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Advances in structural elucidation of glucuronide oleanane-type triterpene carboxylic acid 3,28-*O*-bisdesmosides (1962–1997)Ninghua Tan^{a,*}, Jun Zhou^a, Shouxun Zhao^b^aLaboratory of Phytochemistry, Kunming Institute of Botany, the Chinese Academy of Sciences, Kunming, 650204, P.R. China^bDepartment of Phytochemistry, China Pharmaceutical University, Nanjing, 21009, P.R. China

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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. © 1999 Elsevier Science Ltd. All rights reserved.

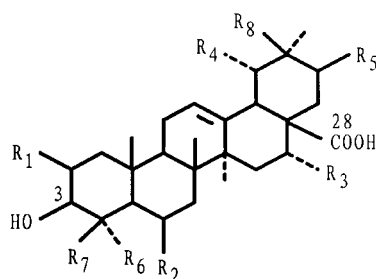
Keywords: Glucuronide oleanane-type triterpene carboxylic acid 3,28-*O*-bisdesmosides (GOTCAB); Triterpenoid saponins; Structural elucidation; Structural data and spectral data summarization; Natural distribution and biological activity

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 *Olex 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 jensseensis* 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 hypoglycaemic 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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(1)

	R ₁	R ₂	R ₃	R ₄	R ₅	R ₆	R ₇	R ₈
1 Bayogenin	OH	H	H	H	H	CH ₂ OH	CH ₃	CH ₃
2 Bredemolic acid	H	H	H	H	H	CH ₃	CH ₂ OH	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 ₂ OH	CH ₃	CH ₃
8 Ilexosapogenin A	H	H	H	OH	H	CH ₂ OH	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 ₂ OH	CH ₃	CH ₃
14 16α-OH Protobassic acid	OH	OH	OH	H	H	CH ₂ OH	CH ₃	CH ₃
15 Quillaic acid	H	H	OH	H	H	CHO	CH ₃	CH ₃
16 Siarsinolic acid	H	H	H	OH	H	CH ₃	CH ₃	CH ₃
17 Spathodic acid	H	H	H	OH	H	CH ₃	CH ₂ OH	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 (G₁); (3) the structure determination of the 28-sugar chain (G₂); (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

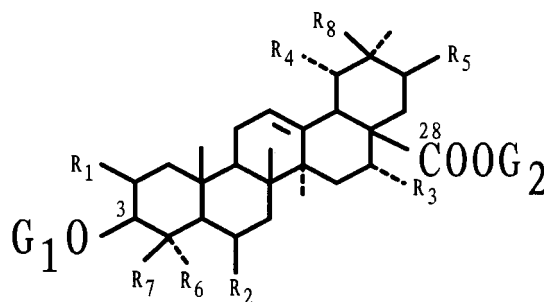


Fig. 1. The skeleton of glucuronide oleanane-type triterpene carboxylic acid 3,28-O-bisdesmosides (GOTCAB).

