PERGAMON

PHYTOCHEMISTRY

Phytochemistry 52 (1999) 153–192

Review Article Number 139

Advances in structural elucidation of glucuronide oleanane-type triterpene carboxylic acid 3,28-*O*-bisdesmosides (1962–1997)

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Received 18 April 1998

Abstract

The structural elucidation of glucuronide oleanane-type triterpene carboxylic acid 3,28-*O*-bisdesmosides (GOTCAB) is quite complicated compared to that of other saponins. In order to determine their structures, it is common to use chemical, enzymatic and spectral methods simultaneously. This review will discuss newer chemical, enzymatic and spectral means, compare structural study strategies in different periods, and summarize main characteristics of NMR spectral data, then propose a systematic method used in their structural elucidation. A compilation of glucuronide oleanane-type triterpene carboxylic acid 3,28-*O*-bisdesmosides isolated during 1962–1997 along with their occurrence, structural data and bioactivity is included.

Keywords: Glucuronide oleanane-type triterpene carboxylic acid 3,28-*O*-bisdesmosides (GOTCAB); Triterpenoid saponins; Structural elucidation; Structural data and spectral data summarization; Natural distribution and biological activity

1. Introduction

Triterpenoid saponins are common in plants and to date there are about 80 families and 231 genera containing this kind of constituent (Zhou, 1988). Glucuronide oleanane-type triterpene carboxylic acid 3,28-*O*-bisdesmosides (GOTCAB) belong to the pentacyclic triterpenoid saponins. They are widely distributed in plants, and so far (1962–1997) 192 saponins of this kind have been isolated from the following 20 families (49 genera and 80 species, see Table 1): Amaranthaceae, Aquifoliaceae, Araliaceae, Asteraceae, Basellaceae, Campanulaceae, Caryophyllaceae, Chenopodiaceae, Compositae, Cucurbitaceae, Euphorbiaceae, Leguminosae, Nyctaginaceae, Olacaceae, Portulacaceae, Rosaceae, Sabiaceae, Sapindaceae, Sapotaceae and Umbelliferae, including diglycosides to undeca-glycosides. Among them squarroside A (**3**) isolated from the roots of *Acanthophyllum squarrosum* showed a concentration dependent immunomodulatory effect in the *in vitro* lymphocyte transformation test (Lacaille-Dubois, Hanquet, Rustaiyan, & Wagner, 1993); achyranthoside A (**5**) and B (**6**) isolated from the roots of *Achyranthes fauriei* were found to have cytotoxic activity against human colon carcinoma and murine melanoma cells (Ida, Satoh, Katoh, Katsumata, Nagasao, Yamaguchi, Kamei, & Shoji, 1994); betavulgaroside III (**52**) isolated from the roots and leaves of *Beta vulgaris* exhibited hypoglycemic activity in an oral glucose tolerance test in rats (Yoshikawa, Murakami, Kadoya, Matsuda, Muraoka, Yamahara, & Murakami, 1996); lucyoside N (**104**) and P (**105**) isolated from the seeds of *Luffa cylindrica* showed strong fibrinolytic activity in an *in vitro* fibrinolysis system (Yoshikawa, Arihara, Wang, Narui, & Okuyama, 1991); olaxoside (**125**) isolated from the leaves, roots and barks of *Olax andronensis*, *O. glabriflora* and *O. psittacorum* had a laxative action when given orally to mice, anti-inflammatory properties, and decreased oedema induced by carragenin (Forgacs & Provost, 1981); two saponins (**144**–**145**) isolated from the roots of *Silene jenisseensis* exhibited only a weak inhibitory effect in the cyclooxygenase inhibition assay (Lacaille-Dubois, Hanquet, Cui, Lou, & Wagner, 1995); tuberoside B (**184**) and C (**185**) isolated from the tubers of *Ullucus tuberosus* showed hypoglucaemic activity (Espada, Jimenez, Dopeso, & Riguera, 1996); zanhasaponin A (**190**), B (**191**) and C (**192**) isolated from the root barks of *Zanha africana* were

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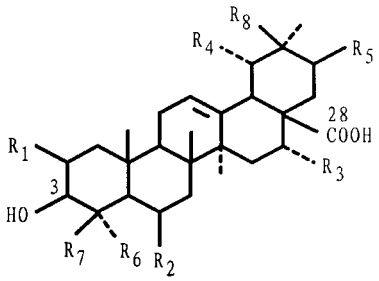
0031-9422/99/$ - see front matter
PII: S0031-9422(98)00454-3



(I)

		R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8
1	Bayogenin	OH	H	H	H	H	CH_2OH	CH_3	CH_3
2	Bredemolic acid	H	H	H	H	H	CH_3	CH_2OH	CH_3
3	Echinocystic acid	H	H	OH	H	H	CH_3	CH_3	CH_3
4	Gypsogenic acid	H	H	H	H	H	COOH	CH_3	CH_3
5	Gypsogenin	H	H	H	H	H	CHO	CH_3	CH_3
6	2β-OH Gypsogenin	OH	H	H	H	H	CHO	CH_3	CH_3
7	Hederagenin	H	H	H	H	H	CH_2OH	CH_3	CH_3
8	Ilexosapogenin A	H	H	H	OH	H	CH_2OH	CH_3	CH_3
9	Machaerinic acid	H	H	H	H	OH	CH_3	CH_3	CH_3
10	Medicagenic acid	OH	H	H	H	H	COOH	CH_3	CH_3
11	Oleanolic acid	H	H	H	H	H	CH_3	CH_3	CH_3
12	2β-OH Oleanolic acid	OH	H	H	H	H	CH_3	CH_3	CH_3
13	Protobassic acid	OH	OH	H	H	H	CH_2OH	CH_3	CH_3
14	16α-OH Protobassic acid	OH	OH	OH	H	H	CH_2OH	CH_3	CH_3
15	Quillaic acid	H	H	OH	H	H	CHO	CH_3	CH_3
16	Siaresinolic acid	H	H	H	OH	H	CH_3	CH_3	CH_3
17	Spathodic acid	H	H	H	OH	H	CH_3	CH_2OH	CH_3
18	Methyl spergulagenate	H	H	H	H	H	CH_3	CH_3	$COOCH_3$
19	Zanhic acid	OH	H	OH	H	H	COOH	CH_3	CH_3

effective in a model of topical inflammation induced by phorbol ester (Cuellar, Giner, Carmen Recio, Just, Manez, Rios, Bilia, Msonthi, & Hostettmann, 1997).

The structural elucidation of GOTCAB is quite complicated compared to that of other saponins because it contains a glucuronic acid at C-3 of the aglycones, more sugar units, and sometimes acyl groups at the 28-sugar chains. The skeleton is shown in Fig. 1. The structural elucidation successively includes the following steps: (1) the structure determination of the aglycone; (2) the structure determination of the 3-sugar chain (G_1); (3) the structure determination of the 28-sugar chain (G_2); (4) and the determination of the positions of the acyl groups. In order to determine their structures, it is common to use chemical and enzymatic methods to obtain a series of aglycones, prosapogenins and oligosaccharides. After determination of the structures of these aglycones, prosapogenins and oligosaccharides based on chemical and spectral means, finally GOTCAB structures can be elucidated step by step. Since aralosides A (**22**) and B (**23**) were

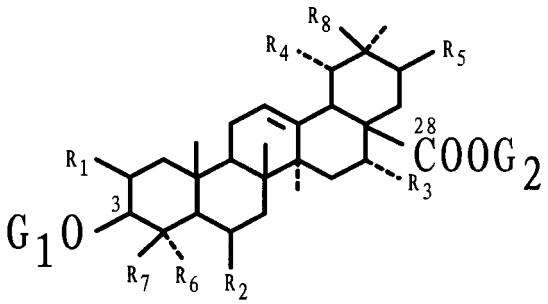


Fig. 1. The skeleton of glucuronide oleanane-type triterpene carboxylic acid 3,28-*O*-bisdesmosides (GOTCAB).

obtained from *Aralia manschurica* in 1962 (Kochetkov, Khorlin, & Vaskovsky, 1962), the three stages in structural elucidation strategies of GOTCAB have been as follows: (1) chemical methods which have been predominant during the 1960s to 1970s; (2) chemical methods which have been widely used together with spec-

Table 1
Glucuronide oleanane-type triterpene carboxylic acid 3,28-*O*-bisdesmosides (GOTCAB, I) isolated from 1962–1997

No.	Source (family, part)	Saponin (No.)	Structure	Structural and spectral data	Bioactivity	Reference
1	*Acanthophyllum gypsophiloides* (Caryophyllaceae)	Acanthophylloside B (1)	Gypsogenin (5) 4 4 gal----ara----glcUA (3β-OH) |2 gal 3 3 4 4 xyl----xyl----xyl----rha----fuc (28-COOH) |2 rha	IR, NMR.		Putieva, Mzhel'skaya, Gorovits, Kondratenko, & Abubakirov, 1976
		Acanthophylloside C (2)	Gypsogenin (5) 4 4 gal----ara----glcUA (3β-OH) 2/ \6 gal glc 3 3 4 4 xyl----xyl----xyl----rha----fuc (28-COOH) |2 rha	IR, NMR.		Putieva et al., 1976
2	*A. Squarrosum* (roots)	Squarroside A (3)	Gypsogenin (5) 2 gal----glcUA (3β-OH) |3 xyl 4 2 xyl----rha----fuc (28-COOH) 3/ \4 ara(f) $COCH_3$	amorphous powder, mp 262-264°, $[\alpha]_D^{20}$ +4°(MeOH, c 0.1), IR, FAB-MS [1537 $(M-H)^-$], PMR, CMR, 2D NMR (COSY, HMQC, HMBC), $C_{71}H_{110}O_{36}$.	immunomodulatory activity	Lacaille-Dubois et al., 1993
3	*Achyranthes aspera* (Amaranthaceae) (seeds)	Saponin B (4)	Oleanolic acid (11) 4 4 rha----glc----glcUA (3β-OH) gal (28-COOH)	methyl ester: mp 200–205°, $[\alpha]_D^{27}$ -8°(MeOH, c 1.2), $C_{55}H_{90}O_{24}$ (EA).		Hariharan et al., 1970
4	*A. fauriei* (roots)	Achyranthoside A (5)	Oleanolic acid (11) glcUA (3β-OH) |3, 4 2' glycolate----α-OCH_2COOH 1''/ \1'' β-OMe α-COOH glc (28-COOH)	methyl ester: white powder, $[\alpha]_D$ +64.3°(MeOH), FAB-MS [1033 $(M+Na)^+$], PMR, CMR, 2D NMR (COSY, H–C COSY, NOE, HMBC), $C_{51}H_{78}O_{20}$, x-ray.	cytotoxic activity	Ida et al., 1994
		Achyranthoside B (6)	Oleanolic acid (11) glcUA (3β-OH) |3, 4 2' glycolate----α-OCH_2COOH 1''/ \1'' β-OH α-COOH glc (28-COOH)	methyl ester: white powder, $[\alpha]_D$ +51.7°(MeOH), FAB-MS [1019 $(M+Na)^+$], PMR, CMR, 2D NMR (HMBC, NOE), $C_{50}H_{76}O_{20}$.	cytotoxic activity	Ida et al., 1994

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Table 1—Continued

No.	Source (family, part)	Saponin (No.)	Structure	Structural and spectral data	Bioactivity	Reference
5	*Actinostemma lobatum* (Cucurbitaceae) (seeds)	Lobatoside I (7)	Gypsogenin (5) 2 gal----glcUA (3β-OH) 4 2 xyl----rha----fuc (28-COOH) |3 glc	white amorphous powder (aqueous MeOH), mp 222–227°(dec.), $[\alpha]_D^{25}+1.7°$(pyridine, c 2.2), FAB-MS [1417 $(M+Na)^+$, 1393 $(M-H)^-$], PMR, CMR, 2D NMR (COSY, H-C COSY, NOESY, ROESY, NOEDS, ROEDS, HOHAHA, DDS), $C_{65}H_{102}O_{32}Na$ (pos. HR-FAB-MS).		Fujioka et al., 1992
		Lobatoside J (8)	Gypsogenin (5) 2 gal----glcUA (3β-OH) 3 4 2 xyl----xyl----rha----fuc (28-COOH) |3 glc	white amorphous powder, mp 229-234° (dec.), $[\alpha]_D^{25}+3.8°$ (pyridine, c 3.2), FAB-MS [1549 $(M+Na)^+$, 1525 $(M-H)^-$], PMR, CMR, 2D NMR (COSY, NOESY, NOEDS, ROEDS, HOHAHA, DDS), $C_{70}H_{110}O_{36}Na$ (pos. HR-FAB-MS).		Fujioka et al., 1992
		Lobatoside K (9)	Oleanolic acid (11) 2 gal----glcUA (3β-OH) 4 2 xyl----rha----fuc (28-COOH) |3 glc	white amorphous powder, mp 235-239° (dec.), $[\alpha]_D^{25}$-3.4°(pyridine, c 1.0), FAB-MS [1403 $(M+Na)^+$, 1379 $(M-H)^-$], PMR, CMR, 2D NMR (COSY, NOESY, NOEDS, ROEDS, HOHAHA, DDS), $C_{65}H_{104}O_{31}Na$ (pos. HR-FAB-MS).		Fujioka et al., 1992
6	*Amaranthus hypochondriacus* (Amaranthaceae) (grains)	Amaranthus-saponin I (10)	2β-OH Oleanolic acid (12) 3 rha----glcUA (3β-OH) glc (28-COOH)	white powder, $[\alpha]_D+23.3°$ (pyridine, c 0.43), FAB-MS [955 $(M-H)^-$], PMR, CMR, methyl ester: $C_{49}H_{78}O_{19}\cdot 2H_2O$ (EA).		Kohda et al., 1991
		Amaranthus-saponin II (11)	2β-OH Gypsogenin (6) 3 rha----glcUA (3β-OH) glc (28-COOH)	white powder, $[\alpha]_D+9.2°$(MeOH, c 0.87), FAB-MS [969 $(M-H)^-$], PMR, CMR, methyl ester: $C_{49}H_{76}O_{20}\cdot 3H_2O$ (EA).		Kohda et al., 1991
7	*Aralia armata* (Araliaceae) (root barks)	Saponin 15 (12)	Oleanolic acid (11) 3 gal----glcUA (3β-OH) glc (28-COOH)	methyl ester: powder, $[\alpha]^{30}+12.4°$(MeOH, c 0.50), IR, SI-MS [993 $(M+Na)^+$], PMR, CMR, $C_{49}H_{78}O_{19}\cdot 2H_2O$ (EA).		Hu, Ogawa, Sashida, & Xiao, 1995
8	*A. chinensis* (roots)	Araliasaponin XVIII (13)	Oleanolic acid (11) 2 glc----glcUA (3β-OH) |4 ara(f) 6 glc----glc (28-COOH)	methyl ester: amorphous powder, $[\alpha]_D^{25}$-33.3°(MeOH, c 3.74), FAB-MS [1228 $(M+Na)^+$], PMR, CMR, 2D NMR (NOE, HMBC), $C_{60}H_{96}O_{28}\cdot 2H_2O$ (EA).		Miyase et al., 1996

9	*A. decaisneana* (root barks)	Ad-III (14)	Oleanolic acid (11) 4 3 gal----gal----glcUA (3β-OH) glc (28-COOH)	white powder, mp 260°(dec.), IR, FAB-MS [1164 (M+2Na)$^+$], PMR, CMR, $C_{54}H_{86}O_{24}$.	Fang et al., 1992
10	*A. elatal* (root barks)	Tarasaponin IV (15)	Oleanolic acid (11) 2 glc----glcUA (3β-OH) |4 ara(f) glc (28-COOH)	methyl ester: powder (MeOH), mp 196-206°(dec.), $[\alpha]_D$-22.6°(MeOH, c 1.10), IR, FAB-MS [1101 (M–H)$^-$], PMR, CMR, 2D NMR (NOE), $C_{54}H_{86}O_{23} \cdot H_2O$ (EA).	Satoh et al., 1994
		Tarasaponin V (16)	Oleanolic acid (11) 2 xyl----glcUA (3β-OH) |3 glc glc (28-COOH)	methyl ester: powder (MeOH), mp 235–245°(dec.), $[\alpha]_D$+5.1°(MeOH, c 1.10), IR, FAB-MS [1101 (M–H)$^-$], PMR, CMR, 2D NMR (NOE), $C_{54}H_{86}O_{23} \cdot 1/2\ H_2O$ (EA).	Satoh et al., 1994
		Tarasaponin VI (17)	Oleanolic acid (11) 2 xyl----glcUA (3β-OH) |3 gal glc (28-COOH)	methyl ester: powder (MeOH), mp 218-230°(dec.), $[\alpha]_D$+48°(MeOH, c 1.10), IR, FAB-MS [1101 M–H)$^-$], CMR, $C_{54}H_{86}O_{23} \cdot 3H_2O$ (EA).	Satoh et al., 1994
	(barks)	Elatoside C (18)	Oleanolic acid (11) 2 xyl----glcUA (3β-OH) |3 gal glc (28-COOH)	colorless fine crystals, mp 208.5-209.5°, $[\alpha]_D$-1.6°(MeOH), IR, FAB-MS [1111 (M+Na)$^+$], PMR, CMR, $C_{53}H_{84}O_{23}$.	Yoshikawa, Harada, Matsuda, Murakami, Yamahara, & Murakami, 1993
		Elatoside D (19)	Oleanolic acid (11) 2 gal----glcUA (3β-OH) |3 gal glc (28-COOH)	colorless fine crystals, mp 188.5-189.5°, $[\alpha]_D$+6.9°(MeOH), IR, FAB-MS [1141 (M+Na)$^+$], PMR, CMR, $C_{54}H_{86}O_{24}$.	Yoshikawa et al., 1993
	(young shoots)	Elatoside K (20)	Oleanolic acid (11) 2 xyl----glcUA (3β-OH) |3 glc glc (28-COOH)	colorless fine crystals (MeOH–H_2O), mp 219.2-222.4°, $[\alpha]_D^{26}$+2.0°(MeOH, c 0.1), IR, FAB-MS [1111 (M+Na)$^+$, 1087 (M-H)$^-$], PMR, CMR, 2D NMR (HMBC), $C_{53}H_{84}O_{23}Na$ (pos. HR-FAB-MS).	Yoshikawa, Yoshizumi, Ueno, Matsuda, Murakami, Yamahara, & Murakami, 1995
	(root barks)	Araloside A (21)	Oleanolic acid (11) 4 ara(f)----glcUA (3β-OH) glc (28-COOH)	methyl ester: white needles (MeOH), mp 213-215°, IR, FAB-MS [979 (M+K)$^+$], PMR, CMR, $C_{48}H_{76}O_{18}$ (EA).	Jiang, Xu, Gu, Ren, Chen, Yao, & Miao, 1992
11	*A. manschurica* (roots)	Araloside A (22)	Oleanolic acid (11) 4 ara(f)----glcUA (3β-OH) glc (28-COOH)	mp 195-196°(dec.) (MeOH), $[\alpha]_D^{20}$-26.7°(MeOH, c 1.9), $C_{47}H_{74}O_{18}$.	Kochetkov et al., 1962
		Araloside B (23)	Oleanolic acid (11) 3 ara(f)----glcUA (3β-OH) |4 ara(f) glc (28-COOH)	permethylated: $[\alpha]_D^{20}$-12.6°($CHCl_3$, c 4.0), $C_{64}H_{106}O_{22}$.	Kochetkov et al., 1962

