The identification of compound I was confirmed by ^{1}H-NMR, ^{13}C-NMR, HMQC, ^{1}H-^{1}H COSY spectrum and by comparison of the reported data (Toyota *et al.*, 1990, Mahato *et al.*, 1992 and Jossang *et al.*, 1996).

On the basis of these results, the structure of compound IV was established as 2α, 3β, 7α, 23- tetrahydroxy-olean-12-en-28-oic acid 28-O-β-D-glucopyranoside.

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