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	<i>Acanthophyllum gypsophiloides</i> (Caryophyllaceae)	Acanthophylloside B (1)	Gypsogenin (5) $\begin{array}{c} 4 \\ \text{gal} \text{---} \text{ara} \text{---} \text{glcUA (}\beta\text{-OH)} \\ \\ 2 \\ 3 \quad 3 \quad 4 \quad 4 \\ \text{xyl} \text{---} \text{xyl} \text{---} \text{rha} \text{---} \text{fuc (28-COOH)} \\ \\ 2 \quad \text{rha} \end{array}$	IR, NMR.		Putieva, Mzhel'skaya, Gorovits, Kondratenko, & Abubakirov, 1976
		Acanthophylloside C (2)	Gypsogenin (5) $\begin{array}{c} 4 \\ \text{gal} \text{---} \text{ara} \text{---} \text{glcUA (}\beta\text{-OH)} \\ \\ 2/ \quad 6 \\ \text{gal} \quad \text{glc} \\ 3 \quad 3 \quad 4 \quad 4 \\ \text{xyl} \text{---} \text{xyl} \text{---} \text{rha} \text{---} \text{fuc (28-COOH)} \\ \\ 2 \quad \text{rha} \end{array}$	IR, NMR.		Putieva et al., 1976
2	<i>A. Squarrosom</i> (roots)	Squarroside A (3)	Gypsogenin (5) $\begin{array}{c} 2 \\ \text{gal} \text{---} \text{glcUA (}\beta\text{-OH)} \\ \\ 3 \\ \text{xyl} \\ 4 \quad 2 \\ \text{xyl} \text{---} \text{rha} \text{---} \text{fuc (28-COOH)} \\ \\ 3/ \quad 4 \\ \text{ara(f)} \quad \text{COCH}_3 \end{array}$	amorphous powder, mp 262–264°, $[\alpha]_D^{20} + 4^\circ$ (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	<i>Achyranthes aspera</i> (Amaranthaceae) (seeds)	Saponin B (4)	Oleanolic acid (11) $\begin{array}{c} 4 \quad 4 \\ \text{rha} \text{---} \text{glc} \text{---} \text{glcUA (}\beta\text{-OH)} \\ \\ \text{gal (28-COOH)} \\ \text{glcUA (}\beta\text{-OH)} \\ \\ 3, 4 \quad 2' \\ \text{glycolate} \text{---} \alpha\text{-OCH}_2\text{COOH} \\ \\ 1''/ \quad 1'' \\ \beta\text{-OMe } \alpha\text{-COOH} \\ \\ \text{glc (28-COOH)} \end{array}$	methyl ester: mp 200–205°, $[\alpha]_D^{27} - 8^\circ$ (MeOH, c 1.2), C ₅₃ H ₉₀ O ₂₄ (EA).		Hariharan et al., 1970
4	<i>A. fauriei</i> (roots)	Achyranthoside A (5)	Oleanolic acid (11) $\begin{array}{c} 4 \quad 4 \\ \text{rha} \text{---} \text{glc} \text{---} \text{glcUA (}\beta\text{-OH)} \\ \\ \text{gal (28-COOH)} \\ \text{glcUA (}\beta\text{-OH)} \\ \\ 3, 4 \quad 2' \\ \text{glycolate} \text{---} \alpha\text{-OCH}_2\text{COOH} \\ \\ 1''/ \quad 1'' \\ \beta\text{-OMe } \alpha\text{-COOH} \\ \\ \text{glc (28-COOH)} \end{array}$	methyl ester: white powder, $[\alpha]_D + 64.3^\circ$ (MeOH), FAB-MS [1033 (M + Na) ⁺], PMR, CMR, 2D NMR (COSY, H–C COSY, NOE, HMBC), C ₅₁ H ₇₆ O ₂₀ , x-ray.	cytotoxic activity	Ida et al., 1994
		Achyranthoside B (6)	Oleanolic acid (11) $\begin{array}{c} 4 \quad 4 \\ \text{rha} \text{---} \text{glc} \text{---} \text{glcUA (}\beta\text{-OH)} \\ \\ \text{gal (28-COOH)} \\ \text{glcUA (}\beta\text{-OH)} \\ \\ 3, 4 \quad 2' \\ \text{glycolate} \text{---} \alpha\text{-OCH}_2\text{COOH} \\ \\ 1''/ \quad 1'' \\ \beta\text{-OH } \alpha\text{-COOH} \\ \\ \text{glc (28-COOH)} \end{array}$	methyl ester: white powder, $[\alpha]_D + 51.7^\circ$ (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	<i>Actinostemma lobatum</i> (Cucurbitaceae) (seeds)	Lobatoside I (7)	Gypso-genin (5) $\begin{array}{c} 2 \\ \text{gal} \cdots \text{glcUA} \text{ (}\beta\text{-OH)} \\ 4 \quad 2 \\ \text{xy} \text{ l} \cdots \text{rha} \cdots \text{fuc} \text{ (28-COOH)} \\ \\ 3 \\ \text{glc} \end{array}$	white amorphous powder (aqueous MeOH), mp 222– 227° (dec.), $[\alpha]_D^{25} + 1.7^\circ$ (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, DDO), C ₆₅ H ₁₀₂ O ₃₂ Na (pos. HR- FAB-MS). white amorphous powder, mp 229–234° (dec.), $[\alpha]_D^{25} + 3.8^\circ$ (pyridine, c 3.2), FAB-MS [1549 (M + Na) ⁺ , 1525 (M – H) [–]], PMR, CMR, 2D NMR (COSY, NOESY, NOEDS, ROEDS, HOHAHA, DDO), C ₆₀ H ₁₁₀ O ₃₆ Na (pos. HR-FAB-MS).		Fujioka et al., 1992
		Lobatoside J (8)	Gypso-genin (5) $\begin{array}{c} 2 \\ \text{gal} \cdots \text{glcUA} \text{ (}\beta\text{-OH)} \\ 3 \quad 4 \quad 2 \\ \text{xy} \text{ l} \cdots \text{xy} \text{ l} \cdots \text{rha} \cdots \text{fuc} \text{ (28-COOH)} \\ \quad \\ 3 \quad \text{glc} \end{array}$			Fujioka et al., 1992
		Lobatoside K (9)	Oleanolic acid (11) $\begin{array}{c} 2 \\ \text{gal} \cdots \text{glcUA} \text{ (}\beta\text{-OH)} \\ 4 \quad 2 \\ \text{xy} \text{ l} \cdots \text{rha} \cdots \text{fuc} \text{ (28-COOH)} \\ \\ 3 \\ \text{glc} \end{array}$	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, DDO), C ₆₃ H ₁₀₄ O ₃₁ Na (pos. HR-FAB-MS).		Fujioka et al., 1992
6	<i>Amaranthus hypochondriacus</i> (Amaranthaceae) (grains)	Amaranthus-saponin I (10)	2β-OH Oleanolic acid (12) $\begin{array}{c} 3 \\ \text{rha} \cdots \text{glcUA} \text{ (}\beta\text{-OH)} \\ \text{glc} \text{ (28-COOH)} \end{array}$	white powder, $[\alpha]_D + 23.3^\circ$ (pyridine, c 0.43), FAB-MS [955 (M – H) [–]], PMR, CMR, methyl ester: C ₄₉ H ₇₈ O ₁₉ · 2H ₂ O (EA).		Kohda et al., 1991
		Amaranthus-saponin II (11)	2β-OH Gypso-genin (6) $\begin{array}{c} 3 \\ \text{rha} \cdots \text{glcUA} \text{ (}\beta\text{-OH)} \\ \text{glc} \text{ (28-COOH)} \end{array}$	white powder, $[\alpha]_D + 9.2^\circ$ (MeOH, c 0.87), FAB-MS [969 (M – H) [–]], PMR, CMR, methyl ester: C ₄₉ H ₇₆ O ₂₀ · 3H ₂ O (EA).		Kohda et al., 1991
7	<i>Aralia amata</i> (Araliaceae) (root barks)	Saponin 15 (12)	Oleanolic acid (11) $\begin{array}{c} 3 \\ \text{gal} \cdots \text{glcUA} \text{ (}\beta\text{-OH)} \\ \text{glc} \text{ (28-COOH)} \end{array}$	methyl ester: powder, [α] _D ²⁵ + 12.4° (MeOH, c 0.50), IR, SI- MS [993 (M + Na) ⁺], PMR, CMR, C ₄₉ H ₇₈ O ₁₉ · 2H ₂ O (EA).		Hu, Ogawa, Sashida, & Xiao, 1995
8	<i>A. chinensis</i> (roots)	Araliasaponin XVIII (13)	Oleanolic acid (11) $\begin{array}{c} 2 \\ \text{glc} \cdots \text{glcUA} \text{ (}\beta\text{-OH)} \\ \\ 4 \\ \text{ara} \text{ (f)} \\ 6 \\ \text{glc} \cdots \text{glc} \text{ (28-COOH)} \end{array}$	methyl ester: amorphous powder, [α] _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 · 2H ₂ O (EA).		Miyase et al., 1996