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Table 1—Continued

No.	Source (family, part)	Saponin (No.)	Structure	Structural and spectral data	Bioactivity	Reference
		Araloside C (24)	Oleanolic acid (11) 3 gal----glcUA (3β-OH) |4 xyl glc (28-COOH)			Hariharan, 1974
12	*A. spinifolia* (roots)	Araloside J (25)	Oleanolic acid (11) 4 ara(f)----glcUA (3β-OH) gal (28-COOH)	white powder, mp 208-210°(dec.), $[\alpha]_D^{20}$-31.1°(MeOH, c 0.1), IR, FAB-MS [949 $(M+Na)^+$], PMR, CMR, $C_{47}H_{74}O_{18} \cdot 3H_2O$ (EA).		Yu et al., 1994
13	*Aster scaber* (Compositae) (ground parts)	Scaberoside Ha (26)	Echinocystic acid (3) glcUA (3β-OH) 2 rha----xyl (28-COOH) |3 rha	methyl ester: white powder, $[\alpha]_D^{25}$-68.9°(MeOH, c 2.0), FAB-MS [1109 $(M+Na)^+$, 1085 $(M-H)^-$], PMR, CMR, 2D NMR (ROEDS), $C_{54}H_{86}O_{22}Na$ (pos. HR-FAB-MS).		Nagao et al., 1993
		Scaberoside Hb_1 (27)	Echinocystic acid (3) glcUA (3β-OH) 4 2 xyl----rha----xyl (28-COOH) |3 rha	methyl ester: white powder, $[\alpha]_D^{28}$-71.0°(MeOH, c 0.9), FAB-MS [1241 $(M+Na)^+$, 1217 $(M-H)^-$], PMR, CMR, 2D NMR (ROEDS), $C_{59}H_{94}O_{26}Na$ (pos. HR-FAB-MS).		Nagao et al., 1993
		Scaberoside Hb_2 (28)	Echinocystic acid (3) glcUA (3β-OH) 3 4 2 xyl----xyl----rha----xyl (28-COOH) |3 rha	methyl ester: Colorless needles (H_2O–MeOH), mp 271°, $[\alpha]_D^{25}$-64.0°(MeOH, c 0.7), FAB-MS [1373 $(M+Na)^+$, 1349 $(M-H)^-$], PMR, CMR, 2D NMR (ROEDS), $C_{64}H_{102}O_{30}Na$ (pos. HR-FAB-MS).		Nagao et al., 1993
		Scaberoside Hc_1 (29)	Echinocystic acid (3) glcUA (3β-OH) 3 3 2 xyl----xyl----rha----xyl (28-COOH) |4 |3 xyl rha	methyl ester: Colorless needles (H_2O–MeOH), mp 238-240°, $[\alpha]_D^{22}$-74.7°(MeOH, c 1.0), FAB-MS [1505 $(M+Na)^+$, 1481 $(M-H)^-$], PMR, CMR, 2D NMR (ROEDS), $C_{69}H_{110}O_{34}Na$ (pos. HR-FAB-MS).		Nagao et al., 1993
		Scaberoside Hc_2 (30)	Echinocystic acid (3) 3 xyl----glcUA (3β-OH) 3 4 2 xyl----xyl----rha----xyl (28-COOH) |3 rha	methyl ester: white powder, $[\alpha]_D^{24}$-67.4°(MeOH, c 1.0), FAB-MS [1505 $(M+Na)^+$, 1481 $(M-H)^-$], PMR, CMR, $C_{69}H_{110}O_{34}Na$ (pos. HR-FAB-MS).		Nagao, Iwase, & Okabe, 1993
		Scaberoside Hd (31)	Echinocystic acid (3) 3 xyl----glcUA (3β-OH) 3 3 2 xyl----xyl----rha----xyl (28-COOH) |4 |3 xyl rha	methyl ester: white powder, $[\alpha]_D^{26}$-73.6°(MeOH, c 0.9), FAB-MS [1637 $(M+Na)^+$, 1613 $(M-H)^-$], PMR, CMR, $C_{74}H_{118}O_{38}Na$ (pos. HR-FAB-MS).		Nagao et al., 1993

	Scaberoside Hf (32)	Echinocystic acid (3) 2 gal----glcUA (3β-OH) 4 2 xyl----rha----xyl (28-COOH) |3 rha	methyl ester: white powder, $[\alpha]_D^{25}$-67.7°(MeOH, c 1.1), FAB-MS [1403 $(M+Na)^+$, 1379 $(M-H)^-$], PMR, CMR, $C_{65}H_{104}O_{31}Na$ (pos. HR-FAB-MS).	Nagao et al., 1993
	Scaberoside Hg (33)	Echinocystic acid (3) 2 gal----glcUA (3β-OH) 3 4 2 xyl----xyl----rha----xyl (28-COOH) |3 rha	methyl ester: colorless needles (H_2O–MeOH), mp 260-261°, $[\alpha]_D^{25}$-67.3° (MeOH, c 1.0), FAB-MS [1535 $(M+Na)^+$, 1511 $(M-H)^-$], PMR, CMR, $C_{70}H_{112}O_{35}Na$ (pos. HR-FAB-MS).	Nagao et al., 1993
	Scaberoside Hh (34)	Echinocystic acid (3) 2 gal----glcUA (3β-OH) |3 xyl 3 4 2 xyl----xyl----rha----xyl (28-COOH) |3 rha	methyl ester: white powder, $[\alpha]_D^{24}$-56.9°(MeOH, c 0.9), FAB-MS [1667 $(M+Na)^+$, 1643 $(M-H)^-$], PMR, CMR, 2D NMR (COSY, ROEDS), $C_{75}H_{120}O_{39}Na$ (pos. HR-FAB-MS).	Nagao et al., 1993
	Scaberoside Hi (35)	Echinocystic acid (3) 2 gal----glcUA (3β-OH) 3 3 2 xyl----xyl----rha----xyl (28-COOH) |4 |3 xyl rha	methyl ester: white powder, $[\alpha]_D^{23}$-64.4°(MeOH, c 0.8), FAB-MS [1667 $(M+Na)^+$, 1643 $(M-H)^-$], PMR, CMR, $C_{75}H_{120}O_{39}Na$ (pos. HR-FAB-MS).	Nagao et al., 1993
(roots)	Scaberoside B_1 (36)	Oleanolic acid (11) glcUA (3β-OH) ara (28-COOH)	methyl ester: colorless needles (H_2O–MeOH), mp 193-195°, $[\alpha]_D^{28}+8.4°$ (MeOH, c 2.5), FAB-MS [779 $(M+H)^+$, 777 $(M-H)^-$], PMR, CMR, $C_{42}H_{67}O_{13}$ (pos. HR-FAB-MS).	Nagao et al., 1991
	Scaberoside B_2 (37)	Oleanolic acid (11) glcUA (3β-OH) xyl (28-COOH)	methyl ester: white powder, $[\alpha]_D^{27}+3.1°$(MeOH, c 0.8), FAB-MS [779$(M+H)^+$, 777 $(M-H)^-$], PMR, CMR, $C_{42}H_{67}O_{13}$ (pos. HR-FAB-MS).	Nagao et al., 1991
	Scaberoside B_3 (38)	Oleanolic acid (11) glcUA (3β-OH) 2 rha----ara (28-COOH)	methyl ester: white powder, $[\alpha]_D^{26}$-37.9°(MeOH, c 1.3), FAB-MS [947 $(M+Na)^+$, 923 $(M-H)^-$], PMR, CMR, 2D NMR (COSY, H–C COSY, NOEDS), $C_{48}H_{76}O_{17}Na$ (pos. HR-FAB-MS).	Nagao et al., 1991
	Scaberoside B_4 (39)	Oleanolic acid (11) glcUA (3β-OH) 2 rha----xyl (28-COOH)	methyl ester: white powder, $[\alpha]_D^{27}$-24.2°(MeOH, c 1.7), FAB-MS [947 $(M+Na)^+$, 923 $(M-H)^-$], PMR, CMR, $C_{48}H_{76}O_{17}Na$ (pos. HR-FAB-MS).	Nagao et al., 1991

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Table 1—Continued

No. Source (family, part)	Saponin (No.)	Structure	Structural and spectral data	Bioactivity	Reference
	Scaberoside B_5 (40)	Oleanolic acid (11) glcUA (3β-OH) 4 2 xyl----rha----ara (28-COOH)	methyl ester: colorless needles (H_2O–MeOH), mp 217-220°, $[\alpha]_D^{23}$-33.3°(MeOH, c 1.0), FAB-MS [1079 ($M+Na^+$), 1055 ($M-H)^-$], PMR, CMR, $C_{53}H_{84}O_{21}Na$ (pos. HR-FAB-MS).		Nagao et al., 1991
	Scaberoside B_6 (41)	Oleanolic acid (11) glcUA (3β-OH) 4 2 xyl----rha----xyl (28-COOH)	methyl ester: colorless needles (H_2O–MeOH), mp 214-216°, $[\alpha]_D^{24}$-27.0°(MeOH, c 1.0), FAB-MS [1079 $(M+Na)^+$, 1055 $(M-H)^-$], PMR, CMR, $C_{53}H_{84}O_{21}Na$ (pos. HR-FAB-MS).		Nagao et al., 1991
	Scaberoside A_1 (42)	Echinocystic acid (3) glcUA (3β-OH) 3 2 api(f)----rha----ara (28-COOH)	methyl ester: amorphous powder, $[\alpha]_D^{29}$-60.6°(MeOH, c 2.25), FAB-MS [1095 $(M+Na)^+$, 1071 $(M-H)^-$], PMR, CMR, $C_{53}H_{84}O_{22}Na$ (pos. HR-FAB-MS).		Nagao et al., 1991
	Scaberoside A_2 (43)	Echinocystic acid (3) glcUA (3β-OH) 4 2 xyl----rha----xyl (28-COOH)	methyl ester: amorphous powder, $[\alpha]_D^{29}$-42.9°(MeOH, c 2.25), FAB-MS [1095 $(M+Na)^+$, 1071 $(M-H)^-$], PMR, CMR, $C_{53}H_{84}O_{22}Na$ (pos. HR-FAB-MS).		Nagao et al., 1991
	Scaberoside A_3 (44)	Echinocystic acid (3) glcUA (3β-OH) 3 2 api(f)----rha----ara (28-COOH) |4 xyl	methyl ester: amorphous powder, $[\alpha]_D^{29}$-64.1°(MeOH, c 2.0), FAB-MS [1227 $(M+Na)^+$, 1203 $(M-H)^-$], PMR, CMR, $C_{58}H_{92}O_{26}Na$ (pos. HR-FAB-MS).		Nagao et al., 1991
	Scaberoside A_4 (45)	Echinocystic acid (3) glcUA (3β-OH) 3 3 2 xyl----xyl----rha----xyl (28-COOH) |4 xyl	methyl ester: amorphous powder, $[\alpha]_D^{29}$-46.2°(MeOH, c 2.25), FAB-MS [1359 $(M+Na)^+$, 1335 $(M-H)^-$], PMR, CMR, 2D NMR (COSY, ROEDS, DDS, HOHAHA), $C_{63}H_{100}O_{30}Na$ (pos. HR-FAB-MS).		Nagao et al., 1991
	Scaberoside B_7 (46)	Oleanolic acid (11) glcUA (3β-OH) 3 2 api(f)----rha----ara (28-COOH) |4 xyl	methyl ester: colorless needles (H_2O–MeOH), mp 230-233°, $[\alpha]_D^{20}$-54.5°(MeOH, c 0.9), FAB-MS [1211 $(M+Na)^+$, 1187 $(M-H)^-$], PMR, CMR, 2D NMR (NOEDS), $C_{58}H_{92}O_{25}Na$ (pos. HR-FAB-MS).		Nagao et al., 1992
	Scaberoside B_9 (47)	Oleanolic acid (11) glcUA (3β-OH) 2 rha----glc (28-COOH) |6 xyl	methyl ester: white powder, $[\alpha]_D^{29}$-31.6°(MeOH, c 0.5), FAB-MS [1109 $(M+Na)^+$, 1085 $(M-H)^-$], PMR, CMR, 2D NMR (ROEDS), $C_{54}H_{86}O_{22}Na$ (pos. HR-FAB-MS).		Nagao et al., 1992

14	*A. tataricus* (ground parts)	Aster saponin Ha (48)	Echinocystic acid (3) glcUA (3β-OH) ara (28-COOH)	methyl ester: amorphous powder, $[\alpha]_D^{27}$-19.3°(MeOH, c 1.9), FAB-MS [817 $(M+Na)^+$], PMR, CMR.		Tanaka et al., 1990
		Aster saponin Hb (49)	Echinocystic acid (3) glcUA (3β-OH) 2 rha----ara (28-COOH)	methyl ester: amorphous powder, $[\alpha]_D^{29}$-54.3°(MeOH, c 2.0), FAB-MS [963 $(M+Na)^+$], PMR, CMR.		Tanaka et al., 1990
		Aster saponin Hc (50)	Echinocystic acid (3) glcUA (3β-OH) 3 4 2 xyl----xyl----rha----ara (28-COOH)	methyl ester: colorless needles (aqueous MeOH), mp 227-228°, $[\alpha]_D^{27}$-47.3°(MeOH, c 2.0), FAB-MS [1227 $(M+Na)^+$], PMR, CMR, $C_{58}H_{92}O_{26} \cdot H_2O$ (EA).		Tanaka et al., 1990
		Aster saponin Hd (51)	Echinocystic acid (3) glcUA (3β-OH) 3 4 2 xyl----xyl----rha----ara (28-COOH) |3 api(f)	methyl ester: colorless needles (aqueous MeOH), mp 235-237°, $[\alpha]_D^{26}$-62.8°(MeOH, c 1.8), FAB-MS [1359 $(M+Na)^+$], PMR, CMR, $C_{63}H_{100}O_{30} \cdot 2H_2O$ (EA).		Tanaka et al., 1990
15	*Beta vulgaris* (Chenopodiaceae) (roots, leaves)	Betavulgaroside III (52)	Oleanolic acid (11) glcUA (3β-OH) |3 3'-3"β-O-carbonylmethyl-2β,3β-dihydroxyl propanic acid glc (28-COOH)	colorless fine crystals, mp 212-214°, $[\alpha]_D^{28}+10.8°$ (MeOH, c 0.1), IR, FAB-MS [979 $(M+Na)^+$, 955 $(M-H)^-$], PMR, CMR, 2D NMR (HMBC), $C_{47}H_{71}O_{20}$ [$(M-H)^-$, neg. HR-FAB-MS)].	hypoglycemic activity	Yoshikawa et al., 1996; Yoshikawa, Murakami, Kadoya, Matsuda, Yamahara, Muraoka, & Murakami, 1995; Yoshikawa, Murakami, Inaduki, Hirano, Yamahara, & Matsuda, 1997
		Betavulgaroside V (53)	Oleanolic acid (11) 2 glc----glcUA (3β-OH) |3 3'-3"-O-carbonylmethyl-2,3-dihydroxyl propanic acid glc (28-COOH)	colorless fine crystals, mp 205-206°, $[\alpha]_D+12.5°$(MeOH), IR, FAB-MS [1141 $(M+Na)^+$, 1117 $(M-H)^-$], PMR, CMR, 2D NMR (HMBC), $C_{53}H_{81}O_{25}$ [$(M-H)^-$, neg. HR-FAB-MS)].		Yoshikawa et al., 1996
16	*Calendula arvensis* (Compositae) (aerial parts)	Saponin 3 (54)	Oleanolic acid (11) 3 gal----glcUA (3β-OH) glc (28-COOH)	$[\alpha]_D+15°$(MeOH), FAB-MS [955 $(M-H)^-$], PMR, CMR, $C_{48}H_{76}O_{19}$.		Pizza, Zhou, & Tommasi, 1987
17	*C. officinalis* (flowers)	Glycoside A (55)	Oleanolic acid (11) 2 glc----glcUA (3β-OH) |3 gal glc (28-COOH)	mp 227-229°(dec.), $[\alpha]_D+12°(H_2O$, c 0.5), FAB-MS [1117 $(M-H)^-$], CMR, $C_{54}H_{86}O_{24}$.		Vidal-Ollivier, Balansard, Faure, & Babadjamian, 1989

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Table 1—Continued

No.	Source (family, part)	Saponin (No.)	Structure	Structural and spectral data	Bioactivity	Reference
18	*Climacoptera transoxana* (Chenopodiaceae)	Copteroside D (56)	Hederagenin (7) 2 xyl----glcUA (3β-OH) glc (28-COOH)			Annaev, Isamukhamedova, & Abubakirov, 1983
		Copteroside E (57)	Oleanolic acid (11) 2 xyl----glcUA (3β-OH) |4 xyl glc (28-COOH)			Annaev, Isaev, & Abubakirov, 1983
		Copteroside F (58)	Hederagenin (7) 2 xyl----glcUA (3β-OH) |4 xyl glc (28-COOH)			Annaev et al., 1983
		Copteroside G (59)	Gypsogenic acid (4) glcUA (3β-OH) glc (28-COOH)			Annaev & Abubakirov, 1984
		Copteroside H (60)	Gypsogenic acid (4) 2 glc----glcUA (3β-OH) glc (28-COOH)			Annaev et al., 1984
19	*Codonopsis lanceolata* (Campanulaceae) (roots)	Codonoside B (61)	Echinocystic acid (3) glcUA (3β-OH) 4 4 2 xyl----rha----glc----ara (28-COOH)	mp 250-256°(aqueous n-butanol), $[\alpha]_D^{20}$-54.4°(aqueous pyridine, c 0.57), IR, CMR, $C_{58}H_{92}O_{27}$.		Alad'ina, El'kin, & Chezhina, 1989
20	*Cucurbita foetidissima* (Cucurbitaceae) (roots)	Foetidissimoside A (62)	Echinocystic acid (3) glcUA (3β-OH) 4 2 xyl----rha----ara (28-COOH)	white amorphous powder, IR, FAB-MS [1057 $(M-H)^-$], PMR, CMR.		Dubois et al., 1988
21	*Cynara cardunculus* (Compositae) (aerial parts)	Cynarasaponin H (63)	Oleanolic acid (11) 2 ara----glcUA (3β-OH) glc (28-COOH)	methyl ester: amorphous powder, $[\alpha]_D^{21}+0.68°$(MeOH, c 1.48), PMR, CMR, $C_{48}H_{76}O_{18}\cdot 2H_2O$ (EA).		Shimizu et al., 1988
		Cynarasaponin J (64)	Machaerinic acid (9) 2 ara----glcUA (3β-OH) glc (28-COOH)	methyl ester: amorphous powder, $[\alpha]_D^{25}+15.6°$(MeOH, c 0.95), PMR, CMR, $C_{48}H_{76}O_{19}\cdot 2H_2O$ (EA).		Shimizu et al., 1988
22	*Deeringia amaranthoides* (Amaranthaceae) (fruits)	(65)	Oleanolic acid (11) 3 rha----glcUA (3β-OH) 2 xyl----glc (28-COOH)	crystals (MeOH), mp 270-274°, IR, FAB-MS [1071 $(M-H)^-$], PMR, CMR.		Sati et al., 1990
23	*Dumasia truncata* (Leguminosae) (aerial parts)	(66)	Hederagenin (7) 3 rha----glcUA (3β-OH) glc (28-COOH)	amorphous powder, $[\alpha]_D$-10.4°(MeOH, c 0.37), FAB-MS [955 $(M-H)^-$], PMR, CMR.		Kinjo, Suyama, & Nohara, 1995