9	<i>A. decaisneana</i> (root barks)	Ad-III (14)	Oleanolic acid (11) 4 gal---gal---glcUA (3 β -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	<i>A. elatal</i> (root barks)	Tarasaponin IV (15)	Oleanolic acid (11) 2 glc---glcUA (3 β -OH) 14 ara(f) glc (28-COOH)	methyl ester: powder (MeOH), mp 196–206°(dec.), [α] _D ²⁰ 22.6°(MeOH, c 1.10), IR, FAB-MS [1101 (M-H) ⁻], PMR, CMR, 2D NMR (NOE), C ₅₄ H ₈₆ O ₂₃ · H ₂ O (EA).	Satoh et al., 1994
		Tarasaponin V (16)	Oleanolic acid (11) 2 xyl---glcUA (3 β -OH) 3 glc glc (28-COOH)	methyl ester: powder (MeOH), mp 235–245°(dec.), [α] _D ²⁰ 5.1°(MeOH, c 1.10), IR, FAB-MS [1101 (M-H) ⁻], PMR, CMR, 2D NMR (NOE), C ₅₄ H ₈₆ O ₂₃ · 1/2 H ₂ O (EA).	Satoh et al., 1994
		Tarasaponin VI (17)	Oleanolic acid (11) 2 xyl---glcUA (3 β -OH) 3 gal glc (28-COOH)	methyl ester: powder (MeOH), mp 218–230°(dec.), [α] _D ²⁰ +48°(MeOH, c 1.10), IR, FAB-MS [1101 (M-H) ⁻], CMR, C ₅₄ H ₈₆ O ₂₃ · 3H ₂ O (EA).	Satoh et al., 1994
	(barks)	Elatoside C (18)	Oleanolic acid (11) 2 xyl---glcUA (3 β -OH) 3 gal glc (28-COOH)	colorless fine crystals, mp 208.5–209.5°, [α] _D ²⁰ -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 (3 β -OH) 3 gal glc (28-COOH)	colorless fine crystals, mp 188.5–189.5°, [α] _D ²⁰ +6.9°(MeOH), IR, FAB-MS [1141 (M+Na) ⁺], PMR, CMR, C ₅₄ H ₈₆ O ₂₄ .	Yoshikawa, Yoshizumi, Ueno, Matsuda, Murakami, Yamahara, & Murakami, 1995
	(young shoots)	Elatoside K (20)	Oleanolic acid (11) 2 xyl---glcUA (3 β -OH) 3 glc glc (28-COOH)	colorless fine crystals (MeOH–H ₂ O), mp 219.2–222.4°, [α] _D ²⁰ +2.0°(MeOH, c 0.1), IR, FAB-MS [1111 (M+Na) ⁺ , 1087 (M-H) ⁻], PMR, CMR, 2D NMR (HMB), C ₅₃ H ₈₄ O ₂₃ Na (pos. HR-FAB-MS).	Jiang, Xu, Gu, Ren, Chen, Yao, & Miao, 1992
	(root barks)	Araloside A (21)	Oleanolic acid (11) 4 ara(f)---glcUA (3 β -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).	Kochetkov et al., 1962
11	<i>A. manschurica</i> (roots)	Araloside A (22)	Oleanolic acid (11) 4 ara(f)---glcUA (3 β -OH) glc (28-COOH)	mp 195–196°(dec.) (MeOH), [α] _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 (3 β -OH) 14 ara(f) glc (28-COOH)	permethylated: [α] _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
12	<i>A. spinifolia</i> (roots)	Araloside C (24)	Oleanolic acid (11) 3 gal---glcUA (3 β -OH) 4 xyl	white powder, mp 208–210°(dec.), [α] _D ²⁰ -31.1°(MeOH, c 0.1), IR, FAB-MS [949 (M+Na) ⁺], PMR, CMR, C ₄₇ H ₇₄ O ₁₈ ·3H ₂ O (EA).		Hariharan, 1974
		Araloside J (25)	Oleanolic acid (11) 4 ara(f)---glcUA (3 β -OH) gal (28-COOH)	methyl ester: white powder, [α] _D ²⁵ -68.9°(MeOH, c 2.0), FAB-MS [1109 (M+Na) ⁺ , 1085 (M-H) ⁻], PMR, CMR, 2D NMR (ROEDS), C ₄₈ H ₈₀ O ₂₃ Na (pos. HR-FAB-MS).		Yu et al., 1994
13	<i>Aster scaber</i> (Compositae) (ground parts)	Scaberoside Ha (26)	Echinocystic acid (3) glcUA (3 β -OH) 2 rha---xyl (28-COOH) 3 rha	methyl ester: white powder, [α] _D ²⁵ -71.0°(MeOH, c 0.9), FAB-MS [1241 (M+Na) ⁺ , 1217 (M-H) ⁻], PMR, CMR, 2D NMR (ROEDS), C ₃₉ H ₆₄ O ₂₃ Na (pos. HR-FAB-MS).		Nagao et al., 1993
		Scaberoside Hb ₁ (27)	Echinocystic acid (3) glcUA (3 β -OH) 4 2 xyl---rha---xyl (28-COOH) 3 rha	methyl ester: Colorless needles (H ₂ O–MeOH), mp 271°, [α] _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 Hb ₂ (28)	Echinocystic acid (3) glcUA (3 β -OH) 3 4 2 xyl---xyl---rha---xyl (28-COOH) 3 rha	methyl ester: Colorless needles (H ₂ O–MeOH), mp 238–240°, [α] _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 ₁ (29)	Echinocystic acid (3) glcUA (3 β -OH) 3 3 2 xyl---xyl---rha---xyl (28-COOH) 4 3 xyl rha	methyl ester: white powder, [α] _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 Hc ₂ (30)	Echinocystic acid (3) 3 xyl---glcUA (3 β -OH) 3 4 2 xyl---xyl---rha---xyl (28-COOH) 3 rha	methyl ester: white powder, [α] _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 Hd (31)	Echinocystic acid (3) 3 xyl---glcUA (3 β -OH) 3 3 2 xyl---xyl---rha---xyl (28-COOH) 4 3 xyl rha			

Scaberoside Hf (32)	Echinocystic acid (3) 2 gal- $\rightarrow$ -glcUA (3 β -OH) 4 2 xyl- $\rightarrow$ -rha- $\rightarrow$ -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- $\rightarrow$ -glcUA (3 β -OH) 3 4 2 xyl- $\rightarrow$ -xyl- $\rightarrow$ -rha- $\rightarrow$ -xyl (28-COOH) 3 rha	methyl ester: colorless needles (H ₂ O–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- $\rightarrow$ -glcUA (3 β -OH) 3 xyl 3 4 2 xyl- $\rightarrow$ -xyl- $\rightarrow$ -rha- $\rightarrow$ -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, ROES), C ₇₅ H ₁₂₀ O ₃₉ Na (pos. HR-FAB-MS).	Nagao et al., 1993
Scaberoside Hi (35)	Echinocystic acid (3) 2 gal- $\rightarrow$ -glcUA (3 β -OH) 3 3 2 xyl- $\rightarrow$ -xyl- $\rightarrow$ -rha- $\rightarrow$ -xyl (28-COOH) 4 3 xyl rha	methyl ester: white powder, $[\alpha]_D^{25}$ -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
Scaberoside B ₁ (36)	Oleanolic acid (11) glcUA (3 β -OH) ara (28-COOH)	methyl ester: colorless needles (H ₂ O–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 (3 β -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 (3 β -OH) 2 rha- $\rightarrow$ -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, NOES), C ₄₈ H ₇₆ O ₁₇ Na (pos. HR-FAB-MS).	Nagao et al., 1991
Scaberoside B ₄ (39)	Oleanolic acid (11) glcUA (3 β -OH) 2 rha- $\rightarrow$ -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 ₂ O–MeOH), mp 217–220°, [α] _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 ₂ O–MeOH), mp 214–216°, [α] _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, [α] _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, [α] _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) 14 xyl	methyl ester: amorphous powder, [α] _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) 14 xyl	methyl ester: amorphous powder, [α] _D ²⁹ -46.2° (MeOH, c 2.25), FAB-MS [1359 (M + Na) ⁺], 1335 (M–H) [–]], PMR, CMR, 2D NMR (COSY, ROES, 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) 14 xyl	methyl ester: colorless needles (H ₂ O–MeOH), mp 230–233°, [α] _D ²⁰ -54.5° (MeOH, c 0.9), FAB- MS [1211 (M + Na) ⁺], 1187 (M– H) [–]], PMR, CMR, 2D NMR (NOES), 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) 16 xyl	methyl ester: white powder, [α] _D ²⁹ - 31.6° (MeOH, c 0.5), FAB-MS [1109 (M + Na) ⁺], 1085 (M–H) [–]], PMR, CMR, 2D NMR (ROES), C ₅₄ H ₈₆ O ₂₂ Na (pos. HR-FAB-MS).		Nagao et al., 1992

14	<i>A. tataricus</i> (ground parts)	Aster saponin Ha (48)	Echinocystic acid (3) glcUA (3 β -OH) ara (28-COOH)	methylester: amorphous powder, [α] _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 (3 β -OH) 2 rha---ara (28-COOH)	methylester: amorphous powder, [α] _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 (3 β -OH) 3 4 2 xyl---xyl---rha---ara (28-COOH)	methylester: colorless needles (aqueous MeOH), mp 227–228°, [α] _D ²⁷ -47.3° (MeOH, c 2.0), FAB- MS [1227 (M + Na) ⁺], PMR, CMR, C ₅₈ H ₉₂ O ₂₆ · H ₂ O (EA).	Tanaka et al., 1990
		Aster saponin Hd (51)	Echinocystic acid (3) glcUA (3 β -OH) 3 4 2 xyl---xyl---rha---ara (28-COOH) 3 api(f)	methylester: colorless needles (aqueous MeOH), mp 235–237°, [α] _D ²⁶ -62.8° (MeOH, c 1.8), FAB- MS [1359 (M + Na) ⁺], PMR, CMR, C ₆₃ H ₁₀₀ O ₃₀ · 2H ₂ O (EA).	Tanaka et al., 1990
15	<i>Beta vulgaris</i> (Chenopodiaceae) (roots, leaves)	Betavulgaroside III (52)	Oleanolic acid (11) glcUA (3 β -OH) 3 3'-3''-O-carbonylmethyl- 2 β ,3 β -dihydroxyl propanoic acid glc (28-COOH)	hypoglycemic activity colorless fine crystals, mp 212- 214°, [α] _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].	Yoshikawa et al., 1996; Yoshikawa, Murakami, Kadoya, Matsuda, Yamahara, Muraoka, & Murakami, 1995; Yoshikawa, Murakami, Inaduki, Hirano, Yamahara, & Matsuda, 1997 Yoshikawa et al., 1996
		Betavulgaroside V (53)	Oleanolic acid (11) 2 glc---glcUA (3 β -OH) 3 3'-3''-O-carbonylmethyl- 2,3-dihydroxyl propanoic acid glc (28-COOH)	colorless fine crystals, mp 205- 206°, [α] _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].	Pizza, Zhou, & Tommasi, 1987
16	<i>Calendula arvensis</i> (Compositae) (aerial parts)	Saponin 3 (54)	Oleanolic acid (11) 3 gal---glcUA (3 β -OH) glc (28-COOH)	[α] _D + 15° (MeOH), FAB-MS [955 (M-H) ⁻], PMR, CMR, C ₄₈ H ₇₆ O ₁₉ .	
17	<i>C. officinalis</i> (flowers)	Glycoside A (55)	Oleanolic acid (11) 2 glc---glcUA (3 β -OH) 3 gal glc (28-COOH)	mp 227–229° (dec.), [α] _D + 12° (H ₂ O, c 0.5), FAB-MS [1117 (M-H) ⁻], CMR, C ₅₄ H ₈₆ O ₂₄ .	Vidal-Ollivier, Balansard, Faure, & Babadjanian, 1989
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Table 1—Continued

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

24	<i>Gypsophila oldhamiana</i> (Caryophyllaceae) (roots)	Saponin 3 (67)	Quillaic acid (15) $\begin{array}{c} 2 \\ \text{gal} \cdots \text{glcUA} (3\beta\text{-OH}) \\ \\ 3 \\ \text{xyl} \\ \\ 3 \\ \text{gle} \cdots \text{rha} (28\text{-COOH}) \\ \\ 4 \end{array}$	light yellow powder, PMR, CMR, 2D NMR (HETCOR, HMBC), $\text{C}_{65}\text{H}_{102}\text{O}_{32}$.	Liu et al., 1995
25	<i>G. pacifica</i> (roots)	Gypsoside (68)	Gypsoenin (5) $\begin{array}{c} 4 \\ \text{gal} \cdots \text{glc} \cdots \text{glcUA} (3\beta\text{-OH}) \\ \\ 3 \\ \text{ara} \\ \\ 3 \quad 2 \\ \text{xyl} \cdots \text{rha} (28\text{-COOH}) \\ \\ 4 \\ \text{fuc} \\ \\ 3 \\ \text{xyl} \end{array}$	permethylated: $[\alpha]_{\text{D}}^{20} + 47.5^{\circ} (\text{CHCl}_3, \text{c } 3.4),$ $\text{C}_{103}\text{H}_{172}\text{O}_{44}$	Kochetkov et al., 1963
26	<i>G. paniculata</i>	MS-1 (69)	Gypsoenin (5) $\begin{array}{c} 2 \\ \text{gal} \cdots \text{glcUA} (3\beta\text{-OH}) \\ \\ 3 \\ \text{ara} \\ \\ 3 \quad 4 \quad 4 \\ \text{xyl} \cdots \text{rha} \cdots \text{fuc} (28\text{-COOH}) \\ \\ 2 \\ \text{qui} \end{array}$	white powder (MeOH–H ₂ O), mp 243–247°(dec.), $[\alpha]_{\text{D}}^{28} + 7.7^{\circ} (\text{H}_2\text{O}, \text{c } 1.68)$, IR, FAB-MS [1641 (M–H) [–]], PMR, CMR, 2D NMR (H–C COSY), $\text{C}_{75}\text{H}_{118}\text{O}_{39} \cdot 1.2\text{H}_2\text{O}$ (EA).	Kim, Higuchi, & Komori, 1992
		MS-2 (70)	Quillaic acid (15) $\begin{array}{c} 2 \\ \text{gal} \cdots \text{glcUA} (3\beta\text{-OH}) \\ \\ 3 \\ \text{ara} \\ \\ 3 \quad 4 \quad 4 \\ \text{xyl} \cdots \text{rha} \cdots \text{fuc} (28\text{-COOH}) \\ \\ 2 \\ \text{qui} \end{array}$	white powder (MeOH–H ₂ O), mp 262–264°(dec.), $[\alpha]_{\text{D}}^{28} + 0.57^{\circ} (\text{H}_2\text{O}, \text{c } 1.33)$, IR, FAB-MS [1657 (M–H) [–]], PMR, CMR, $\text{C}_{75}\text{H}_{118}\text{O}_{40} \cdot 1/2\text{H}_2\text{O}$ (EA).	Kim et al., 1992
27	<i>G. paniculata</i> and <i>G. arrostii</i> (roots)	G1 (71)	Quillaic acid (15) $\begin{array}{c} 2 \\ \text{gal} \cdots \text{glcUA} (3\beta\text{-OH}) \\ \\ 3 \\ \text{xyl} \\ \\ 3 \quad 2 \\ \text{gle} \cdots \text{rha} \cdots \text{fuc} (28\text{-COOH}) \\ \\ 4 \\ \text{xyl} \end{array}$	amorphous powder, mp 210–213°, FAB-MS [1541 (M–H) [–]], PMR, CMR, 2D NMR (HOHAHA, H–C COSY, H–C RELAY, HMBC), $\text{C}_{70}\text{H}_{110}\text{O}_{37}$.	Frechet et al., 1991
		G2 (72)	Quillaic acid (15) $\begin{array}{c} 2 \\ \text{gal} \cdots \text{glcUA} (3\beta\text{-OH}) \\ \\ 3 \\ \text{xyl} \\ \\ 4 \quad 3 \quad 4 \quad 2 \\ \text{ara} \cdots \text{rha} \cdots \text{xyl} \cdots \text{rha} \cdots \text{fuc} (28\text{-COOH}) \end{array}$	amorphous powder, mp 213–215°, FAB-MS [1643 (M–H) [–]], PMR, CMR, 2D NMR (HOHAHA, H–C COSY, H–C RELAY, HMBC), $\text{C}_{74}\text{H}_{116}\text{O}_{40}$.	Frechet et al., 1991