24	*Gypsophila oldhamiana* (Caryophyllaceae) (roots)	Saponin 3 (67)	Quillaic acid (15) 2 gal----glcUA (3β-OH) |3 xyl 3 glc----rha (28-COOH) |4 fuc	light yellow powder, PMR, CMR, 2D NMR (HETCOR, HMBC), $C_{65}H_{102}O_{32}$.	Liu et al., 1995
25	*G. pacifica* (roots)	Gypsoside (68)	Gypsogenin (5) 4 4 gal----glc----glcUA (3β-OH) |3 ara 3 2 xyl----xyl----rha (28-COOH) |4 fuc |3 xyl	permethylated: $[\alpha]_D^{20}+47.5°$($CHCl_3$, c 3.4), $C_{103}H_{172}O_{44}$.	Kochetkov et al., 1963
26	*G. paniculata*	MS-1 (69)	Gypsogenin (5) 2 gal----glcUA (3β-OH) |3 ara 3 4 4 xyl----xyl----rha----fuc (28-COOH) |2 qui	white powder (MeOH–H_2O), mp 243-247°(dec.), $[\alpha]_D^{28}+7.7°$(H_2O, c 1.68), IR, FAB-MS [1641 $(M-H)^-$], PMR, CMR, 2D NMR (H–C COSY), $C_{75}H_{118}O_{39}\cdot 1.2H_2O$ (EA).	Kim, Higuchi, & Komori, 1992
		MS-2 (70)	Qullaic acid (15) 2 gal----glcUA (3β-OH) |3 ara 3 4 4 xyl----xyl----rha----fuc (28-COOH) |2 qui	white powder (MeOH–H_2O), mp 262–264°(dec.), $[\alpha]_D^{28}+0.57°$(H_2O, c 1.33), IR, FAB-MS [1657 $(M-H)^-$], PMR, CMR, $C_{75}H_{118}O_{40}\cdot 1/2H_2O$ (EA).	Kim et al., 1992
27	*G. paniculata* and *G. arrostii* (roots)	G1 (71)	Qullaic acid (15) 2 gal----glcUA (3β-OH) |3 xyl 3 2 glc----rha----fuc (28-COOH) |4 xyl	amorphous powder, mp 210-213°, FAB-MS [1541 $(M-H)^-$], PMR, CMR, 2D NMR (HOHAHA, H–C COSY, H–C RELAY, HMBC), $C_{70}H_{110}O_{37}$.	Frechet et al., 1991
		G2 (72)	Qullaic acid (15) 2 gal----glcUA (3β-OH) |3 xyl 4 3 4 2 ara----ara----xyl----rha----fuc (28-COOH)	amorphous powder, mp 213–215°, FAB-MS [1643 $(M-H)^-$], PMR, CMR, 2D NMR (HOHAHA, H–C COSY, H–C RELAY, HMBC), $C_{74}H_{116}O_{40}$.	Frechet et al., 1991

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No.	Source (family, part)	Saponin (No.)	Structure	Structural and spectral data	Bioactivity	Reference
		G3 (73)	Gypsogenin (5) 2 glc----glcUA (3β-OH) 3 2 glc----rha----fuc (28-COOH) |4 xyl	amorphous powder, mp 207-211°, FAB-MS [1393 $(M-H)^-$], PMR, CMR, 2D NMR (HOHAHA, H–C COSY, H–C RELAY, HMBC), $C_{65}H_{102}O_{32}$.		Frechet et al., 1991
		G4 (74)	Gypsogenin (5) 2 gal----glcUA (3β-OH) |3 xyl 3 2 glc----rha----fuc (28-COOH) |4 xyl	amorphous powder, mp 215-218°, FAB-MS [1525 $(M-H)^-$], PMR, CMR, 2D NMR (HOHAHA, H–C COSY, H–C RELAY, HMBC), $C_{70}H_{110}O_{36}$.		Frechet et al., 1991
28	*G. patrinii* (roots)	Phyloside A (75)	Gypsogenin (5) 2 3 xyl----gal----glcUA (3β-OH) 2/ \4 xyl gal 4 2 rha----glc----fuc (28-COOH) |6 rha			Bukharov, Karlin, Bukharova, & Surkova, 1975a
		Phyloside B (76)	Gypsogenin (5) 2 2 3 ara----xyl----gal----glcUA (3β-OH) 2/ \4 xyl gal 4 2 rha----ara----fuc (28-COOH)			Bukharov, Karlin, Bukharova, & Surkova, 1975b
29	*G. trichotoma*	Trichoside A (77)	Gypsogenin (5) 3 glc----glcUA (3β-OH) gal (28-COOH)			Luchanskaya, Kondratenko, Gorovits, & Abubakirov, 1971
		Trichoside C (78)	Gypsogenin (5) 3 glc----glcUA (3β-OH) 4 4 gal----rha----fuc (28-COOH)			Luchanskaya, Kondratenko, & Abubakirov, 1972
30	*Hemsleya chinensis* (Cucurbitaceae) (rhizomes)	Hemsloside H_1 (79)	Oleanolic acid (11) 2 glc---glcUA (3β-OH) |3 ara 6 glc----glc (28-COOH)	white powder (MeOH–EtOAc), $[\alpha]_D^{27}+2.9°$(MeOH, c 1.32), CMR, $C_{59}H_{94}O_{28}\cdot 5/2H_2O$ (EA).		Morita et al., 1986
31	*H. graciliflora* (rhizomes)	Hemsloside G1 (80)	Oleanolic acid (11) 3 ara----glcUA (3β-OH) 6 glc----glc (28-COOH)	white powder, $[\alpha]_D^{18}+7.6°$(MeOH, c 0.9), PMR, CMR, $C_{53}H_{84}O_{23}\cdot 2H_2O$ (EA).		Kasai, Tanaka, Nie, Miyakoshi, Zhou, & Tanaka, 1990

		Hemsloside G2 (81)	Oleanolic acid (11) 2 glc----glcUA (3β-OH) 6 glc----glc (28-COOH)	white powder, $[\alpha]_D^{18}$-6.1°(MeOH, c 0.9), PMR, CMR, $C_{54}H_{86}O_{24} \cdot 2H_2O$ (EA).	Kasai et al., 1990
32	*H. macrosperma* (rhizomes)	Hemsloside-Mal (82)	Oleanolic acid (11) 3 ara----glcUA (3β-OH) glc (28-COOH)	colorless prisms (MeOH–H_2O), mp 230-233°, $[\alpha]_D^{21}$ + 15.8°(MeOH, c 1.03), CMR, $C_{47}H_{74}O_{18} \cdot 4H_2O$ (EA).	Nie et al., 1984
		Hemsloside-Ma2 (83)	Oleanolic acid (11) 2 xyl----glcUA (3β-OH) |3 ara glc (28-COOH)	white powder (MeOH–EtOAc), $[\alpha]_D^{14}$ + 15.4°(MeOH, c 1.03), CMR, $C_{52}H_{82}O_{22} \cdot 7/2H_2O$ (EA).	Nie et al., 1984
		Hemsloside-Ma3 (84)	Oleanolic acid (11) 2 glc----glcUA (3β-OH) |3 ara glc (28-COOH)	colorless needles (MeOH–H_2O), mp 249-252°, $[\alpha]_D^{21}$ + 16.0°(MeOH, c 1.00), CMR, $C_{53}H_{84}O_{23} \cdot 5H_2O$ (EA).	Nie et al., 1984
33	*Herniaria fontanesii* (Caryophyllaceae) (aerial parts)	Herniaria saponin C (85)	Zanhic acid (19) 2 rha----glcUA (3β-OH) 2 rha----fuc (28-COOH) 3/ \4 rha $COCH_3$	amorphous powder, $[\alpha]_D^{18}$-26°(MeOH, c 0.6), FAB-MS [1319 $(M–H)^-$], PMR, CMR, 2D NMR (COSY, H–C COSY, HOHAHA), $C_{62}H_{96}O_{30}$.	M'Bark, Gutllaume, Kol, & Charrouf, 1996
		Herniaria saponin D (86)	Zanhic acid (19) 2 rha----glcUA (3β-OH) 2 rha----fuc (28-COOH) |3 rha	amorphous powder, $[\alpha]_D^{18}$-26°(MeOH, c 0.35), FAB-MS [1277 $(M–H)^-$], PMR, CMR.	M'Bark et al., 1996
34	*H. glabra* (ground parts)	Herniaria saponin 1 (87)	Medicagenic acid (10) glcUA (3β-OH) 3 2 glc----rha----fuc (28-COOH) 3/ \4 $COCH_3$ $COCH_3$		Schroder et al., 1993
		Herniaria saponin 3 (88)	Medicagenic acid (10) glcUA (3β-OH) 3 2 glc----rha----fuc (28-COOH) 3/ \4 glc $COCH_3$	powder, mp 275–276°, $[\alpha]_D^{20}$-6.12°(c 0.2), FAB-MS [1336 (M)], PMR, CMR, 2D NMR (COSY, TOCSY, HMQC, NOESY, ROESY, HMBC).	Schroder et al., 1993
		Herniaria saponin (89)	Medicagenic acid (10) glcUA (3β-OH) 3 2 glc----rha----fuc (28-COOH) 3/ \4 api(f) $COCH_3$	mp 259-261°, $[\alpha]_D^{20}$-13.6°.	Freiler, Reznicek, Schubert-Zsilavecz, Reiner, Haslinger, Jurenitsch, & Kubelka, 1996
35	*Ilex rotunda* (Aquifoliaceae) (leaves)	Ilexoside XXXI (90)	Siaresinolic acid (16) glcUA (3β-OH) glc (28-COOH)	white powder, $[\alpha]_D$-2.0°(MeOH, c 3.1), FAB-MS [809 $(M–H)^-$], PMR, CMR, 2D NMR (HMBC), $C_{42}H_{66}O_{15} \cdot 2H_2O$ (EA).	Amimoto et al., 1992

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Table 1—Continued

No.	Source (family, part)	Saponin (No.)	Structure	Structural and spectral data	Bioactivity	Reference
		Ilexoside XLVI (91)	Ilexosapogenin A (8) glcUA (3β-OH) glc (28-COOH)	white powder, $[\alpha]_D^{22}$-0.6°(MeOH, c 3.2), FAB-MS [825 $(M-H)^-$], PMR, CMR, $C_{42}H_{66}O_{16} \cdot 2\ H_2O$ (EA).		Amimoto et al., 1993
		Ilexoside XLVII (92)	Spathodic acid (17) glcUA (3β-OH) glc (28-COOH)	colorless needles (MeOH), mp 238-239°, $[\alpha]_D^{22}$-11.3°(MeOH, c 0.7), FAB-MS [825 $(M-H)^-$], PMR, CMR, 2D NMR (NOESY, HMBC), $C_{42}H_{66}O_{16} \cdot 3H_2O$ (EA).		Amimoto et al., 1993
		Ilexoside XLVIII (93)	Hederagenin (7) glcUA (3β-OH) glc (28-COOH)	colorless needles (MeOH), mp 200-201°, $[\alpha]_D^{22}+19.3$°(MeOH, c 7.2), FAB-MS [809 $(M-H)^-$], PMR, CMR, $C_{42}H_{66}O_{15} \cdot H_2O$ (EA).		Amimoto et al., 1993
		Ilexoside XLIX (94)	Hederagenin (7) 2 gal----glcUA (3β-OH) glc (28-COOH)	white powder, $[\alpha]_D^{22}+18.9$°(MeOH, c 1.1), FAB-MS [971 $(M-H)^-$], PMR, CMR, $C_{48}H_{76}O_{20} \cdot 3H_2O$ (EA).		Amimoto et al., 1993
		Ilexoside L (95)	Bredemolic acid (2) glcUA (3β-OH) glc (28-COOH)	colorless needles (MeOH), mp 250-252°, $[\alpha]_D^{22}+5.3$°(MeOH, c 7.9), FAB-MS [809 $(M-H)^-$], PMR, CMR, 2D NMR (NOESY), $C_{42}H_{66}O_{15} \cdot 2H_2O$ (EA).		Amimoto et al., 1993
		Ilexoside LI (96)	Siaresinolic acid (16) 2 gal----glcUA (3β-OH) glc (28-COOH)	colorless needles (MeOH), mp 207-209°, $[\alpha]_D^{22}$-1.3°(MeOH, c 0.8), FAB-MS [971 $(M-H)^-$], PMR, CMR, $C_{48}H_{76}O_{20} \cdot 3\ H_2O$ (EA).		Amimoto et al., 1993
36	*Kalimeris shimadae* (Compositae) (roots)	Shimadoside A (97)	Echinocystic acid (3) glcUA (3β-OH) 3 4 2 xyl----xyl----rha----xyl (28-COOH)	needles, mp 215-216°, $[\alpha]_D$-29.4°(MeOH, c 0.5), IR, FAB-MS [1189 $(M-H)^-$], PMR, CMR, 2D NMR (COSY, HOHAHA, HMQC, ROESY), $C_{57}H_{90}O_{26}$.		Shao et al., 1996
37	*Kochia scoparia* (Chenopodiaceae) (fruits)	Saponin 5 (98)	Oleanolic acid (11) 2 glc----glcUA (3β-OH) |3 xyl glc (28-COOH)	white powder, mp 237-240°, $[\alpha]_D^{18}+10.0$°(MeOH, c 0.1), IR, FAB-MS [1111 $(M+Na)^+$], PMR, CMR, $C_{53}H_{84}O_{23} \cdot 6H_2O$ (EA).		Wen, Chen, Cui, Li, & Wang, 1995
38	*Ladyginia bucharica* (Umbelliferae) (roots)	Ladyginoside D (99)	Hederagenin (7) 4 glc----glcUA (3β-OH) 4 6 gal----glc----glc (28-COOH)			Patkhullaeva, Mzhel'skaya, & Abubakirov, 1975

		Ladyginoside E (100)	Oleanolic acid (11) 4 glc----glcUA (3β-OH) 6 6 6 glc----glc----glc----glc (28-COOH) |4 gal	mp 200-202°.		Patkullaeva Mzhel'skaya, & Abubakirov, 1975
		Ladyginoside F (101)	Hederagenin (7) 4 glc----glcUA (3β-OH) 6 6 6 glc----glc----glc----glc (28-COOH) |4 gal			Patkullaeva et al., 1975
39	*Luffa acutangula* (Cucurbitaceae) (seeds)	Acutoside H (102)	Oleanolic acid (11) 3 ara----glcUA (3β-OH) 3 4 2 xyl----xyl----rha----ara (28-COOH) |3 xyl	methyl ester: colorless fine needles (80% MeOH), mp 235-238°, $[\alpha]_D^{24}$-53.1°(50% MeOH, c 0.58), FAB-MS [1475 $(M+Na)^+$, 1451 $(M-H)^-$], PMR, CMR, 2D NMR (COSY, H–C COSY, HOHAHA, ROEDS), $C_{68}H_{108}O_{33}Na$ (pos. HR-FAB-MS).		Nagao et al., 1991
		Acutoside I (103)	Oleanolic acid (11) 3 ara----glcUA (3β-OH) 3 4 2 ara----xyl----rha----ara (28-COOH) |3 xyl	methyl ester: colorless needles (80% MeOH), mp 234-237°, $[\alpha]_D^{24}$-28.7°(50% MeOH, c 2.0), FAB-MS [1475 $(M+Na)^+$, 1451 $(M-H)^-$], PMR, CMR, $C_{68}H_{108}O_{33}Na$ (pos. HR-FAB-MS).		Nagao et al., 1991
40	*L. cylindrica* (seeds)	Lucyoside N (104)	Quillaic acid (15) 2 gal----glcUA (3β-OH) 4 2 xyl----rha----ara (28-COOH) |3 glc	colorless fine needles, mp 268-270°, $[\alpha]_D$-36.1°(pyridine, c 2.4), IR, FAB-MS [1395 $(M-H)^-$], PMR, CMR, $C_{64}H_{100}O_{33} \cdot 7/2H_2O$ (EA).	fibrinolytic activity	Yoshikawa et al., 1991
		Lucyoside P (105)	Gypsogenin (5) 2 gal----glcUA (3β-OH) 4 2 xyl----rha----ara (28-COOH) |3 glc	colorless fine needles, mp 228-230°, $[\alpha]_D$-12.2°(pyridine, c 6.5), IR, FAB-MS [1379 $(M-H)^-$], PMR, CMR, $C_{64}H_{100}O_{32} \cdot 6H_2O$ (EA).	fibrinolytic activity	Yoshikawa et al., 1991
41	*L. operculata* (whole plants)	Luperoside I (106)	Gypsogenin (5) 2 gal----glcUA (3β-OH) |3 ara 4 2 xyl----rha----qui (28-COOH) |3 rha	methyl ester: fine needles (MeOH), mp 242-245°(dec.), $[\alpha]_D^{27}$-6.4°(80% MeOH, c 1.30), FAB-MS [1547 $(M+Na)^+$, 1523 $(M-H)^-$], PMR, CMR, 2D NMR (COSY, H–C COSY, NOEDS), $C_{71}H_{112}O_{35} \cdot 2H_2O$ (EA).		Okabe et al., 1989

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Table 1—Continued

No.	Source (family, part)	Saponin (No.)	Structure	Structural and spectral data	Bioactivity	Reference
		Luperoside J (107)	Gypsogenin (5) 2 gal---glcUA (3β-OH) |3 ara 3 4 2 xyl---xyl---rha---qui (28-COOH) |3 rha	methyl ester: fine needles (MeOH), mp 237–240°, $[\alpha]_D^{28}$-9.8°(80% MeOH, c 1.10), FAB-MS [1679 $(M+Na)^+$, 1655 $(M-H)^-$], PMR, CMR, 2D NMR (COSY, H–C COSY), $C_{76}H_{120}O_{39} \cdot 4H_2O$ (EA).		Okabe et al., 1989
		Luperoside K (108)	Quillaic acid (15) 2 gal---glcUA (3β-OH) |3 ara 4 2 xyl---rha---qui (28-COOH) |3 rha	methyl ester: amorphous powder (EtOH), mp 242–244°, $[\alpha]_D^{28}$-18.2°(80% MeOH, c 1.30), FAB-MS [1563 $(M+Na)^+$], PMR, CMR, 2D NMR (COSY), $C_{71}H_{112}O_{36} \cdot 7/2H_2O$ (EA).		Okabe et al., 1989
		Luperoside L (109)	Quillaic acid (15) 2 gal---glcUA (3β-OH) |3 ara 3 4 2 xyl---xyl---rha---qui (28-COOH) |3 rha	methyl ester: amorphous powder (EtOH), mp 246–248°(dec.), $[\alpha]_D^{28}$-21.6°(70% MeOH, c 1.40), FAB-MS [1695 $(M+Na)^+$], PMR, CMR, $C_{76}H_{120}O_{40} \cdot 5H_2O$ (EA).		Okabe et al., 1989
42	*Madhuca butyracea* (Sapotaceae) (seeds)	Butyroside C (110)	Protobassic acid (13) glcUA (3β-OH) 3 4 2 rha---xyl---rha---ara (28-COOH)	powder (MeOH), mp 216-220°(dec.), $[\alpha]_D^{16}$-20°(MeOH, c 0.8), FAB-MS [1235 $(M-H)^-$], PMR, CMR, $C_{58}H_{92}O_{28}$.		Li et al., 1994
		Butyroside D (111)	16α-OH Protobassic acid (14) glcUA (3β-OH) 3 4 2 api(f)---xyl---rha---ara (28-COOH)	powder (MeOH), mp 213-215°(dec.), $[\alpha]_D^{16}$-53°(MeOH, c 1.03), FAB-MS [1237 $(M-H)^-$], PMR, CMR, $C_{57}H_{90}O_{29}$.		Li et al., 1994
43	*Melanthera scandens* (Asteraceae) (leaves)	Saponin 5 (112)	Oleanolic acid (11) 4 xyl---glcUA (3β-OH) glc (28-COOH)	methyl ester of acetylated: PMR, CMR, 2D NMR (COSY).		Penders & Delaude, 1994
44	*Meliosma lanceolata* (Sabiaceae) (barks)	(113)	Bayogenin (1) glcUA (3β-OH) glc (28-COOH)	methyl ester: $[\alpha]_D^{22}+20.5°$[MeOH, c 0.56], FAB-MS [863 $(M+Na)^+$], PMR, CMR, 2D NMR (COSY, HMBC), $C_{43}H_{68}O_{16}Na$ (pos. HR-FAB-MS).		Abe et al., 1996
		(114)	Bayogenin (1) glcUA (3β-OH) glc (28-COOH)	$[\alpha]_D^{22}+14.7°$[MeOH, c 1.09], FAB-MS [871 $(M+2Na)^+$], PMR, CMR, $C_{42}H_{65}O_{16} \cdot 2Na$ (pos. HR-FAB-MS).		Abe et al., 1996