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Table 1—Continued

No.	Source (family, part)	Saponin (No.)	Structure	Structural and spectral data	Bioactivity	Reference
28	<i>G. patrinii</i> (roots)	G3 (73)	Gypsogenin (5) 2 glc---glcUA (3 β -OH) 3 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 ₆₃ H ₁₀₂ O ₃₂ .		Frechet et al., 1991
		G4 (74)	Gypsogenin (5) 2 gal---glcUA (3 β -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
		Phyloside A (75)	Gypsogenin (5) 2 3 xyl---gal---glcUA (3 β -OH) 2/ 4 4 2 xyl gal rha---glc---fuc (28-COOH) 6 rha			Bukharov, Karlin, Bukharova, & Surkova, 1975a
29	<i>G. trichotoma</i>	Phyloside B (76)	Gypsogenin (5) 2 3 ara---xyl---gal---glcUA (3 β -OH) 2/ 4 4 2 xyl gal rha---ara---fuc (28-COOH)			Bukharov, Karlin, Bukharova, & Surkova, 1975b
		Trichoside A (77)	Gypsogenin (5) 3 glc---glcUA (3 β -OH) gal (28-COOH)			Luchanskaya, Kondratenko, Gorovits, & Abubakirov, 1971
		Trichoside C (78)	Gypsogenin (5) 3 glc---glcUA (3 β -OH) 4 4 gal---rha---fuc (28-COOH)			Luchanskaya, Kondratenko, & Abubakirov, 1972
30	<i>Hemsleya clinensis</i> (Cucurbitaceae) (rhizomes)	Hemsloside H ₁ (79)	Oleanolic acid (11) 2 glc---glcUA (3 β -OH) 3 ara 6	white powder (MeOH–EtOAc), [α] _D ²⁷ + 2.9° (MeOH, c 1.32), CMR, C ₅₉ H ₉₄ O ₂₈ · 5/2H ₂ O (EA).		Morita et al., 1986
		Hemsloside G1 (80)	Oleanolic acid (11) 3 ara---glcUA (3 β -OH) 6 glc---glc (28-COOH)	white powder, [α] _D ¹⁸ + 7.6° (MeOH, c 0.9), PMR, CMR, C ₅₃ H ₈₄ O ₂₃ · 2H ₂ O (EA).		Kasai, Tanaka, Nie, Miyakoshi, Zhou, & Tanaka, 1990

	Hemloside G2 (81)	Oleanolic acid (11) 2 glc---glcUA (3 β -OH) 6 glc---glc (28-COOH)	white powder, $[\alpha]_D^{18}$ -6.1°(MeOH, c 0.9), PMR, CMR, $C_{34}H_{60}O_{24} \cdot 2H_2O$ (EA).	Kasai et al., 1990
32	<i>H. macrosperma</i> (rhizomes)	Hemloside-Ma1 (82)	Oleanolic acid (11) 3 ara---glcUA (3 β -OH) glc (28-COOH)	Nie et al., 1984
		Hemloside-Ma2 (83)	Oleanolic acid (11) 2 xyl---glcUA (3 β -OH) 3 ara	Nie et al., 1984
		Hemloside-Ma3 (84)	glc (28-COOH) Oleanolic acid (11) 2 glc---glcUA (3 β -OH) 3 ara	Nie et al., 1984
33	<i>Herniaria fontanesii</i> (Caryophyllaceae) (aerial parts)	Herniaria saponin C (85)	glc (28-COOH) Zanhic acid (19) 2 rha---glcUA (3 β -OH) 2 rha---fuc (28-COOH) 3/ \4 rha COCH ₃	M'Bark, Gutllaume, Kol, & Charrouf, 1996
		Herniaria saponin D (86)	Zanhic acid (19) 2 rha---glcUA (3 β -OH) 2 rha---fuc (28-COOH) 3 rha	M'Bark et al., 1996
34	<i>H. glabra</i> (ground parts)	Herniaria saponin 1 (87)	Medicagenic acid (10) glcUA (3 β -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 (3 β -OH) 3 2 glc---rha---fuc (28-COOH) 3/ \4 glc COCH ₃	Schroder et al., 1993
		Herniaria saponin (89)	Medicagenic acid (10) glcUA (3 β -OH) 3 2 glc---rha---fuc (28-COOH) 3/ \4 api(f) COCH ₃	Freiler, Reznicek, Schubert-Zsilavecz, Reiner, Haslinger, Jurenitsch, & Kubelka, 1996
35	<i>Ilex rotunda</i> (Aquifoliaceae) (leaves)	Ilexoside XXXI (90)	Siaresinolic acid (16) glcUA (3 β -OH) glc (28-COOH)	Amimoto et al., 1992

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Table 1—Continued

No.	Source (family, part)	Saponin (No.)	Structure	Structural and spectral data	Bioactivity	Reference
36	<i>Kalimeris shimadae</i> (Compositae) (roots)	Ilexoside XLVI (91)	Ilexosapogenin A (8) glcUA (3 β -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 · 2 H ₂ O (EA).		Amimoto et al., 1993
		Ilexoside XLVII (92)	Spathodic acid (17) glcUA (3 β -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 · 3H ₂ O (EA).		Amimoto et al., 1993
		Ilexoside XLVIII (93)	Hederagenin (7) glcUA (3 β -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 · H ₂ O (EA).		Amimoto et al., 1993
		Ilexoside XLIX (94)	Hederagenin (7) 2 gal----glcUA (3 β -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 · 3H ₂ O (EA).		Amimoto et al., 1993
		Ilexoside L (95)	Bredemolic acid (2) glcUA (3 β -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 · 2H ₂ O (EA).		Amimoto et al., 1993
37	<i>Kochia scoparia</i> (Chenopodiaceae) (fruits)	Ilexoside LI (96)	Siaresinolic acid (16) 2 gal----glcUA (3 β -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 · 3 H ₂ O (EA).		Amimoto et al., 1993
		Shimadoside A (97)	Echinocystic acid (3) glcUA (3 β -OH) 3 4 2 xyl----xyl----rha----xyl (28-COOH)	needles, mp 215–216°, $[\alpha]_D^{22}$ -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
38	<i>Ladyginia bucharica</i> (Umbelliferae) (roots)	Saponin 5 (98)	Oleanolic acid (11) 2 glc----glcUA (3 β -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 · 6H ₂ O (EA).		Wen, Chen, Cui, Li, & Wang, 1995
		Ladyginoside D (99)	Hederagenin (7) 4 glc----glcUA (3 β -OH) 4 6 gal----glc----glc (28-COOH)			Patkullaeva, Mzhel'skaya, & Abubakirov, 1975