		(115)	Bayogenin (1) 4 gal----glcUA (3β-OH) glc (28-COOH)	methyl ester: prisms, mp 220-230°, $[\alpha]_D^{26}+27.2°$[MeOH, c 0.53], FAB-MS [1025 $(M+Na)^+$], PMR, CMR, $C_{49}H_{78}O_{21}Na$ (pos. HR-FAB-MS).	Abe et al., 1996
		(116)	Bayogenin (1) 4 gal----glcUA (3β-OH) glc (28-COOH)	prisms, mp 290-300°(dec.), $[\alpha]_D^{27}+20.7°$[MeOH, c 1.19], FAB-MS [1011 $(M+Na)^+$], PMR, CMR, $C_{48}H_{76}O_{21}Na$ (pos. HR-FAB-MS).	Abe et al., 1996
		(117)	Bayogenin (1) 4 ara----glcUA (3β-OH) glc (28-COOH)	methyl ester: $[\alpha]_D^{26}+28.1°$[MeOH, c 0.26], FAB-MS [995 $(M+Na)^+$], PMR, CMR, 2D NMR (COSY), $C_{48}H_{76}O_{20}Na$ (pos. HR-FAB-MS).	Abe et al., 1996
		(118)	Hederagenin (7) 4 gal----glcUA (3β-OH) glc (28-COOH)	methyl ester: $[\alpha]_D^{26}+28.1°$[MeOH, c 0.26], FAB-MS [1009 $(M+Na)^+$], PMR, CMR, $C_{49}H_{78}O_{20}Na$ (pos. HR-FAB-MS).	Abe et al., 1996
		(119)	Hederagenin (7) 4 gal----glcUA (3β-OH) glc (28-COOH)	$[\alpha]_D^{21}+6.61°$[MeOH, c 0.59], FAB-MS [995 $(M+Na)^+$], PMR, CMR, $C_{48}H_{76}O_{19}Na$ (pos. HR-FAB-MS).	Abe et al., 1996
45	*Mimusops elengi* (Sapotaceae) (seed kernels)	Saponin 4 (120)	Protobassic acid (13) glcUA (3β-OH) 3 4 2 rha----xyl----rha----ara (28-COOH) |3 rha	$[\alpha]_D$-37.7°[MeOH, c 0.305], FAB-MS [1381.4 $(M-H)^-$], PMR, CMR, 2D NMR (COSY, HMQC, HOHAHA, ROESY), $C_{64}H_{101}O_{32}$ (neg. FAB-MS).	Lavaud et al., 1996
46	*M. hexandra* (seed kernels)	Saponin 5 (121)	16α-OH Protobassic acid (14) glcUA (3β-OH) 3 4 2 rha----xyl----rha----ara (28-COOH)	$[\alpha]_D$-49.4°[MeOH, c 0.563], FAB-MS [1275.6 $(M+Na)^+$], PMR, CMR, 2D NMR (COSY).	Lavaud et al., 1996
47	*Momordica cochinchinensis* (Cucurbitaceae) (seed kernels)	Momordica saponin I (122)	Gypsogenin (5) 2 gal----glcUA (3β-OH) |3 rha 3 3 2 xyl----glc----rha----fuc (28-COOH) |4 xyl	white powder (MeOH), mp 241-244°(dec.), $[\alpha]_D^{19}$-14.8°[MeOH–H_2O (1:2), c 0.7], IR.	Iwamoto et al., 1985
		Momordica saponin II (123)	Quillaic acid (15) 2 gal----glcUA (3β-OH) |3 rha 3 3 2 xyl----glc----rha----fuc (28-COOH) |4 xyl	white powder (MeOH), mp 252-255°(dec.), $[\alpha]_D^{19}$-28.5°[MeOH–H_2O (1:2), c 0.67], IR.	Iwamoto et al., 1985

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Table 1—Continued

No.	Source (family, part)	Saponin (No.)	Structure	Structural and spectral data	Bioactivity	Reference
	(roots)	Momordin IId (124)	Oleanolic acid (11) 2 xyl----glcUA (3β-OH) |3 xyl glc (28-COOH)	white powder (MeOH–EtOAc), $[\alpha]_D^{23}+1.98°$[MeOH, c 1.06], IR, SIMS [1097 $(M+K)^+$], PMR, CMR, $C_{52}H_{82}O_{22}\cdot H_2O$ (EA).		Kawamura et al., 1988
48	*Olax andronensis* *O. glabriflora* *O. psittacorum* (Olacaceae) (leaves, roots, barks)	Olaxoside (125)	Oleanolic acid (11) 4 rha----glcUA (3β-OH) glc (28-COOH)	colorless crystals [EtOH–H_2O (1:1)], mp 216-218°, $C_{48}H_{76}O_{18}\cdot H_2O$.	anti-inflammatory and laxative activities	Forgacs et al., 1981
49	*Panax japonicum* (Araliaceae) (rhizomes)	Chikusetsusaponin V (126)	Oleanolic acid (11) 2 glc----glcUA (3β-OH) glc (28-COOH)	white powder (MeOH–AcOEt), mp 240-241°, $[\alpha]_D^{22}+2.85°$[MeOH, c 2.01], IR, $C_{48}H_{76}O_{19}\cdot 2\ H_2O$ (EA).		Kondo, Marumoto, & Shoji, 1971
50	*P. pseudoginseng* subsp. *himalaicus* (rhizomes)	Pseudo-ginsenoside RT_1 (127)	Oleanolic acid (11) 2 xyl----glcUA (3β-OH) glc (28-COOH)	colorless needles (MeOH), mp 235–238°(dec.), $[\alpha]_D^{20}+8.4°$[MeOH, c 0.11], CMR, $C_{47}H_{74}O_{18}\cdot 4H_2O$ (EA).		Tanaka, Morita, Kasai, Kinouchi, Sanada, Ida, & Shoji, 1985
51	*P. pseudoginseng* subsp. *himalaicus* var. *angustifolius* (rhizomes)	Saponin C (128)	Oleanolic acid (11) glcUA (3β-OH) glc (28-COOH)	white powder (aqueous BuOH), mp 216°(dec.), $[\alpha]_D^{18}+15.8°$(MeOH, c 0.62), IR, $C_{42}H_{66}O_{14}\cdot 3H_2O$ (EA).		Kondo & Shoji, 1975
52	*P. stipuleanatus* (rhizomes)	Stipuleanoside R_2 (129)	Oleanolic acid (11) 3 glc----glcUA (3β-OH) |4 ara(f) glc (28-COOH)	white amorphous powder, mp 200–210°, CMR, $C_{53}H_{84}O_{23}\cdot 4H_2O$ (EA).		Yang, Jiang, Zhou, Kasai, & Tanaka, 1985
53	*Pisonia umbellifera* (Nyctaginaceae) (leaves)	Saponin 4 (130)	Oleanolic acid (11) 2 3 glc----xyl----glcUA (3β-OH) |2 glc glc (28-COOH)	$[\alpha]_D+2.3°(CD_3OD$, c 0.7), FAB-MS [1273 $(M+Na)^+$], PMR, CMR, 2D NMR (COSY, HOHAHA, HMQC, ROESY), $C_{59}H_{94}O_{28}$.		Lavaud et al., 1996
		Saponin 5 (131)	Oleanolic acid (11) glcUA (3β-OH) |3 O-CH (OCH_2COOH) COOH glc (28-COOH)	$[\alpha]_D+6.8°(CD_3OD$, c 0.3), FAB-MS [945.9 $(M+Na+H)^+$, 925.3 $(M-H)^-$], PMR, CMR, 2D NMR (COSY, HOHAHA, HMQC, HMBC), $C_{46}H_{70}O_{19}$.		Lavaud et al., 1996
54	*Polyscias scutellaria* (Araliaceae) (leaves)	Saponin C (132)	Oleanolic acid (11) 3 glc----glcUA (3β-OH) glc (28-COOH)	white powder, mp 260°, FAB-MS [955 $(M-H)^-$], $C_{48}H_{75}O_{19}$.		Paphassarang et al., 1989
		Polysciasaponin P_1 (133)	Oleanolic acid (11) 4 2 glc----glc----glcUA (3β-OH) glc (28-COOH)	white powder, mp 263°, FAB-MS [1117 $(M-H)^-$], CMR.		Paphassarang et al., 1990

55	*Pseudostellaria heterophylla* (Caryophyllaceae) (roots)	Pseudostellarinoside A (134)	Gypsogenin (5) 3 glc----glcUA (3β-OH) |4 glc glc (28-COOH)	white needles (MeOH), mp 278-280°, FAB-MS [1157 $(M+Na)^+$], CMR, 2D NMR (COSY, H–C COSY).	Wang, Xu, Zhang, Qiu, Su, Zhang, Chen, & Yao, 1992
56	*Putranjiva roxburghii* (Euphorbiaceae) (leaves)	Putranjiva saponin C (135)	Oleanolic acid (11) 2 3 rha----glc----glcUA (3β-OH) glc (28-COOH)	methyl ester: colorless crystals (MeOH–ether), mp 203-205°, $[\alpha]_D$-12.9°(MeOH, c 0.77), $C_{55}H_{90}O_{24}$ (EA).	Rangaswami & Seshadri, 1971; Seshadri & Rangaswami, 1975
		Putranjiva saponin D (136)	Oleanolic acid (11) 2 3 rha----glc----glcUA (3β-OH) |4 xyl glc (28-COOH)	methyl ester: colorless crystals (MeOH–ether), mp 196-199°, $[\alpha]_D$-18.6°(MeOH, c 0.975), $C_{60}H_{96}O_{20} \cdot 2H_2O$ (EA).	Rangaswami et al., 1971; Seshadri et al., 1975
	(seed coats)	Putranoside C (137)	Oleanolic acid (11) 3 rha----glcUA (3β-OH) glc (28-COOH)	methyl ester: mp 190-194°, $C_{49}H_{78}O_{18}$ (EA).	Hariharan, 1974
		Putranoside D (138)	Oleanolic acid (11) 3 rha----glcUA (3β-OH) |4 xyl glc (28-COOH)	methyl ester: mp 218-222°, $[\alpha]_D$-8.5°(MeOH), $C_{54}H_{86}O_{22} \cdot 2H_2O$ (EA).	Hariharan, 1974
57	*Quillaja saponaria* (Rosaceae) (barks)	QS-III (139)	Quillaic acid (15) 2 gal----glcUA (3β-OH) |3 xyl 3 4 2 api(f)----xyl----rha----fuc (28-COOH) |3 |3 glc 3,5-dihydroxy-6-methyl-octanoyl |5 3,5-dihydroxy-6-methyl-octanoyl |5 ara(f) |2 rha	amorphous powder, mp 203-206°(dec.), $[\alpha]_D$-37.5°[MeOH, c 1.23], IR, FAB-MS [2295 $(M-H)^-$], CMR, $C_{104}H_{168}O_{55} \cdot 8H_2O$ (EA).	Higuchi et al., 1987; Higuchi et al., 1988
58	*Salsola micranthera* (Chenopodiaceae)	Salsoloside E (140)	Oleanolic acid (11) 2 glc----glcUA (3β-OH) |4 xyl glc (28-COOH)		Annaev, Isamukhamedova, & Abubakirov, 1984
59	*Saponaria officinalis* (Caryophyllaceae) (roots)	Saponoside A (141)	Gypsogenin (5) glcUA (3β-OH) 3 glc----glc (28-COOH) |6 glc	mp 132–134°, $[\alpha]_D^{20}+35°$(MeOH, c 2).	Chirva & Kintya, 1970

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Table 1—Continued

No.	Source (family, part)	Saponin (No.)	Structure	Structural and spectral data	Bioactivity	Reference
		Saponoside D (142)	Gypsogenin (5) 2 3 gal----xyl----glcUA (3β-OH) |4 |4 ara rha 2 3 gal^a----xyl----fuc (28-COOH) |4 |4 glc^a rha			Lazur'evskii, Kintya, & Chirva, 1970
60	*Schefflera delavayi* (Araliaceae) (barks)	Scheffleraside II (143)	Oleanolic acid (11) glcUA (3β-OH) 4 6 rha----glc----glc (28-COOH)	mp 240–244°, PMR, CMR.		Jiang & Xiao, 1990
61	*Silene jenisseensis* (Caryophyllaceae) (roots)	(144)	Quillaic acid (15) 2 gal----glcUA (3β-OH) 2 2 glc----rha----fuc (28-COOH) |4 trans-p-methoxy cinnamoyl	amorphous powder, IR, UV, FAB-MS [1437 (M–H)$^-$], PMR, CMR, 2D NMR (COSY, HMQC, HMBC), $C_{70}H_{102}O_{31}$.	cyclooxygenase inhibitory activity	Lacaille-Dubois et al., 1995
		(145)	Quillaic acid (15) 2 gal----glcUA (3β-OH) 2 2 glc----rha----fuc (28-COOH) |4 cis-p-methoxy cinnamoyl	amorphous powder, IR, UV, FAB-MS [1437 (M–H)$^-$], PMR, CMR, 2D NMR (COSY, HMQC, HMBC), $C_{70}H_{102}O_{31}$.	cyclooxygenase inhibitory activity	Lacaille-Dubois et al., 1995
62	*S. rubicunda* (roots)	Rubicunoside A (146)	Quillaic acid (15) 2 gal----glcUA (3β-OH) |3 xyl 3 4 4 xyl----xyl----rha----fuc (28-COOH) 2/ \3 qui $COCH_3$ |2 $COCH_3$	colorless crystals (MeOH), mp 244–246°, $[\alpha]_D^{16}$-18.03°(pyrindine, c 1.1), IR, FAB-MS [1742 (M)$^-$], PMR, CMR, $C_{79}H_{122}O_{42}$.		Tan et al., 1995
		Rubicunoside B (147)	Quillaic acid (15) 2 gal----glcUA (3β-OH) |3 xyl 3 4 4 xyl----xyl----rha----fuc (28-COOH) 2/ \3 qui $COCH_3$ |4 glc	amorphous powder, $[\alpha]_D^{15}$-11.31°(pyrindine, c 1.5), IR, FAB-MS [1861 (M–H)$^-$], CMR, $C_{83}H_{130}O_{46}$.		Tan et al., 1996

		Rubicunoside C (148)	Quillaic acid (15) 2 gal----glcUA (3β-OH) |3 xyl 4 4 xyl----rha----fuc (28-COOH) |2 glc |4 $COCH_3$	amorphous powder, $[\alpha]_D^{16}$-15.97°(pyrindine, c 0.9), IR, FAB-MS [1585 $(M-H)^-$], CMR, $C_{72}H_{114}O_{38}$.	Tan et al., 1996
		Rubicunoside D (149)	Quillaic acid (15) 2 gal----glcUA (3β-OH) 3/ \6 xyl $OCH_2CH_2CH_2CH_3$ 3 4 4 xyl----xyl----rha----fuc (28-COOH) 2/ \3 qui $COCH_3$ |2 $COCH_3$	amorphous powder, $[\alpha]_D^{15}$-11.64°(pyrindine, c 1.5), IR, FAB-MS [1797 $(M-H)^-$], CMR.	Tan et al., 1996
63	*Silphium perfoliatum* (Compositae) (epigeal parts)	Silphioside A (150)	Oleanolic acid (11) glcUA (3β-OH) glc (28-COOH)	methyl ester: mp 197–199°, $[\alpha]_D^{25}$+4.5°(MeOH, c 1.0), PMR, $C_{43}H_{68}O_{14}$.	Davidyants, Putieva, Bandyukova, & Abubakirov, 1986
64	*Swartzia madagascariensis* (Leguminosea) (fruits)	Saponin 5 (151)	Oleanolic acid (11) 2 glc----glcUA (3β-OH) |3 rha glc (28-COOH)	white powder, mp 215–223°(dec.), FAB-MS [1101 $(M-H)^-$], PMR, CMR.	Borel & Hostettmann, 1987
65	*S. simplex* (leaves)	Saponin 2 (152)	Gypsogenin (5) glcUA (3β-OH) glc (28-COOH)	mp 220–235°(dec.), FAB-MS [807 $(M-H)^-$], CMR.	Borel, Gupta, & Hostettmann, 1987
		Saponin 5 (153)	Oleanolic acid (11) 4 glc----glcUA (3β-OH) glc (28-COOH)	mp 200–208°(dec.), FAB-MS [955 $(M-H)^-$], CMR.	Borel et al., 1987
		Saponin 6 (154)	Oleanolic acid (11) 2 xyl----glcUA (3β-OH) |3 rha glc (28-COOH)	mp 248–258°(dec.), FAB-MS [1071 $(M-H)^-$], CMR.	Borel et al., 1987
66	*Talinum tenuissimum* (Portulacaceae) (tubers)	(155)	Oleanolic acid (11) 3 xyl----glcUA (3β-OH) glc (28-COOH)	white powder, mp 270–275°(dec.), $[\alpha]_D^{22}$+4°(MeOH, c 1.0), FAB-MS [925 $(M-H)^-$], CMR.	Gafner et al., 1985
67	*T. triangulare* (roots)	Talinumoside I (156)	Methyl spergulagenate (18) glcUA (3β-OH) glc (28-COOH)	white powder, $[\alpha]_D$+57.5°(pyrindine, c 0.8), FAB-MS [837 $(M-H)^-$], CMR, $C_{43}H_{66}O_{16} \cdot 5H_2O$ (EA).	Kohda et al., 1992

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Table 1—Continued

No.	Source (family, part)	Saponin (No.)	Structure	Structural and spectral data	Bioactivity	Reference
68	*Tetrapanax papyriferum* (Araliaceae) (roots)	R-Ia (157)	Oleanolic acid (11) 2 gal----glcUA (3β-OH) |4 ara(f) glc (28-COOH)	methyl ester: colorless needles (MeOH), mp 226-228°, $[\alpha]_D^{22}$-21.8°(MeOH, c 0.5), IR, PMR, CMR, $C_{54}H_{86}O_{23} \cdot 3H_2O$ (EA).		Takabe, Takeda, Chen, & Ogihara, 1985
		R-Ib (158)	Oleanolic acid (11) 4 ara----glcUA (3β-OH) 4 6 rha----glc----glc (28-COOH)	methyl ester: white prisms (MeOH), mp 203–205°, $[\alpha]_D^{22}$-27.0°(MeOH, c 0.6), IR, PMR, CMR, $C_{60}H_{96}O_{27} \cdot 4H_2O$ (EA).		Takabe et al., 1985
		R-Ic (159)	Oleanolic acid (11) 2 gal----glcUA (3β-OH) glc (28-COOH)	methyl ester: white powder, mp 190–193°, $[\alpha]_D^{22}$-8.7°(MeOH, c 0.5), IR, PMR, CMR, $C_{49}H_{78}O_{19} \cdot 3H_2O$ (EA).		Takabe et al., 1985
69	*Thladiantha dubia* (Cucurbitaceae) (tubers)	Dubioside A (160)	Quillaic acid (15) 2 gal----glcUA (3β-OH) 2 rha----ara (28-COOH)	methyl ester: amorphous powder, mp 210-215°(dec.), $[\alpha]_D^{25}$-31.9°(MeOH, c 2.7), FAB-MS [1139 $(M+Na)^+$], PMR, CMR, $C_{54}H_{84}O_{24} \cdot 3H_2O$ (EA).		Nagao, Okabe, Mihashi, & Yamauchi, 1989
		Dubioside B (161)	Quillaic acid (15) 2 gal----glcUA (3β-OH) 4 2 xyl----rha----ara (28-COOH)	methyl ester: fine needles (MeOH), mp 225-226°, $[\alpha]_D^{24}$-26.1°(MeOH, c 1.0), FAB-MS [1271 $(M+Na)^+$)], PMR, CMR, $C_{59}H_{92}O_{28} \cdot 3H_2O$ (EA).		Nagao et al., 1989
		Dubioside C (162)	Quillaic acid (15) 2 gal----glcUA (3β-OH) 3 4 2 xyl----xyl----rha----ara (28-COOH)	methyl ester: fine needles (MeOH), mp 229-231°, $[\alpha]_D^{24}$-27.6°(70% MeOH, c 0.8), FAB-MS [1403 $(M+Na)^+$], PMR, CMR, $C_{64}H_{100}O_{32} \cdot 2H_2O$ (EA).		Nagao et al., 1989
70	*T. hookeri* var. *pentadactyla* (tubers)	Thladioside-H1 (163)	Gypsogenin (5) 2 gal----glcUA (3β-OH) 3 4 2 xyl----xyl----rha----xyl (28-COOH)	white powder, $[\alpha]_D^{22}$+3.8°(H_2O, c 0.89), IR, PMR, CMR, $C_{63}H_{98}O_{31} \cdot 2H_2O$ (EA).		Nie et al., 1989
71	*Tragopogon porrifolius* (Compositae) (roots)	Tragopogonsaponin B (164)	Echinocystic acid (3) glcUA (3β-OH) xyl (28-COOH) |2 4 CO-CH=CH-$\varnothing$----OH	methyl ester: amorphous powder, $[\alpha]_D^{25}$+24.9°(MeOH, c 1.27), UV, FAB-MS [963 $(M+Na)^+$], PMR, CMR, $C_{51}H_{72}O_{16} \cdot 3H_2O$ (EA).		Warashina et al., 1991
		Tragopogonsaponin C (165)	Echinocystic acid (3) glcUA (3β-OH) xyl (28-COOH) |2 4 CO-CH=CH-$\varnothing$----OH \3 OMe	methyl ester: amorphous powder, $[\alpha]_D^{25}$+24.3°(MeOH, c 0.9), UV, FAB-MS [993 $(M+Na)^+$], PMR, CMR, 2D NMR (NOEDS), $C_{52}H_{74}O_{17} \cdot 2H_2O$ (EA).		Warashina et al., 1991

Tragopogonsaponin D (166)	Echinocystic acid (3) glcUA (3β-OH) xyl (28-COOH) |2 4 CO-CH=CH-$\varnothing$----Oglc \3 OMe	methyl ester: amorphous powder, $[\alpha]_D^{25}$-4.4°(MeOH, c 0.6), UV, FAB-MS [1155 $(M+Na)^+$], PMR, CMR, 2D NMR (NOEDS), $C_{58}H_{84}O_{22} \cdot 3H_2O$ (EA).	Warashina et al., 1991
Tragopogonsaponin E (167)	Echinocystic acid (3) glcUA (3β-OH) ara (28-COOH) |2 4 CO-CH=CH-$\varnothing$----Oglc \3 OMe	methyl ester: amorphous powder, $[\alpha]_D^{25}$+7.3°(MeOH, c 1.1), UV, FAB-MS [1155 $(M+Na)^+$], PMR, CMR, $C_{58}H_{84}O_{22} \cdot 7/2H_2O$ (EA).	Warashina et al., 1991
Tragopogonsaponin F (168)	Echinocystic acid (3) glcUA (3β-OH) 3 glc----xyl (28-COOH) |2 4 CO-CH=CH-$\varnothing$----OH	methyl ester: amorphous powder, $[\alpha]_D^{25}$+20.9°(MeOH, c 1.29), UV, FAB-MS [1125 $(M+Na)^+$], PMR, CMR, 2D NMR (NOEDS), $C_{57}H_{82}O_{21} \cdot 4H_2O$ (EA).	Warashina et al., 1991
Tragopogonsaponin G (169)	Echinocystic acid (3) glcUA (3β-OH) 3 glc----xyl (28-COOH) |2 4 CO-CH_2-CH_2-$\varnothing$----OH	methyl ester: amorphous powder, $[\alpha]_D^{25}$-11.7°(MeOH, c 0.95), UV, FAB-MS [1127 $(M+Na)^+$], PMR, CMR, $C_{57}H_{84}O_{21} \cdot 3H_2O$ (EA).	Warashina et al., 1991
Tragopogonsaponin H (170)	Echinocystic acid (3) glcUA (3β-OH) 3 glc----ara (28-COOH) |2 4 CO-CH=CH-$\varnothing$----OH	methyl ester: amorphous powder, $[\alpha]_D^{25}$+7.2°(MeOH, c 0.65), UV, FAB-MS [1125 $(M+Na)^+$], PMR, CMR, 2D NMR (NOEDS), $C_{57}H_{82}O_{21} \cdot 5/2H_2O$ (EA).	Warashina et al., 1991
Tragopogonsaponin I (171)	Echinocystic acid (3) glcUA (3β-OH) 3 glc----ara (28-COOH) |2 4 CO-CH_2-CH_2-$\varnothing$----OH	methyl ester: amorphous powder, FAB-MS [1127 $(M+Na)^+$], PMR, CMR.	Warashina et al., 1991
Tragopogonsaponin J (172)	Echinocystic acid (3) glcUA (3β-OH) 3 glc----ara (28-COOH) |2 4 CO-CH_2-CH_2-$\varnothing$----OH \3 OMe	methyl ester: amorphous powder, FAB-MS [1157 $(M+Na)^+$], PMR, CMR.	Warashina et al., 1991
Tragopogonsaponin N (173)	Echinocystic acid (3) glcUA (3β-OH) 3 glc----xyl (28-COOH) |2 4 CO-CH=CH-$\varnothing$----Oglc	methyl ester: amorphous powder, $[\alpha]_D^{25}$-6.7°(MeOH, c 0.5), UV, FAB-MS [1287 $(M+Na^+)$], PMR, CMR, 2D NMR (NOEDS), $C_{63}H_{92}O_{26} \cdot 6H_2O$ (EA).	Warashina et al., 1991

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Table 1—Continued

No.	Source (family, part)	Saponin (No.)	Structure	Structural and spectral data	Bioactivity	Reference
		Tragopogonsaponin O (174)	Echinocystic acid (3) glcUA (3β-OH) 3 glc----xyl (28-COOH) |2 4 CO-CH_2-CH_2-∅----Oglc	methyl ester: amorphous powder, $[\alpha]_D^{25}$ 0°(MeOH, c 0.4), UV, FAB-MS [1289 $(M+Na)^+$], PMR, CMR, 2D NMR (NOEDS), $C_{63}H_{94}O_{26} \cdot 11/2H_2O$ (EA).		Warashina et al., 1991
		Tragopogonsaponin P (175)	Echinocystic acid (3) glcUA (3β-OH) 3 glc----ara (28-COOH) |2 4 CO-CH_2-CH_2-∅----Oglc	methyl ester: amorphous powder, $[\alpha]_D^{25}$-7.2°(MeOH, c 0.9), UV, FAB-MS [1289 $(M+Na)^+$], PMR, CMR, 2D NMR (NOEDS), $C_{63}H_{94}O_{26} \cdot 11/2H_2O$ (EA).		Warashina et al., 1991
		Tragopogonsaponin R (176)	Echinocystic acid (3) glcUA (3β-OH) 3 glc----ara (28-COOH) |2 4 CO-CH_2-CH_2-∅----Oglc \3 OMe	methyl ester: amorphous powder, $[\alpha]_D^{25}$-12.3°(MeOH, c 0.5), UV, FAB-MS [1319 $(M+Na)^+$], PMR, CMR, 2D NMR (NOEDS), $C_{64}H_{96}O_{27} \cdot 9/2H_2O$ (EA).		Warashina et al., 1991
72	*T. pratensis* (whole plants)	Tragopogonoside A (177)	Echinocystic acid (3) glcUA (3β-OH) xyl (28-COOH)	methyl ester: amorphous powder, $[\alpha]_D^{24}$-21.9°(MeOH, c 0.48), FAB-MS [817 $(M+Na)^+$], PMR, CMR, 2D NMR (NOES), $C_{42}H_{66}O_{14} \cdot 3/2H_2O$ (EA).		Miyase et al., 1992
		Tragopogonoside C (178)	Echinocystic acid (3) 2 gal----glcUA (3β-OH) xyl (28-COOH)	methyl ester: amorphous powder, $[\alpha]_D^{24}$-16.3°(MeOH, c 1.63), FAB-MS [979 $(M+Na)^+$], PMR, CMR, 2D NMR (NOES), $C_{48}H_{76}O_{19} \cdot 7/2H_2O$ (EA).		Miyase et al., 1992
		Tragopogonoside D (179)	Echinocystic acid (3) glcUA (3β-OH) 3 glc----xyl (28-COOH)	methyl ester: amorphous powder, $[\alpha]_D^{23}$-27.8°(MeOH, c 0.45), FAB-MS [979 $(M+Na)^+$], PMR, CMR, 2D NMR (NOES), $C_{48}H_{76}O_{19} \cdot 2H_2O$ (EA).		Miyase et al., 1992
		Tragopogonoside E (180)	Echinocystic acid (3) 2 gal----glcUA (3β-OH) 3 glc----xyl (28-COOH)	methyl ester: amorphous powder, $[\alpha]_D^{24}$-22.9°(MeOH, c 0.35), FAB-MS [1141 $(M+Na)^+$], PMR, CMR, $C_{54}H_{86}O_{24} \cdot 11/2H_2O$ (EA).		Miyase et al., 1992
		Tragopogonoside F (181)	Echinocystic acid (3) 2 gal----glcUA (3β-OH) 3 glc----xyl (28-COOH) |2 4 CO-CH=CH-∅----OH	methyl ester: amorphous powder, $[\alpha]_D^{24}$+1.3°(MeOH, c 1.16), UV, FAB-MS [1288 $(M+Na)^+$], PMR, CMR.		Miyase et al., 1992

		Tragopogonoside G (182)	Echinocystic acid (3) 2 gal----glcUA (3β-OH) xyl (28-COOH) |2 4 CO-CH=CH-∅----OH	methyl ester: amorphous powder, FAB-MS [1125 $(M+Na)^+$], PMR, CMR.		Miyase et al., 1992
		Tragopogonoside H (183)	Echinocystic acid (3) 2 gal----glcUA (3β-OH) xyl (28-COOH) |2 4 CO-CH=CH-∅----OH \3 OMe	methyl ester: amorphous powder, FAB-MS [1153 $(M+Na)^+$], PMR, CMR.		Miyase et al., 1992
73	*Ullucus tuberosus* (Basellaceae) (tubers)	Tuberoside B (184)	Oleanolic acid (11) 2 xyl----glcUA (3β-OH) |4 glc glc (28-COOH)	sodium/choline salt: microcrystalline white powder, mp 203–206°, FAB-MS [1111 $(M \cdot Na+H)^+$, 1087 $(M)^-$], PMR, CMR, 2D NMR (COSY, HMQC, HMBC, ROESY), $C_{53}H_{84}O_{23}Na$ (pos. HR-FAB-MS).	hypoglucaemic activity	Espada et al., 1996
		Tuberoside C (185)	Hederagenin (7) 2 xyl----glcUA (3β-OH) |4 glc glc (28-COOH)	sodium/choline salt: FAB-MS [1149 $(M \cdot Na+Na)^+$], PMR, CMR, $C_{53}H_{83}O_{24}Na_2$ (pos. HR-FAB-MS).	hypoglucaemic activity	Espada et al., 1996

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Table 1—Continued

No.	Source (family, part)	Saponin (No.)	Structure	Structural and spectral data	Bioactivity	Reference
74	*Vaccaria segetalis* (Caryophyllaceae)	Vaccegoside B (186)	Gypsogenin (5) 2 gal----glcUA (3β-OH) 3/ \6 gal ara 4 3 xyl----rha----fuc (28-COOH)			Baeva, Karryev, & Abubakirov, 1975
		Vaccegoside C (187)	Gypsogenin (5) 2 gal----glcUA (3β-OH) 3/ |4 \6 gal xyl ara 3 4 3 rha----xyl----rha----fuc (28-COOH) |4 qui			Baeva, Karryev, & Abubakirov, 1976
75	*Viscaria viscosa* (Caryophyllaceae)	Viscoside (188)	Gypsogenin (5) 2 3 xyl----gal----glcUA (3β-OH) 2/ \4 xyl gal 2 2 glc----rha----fuc (28-COOH)			Bukharov, Chirva, & Bukharova, 1975
76	*Ximenia americana* (Olacaceae) (roots)	(189)	Oleanolic acid (11) 2 3 rha----galUA----glcUA (3β-OH) glc (28-COOH)			Agostino, Biagi, Simone, & Pizza, 1994
77	*Zanha africana* (Sapindaceae) (root barks)	Zanhasaponin A (190)	Zanhic acid (19) glcUA (3β-OH) 2 rha----rha (28-COOH)	crystals, mp 245–247°, $[\alpha]_D$-9°(MeOH, c 0.1), CMR.	anti-inflammatory activity	Cuellar et al., 1997
		Zanhasaponin B (191)	Zanhic acid (19) glcUA (3β-OH) 2 2 xyl----rha----rha (28-COOH)	amorphous, mp 258–260°, $[\alpha]_D$+6°(MeOH, c 0.1), CMR.	anti-inflammatory activity	Cuellar et al., 1997
		Zanhasaponin C (192)	Zanhic acid (19) glcUA (3β-OH) 3 2 2 xyl----xyl----rha----rha (28-COOH)	amorphous, mp 260–262°, $[\alpha]_D$+3°(MeOH, c 0.1), CMR.	anti-inflammatory activity	Cuellar et al., 1997

[a] It can be interchangeable.

tral techniques during the 1980s; (3) spectral means which are predominant during the 1990s.

Chemical investigations on triterpenoid saponins began in the 19th century. But their structural elucidations started only from the 30s of the 20th century on. Since the late 1960s various spectroscopic methods including IR, UV, NMR, MS, CD, X-ray have been wildly applied to determine structures of natural products. Especially since the 1980s a lot of structures of complicated triterpenoid saponins have been published constantly along with the development of various separation and purification technologies, and they became a good model of structural elucidation of natural products, fully using various chemical, enzymatic and spectral methods.

With regard to the structural elucidation of GOTCAB in this review newer chemical, enzymatic and spectral means are discussed, structural study strategies in different periods are compared, and the main characteristics of NMR spectral data are summarized. A systematic method used in their structural elucidation is also proposed. Finally a compilation of GOTCAB during 1962–1997 along with their occurrence, structural data and bioactivity is included (see Table 1).

2. Structural study strategies in different periods

2.1. The initial period (1960s–1970s)

The structures of GOTCAB which were determined during this period were quite simple, and the amounts available were small. They were mostly determined according to the following steps in which chemical methods are predominant (Hariharan & Rangaswami, 1970; Kochetkov, Khorlin, & Ovodov, 1963):

(1) Acid hydrolysis afforded aglycones and sugars. Aglycones were identified with authentic samples by means of their mp and TLC, and sugars were examined in PC.

(2) Permethylation and methanolysis gave methylated monosaccharides, which were identified with authentic samples by means of their corresponding derivatives in PC.

(3) Partial acid and basic hydrolysis yielded 3-prosapogenins and 28-oligosaccharides, of which the former were determined using steps (1) and (2).

(4) Periodate oxidation, $LiAlH_4$ or $NaBH_4$ reduction and partial hydrolysis gave 3, 28-prosapogenins in reduced aglycones, which were determined using steps (1) and (2).

(5) Methylation and reduction afforded 3-methylated prosapogenins in reduced aglycones, 3- and 28-methylated oligosaccharides which were determined using step (2).

(6) With regard to the configuration at the anomeric carbons of sugar units it is a general observation that D-sugars occur with β-glycosidic linkages and L-sugars with α-glycosidic linkages. Compared with observed and calculated values of molecular rotation on the basis of Klyne's rule, configurations of sugars could be deduced.

2.2. The developing period (1980s)

During this period chemical methods have been widely used together with spectral techniques:

(1) PMR and CMR assignments of GOTCAB were increasingly reported following the development of various NMR techniques. Glycosylation and esterification shift rules as well as CMR data comparison were widely used to determine interglycosidic linkages, attached positions of sugar chains to aglycones and acyl groups to sugar chains, and compositions of sugars (Higuchi, Tokimitsu, & Komori, 1988; Gafner, Msonthi, & Hostettmann, 1985). Anomeric configurations were deduced by J values of anomeric proton signals in PMR (Nie, Morita, Kasai, Zhou, Wu, & Tanaka, 1984).

(2) Various MS techniques (i.e. negative FAB-MS, positive FAB-MS, FD-MS, SI-MS, EI-MS) were applied to establish molecular formulas and sugar sequences of saponins and their derivatives (Okabe, Nagao, Hachiyama, & Yamauchi, 1989; Kawamura, Watanabe, & Oshio, 1988; Higuchi, Tokimitsu, & Komori, 1988).

(3) In order to analyze sugar sequences, methylated alditol acetates were detected by GC-MS after methylated monosaccharides were subjected to reduction with $NaBH_4$ followed by acetylation (Nie et al., 1984). Aglycones and prosapogenins were elucidated by comparison with authentic samples (TLC, PMR, CMR, MS) (Shimizu, Ishihara, Umehara, Miyase, & Ueno, 1988; Iwamoto, Okabe, Yamauchi, Tanaka, Rokutani, Hara, Mihashi, & Higuchi, 1985; Gafner et al., 1985).

2.3. The present period (1990s)

During this period various homo- and heteronuclear 2D NMR techniques including COSY, TOCSY, relayed COSY, ^{1}H-^{13}C COSY, HMQC, HSQC, COLOC, HMBC, NOEDS, NOESY, ROESY, HOHAHA, DDS were widely applied to determine sugar residues, sequences, interglycosidic linkages as well as aglycone structures, attached positions of sugar chains to aglycones as well as acyl groups to sugar chains. Therefore, complete assignments of carbon signals and partial elucidations of proton coupling networks were continuously reported in the literatures (Lacaille-Dubois et al., 1993; Fujioka, Nagao, Okabe, & Mihashi, 1992; Nagao, Tanaka, Iwase, & Okabe, 1993; Nagao, Tanaka, & Okabe, 1991; Nagao, Tanaka, Shimokawa, & Okabe, 1991; Frechet, Christ, Sorbier, Fischer, & Vuilhorgne, 1991; Schroder, Schubert-Zsilavecz, Reznicek, Cart, Jur-

enitsch, & Haslinger, 1993; Amimoto, Yoshikawa, & Arihara, 1993; Shao, Poobrasert, Ho, Chin, & Cordell, 1996; Nagao, Tanaka, & Okabe, 1991; Lavaud, Massiot, Becchi, Misra, & Nigan, 1996; Lavaud, Beauviere, Massiot, Men-Olivier, & Bourdy, 1996; Lacaille-Dubois, Hanquet, Cui, Lou, & Wagner, 1995; Warashina, Miyase, & Ueno, 1991; Espada et al., 1996).

3. Newer chemical and enzymatic degradation reactions

3.1. Chemical reactions

Since the middle 1970s more efforts have been made to introduce new chemical methods to obtain genuine aglycones, 3- and 28-prosapogenins, 3- and 28-oligosaccharides. The following methods have successively been used: (1) selective cleavages of 3-glucuronides to afford aglycones and 3-oligosaccharides as well as 28-prosapogenins including photolysis (Kitagawa, Yoshikawa, Imakura, & Yosioka, 1974), lead tetraacetate oxidation followed by alkali treatment (Kitagawa, Yoshikawa, Im, & Ikenishi, 1977; Kitagawa, Yoshikawa, & Kadota, 1978; Kitagawa, Kamigauchi, Ikeda, & Yoshikawa, 1984), acetic anhydride and pyridine treatment (Kitagawa, Ikenishi, Yoshikawa, & Im, 1977), acetic anhydride and triethylamine (Iwamoto et al., 1985), anodic oxidation (Kitagawa, Kamigauchi, Ohmori, & Yoshikawa, 1980), diazomethane–ether treatment in methanol (Higuchi, Tokimitsu, Hamada, Komori, & Kawasaki, 1985; Higuchi, Tokimitsu, & Komori, 1988), thermal degradation (Huguchi, Kitamura, & Komori, 1986); (2) selective cleavages of 28-ester glycosidic linkages to give 3-prosapogenins and 28-oligosaccharides including treatment with anhydrous LiI, 2,6-lutidine and anhydrous methanol (Ohtami, Mizutani, Kasai, & Tanaka, 1984), and hydrothermolysis with water or water/1,4-dioxane (Kim, Higuchi, & Komori, 1992). Especially treatment with anhydrous LiI, 2,6-lutidine and anhydrous methanol has widely been used; hydrothermolysis with water or water/1,4-dioxane, a newer method, will be discussed in more detail.