39	<i>Luffia acutangula</i> (Cucurbitaceae) (seeds)	Ladyginoside E (100)	Oleanolic acid (11) 4 glc---glcUA (3 β -OH) 6 6 glc---glc---glc---glc (28-COOH) 4 gal	mp 200–202°.	Patkullaeva Mzh- el'skaya, & Abubaki- rov, 1975
		Ladyginoside F (101)	Hederagenin (7) 4 glc---glcUA (3 β -OH) 6 6 glc---glc---glc---glc (28-COOH) 4 gal		Patkullaeva et al., 1975
40	<i>L. cylindrica</i> (seeds)	Acutoside H (102)	Oleanolic acid (11) 3 ara---glcUA (3 β -OH) 3 4 2 xyl---xyl---rha---ara (28-COOH) 3 xyl	methyl ester: colorless fine needles (80% MeOH), mp 235–238°, [α] _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, ROES), C ₆₈ H ₁₀₈ O ₃₃ Na (pos. HR- FAB-MS).	Nagao et al., 1991
		Acutoside I (103)	Oleanolic acid (11) 3 ara---glcUA (3 β -OH) 3 4 2 ara---xyl---rha---ara (28-COOH) 3 xyl	methyl ester: colorless needles (80% MeOH), mp 234–237°, [α] _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
41	<i>L. operculata</i> (whole plants)	Lucyoside N (104)	Quillaic acid (15) 2 gal---glcUA (3 β -OH) 4 2 xyl---rha---ara (28-COOH) 3 glc	colorless fine needles, mp 268- 270°, [α] _D ²⁴ –36.1° (pyridine, c 2.4), IR, FAB-MS [1395 (M-H) ⁻], PMR, CMR, C ₆₄ H ₁₀₀ O ₃₃ ·7/2H ₂ O (EA).	Yoshikawa et al., 1991
		Lucyoside P (105)	Gypsogenin (5) 2 gal---glcUA (3 β -OH) 4 2 xyl---rha---ara (28-COOH) 3 glc	fibrinolytic activity	Yoshikawa et al., 1991
41	<i>L. operculata</i> (whole plants)	Luperoside I (106)	Gypsogenin (5) 2 gal---glcUA (3 β -OH) 3 ara 4 2 xyl---rha---qui (28-COOH) 3 rha	colorless fine needles, mp 228- 230°, [α] _D ²⁴ –12.2° (pyridine, c 6.5), IR, FAB-MS [1379 (M-H) ⁻], PMR, CMR, C ₆₄ H ₁₀₀ O ₃₂ ·6H ₂ O (EA).	Okabe et al., 1989
				methyl ester: fine needles (MeOH), mp 242–245° (dec.), [α] _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 ·2H ₂ O (EA).	Continued overleaf

Table 1—Continued

No.	Source (family, part)	Saponin (No.)	Structure	Structural and spectral data	Bioactivity	Reference
42	<i>Madhuca butyracea</i> (Sapotaceae) (seeds)	Luperoside J (107)	Gypsogenin (5) 2 gal---glcUA (3 β -OH) 3 ara 3 4 2 xyl---xyl---rha---qui (28-COOH) 3 rha	methyl ester: fine needles (MeOH), mp 237–240°, [α] _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 ₇₀ H ₁₂₀ O ₃₉ · 4H ₂ O (EA).		Okabe et al., 1989
		Luperoside K (108)	Quillaic acid (15) 2 gal---glcUA (3 β -OH) 3 ara 4 2 xyl---rha---qui (28-COOH) 3 rha	methyl ester: amorphous powder (EtOH), mp 242–244°, [α] _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 · 7/2H ₂ O (EA).		Okabe et al., 1989
		Luperoside L (109)	Quillaic acid (15) 2 gal---glcUA (3 β -OH) 3 ara 3 4 2 xyl---xyl---rha---qui (28-COOH) 3 rha	methyl ester: amorphous powder (EtOH), mp 246–248° (dec.), [α] _D ²⁸ , 21.6° (70% MeOH, c 1.40), FAB- MS [1695 (M + Na) ⁺], PMR, CMR, C ₇₆ H ₁₂₀ O ₄₀ · 5H ₂ O (EA).		Okabe et al., 1989
43	<i>Melastoma butyracea</i> (Sapotaceae) (seeds)	Butyroside C (110)	Protobassic acid (13) 3 4 2 glcUA (3 β -OH) rha---xyl---rha---ara (28-COOH)	powder (MeOH), mp 216- 220° (dec.), [α] _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)	16 α -OH Protobassic acid (14) 3 4 2 glcUA (3 β -OH) api(f)---xyl---rha---ara (28-COOH)	powder (MeOH), mp 213- 215° (dec.), [α] _D ¹⁶ , 53° (MeOH, c 1.03), FAB-MS [1237 (M-H) ⁻], PMR, CMR, C ₅₇ H ₉₀ O ₂₉ .		Li et al., 1994
		Saponin 5 (112)	Oleanolic acid (11) 4 xyl---glcUA (3 β -OH) glc (28-COOH)	methyl ester of acetylated: PMR, CMR, 2D NMR (COSY).		Penders & Delaude, 1994
44	<i>Meliosma lanceolata</i> (Sabiaceae) (barks)	(113)	Bayogenin (1) glcUA (3 β -OH) glc (28-COOH)	methyl ester: [α] _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 (3 β -OH) glc (28-COOH)	[α] _D ²² + 14.7° (MeOH, c 1.09), FAB-MS [871 (M + 2Na) ⁺], PMR, CMR, C ₄₂ H ₆₅ O ₁₆ · 2Na (pos. HR- FAB-MS).		Abe et al., 1996

(115)	Bayogenin (1)	gal $\rightarrow$ glcUA (3 β -OH) glc (28-COOH)	methylester: prisms, mp 220–230°, [α] _D ²⁶ + 27.2° [MeOH, c 0.53], FAB-MS [1025 (M + Na) ⁺], PMR, CMR, C ₄₀ H ₇₈ O ₂₁ Na (pos. HR-FAB-MS).	Abe et al., 1996
(116)	Bayogenin (1)	gal $\rightarrow$ glcUA (3 β -OH) glc (28-COOH)	prisms, mp 290–300° (dec.), [α] _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)	ara $\rightarrow$ glcUA (3 β -OH) glc (28-COOH)	methylester: [α] _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)	gal $\rightarrow$ glcUA (3 β -OH) glc (28-COOH)	methylester: [α] _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)	gal $\rightarrow$ glcUA (3 β -OH) glc (28-COOH)	[α] _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	<i>Mimusops elengi</i> (Sapotaceae) (seed kernels)	Protobassic acid (13) glcUA (3 β -OH) rha $\rightarrow$ xy $\rightarrow$ rha $\rightarrow$ ara (28-COOH) ₃ rha	[α] _D ²⁷ 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	<i>M. hexandra</i> (seed kernels)	16 α -OH Protobassic acid (14) glcUA (3 β -OH) rha $\rightarrow$ xy $\rightarrow$ rha $\rightarrow$ ara (28-COOH) ₃ rha	[α] _D ²⁶ 49.4° [MeOH, c 0.563], FAB-MS [1275.6 (M + Na) ⁺], PMR, CMR, 2D NMR (COSY).	Lavaud et al., 1996
47	<i>Momordica cochinchinensis</i> (Cucurbitaceae) (seed kernels)	Gypsogenin (5) gal $\rightarrow$ glcUA (3 β -OH) ₃ rha ₃ 3 3 2 xyl $\rightarrow$ glc $\rightarrow$ rha $\rightarrow$ fuc (28-COOH) ₄ xyl	white powder (MeOH), mp 241–244° (dec.), [α] _D ¹⁹ 14.8° [MeOH–H ₂ O (1:2), c 0.7], IR.	Iwamoto et al., 1985
	Momordica saponin I (122)	Quillic acid (15) gal $\rightarrow$ glcUA (3 β -OH) ₃ rha ₃ 3 3 2 xyl $\rightarrow$ glc $\rightarrow$ rha $\rightarrow$ fuc (28-COOH) ₄ xyl	white powder (MeOH), mp 252–255° (dec.), [α] _D ¹⁹ 28.5° [MeOH–H ₂ O (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 (3 β -OH) 3 xyl glc (28-COOH)	white powder (MeOH-EtOAc), [α] _D ²³ +1.98° [MeOH, c 1.06], IR, SIMS [1097 (M+K) ⁺], PMR, CMR, C ₅₃ H ₈₅ O ₂₂ · H ₂ O (EA).		Kawamura et al., 1988
48	<i>Ola</i> <i>andronensis</i> <i>O. glabriflora</i> <i>O. psittacorum</i> (Olacaceae) (leaves, roots, barks)	Olaxoside (125)	Oleanolic acid (11) 4 rha-----glcUA (3 β -OH) glc (28-COOH)	colorless crystals [EtOH-H ₂ O (1:1)], mp 216–218°, C ₄₃ H ₇₆ O ₁₈ · H ₂ O.	anti-inflammatory and laxative activities	Forgacs et al., 1981
49	<i>Panax japonicum</i> (Araliaceae) (rhizomes)	Chikusetsusaponin V (126)	Oleanolic acid (11) 2 glc-----glcUA (3 β -OH) glc (28-COOH)	white powder (MeOH-AcOEt), mp 240–241°, [α] _D ²² +2.85° [MeOH, c 2.01], IR, C ₄₃ H ₇₆ O ₁₉ · 2 H ₂ O (EA).		Kondo, Marumoto, & Shoji, 1971
50	<i>P. pseudoginseng</i> subsp. <i>himalaicus</i> (rhizomes)	Pseudo-ginsenoside RT ₁ (127)	Oleanolic acid (11) 2 xyl-----glcUA (3 β -OH) glc (28-COOH)	colorless needles (MeOH), mp 235–238° (dec.), [α] _D ²⁰ +8.4° [MeOH, c 0.11], CMR, C ₄₇ H ₇₄ O ₁₈ · 4H ₂ O (EA).		Tanaka, Morita, Kasai, Kinouchi, Sanada, Ida, & Shoji, 1985
51	<i>P. pseudoginseng</i> subsp. <i>himalaicus</i> var. <i>angustifolius</i> (rhizomes)	Saponin C (128)	Oleanolic acid (11) glcUA (3 β -OH) glc (28-COOH)	white powder (aqueous BuOH), mp 216° (dec.), [α] _D ¹⁸ +15.8° [MeOH, c 0.62], IR, C ₄₃ H ₆₆ O ₁₄ · 3H ₂ O (EA).		Kondo & Shoji, 1975
52	<i>P. stipuleanatus</i> (rhizomes)	Stipuleanoside R ₂ (129)	Oleanolic acid (11) 3 glc-----glcUA (3 β -OH) 4 ara(f) glc (28-COOH)	white amorphous powder, mp 200–210°, CMR, C ₅₃ H ₈₄ O ₂₃ · 4H ₂ O (EA).		Yang, Jiang, Zhou, Kasai, & Tanaka, 1985
53	<i>Pisonia umbellifera</i> (Nyctaginaceae) (leaves)	Saponin 4 (130)	Oleanolic acid (11) 2 3 glc-----xyl-----glcUA (3 β -OH) 12 glc glc (28-COOH)	[α] _D ²³ +2.3° (CD ₃ OD, 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 (3 β -OH) 13 O-CH (OCH ₂ COOH) COOH glc (28-COOH)	[α] _D ²³ +6.8° (CD ₃ OD, 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 ₇₆ O ₁₉ .		Lavaud et al., 1996
54	<i>Polyscias scutellaria</i> (Araliaceae) (leaves)	Saponin C (132)	Oleanolic acid (11) 3 glc-----glcUA (3 β -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 (3 β -OH) glc (28-COOH)	white powder, mp 263°, FAB-MS [1117 (M-H) ⁻], CMR.		Paphassarang et al., 1990