Kim et al. (1992) found that heating of water-soluble and water-insoluble glycosides including triterpenoid and steroid glycosides with water and water/1,4-dioxane, respectively, at 100° to 140° causes cleavage of the glycosidic linkages to give the corresponding aglycones and prosapogenins. For example, DS-2 (**193**), which is a desacylsaponin isolated from *Quillaja saponaria* (Higuchi, Tokimitsu, Fujioka, Komori, Kawasaki, & Oakenful, 1987), has been heated with H_2O at 100° for 17 h and afforded its 3-prosapogenin (**194**) and reduced 28-oligosaccharide (**195**) in good yield (Fig. 2). Therefore, they thought that hydrothermolysis of triterpenoid 3,28-*O*-bisdesmosides leads to selective cleavage of their ester glycosidic linkages to give their 3-prosapogenins and reduced 28-sugar moieties.

3.2. Enzymatic hydrolysis

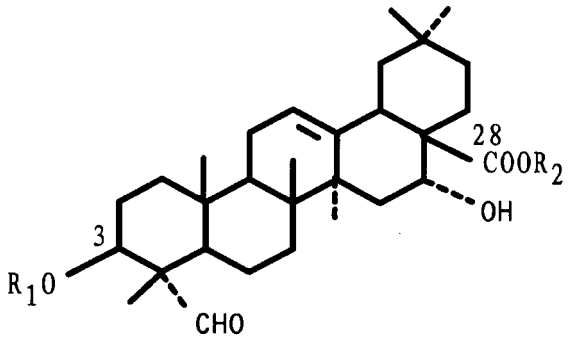
Since 1985 six enzymes have been used in enzymatic hydrolysis of GOTCAB. Using cellulase followed by methylation with CH_2N_2, aster saponin Hc methyl ester (**50**) liberated its 3-prosapogenins and 28-prosapogenins (Tanaka, Nagao, Okabe, & Yamauchi, 1990); with the same cellulase lucyoside N (**104**) provided its 3,28-prosapogenins after cleavage of the terminal sugars (gal and glc) (Yoshikawa et al., 1991); and 28-methyl protrioside of momordica saponin I (**122**) and II (**123**) yielded monosaccharide moieties following cellulase hydrolysis (Iwamoto et al., 1985). β-D-Glucuronidase eliminated 3-sugar chain and/or 28-terminal xyl from foetidissimoside A (**62**) and thladioside-H1 (**163**), to obtain 28-prosapogenins (Dubois, Bauer, Cagiotti, & Wagner, 1988; Nie, Tanaka, Miyakoshi, Kasai, Morita, Zhou, & Tanaka, 1989). β-Glucosidase and β-glucuronidase were applied to successively hydrolyze saponin C (**132**) and polysciasaponin P_1 (**133**) to produce aglycones (Paphassarang, Raymaud, Lussignol, & Becchi, 1989; Paphassarang, Raymaud, Lussignol, & Cabalion, 1990). On enzymatic hydrolysis with crude hesperidinase talinumoside I (**156**) and thaldioside-H1 (**163**) liberated their aglycones (Kohda, Yamaoka, Morinaga, Ishak, & Darise, 1992; Nie et al., 1989). On treatment with crude pectinase achyranthoside A (**5**) and tarasaponin IV (**15**) liberated its glucose ester to afford its 3-prosapogenins (Ida et al., 1994; Satoh, Sakai, Katsumata, Nagasao, Miyakoshi, Ida, & Shoji, 1994).

Glycyrrhizinic acid hydrolase produced by *Aspergillus niger* selectively hydrolyzes the 3-*O*-β-D-glucuronide linkages of GOTCAB with free 4-OH and 6-COOH in the glucuronide moiety to give 3-oligosaccharides and 28-prosapogenins (Muro, Kuramoto, Imoto, & Okada, 1986; Sasaki, Morita, Kuramoto, Mizutani, Ikeda, & Tanaka, 1988; Ohtani, Ogawa, Kasai, Yang, Yamasaki, Zhou, & Tanaka, 1992). For example, saponins (**196**–**200**) afforded the common 28-prosapogenin (**201**) and different 3-oligosaccharides (**202**–**206**) (Fig. 3). In the structural elucidation of rubicunoside A (**207**) isolated from *Silene rubicunda* we successfully utilized glycyrrhizinic acid hydrolase to obtain its aglycone quillaic acid (**208**), 3-oligosaccharides (**209**–**210**) and three 28-prosapogenins (**211**–**213**). The last two 28-prosapogenins (**212**–**213**) indicated that the enzyme selectively eliminated the terminal xylose and acetyl group, which was a new characteristic of the hydrolase (Tan, Zhao, Zhou, & Chen, 1995) (Fig. 3).

4. Newer spectral techniques and characteristics of NMR data

4.1. MS

Mass spectra were used to establish molecular formulas and sugar sequences of saponins and their derivatives.

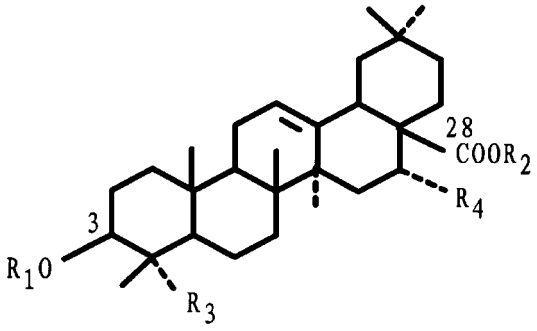


	R_1	R_2
193	glcUA(2)----gal(3)|xyl	fuc(2)----rha(4)----xyl(3)|glc----api(f)
194	glcUA(2)----gal(3)|xyl	H
195*		(α and β) fuc(2)----rha(4)----xyl(3)|glc----api(f)

$$(193) \xrightarrow[100°C,\ 17\ hrs]{H_2O} (194) + (195)$$

(100 mg) (54 mg) (40 mg)

Fig. 2. Hydrothermolysis of DS-2 (**193**) by mere heating with water solution (*indicates 28-oligosaccharides).



	R_1	R_2	R_3	R_4
196	glcUA 2	glc	CH_3	H
197	glcUA----glc 2	glc	CH_3	H
198	glcUA----xyl 3	glc	CH_3	H
199	glcUA----ara 2	glc	CH_3	H
200	glcUA----glc |3 ara	glc	CH_3	H
201	H	glc	CH_3	H
202*	glcUA 2			
203*	glcUA----glc 2			
204*	glcUA----xyl 3			
205*	glcUA----ara 2			
206*	glcUA----glc |3 ara			

Fig. 3. Structures of compounds (**196–213**) (*indicates 3-oligosaccharides).

207	2 glcUA----gal |3 xyl	4 4 3 fuc----rha----xyl----xyl |2 \3 qui $COCH_3$ |2 $COCH_3$	CHO	OH
208	H	H	CHO	OH
209*	2 (β-OH)glcUA----gal |3 xyl			
210*	2 (α-OH)glcUA----gal |3 xyl			
211	H	4 4 3 fuc----rha----xyl----xyl |2 \3 qui $COCH_3$ |2 $COCH_3$	CHO	OH
212	H	4 4 3 fuc----rha----xyl----xyl |2 \3 qui $COCH_3$	CHO	OH
213	H	4 4 fuc----rha----xyl |2 \3 qui $COCH_3$	CHO	OH

Fig. 3. Continued.

Usually molecular weights and formulas of this kind of saponins were taken by fast atom bombardment mass spectrometry (FAB-MS, negative- or positive-ion mode) together with some important fragment ions relative to sequences of sugar chains; they were also measured by FD-MS; but molecular weights and formulas of their aglycones were often recorded by EI-MS (Okabe et al., 1989; Higuchi et al., 1988; Tan et al., 1995; Tan, Zhou, Zhao, & Chen, 1996). Sometimes their trimethylsilyl ether (TMSi) derivatives exhibited fragment ions of terminal sugars (Nie et al., 1984).

4.2. NMR

During the 1990s various 1D- and 2D-NMR techniques have been utilized to determine structures of GOTCAB:

(1) Structures of aglycones were elucidated with PMR, CMR, distortionless enhancement by polarization transfer (DEPT), ^{1}H–^{1}H shift correlation spectroscopy (^{1}H–^{1}H COSY or COSY), total correlation spectroscopy (TOCSY), ^{1}H-detected heteronuclear multiple bond coherence spectrum (HMBC), ^{1}H nuclear Overhauser enhancement and exchange spectroscopy (NOESY), rotating frame nuclear Overhauser enhancement and exchange spectroscopy (ROESY) (Schroder et al., 1993).

(2) Proton coupling networks of sugar moieties were indicated with PMR, COSY, TOCSY, one-dimensional homonuclear Hartmann–Hahn spectrum (1D-HOHAHA), decoupling difference spectrum (DDS); and their assignments of carbon signals were deduced with CMR, DEPT, ^{1}H–^{13}C COSY, ^{1}H–^{13}C relayed COSY, ^{1}H-detected heteronuclear multiple-Quantum coherence spectrum (HMQC), DEPT-HMQC, heteronuclear single quantum coherence spectrum (HSQC) (Lacaille-Dubois et al., 1993; Fujioka et al., 1992; Miyase, Sutoh, Zhang, & Ueno, 1996; Nagao et al., 1991; Frechet et al., 1991; Schroder et al., 1993; Shao et al., 1996).

(3) Sequences and interglycosidic linkages of sugar moieties, and attached positions of sugar chains to aglycones as well as acyl groups to sugar chains were determined with nuclear Overhauser effect difference spectrum (NOEDS), rotating-frame Overhauser effect difference spectrum (ROEDS), NOESY, ROESY, selective 1D ROESY, selective 1D NOESY, DDS, HMBC (Lacaille-Dubois et al., 1993; Fujioka et al., 1992; Nagao et al., 1991; Nagao et al., 1991; Schroder et al., 1993; Amimoto, Yoshikawa, & Arihara, 1992; Shao et al., 1996).

4.2.1. ^{13}C NMR characteristics of GOTCAB aglycones

In comparison with data in the references, we selected the typical data of 18 aglycones and their derivatives including aglycones of 3-prosapogenins and 28-prosapogenins as well as 3,28-saponins shown in Table 2. From Table 2 we summarized some CMR characteristics of GOTCAB aglycones as follows:

(1) Values of 3-glycosylation shifts are about 8.8–12.8 ppm, i.e. C_3 δ values *down*shift from 71.6–78.4 to 81.8–90.5 ppm. Meantime C_2 and C_4 *up*shift about 0.0–2.0 ppm, and C_{23}, C_{24} *down*shift about 0.4–3.1 ppm only when C_{23}–CH_3 was replaced by CHO, respectively (Kohda, Tanaka, Yamaoka, & Ohhara, 1991; Shimizu et al., 1988; Nie et al., 1984; Amimoto et al., 1993; Li, Liu, Wang, Yang, Nigam, & Misra, 1994; Abe, Yamauchi, Shibuya, & Kitagawa, 1996; Iwamoto et al., 1985; Tan et al., 1995; Kohda et al., 1992; Nie et al., 1989; Warashima et al., 1991).

(2) Values of 28-glycosylation shifts are about 2.9–4.3 ppm, i.e. C_{28} δ values *up*shift from 179.9–181.0 to 175.6–177.6 ppm (Kohda et al., 1991; Shimizu et al., 1988; Nie et al., 1984; Amimoto et al., 1993; Li et al., 1994; Abe et al., 1996; Iwamoto et al., 1985; Tan et al., 1995; Kohda et al., 1992; Nie et al., 1989; Warashima et al., 1991).

(3) When C_{23}–αCH_3 was replaced with CHO, C_{23} and C_4 δ values *down*shift from 28.0–28.7 to 207.0–210.1, 39.3–39.4 to 54.9–56.3 ppm, respectively. C_2, C_3, C_5, and C_{24} δ values *up*shift about 1.1–7.9 ppm; but C_6 *down*shift about 2.0–2.4 ppm (Nie et al., 1984; Iwamoto et al., 1985; Nie et al., 1989).

(4) When C_{23}–αCH_3 was replaced with COOH, C_{23} and C_4 δ values *down*shift from 29.9 to 182.2, 38.8 to 53.6 ppm, respectively. C_3, C_5, and C_{24} δ values *up*shift about 2.9–4.3 ppm; but C_6 *down*shift about 3.4 ppm (Nie et al., 1984; Schroder et al., 1993). And when C_{30}–βCH_3 was replaced with $COOCH_3$, C_{30} and C_{20} δ values *down*shift from 23.6–23.8 to 176.1–179.5, 30.7–31.0 to 44.0 ppm, respectively. C_{19}, C_{21} and C_{29} δ values *up*shift about 3.0–4.9 ppm, but C_{18} and C_{22} *down*shift about 0.7–1.6 ppm (Nie et al., 1984; Kohda et al., 1992).

(5) When C_2–βH was replaced with OH, C_2 δ values *down*shift from 26.3–28.2 to 69.6–71.5 ppm; and C_1, C_{23}, C_{24} and C_{25} δ values *down*shift about 1.2–6.5 ppm (Kohda et al., 1991; Nie et al., 1984). When C_6–βH was replaced with OH, C_6 δ values *down*shift from 17.9–18.0 to 67.6–67.7 ppm; and C_1, C_4, C_5, C_7, C_{24}, C_{25} and C_{26} δ values *down*shift about 1.0–8.4 ppm (Li et al., 1994; Abe et al., 1996). When C_{16}–αH was replaced with OH, C_{16} δ values *down*shift from 23.6–23.8 to 73.9–74.8 ppm; and C_{15}, C_{17}, and C_{21} δ values *down*shift about 1.7–8.4 ppm (Nie et al., 1984; Warashina et al., 1991). When C_{19}–αH was replaced with OH, C_{19} δ values *down*shift from 46.2 to 81.2 ppm; and C_{16}, C_{18}, C_{20} and C_{30} δ values *down*shift about 1.5–5.0 ppm, but C_{21} and C_{29} *up*shift about 4.1–4.4 ppm (Nie et al., 1984; Amimoto et al., 1993). When C_{21}–βH was replaced with OH, C_{21} δ values *down*shift from 33.7–34.2 to 72.2–72.4 ppm; and C_{17}, C_{20}, and C_{22} δ values *down*shift about 2.2–8.6 ppm, but C_{29} and C_{30} *up*shift about 3.3–5.9 ppm (Shimizu et al., 1988; Nie et al., 1984). When C_{23}–αCH_3 was replaced with CH_2OH, C_{23} δ values *down*-

Table 2
^{13}C-NMR chemical shifts of GOTCAB aglycone moieties in C_5D_5N

	1[b]	1[d]	2[d]	3[a]	3[b]	3[c]	3[d]	5[ae]	5[be]	5[c]	5[d]	6[d]	7[b]	7[d]	8[a]	8[b]	8[d]	9[af]	9[b]	9[d]	10[dg]
1	44.3	44.3	38.5	39.0	38.7	39.0	38.9	38.4	38.0	38.6	38.0	45.0	38.8	38.8	38.6	38.5	38.5	38.5	38.8	38.9	45.1
2	70.3	71.0	26.8	28.0	26.7	28.2	26.9	27.0	25.2	27.0	25.1	67.9	25.8	26.1	27.7	26.1	26.1	27.2	26.7	26.8	70.4
3	83.4	82.8	89.0	78.1	89.2	78.1	89.5	71.6	84.2	71.6	82.0	84.6	82.3	81.8	73.3	82.1	82.1	79.0	89.3	89.3	87.0
4	42.8	42.9	44.4	39.4	39.6	39.4	39.8	56.2	54.9	56.3	54.9	54.4	42.3	43.6	42.9	43.6	43.6	38.7	39.6	39.6	53.6
5	47.8	47.6	56.1	55.9	55.9	55.9	56.1	47.9	48.7	48.0	48.6	49.6	48.2	47.6	48.6	48.4	48.4	55.3	55.9	56.0	53.1
6	18.0	17.9	18.9	18.8	18.5	18.6	18.5	21.0	20.4	21.2	20.6	20.1	18.2	18.3	18.7	18.4	18.4	18.3	18.5	18.6	21.9
7	33.0	32.8	32.6	32.8	33.5	33.2	33.2	33.1	33.3	32.5	32.5	32.4	32.9	32.7	33.0	33.0	32.9	32.7	33.2	33.4	33.7
8	39.9	40.0	39.9	39.9	39.9	40.0	40.2	40.0	39.9	40.2	40.1	40.2	39.8	40.1	40.0	40.1	40.3	39.3	39.7	40.0	41.1
9	48.5	48.5	47.9	47.3	47.2	47.2	47.3	47.6	47.8	48.0	47.8	48.4	47.8	48.2	48.4	47.7	47.7	47.6	48.0	48.1	49.5
10	37.0	36.9	36.7	37.4	37.0	37.5	37.2	36.1	36.2	36.2	36.2	36.4	37.0	37.0	37.4	37.1	37.1	37.1	36.8	36.8	37.4
11	24.0	23.9	23.4	23.9	23.8	23.8	24.0	23.8	23.8	23.6	23.6	23.3	23.8	23.5	24.2	24.2	24.2	23.4	23.8	23.9	22.9
12	122.8	123.0	122.9	122.5	122.4	123.1	123.1	122.1	122.1	122.5	122.5	122.8	122.6	123.0	123.4	123.4	123.4	123.0	123.3	123.3	123.4
13	144.7	144.1	144.1	145.1	145.2	144.4	144.5	144.8	144.7	144.1	144.0	144.1	144.8	144.3	144.9	144.9	144.4	142.4	143.5	143.5	144.7
14	42.3	42.2	42.2	42.1	42.1	42.1	42.3	42.2	42.1	42.4	42.2	42.3	42.3	42.3	42.1	42.2	42.1	41.7	42.1	42.3	43.1
15	28.2	28.2	28.3	36.2	36.2	36.4	36.4	28.2	28.2	28.5	28.4	28.1	28.5	28.4	28.4	28.4	28.0	27.7	28.3	28.5	29.0
16	23.7	23.3	24.0	74.6	74.8	73.9	74.0	23.8	23.8	23.2	23.6	24.0	23.9	24.0	29.2	29.2	29.1	24.4	25.0	25.0	24.2
17	46.6	46.9	47.0	48.9	48.9	49.1	49.3	46.5	46.5	47.2	47.2	46.9	46.8	47.1	46.1	46.1	46.5	48.4	48.9	49.0	47.9
18	42.0	41.7	41.8	41.5	41.5	41.0	41.2	41.9	42.1	41.9	41.9	41.7	42.3	41.8	44.8	44.8	44.6	40.9	41.6	41.6	42.8
19	46.3	46.1	46.2	47.3	47.3	47.2	47.3	46.4	46.5	46.3	46.7	46.1	46.8	46.3	81.2	81.2	81.0	46.4	47.1	47.2	47.3
20	30.9	30.7	30.8	31.0	31.1	30.8	31.1	30.9	30.9	30.8	30.7	30.7	31.0	30.9	35.7	35.8	35.6	36.1	37.0	37.1	31.4
21	34.2	34.0	34.0	36.0	36.2	35.9	36.2	34.2	34.2	34.0	34.1	33.9	34.3	34.1	29.2	29.2	29.0	73.4	72.2	72.4	34.8
22	32.4	32.5	33.4	33.6	32.9	32.3	32.6	32.5	32.5	32.7	32.5	32.5	33.3	32.9	33.6	33.7	33.1	40.0	41.4	41.1	33.0
23	65.4	64.5	23.4	28.8	28.2	28.8	28.4	207.0	210.1	207.8	210.0	206.2	64.5	64.4	67.8	64.5	64.5	28.1	28.0	28.0	182.2
24	14.9	14.9	63.3	16.6	17.0	16.6	17.2	9.6	11.1	9.7	10.0	11.3	13.7	13.8	13.0	13.6	13.6	15.3	15.5	15.7	14.2
25	17.3	17.2	15.4	15.7	15.6	15.7	15.9	15.7	15.5	15.8	15.7	17.1	16.1	16.3	15.8	16.0	16.1	15.5	16.5	16.5	17.4
26	17.5	17.5	17.4	17.5	17.5	17.1	17.3	17.3	17.2	17.4	17.3	17.6	17.6	17.7	17.5	17.6	17.7	16.8	17.2	17.6	18.1
27	26.2	26.1	26.1	27.2	27.3	27.0	27.3	26.1	26.1	25.9	25.8	26.1	26.3	26.3	24.8	24.9	24.7	25.7	26.1	26.1	26.3
28	180.1	176.3	176.5	179.9	180.0	175.6	175.9	180.0	180.0	176.4	176.4	176.4	180.2	176.7	181.0	180.9	177.3	176.7	177.2	175.7	177.6
29	33.2	33.0	33.2	33.3	33.4	33.2	33.4	33.3	33.3	33.1	33.1	33.1	33.3	33.3	28.9	28.9	28.8	28.9	29.8	29.8	33.5
30	23.7	23.6	23.7	24.7	24.8	24.4	24.7	23.8	23.8	23.6	23.6	23.6	23.9	23.8	24.8	24.9	25.0	17.0	17.8	17.7	24.2
OMe[i]																		51.6	51.7		
Ref.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21

	11[a]	11[b]	11[c]	11[d]	12[a]	12[d]	13[b]	13[d]	14[b]	14[d]	15[al]	15[bl]	15[cl]	15[dl]	16[a]	16[d]	17[d]	18[a]	18[b]	18[d]	19[dh]
1	38.9	38.4	39.0	38.6	45.0	45.1	46.5	46.4	46.8	46.8	38.7	38.2	38.8	39.0	38.8	38.7	38.9	38.7	38.7	38.7	44.4
2	28.2	26.4	28.1	26.3	71.5	69.6	71.2	71.2	71.0	71.2	27.2	25.2	27.2	26.0	28.1	26.8	26.8	28.1	26.3	26.3	70.9
3	78.0	89.1	78.1	89.1	78.4	90.5	82.8	83.0	83.0	83.2	71.8	84.5	71.7	84.6	78.2	89.6	89.1	78.1	89.3	89.3	86.7
4	39.4	39.4	39.3	39.3	38.8	38.8	44.1	44.0	44.1	44.1	56.4	55.2	56.4	55.2	39.3	39.8	44.4	39.5	39.5	39.5	53.3
5	55.8	55.6	55.8	55.6	56.0	56.0	49.2	49.2	49.0	49.0	48.0	48.6	48.0	48.9	56.0	56.1	56.2	55.9	55.9	55.9	53.0
6	18.8	18.4	18.8	18.3	18.7	18.5	67.6	67.7	67.7	67.9	21.2	20.6	21.3	20.5	18.9	18.9	19.1	18.8	18.5	18.5	21.2
7	33.3	33.2	33.2	33.1	33.4	33.1	41.2	41.2	41.4	41.4	33.0	32.9	33.0	33.2	33.2	33.3	33.6	33.2	33.2	33.2	33.8
8	39.8	39.6	39.9	39.7	40.0	40.1	39.3	39.5	39.5	39.7	40.3	40.3	40.5	40.3	40.0	40.4	40.2	39.9	39.9	39.9	42.3
9	48.1	47.9	48.1	47.9	48.6	48.4	48.8	48.8	48.3	48.4	47.3	47.1	47.2	47.0	47.3	48.4	48.1	48.0	48.0	48.0	49.0
10	37.4	36.9	37.4	36.8	37.4	37.1	37.0	36.9	37.1	37.0	36.3	36.4	36.3	36.3	37.5	37.2	36.8	37.0	37.0	37.0	36.3
11	23.8	23.7	23.7	23.6	23.8	23.4	24.1	24.2	24.2	24.3	23.9	23.9	23.9	24.0	24.1	24.3	24.3	23.8	23.8	23.8	24.6
12	122.5	122.7	122.9	122.5	123.0	123.3	123.3	123.3	123.1	123.5	122.2	122.2	122.3	122.3	123.3	123.4	124.3	123.5	123.5	123.5	123.4
13	144.8	144.7	144.1	144.0	144.9	144.0	144.2	143.8	144.5	143.9	145.3	145.3	144.5	144.5	144.3	144.5	144.7	143.8	143.8	143.8	144.3
14	42.0	42.0	42.1	41.9	42.4	42.3	42.9	42.9	42.9	42.9	42.3	42.2	42.3	42.2	42.1	42.3	42.1	42.0	42.0	42.0	42.3
15	28.3	28.1	28.1	28.0	28.3	28.1	28.3	28.3	36.3	36.3	36.2	36.2	36.0	36.0	29.0	29.1	28.9	28.8	28.4	28.4	36.2
16	23.8	23.7	23.7	23.6	24.0	24.0	23.8	23.4	74.9	74.2	74.7	74.8	74.5	74.4	28.1	28.1	29.1	23.6	23.6	23.6	76.6
17	46.7	46.6	47.0	46.8	46.7	47.0	46.7	47.5	49.0	49.9	49.0	49.0	49.3	49.3	46.4	46.7	46.5	46.5	46.5	46.5	49.8[k]
18	42.0	42.0	41.7	41.6	42.1	41.7	42.1	41.9	41.6	41.6	41.6	41.6	41.7	41.7	44.6	44.8	44.6	43.2	43.2	43.2	42.8
19	46.7	46.6	46.3	46.2	46.5	46.2	46.8	46.7	47.3	47.2	47.4	47.4	47.5	47.0	81.0	81.2	81.0	42.5	43.2	42.5	47.7
20	31.0	30.9	30.8	30.7	31.0	30.7	31.0	31.0	31.1	31.0	31.1	31.1	30.8	30.8	35.6	35.7	35.6	44.0	44.0	44.0	31.1
21	34.3	34.2	34.1	33.7	34.3	34.0	34.3	34.3	36.2	36.1	36.3	36.4	36.3	36.3	29.0	29.3	29.2	30.6	31.2	30.6	37.3
22	33.3	33.2	32.5	32.5	33.3	32.6	33.3	33.2	32.9	33.3	30.0	30.0	31.9	33.0	33.2	33.4	33.1	34.0	34.8	34.0	31.4
23	28.7	28.1	28.7	28.0	30.3	29.9	65.2	65.4	65.3	65.5	207.3	210.0	207.6	210.4	28.2	28.4	23.4	28.4	28.4	28.4	182.2
24	16.5	16.9	16.5	16.8	18.2	18.5	16.8	16.8	16.8	16.8	9.7	11.1	9.8	11.2	16.5	16.8	63.2	17.1	17.1	17.1	13.6
25	15.5	15.3	15.6	15.4	16.7	16.8	19.0	19.1	19.1	19.2	15.9	15.8	16.0	15.9	15.5	15.7	15.2	15.6	15.6	15.6	16.7
26	17.5	17.4	17.5	17.3	17.5	17.7	18.5	18.7	18.7	18.9	17.5	17.6	17.6	17.5	17.4	17.8	17.4	17.5	17.5	17.5	18.0
27	26.2	26.1	26.1	26.0	26.3	26.1	26.5	26.3	27.5	27.5	27.3	27.3	27.2	27.1	24.7	24.9	24.7	26.2	26.2	26.2	27.3

continued

Table 2 Continued

28	180.2	180.2	176.3	176.3	180.2	176.4	180.2	176.3	180.1	176.2	180.0	180.2	176.1	176.0	178.7	177.6	177.2	179.9	180.0	177.0	175.8
29	33.3	33.2	33.2	33.1	33.3	33.1	33.3[j]	33.2	33.4	33.3	33.4	33.4	33.2	33.2	28.8	29.0	28.8	28.4	29.1	28.4	33.2
30	23.8	23.7	23.7	23.6	23.8	23.6	23.8	23.8	24.9	25.1	24.8	24.9	24.6	24.6	24.9	25.1	24.9	177.2	179.5	176.1	25.3
OMe[i]															51.7			51.7[m]		51.7[m]	
Ref.	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42

[a]Free aglycones. [b]Aglycones of 3-prosapogenins. [c]Aglycones of 28-prosapogenins. [d]Aglycones of 3,28-saponins. [e]The solvent was not indicated in the literature. [f]Data measured in $CDCl_3$. [g]Data measured in CD_3OD:C_5D_5N(3:2). [h]Data measured in CD_3OD:AcOD. [i]It linked in C-28 or C-30 COOH. [j]It was 23.3 in the literature (Li et al., 1994), but we corrected it as 33.3 compared with relative data in the literature. [k]It was not observed in the literature (Cuellar et al., 1997), but we added it as 49.8 compared with relative data in the literature (M'Bark et al., 1996). [l]Original data were four digits, and now we changed these data to three digits for being identical. [m]It showed C-30 COO*Me*.

[1] Abe et al., 1996. [2] Abe et al., 1996. [3] Amimoto et al., 1993. [4] Warashina et al., 1991. [5] Warashina et al., 1991. [6] Warashina et al., 1991. [7] Warashina et al., 1991. [8] Iwamoto et al., 1985. [9] Iwamoto et al., 1985. [10] Nie et al., 1989. [11] Nie et al., 1989. [12] Kohda et al., 1991. [13] Nie et al., 1989. [14] Amimoto et al., 1993. [15] Amimoto et al., 1993. [16] Amimoto et al., 1993. [17] Amimoto et al., 1993. [18] Shimizu et al., 1988. [19] Shimizu et al., 1988. [20] Shimizu et al., 1988. [21] Schroder et al., 1993. [22] Nie et al., 1984. [23] Nie et al., 1984. [24] Nie et al., 1984. [25] Nie et al., 1984. [26] Kohda et al., 1991. [27] Kohda et al., 1991. [28] Li et al., 1994. [29] Li et al., 1994. [30] Li et al., 1994. [31] Li et al., 1994. [32] Tan et al., 1995. [33] Tan et al., 1995. [34] Tan et al., 1995. [35] Tan et al., 1995. [36] Amimoto et al., 1993. [37] Amimoto et al., 1993. [38] Amimoto et al., 1993. [39] Kohda et al., 1992. [40] Kohda et al., 1992. [41] Kohda et al., 1992. [42] Cuellar et al., 1997.

shift from 28.0–28.1 to 64.4–64.5 ppm; and C_4 δ values *down*shift about 2.9–4.3 ppm and C_3, C_5, C_{24} *up*shift about 3.0–8.0 ppm (Nie et al., 1984; Amimoto et al., 1993). When C_{24}–βCH_3 was replaced with CH_2OH, C_{24} δ values *down*shift from 16.8 to 63.3 ppm; and C_4 δ values *down*shift about 5.1 ppm and C_{23} *up*shift about 4.6 ppm (Nie et al., 1984; Amimoto et al., 1993).

4.2.2. ^{13}C NMR characteristics of GOTCAB monosaccharide moieties and their derivatives with different glycosidic and acyl linkages

Up to date monosaccharide moieties in GOTCAB are different from two to eleven ones including linear and branched sugar chains, mono- and di- as well as triglycosidic or acyl sugar residues. Common monosaccharides include glucuronic acid (glcUA), glucose (glc), galactose (gal), fucose (fuc), rhamnose (rha), quinovose (qui), arabinose (ara), xylose (xyl), and apiose (api) in structures of this kind of saponins. Comparison with data in the references we selected the typical data of monosaccharide moieties mentioned above and their derivatives with different glycosidic and acyl linkages shown in Table 3. From Table 3 we summarized their some CMR characteristics as follows (Lacaille-Dubois et al., 1993; Fujioka et al., 1992; Fang, Zhou, & Zeng, 1992; Satoh et al., 1994; Yu, Yu, & Liang, 1994; Nagao et al., 1993; Nagao et al., 1991; Nagao et al., 1991; Nagao & Okabe, 1992; Sati, Bahuguna, Uniyal, Sakakibara, Kaiya, & Nakamura, 1990; Liu, Li, Owen, Grant, Cates, & Jia, 1995; Frechet et al., 1991; Morita, Nie, Fujino, Ito, Matsufuji, Kasai, Zhou, Wu, Yata, & Tanaka, 1986; Nie et al., 1984; Shao et al., 1996; Okabe et al., 1989; Abe et al., 1996; Lavaud et al., 1996; Paphassarang et al., 1990; Higuchi et al., 1988; Lacaille-Dubois et al., 1995; Tan et al., 1995; Tan et al., 1996; Warashina et al., 1991; Miyase, Kohsaka, & Ueno, 1992; Cuellar et al., 1997):

(1) Glycosylation shift values are approximate 7.2–9.7 and 3.7–8.5 ppm in mono- and diglycosidic linkages, respectively.

(2) Esterification shift values are smaller than glycosylation shift values, and about 2.2–3.0 ppm.

(3) After monosaccharides were linked by glycosidic bonds and acyl groups their β position carbons usually upshift about 0.2–3.4 ppm.

5. Conclusion

In the structural elucidation of GOTCAB two different strategies can be applied:

(1) The degradation and integration way: using chemical and enzymatic methods GOTCAB afford a series of aglycones, prosapogenins and oligosaccharides. After determination of these derivative structures by means of chemical and spectral methods, GOTCAB structures are finally deduced step by step. Therefore, we have emphasises the methodology to obtain genuine aglycones, prosapogenins and oligosaccharides. The following steps are proposed for the GOTCAB structural elucidation: (1) Using acid hydrolysis and mild hydrolysis (especially glycyrrhizinic acid hydrolase) genuine aglycones and sugars are obtained in which aglycones are determined by means of TLC, NMR, MS. The sugar compositions and sequences are deduced by PC, GC-MS. (2) By means of selective cleavages (especially treatment with anhydrous LiI and 2,6-Lutidine as well as anhydrous methanol, glycyrrhizinic acid hydrolase, partial acid hydrolysis, basic hydrolysis) 3- and 28-prosapogenins and their oligosaccharides are obtained and their structures are elucidated using NMR, MS, methylation-methanolysis. (3) Finally GOTCAB structures are established after summarizing information obtained as discussed above.

(2) The NMR complete interpretation way: After identifying sugar moieties, their anomeric configurations,

Table 3
^{13}C-NMR chemical shifts of GOTCAB monosaccharide moieties and their derivatives with different glycosidic and acyl linkages in C_5D_5N

	free	2-osidic	3-osidic	4-osidic	2,3-osidic	3,4-osidic	2,4-osidic
3-glcUA							
1	107.1	105.3	105.1	104.0	105.2	106.5	105.5
2	75.4	82.8	74.2	75.0	79.1	74.1	81.7
3	78.0	77.1	85.7	76.8	86.1	82.7	75.0
4	73.4	73.2	72.5	82.0	72.8	79.5	78.3
5	77.7	77.9	77.2	74.3	77.2	75.9	77.1
6	173.3	172.6	172.0	173.0	171.7	170.0	169.8
OMe						52.7	52.7
Ref.	Nie et al., 1984	Nie et al., 1984	Nie et al., 1984	Abe et al., 1996	Nie et al., 1984	Satoh et al., 1994[e]	Satoh et al., 1994[e]
	free	4-osidic	4-acyl				
glc							
1	103.7	104.8	105.6				
2	76.3	73.9	72.1				
3	78.8	78.1	77.3				
4	72.5	81.0	75.5				
5	77.8	77.6	76.2				
6	63.3	62.4	62.8				
CH_3COO			171.5				
CH_3COO			20.9				
Ref.	Nie et al., 1984	Paphassarang et al., 1990[f]	Tan et al., 1996[f]				
	free	2-osidic	6-osidic	2,6-osidic			
28-glc							
1	95.6	99.7	95.7	94.7			
2	74.1	79.2	75.2	75.4			
3	78.8	78.3	78.4	79.5			
4	71.1	71.4	71.5	71.3			
5	79.1	78.0	78.7	77.8			
6	62.2	64.0	69.4	69.1			
Ref.	Nie et al., 1984	Sati et al., 1990[a]	Morita et al., 1986	Nagao and Okabe, 1992[e]			
	free	4-osidic					
gal							
1	103.5	104.3					
2	73.8	72.3					
3	74.8	75.3					
4	70.4	78.3					
5	76.8	77.4					
6	62.1	62.4					
Ref.	Tan et al., 1995[f]	Fang et al., 1992[f]					

	free
28-gal	
1	95.6
2	71.2
3	74.0
4	70.3
5	76.2
6	62.0
Ref.	Yu et al., 1994

	2-osidic	2-osidic-3-acyl	2-osidic-4-acyl	2,3-osidic-4-acyl	2,4-osidic	2,4-osidic-3-acyl
28-fuc						
1	95.3	94.9	92.7	94.0	94.8	94.8
2	76.0	72.8	73.9	73.7	75.2	74.0
3	75.3	74.2	72.5	80.9	71.0	75.9
4	72.9	70.7	73.4	73.8	84.1	83.2
5	72.5	75.4	69.0	69.9	71.9	70.7
6	17.1	16.7	16.0	17.1	17.4	17.2
CH_3COO				172.6		170.5
CH_3COO				21.6		21.0
Ref.	Fujioka et al., 1992[d]	Higuchi et al., 1988	Lacaille-Dubois et al., 1995[c]	Lacaille-Dubois et al., 1993[c]	Tan et al., 1995[f]	Tan et al., 1995[f]

	free	2-osidic-β-OMe	2-osidic-α-OMe	2,4-osidic-α-OMe	2,4-osidic-α-OH	2,4-osidic-β-OH
fuc						
1	98.7	103.8	100.6	104.6	93.5	97.4
2	70.8	77.0	78.8	78.7	79.1	79.4
3	73.5	75.6	69.9	70.7	70.8	72.2
4	72.4	73.0	73.3	84.0	84.6	84.5
5	71.9	71.2	66.7	66.2	65.8	70.6
6	15.6	17.1	17.1	17.3	17.7	17.7
OMe		56.1	55.0	55.2		
Ref.	Liu et al., 1995	Fujioka et al., 1992[d]	Fujioka et al., 1992[d]	Tan et al., 1995[f]	Tan et al., 1995[f]	Tan et al., 1995[f]

	free	2-osidic	3-osidic	4-osidic	3,4-osidic
rha					
1	100.8	99.5	101.5	101.5	102.3
2	72.2	81.3	71.7	71.9	70.9
3	72.8	70.1	80.3	72.5	82.7
4	74.1	72.0	73.6	83.8	78.7
5	70.1	68.7	71.7	68.5	69.1
6	18.7	18.1	18.5	18.8	19.1
Ref.	Tan et al., 1995[f]	Lacaille-Dubois et al., 1995[c]	Nagao et al., 1991	Tan et al., 1995[f]	Fujioka et al., 1992[d]

	2-osidic	3,4-osidic
28-rha		
1	95.1	94.0
2	79.6	70.0
3	72.1	81.9
4	73.7	77.1
5	70.8	69.9
6	18.9	17.2
Ref.	Cuellar et al., 1997[b]	Liu et al., 1995

continued

Table 3 Continued

	free	2-acyl	4-osidic	2,3-osidic-α-OMe		
qui						
1	106.3	105.8	105.6	99.8		
2	76.0	78.2	76.1	82.5		
3	78.5	75.1	77.5	79.9		
4	76.8	76.2	84.9	75.5		
5	73.4	73.2	70.6	68.2		
6	18.7	17.7	17.9	18.4		
CH_3COO		170.2				
CH_3COO		20.7				
OMe				54.7		
Ref.	Tan et al., 1995[f]	Tan et al., 1995[f]	Tan et al., 1996[f]	Okabe et al., 1989[e]		
	free	2-osidic	2-acyl	3-osidic-2-acyl		
28-ara						
1	95.8	93.5	93.4	93.7		
2	71.3	75.0	71.3	70.3		
3	73.8	70.4	72.3	80.7		
4	67.9	66.3	68.8	69.1		
5	66.0	63.2	67.1	68.1		
Ref.	Nagao et al., 1991[e]	Nagao et al., 1991[e]	Warashina et al., 1991	Warashina et al., 1991		
	free	4-osidic	2-osidic-α-OMe	2-osidic-β-OMe	free (f)	2-osidic (f)
ara						
1	106.5	104.3	103.6	101.1	110.9	106.3
2	71.3	72.0	76.8	78.7	82.9	88.2
3	74.5	73.1	74.2	69.1	77.5	77.0
4	69.0	77.4	69.2	70.6	85.2	84.8
5	67.0	65.4	65.9	63.5	61.6	62.1
OMe			55.9	55.1		
Ref.	Nie et al., 1984	Frechet et al., 1991[f]	Nagao et al., 1991[e]	Nagao et al., 1991[e]	Lacaille-Dubois et al., 1993[c]	Higuchi et al., 1988
	free	2-osidic	2-acyl	2-acyl-3-osidic	3-osidic	2,3-osidic
28-xyl						
1	96.2	95.1	93.6	93.5	95.8	94.0
2	73.6	75.9	73.6	71.1	72.5	74.8
3	78.1	77.0	76.1	85.5	88.1	79.5
4	70.8	70.6	71.0	69.4	69.2	68.3
5	67.6	66.9	68.0	67.1	67.2	65.2
Ref.	Nagao et al., 1991[e]	Shao et al., 1996	Warashina et al., 1991	Warashina et al., 1991	Miyase et al., 1992	Nagao et al., 1993[e]

	free	2-osidic	2-osidic-α-OMe	2-osidic-β-OMe	3-osidic	2,3-osidic-α-OMe	2,3-osidic-β-OMe
xyl							
1	104.9	101.9	100.5	104.3	106.0	100.0	103.8
2	75.2	84.3	81.4	78.7	74.8	82.5	79.1
3	78.5	77.2	74.1	79.0	87.4	79.9	86.0
4	70.8	71.0	71.5	71.2	69.2	69.8	69.8
5	67.3	66.6	62.7	67.0	66.9	62.7	66.5
OMe			54.9	56.2		54.8	56.1
Ref.	Tan et al., 1995[f]	Lavaud et al., 1996[a]	Nagao et al., 1991[e]	Nagao et al., 1991[e]	Tan et al., 1995[f]	Nagao et al., 1993[e]	Nagao et al., 1993[e]
	free						
api							
1	111.2						
2	77.7						
3	80.1						
4	75.0						
5	65.6						
Ref.	Higuchi et al., 1988						

[a]Data measured in CD_3OD. [b]Data measured in CD_3OD-AcOD. [c]Data measured in DMSO-d_6. [d]Data measured in C_5D_5N–D_2O. [e]The solvent was not indicated in the literature. [f]Original data were four digits, and now we changed these data to three digits for being identical.

sequences, interglycosidic linkages and sites of appended acyl groups as well as aglycones and attached positions of glycosidic linkages with 1D- and 2D-NMR techniques, GOTCAB structures are finally determined non-destructively. The key of this way is to assign all proton and carbon signals unambiguously.

Although both strategies are useful to elucidate the complex structures of GOTCAB, we prefer to assign unambiguously ^1H and ^{13}C NMR chemical shifts of GOTCAB and their derivatives. We hope that various homo- and heteronuclear 2D NMR techniques will be more widely used to the structural elucidation of not only GOTCAB, but also of other natural products.

References

Abe, F., Yamauchi, T., Shibuya, H., & Kitagawa, I. (1996). *Phytochemistry*, *42*, 809.

Agostino, M. D., Biagi, C., Simone, F. De., & Pizza, C. (1994). *Fitoterapia*, *65*, 59.

Alad'ina, N. G., El'kin, Yu. N., & Chezhina, E. A. (1989). *Chem. Nat. Compd.*, *25*, 317.

Amimoto, K., Yoshikawa, K., & Arihara, S. (1992). *Chem. Pharm. Bull.*, *40*, 3138.

Amimoto, K., Yoshikawa, K., & Arihara, S. (1993). *Chem. Pharm. Bull.*, *41*, 77.

Annaev, Ch., & Abubakirov, N. K. (1984). *Khim. Prir. Soedin*, 60.

Annaev, Ch., Isaev, M. I., & Abubakirov, N. K. (1983). *Khim. Prir. Soedin*, 596.

Annaev, Ch., Isamukhamedova, M., & Abubakirov, N. K. (1983). *Khim. Prir. Soedin*, 453.

Annaev, Ch., Isamukhamedova, M., & Abubakirov, N. K. (1984). *Khim. Prir. Soedin*, 65.

Baeva, R. T., Karryev, M. O., & Abubakirov, N. K. (1975). *CA*, *82*, 135692r.

Baeva, R. T., Karryev, M. O., & Abubakirov, N. K. (1976). *CA*, *84*, 59922q.

Borel, C., Gupta, M. P., & Hostettmann, K. (1987). *Phytochemistry*, *26*, 2685.

Borel, C., & Hostettmann, K. (1987). *Helv. Chim. Acta*, *70*, 570.

Bukharov, V. G., Chirva, V. Ya., & Bukharova, I. L. (1975). *CA*, *83*, 179495d.

Bukharov, V. G., Karlin, V. V., Bukharova, I. L., & Surkova, L. N. (1975a). *CA*, *82*, 73386h.

Bukharov, V. G., Karlin, V. V., Bukharova, I. L., & Surkova, L. N. (1975b). *CA*, *82*, 73390e.

Chirva, V. Ya., & Kintya, P. K. (1970). *CA*, *72*, 13007u.

Cuellar, M. J., Giner, R. M., Carmen Recio, M., Just, M. J., Manez, S., Rios, J. L., Bilia, A. R., Msonthi, J., & Hostettmann, M. (1997). *J. Nat. Prod.*, *60*, 191.

Davidyants, E. S., Putieva, Zh. M., Bandyukova, V. A., & Abubakirov, N. K. (1986). *Chem. Nat. Compd.*, *22*, 58.

Dubois, M.-A., Bauer, R., Cagiotti, M. R., & Wagner, H. (1988). *Phytochemistry*, *27*, 881.

Espada, A., Jimenez, C., Dopeso, J., & Riguera, R. (1996). *Liebigs Ann.*, 781.

Fang, Z.-P., Zhou, Y.-X., & Zeng, X.-Y. (1992). *Acta Bot. Sin.*, *34*, 461.

Forgacs, P., & Provost, J. (1981). *Phytochemistry*, *20*, 1689.

Frechet, D., Christ, B., Sorbier, B. M., Fischer, H., & Vuilhorgne, M. (1991). *Phytochemistry*, *30*, 927.

Freiler, M., Reznicek, G., Schubert-Zsilavecz, M., Reiner, J., Haslinger, E., Jurenitsch, J., & Kubelka, W. (1996). *Sci. Pharm.*, *64*, 359.

Fujioka, T., Nagao, T., Okabe, H., & Mihashi, K. (1992). *Chem. Pharm. Bull.*, *40*, 1105.
Gafner, F., Msonthi, J. D., & Hostettmann, K. (1985). *Helv. Chim. Acta*, *68*, 555.
Hariharan, V., & Rangaswami, S. (1970). *Phytochemistry*, *9*, 409.
Hariharan, V. (1974). *Ind. J. Chem.*, *12*, 447.
Higuchi, R., Tokimitsu, Y., Fujioka, T., Komori, T., Kawasaki, T., & Oakenful, D. G. (1987). *Phytochemistry*, *26*, 229.
Higuchi, R., Tokimitsu, Y., Hamada, N., Komori, T., & Kawasaki, T. (1985). *Liebigs Ann. Chem.*, 1192.
Higuchi, R., Tokimitsu, Y., & Komori, T. (1988). *Phytochemistry*, *27*, 1165.
Hu, M., Ogawa, K., Sashida, Y., & Xiao, P.-G. (1995). *Phytochemistry*, *39*, 179.
Huguchi, R., Kitamura, Y., & Komori, T. (1986). *Liebigs Ann. Chem.*, 638.
Huguchi, R., Tokimitsu, Y., & Komori, T. (1988). *Liebigs Ann. Chem.*, 249.
Ida, Y., Satoh, Y., Katoh, M., Katsumata, M., Nagasao, M., Yamaguchi, K., Kamei, H., & Shoji, J. (1994) *Tetrahedron Lett.*, *35*, 6887.
Iwamoto, M., Okabe, H., Yamauchi, T., Tanaka, M., Rokutani, Y., Hara, S., Mihashi, K., & Higuchi, R. (1985). *Chem. Pharm. Bull.*, *33*, 464.
Jiang, Q.-P., & Xiao, Z.-Y. (1990). *West China J. Pharm. Sci.*, *5*, 133.
Jiang, Y.-T., Xu, S.-X., Gu, X.-H., Ren, L., Chen, Y.-J., Yao, X.-S., & Miao, Z.-C. (1992). *Acta Pharm. Sin.*, *27*, 528.
Kasai, R., Tanaka, T., Nie, R.-L., Miyakoshi, M., Zhou, J., & Tanaka, O. (1990). *Chem. Pharm. Bull.*, *38*, 1320.
Kawamura, N., Watanabe, H., & Oshio, H. (1988). *Phytochemistry*, *27*, 3585.
Kim, Y. C., Higuchi, R., & Komori, T. (1992). *Liebigs Ann. Chem*, 453.
Kim, Y. C., Higuchi, R., & Komori, T. (1992). *Liebigs Ann. Chem.*, 941.
Kinjo, J., Suyama, K., & Nohara, T. (1995). *Phytochemistry*, *40*, 1765.
Kitagawa, I., Ikenishi, Y., Yoshikawa, M., & Im, K. S. (1977). *Chem. Pharm. Bull.*, *25*, 1408.
Kitagawa, I., Kamigauchi, T., Ikeda, Y., & Yoshikawa, M. (1984). *Chem. Pharm. Bull.*, *32*, 4858.
Kitagawa, I., Kamigauchi, T., Ohmori, H., & Yoshikawa, M. (1980). *Chem. Pharm. Bull*, *28*, 3078.
Kitagawa, I., Yoshikawa, M., Im, K. S., & Ikenishi, Y. (1977). *Chem. Pharm. Bull.*, *25*, 657.
Kitagawa, I., Yoshikawa, M., Imakura, Y., & Yosioka, I. (1974). *Chem. Pharm. Bull.*, *22*, 1339.
Kitagawa, I., Yoshikawa, M., & Kadota, A. (1978). *Chem. Pharm. Bull.*, *26*, 484.
Kochetkov, N. K., Khorlin, A. J., & Ovodov, Ju. S. (1963). *Tetrahedron Lett.*, 477.
Kochetkov, N. K., Khorlin, A. J., & Vaskovsky, V. E. (1962). *Tetrahedron Lett.*, *16*, 713.
Kohda, H., Tanaka, S., Yamaoka, Y., & Ohhara, Y. (1991). *Chem. Pharm. Bull.*, *39*, 2609.
Kohda, H., Yamaoka, Y., Morinaga, S., Ishak, M., & Darise, M. (1992). *Chem. Pharm. Bull.*, *40*, 2557.
Kondo, N., Marumoto, Y., & Shoji, J. (1971). *Chem. Pharm. Bull.*, *19*, 1103.
Kondo, N., & Shoji, J. (1975). *Chem. Pharm. Bull.*, *23*, 3282.
Lacaille-Dubois, M.-A., Hanquet, B., Cui, Z.-H., Lou, Z.-C., & Wagner, H. (1995). *Phytochemistry*, *40*, 509.
Lacaille-Dubois, M.-A., Hanquet, B., Rustaiyan, A., & Wagner, H. (1993). *Phytochemistry*, *34*, 489.
Lavaud, C., Beauviere, S., Massiot, G., Men-Olivier, L., & Bourdy, G. (1996). *Phytochemistry*, *43*, 189.
Lavaud, C., Massiot, G., Becchi, M., Misra, G., & Nigam, S. K. (1996). *Phytochemistry*, *41*, 887.
Lazur'evskii, G. V., Kintya, P. K., & Chirva, V. Ya. (1970). *CA*, *72*, 67224f.
Li, X.-C., Liu, Y.-Q., Wang, D.-Z., Yang, C.-R., Nigam, S. K., & Misra, G. (1994). *Phytochemistry*, *37*, 827.
Liu, Z.-M., Li, D., Owen, N. L., Grant, D. M., Cates, R. G., & Jia, Z.-J. (1995). *J. Nat. Prod.*, *58*, 1632.
Luchanskaya, V. N., Kondratenko, E. S., & Abubakirov, N. K. (1972). *CA*, *76*, 59967t.
Luchanskaya, V. N., Kondratenko, E. S., Gorovits, T. T., & Abubakirov, N. K. (1971). *CA*, *75*, 49495c.
M'Bark, A. N., Gutllaume, D., Kol, O., & Charrouf, Z. (1996). *Phytochemistry*, *43*, 1075.
Miyase, T., Kohsaka, H., & Ueno, A. (1992). *Phytochemistry*, *31*, 2087.
Miyase, T., Sutoh, N., Zhang, D.-M., & Ueno, A. (1996). *Phytochemistry*, *42*, 1123.
Morita, T., Nie, R.-L., Fujino, H., Ito, K., Matsufuji, N., Kasai, R., Zhou, J., Wu, C.-Y., Yata, N., & Tanaka, O. (1986). *Chem. Pharm. Bull.*, *34*, 401.
Muro, T., Kuramoto, T., Imoto, K., & Okada, S. (1986). *Agric. Biol. Chem.*, *50*, 687.
Nagao, T., Iwase, Y., & Okabe, H. (1993). *Chem. Pharm. Bull.*, *41*, 1562.
Nagao, T., Okabe, H., Mihashi, K., & Yamauchi, T. (1989). *Chem. Pharm. Bull.*, *37*, 925.
Nagao, T., & Okabe, H. (1992). *Chem. Pharm. Bull.*, *40*, 886.
Nagao, T., Tanaka, R., Iwase, Y., & Okabe, H. (1993). *Chem. Pharm. Bull.*, *41*, 659.
Nagao, T., Tanaka, R., & Okabe, H. (1991). *Chem. Pharm. Bull.*, *39*, 1699.
Nagao, T., Tanaka, R., & Okabe, H. (1991). *Chem. Pharm. Bull.*, *39*, 889.
Nagao, T., Tanaka, R., Shimokawa, H., & Okabe, H. (1991). *Chem. Pharm. Bull.*, *39*, 1719.
Nie, R.-L., Morita, T., Kasai, R., Zhou, J., Wu, C.-Y., & Tanaka, O. (1984). *Planta Med.*, *48*, 322.
Nie, R.-L., Tanaka, T., Miyakoshi, M., Kasai, R., Morita, T., Zhou, J., & Tanaka, O. (1989). *Phytochemistry*, *28*, 1711.
Ohtani, K., Mizutani, K., Kasai, R., & Tanaka, O. (1984). *Tetrahedron Lett.*, *25*, 4537.
Ohtani, K., Ogawa, K., Kasai, R., Yang, C.-R., Yamasaki, K., Zhou, J., & Tanaka, O. (1992). *Phytochemistry*, *31*, 1747.
Okabe, H., Nagao, T., Hachiyama, S., & Yamauchi, T. (1989). *Chem. Pharm. Bull.*, *37*, 895.
Paphassarang, S., Raynaud, J., Lussignol, M., & Becchi, M. (1989). *Phytochemistry*, *28*, 1539.
Paphassarang, S., Raynaud, J., Lussignol, M., & Cabalion, P. (1990). *J. Nat. Prod.*, *53*, 163.
Patkhullaeva, M., Mzhel'skaya, L. G., & Abubakirov, N. K. (1975). *CA*, *82*, 28554a.
Patkhullaeva, M., Mzhel'skaya, L. G., & Abubakirov, N. K. (1975). *CA*, *82*, 28561a.
Penders, A., & Delaude, C. (1994). *Phytochemistry*, *37*, 821.
Pizza, C., Zhou, Z.-L., & Tommasi, N. (1987). *J. Nat. Prod.*, *50*, 927.
Putieva, Zh. M., Mzhel'skaya, L. G., Gorovits, T. T., Kondratenko, E. S., & Abubakirov, N. K. (1976). *CA*, *84*, 150898x.
Rangaswami, S., & Seshadri, R. (1971). *Ind. J. Chem.*, *9*, 189.
Sasaki, Y., Morita, T., Kuramoto, T., Mizutani, K., Ikeda, R., & Tanaka, O. (1988). *Agric. Biol. Chem.*, *52*, 207.
Sati, O. P., Bahuguna, S., Uniyal, S., Sakakibara, J., Kaiya, T., & Nakamura, A. (1990). *J. Nat. Prod.*, *53*, 466.
Satoh, Y., Sakai, S., Katsumata, M., Nagasao, M., Miyakoshi, M., Ida, Y., & Shoji, J. (1994). *Phytochemistry*, *36*, 147.
Schroder, H., Schubert-Zsilavecz, M., Reznicek, G., Cart, J., Jurenitsch, J., & Haslinger, E. (1993). *Phytochemistry*, *34*, 1609.
Seshadri, R., & Rangaswami, S. (1975). *Ind. J. Chem.*, *13*, 447.
Shao, Y., Poobrasert, O., Ho, C.-T., Chin, C.-K., & Cordell, G. A. (1996). *Phytochemistry*, *43*, 195.
Shimizu, S., Ishihara, N., Umehara, K., Miyase, T., & Ueno, A. (1988). *Chem. Pharm. Bull.*, *36*, 2466.

Takabe, S., Takeda, T., Chen, Y.-J., & Ogihara, Y. (1985). *Chem. Pharm. Bull.*, *33*, 4701.

Tan, N.-H., Zhao, S.-X., Zhou, J., & Chen, C.-X. (1995). *Acta Chim. Sin.*, *53*, 1024.

Tan, N.-H., Zhou, J., Zhao, S.-X., & Chen, C.-X. (1996). *Acta Chim. Sin.*, *54*, 722.

Tanaka, O., Morita, T., Kasai, R., Kinouchi, J., Sanada, S., Ida, Y., & Shoji, J. (1985). *Chem. Pharm. Bull.*, *33*, 2323.

Tanaka, R., Nagao, T., Okabe, H., & Yamauchi, T. (1990). *Chem. Pharm. Bull.*, *38*, 1153.

Vidal-Ollivier, E., Balansard, G., Faure, R., & Babadjamian, A. (1989). *J. Nat. Prod.*, *52*, 1156.

Wang, Z.-X., Xu, S.-X., Zhang, G.-G., Qiu, F., Su, X.-F., Zhang, X.-Q., Chen, Y.-J., & Yao, X.-S. (1992). *Chin. J. Med. Chem.*, *2*, 65.

Warashina, T., Miyase, T., & Ueno, A. (1991). *Chem. Pharm. Bull.*, *39*, 388.

Wen, Y., Chen, Y.-J., Cui, J.-P., Li, J.-H., & Wang, Z.-X. (1995). *Planta Med.*, *61*, 450.

Yang, C.-R., Jiang, Z.-D., Zhou, J., Kasai, R., & Tanaka, O. (1985). *Acta Bot. Yunnanica*, *7*, 103.

Yoshikawa, K., Arihara, S., Wang, J.-D., Narui, T., & Okuyama, T. (1991). *Chem. Pharm. Bull.*, *39*, 1185.

Yoshikawa, M., Harada, E., Matsuda, H., Murakami, T., Yamahara, J., & Murakami, N. (1993). *Chem. Pharm. Bull.*, *41*, 2069.

Yoshikawa, M., Murakami, T., Inaduki, M., Hirano, K., Yamahara, J., & Matsuda, H. (1997). *Chem. Pharm. Bull.*, *45*, 561.

Yoshikawa, M., Murakami, T., Kadoya, M., Matsuda, H., Muraoka, O., Yamahara, J., & Murakami, N. (1996). *Chem. Pharm. Bull.*, *44*, 1212.

Yoshikawa, M., Murakami, T., Kadoya, M., Matsuda, H., Yamahara, J., Muraoka, O., & Murakami, N. (1995). *Heterocycles*, *41*, 1621.

Yoshikawa, M., Yoshizumi, S., Ueno, T., Matsuda, H., Murakami, T., Yamahara, J., & Murakami, N. (1995). *Chem. Pharm. Bull.*, *43*, 1878.

Yu, S.-S., Yu, D.-Q., & Liang, X.-T. (1994). *J. Nat. Prod.*, *57*, 978.

Zhou, Y.-H. (1988). *Chemotaxonomy of Medicinal Plants* (pp. 140). Shanghai: Shanghai Scientific and Technological Press.