55	<i>Pseudostellaria heterophylla</i> (Caryophyllaceae) (roots)	Pseudostellarinoside A (134)	Gypsogenin (5) 3 glc---glcUA (3 β -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	<i>Putranjiva roxburghii</i> (Euphorbiaceae) (leaves)	Putranjiva saponin C (135)	Oleanolic acid (11) 2 3 rha---glc---glcUA (3 β -OH) glc (28-COOH)	methyl ester: colorless crystals (MeOH-ether), mp 203-205°, [α] _D ²⁰ 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 (3 β -OH) 4 xyl	methyl ester: colorless crystals (MeOH-ether), mp 196-199°, [α] _D ²⁰ 18.6° (MeOH, c 0.975), C ₆₀ H ₉₆ O ₂₀ · 2H ₂ O (EA).	Rangaswami et al., 1971; Seshadri et al., 1975
	(seed coats)	Putranoside C (137)	Oleanolic acid (11) 3 rha---glcUA (3 β -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 (3 β -OH) 4 xyl	methyl ester: mp 218-222°, [α] _D ²⁰ 8.5° (MeOH), C ₅₄ H ₈₆ O ₂₂ · 2H ₂ O (EA).	Hariharan, 1974
57	<i>Quillaja saponaria</i> (Rosaceae) (barks)	QS-III (139)	Quillic acid (15) 2 gal---glcUA (3 β -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.), [α] _D ²⁰ -37.5° [MeOH, c 1.23], IR, FAB-MS [2295 (M- H) ⁻], CMR, C ₁₀₄ H ₁₆₈ O ₅₅ · 8H ₂ O (EA).	Higuchi et al., 1987; Higuchi et al., 1988
58	<i>Salsola micranthera</i> (Chenopodiaceae)	Salsoloside E (140)	Oleanolic acid (11) 2 glc---glcUA (3 β -OH) 4 xyl		Annaev, Isamukhamedova, & Abubakirov, 1984
59	<i>Saponaria officinalis</i> (Caryophyllaceae) (roots)	Saponoside A (141)	Gypsogenin (5) glcUA (3 β -OH) 3 glc---glc (28-COOH) 6 glc	mp 132-134°, [α] _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
60	<i>Schefflera delavayi</i> (Araliaceae) (barks)	Saponoside D (142)	Gypogenin (5) 2 3 gal---xyl---glcUA (3 β -OH) 4 4 ara rha	mp 240–244 $^{\circ}$, PMR, CMR.		Lazur'evskii, Kintya, & Chirva, 1970
61	<i>Silene jenkinsensis</i> (Caryophyllaceae) (roots)	Scheffleraside II (143) (144)	gal ¹⁶ ---xyl ¹ ---fuc (28-COOH) 2 3 4 4 gic ¹⁶ rha Oleanolic acid (11) glcUA (3 β -OH) 4 6 rha---glc---glc (28-COOH) Quillaic acid (15) 2 gal---glcUA (3 β -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	Jiang & Xiao, 1990
62	<i>S. rubicunda</i> (roots)	Rubicunoside A (146)	Quillaic acid (15) 2 gal---glcUA (3 β -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
		Rubicunoside B (147)	Quillaic acid (15) 2 gal---glcUA (3 β -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 $^{\circ}$, [α] _D ¹⁶ -18.03 $^{\circ}$ (pyrindine, c 1.1), IR, FAB-MS [1742 (M) ⁻], PMR, CMR, C ₇₉ H ₁₂₂ O ₄₂ .		Tan et al., 1995
			Quillaic acid (15) 2 gal---glcUA (3 β -OH) 3 xyl 3 4 4 xyl---xyl---rha---fuc (28-COOH) 2/ \3 qui COCH ₃ 4 glc	amorphous powder, [α] _D ¹⁵ - 11.31 $^{\circ}$ (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 (3 β -OH) 3 xyl 4 4 xyl---rha---fuc (28-COOH) 2 glc 4 COCH ₃	amorphous powder, $[\alpha]_D^{16}$ -15.97° (pyridine, 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 (3 β -OH) 3/ 6 xyl OCH ₂ CH ₂ CH ₂ CH ₃ 3 4 4 xyl---rha---fuc (28-COOH) 2/ 3 qui COCH ₃ 2 COCH ₃	amorphous powder, $[\alpha]_D^{15}$ -11.64° (pyridine, c 1.5), IR, FAB-MS [1797 (M-H) ⁻]. CMR.	Tan et al., 1996
63	<i>Silphium perfoliatum</i> (Compositae) (epigeal parts)	Silphioside A (150) Oleanolic acid (11) glcUA (3 β -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 Borel & Hostettmann, 1987
64	<i>Swartzia madagascariensis</i> (Leguminosae) (fruits)	Saponin 5 (151) Oleanolic acid (11) 2 glc---glcUA (3 β -OH) 3 rha glc (28-COOH) Gypsogenin (5) glcUA (3 β -OH) glc (28-COOH) Oleanolic acid (11) 4 glc---glcUA (3 β -OH) glc (28-COOH) Oleanolic acid (11) 2 xyl---glcUA (3 β -OH) 3 rha glc (28-COOH) Oleanolic acid (11) 3 xyl---glcUA (3 β -OH) glc (28-COOH) Methyl spergulagenate (18) glcUA (3 β -OH) glc (28-COOH)	white powder, mp 215–223° (dec.), FAB-MS [1101 (M-H) ⁻]. PMR, CMR. mp 220–235° (dec.), FAB-MS [807 (M-H) ⁻]. CMR. mp 200–208° (dec.), FAB-MS [955 (M-H) ⁻]. CMR. mp 248–258° (dec.), FAB-MS [1071 (M-H) ⁻]. CMR. white powder, mp 270–275° (dec.), $[\alpha]_D^{22}$ +4° (MeOH, c 1.0), FAB-MS [925 (M-H) ⁻]. CMR. white powder, $[\alpha]_D^{22}$ +57.5° (pyridine, c 0.8), FAB-MS [837 (M-H) ⁻]. CMR, C ₄₃ H ₆₆ O ₁₆ · 5H ₂ O (EA).	Borel, Gupta, & Hostettmann, 1987 Borel et al., 1987 Borel et al., 1987 Gafner et al., 1985 Kohda et al., 1992
65	<i>S. simplex</i> (leaves)	Saponin 2 (152) Saponin 5 (153) Saponin 6 (154)		
66	<i>Talinum tenuissimum</i> (Portulacaceae) (tubers)	(155)		
67	<i>T. triangulare</i> (roots)	Talinumoside I (156)		

Continued overleaf

Table 1—Continued

No.	Source (family, part)	Saponin (No.)	Structure	Structural and spectral data	Bioactivity	Reference
68	<i>Tetrapanax papyriferum</i> (Araliaceae) (roots)	R-Ia (157)	Oleanolic acid (11) 2 gal---glcUA (3 β -OH) 4 ara(f)	methyl ester: colorless needles (MeOH), mp 226–228°, [α] _D ²⁵ - 21.8° (MeOH, c 0.5), IR, PMR, CMR, C ₅₄ H ₈₆ O ₂₃ · 3H ₂ O (EA).		Takabe, Takeda, Chen, & Ogihara, 1985
		R-Ib (158)	glc (28-COOH) Oleanolic acid (11) 4 ara---glcUA (3 β -OH) 4 rha---glc---glc (28-COOH)	methyl ester: white prisms (MeOH), mp 203–205°, [α] _D ²² - 27.0° (MeOH, c 0.6), IR, PMR, CMR, C ₆₀ H ₉₆ O ₂₇ · 4H ₂ O (EA).		Takabe et al., 1985
		R-Ic (159)	Oleanolic acid (11) 2 gal---glcUA (3 β -OH) glc (28-COOH)	methyl ester: white powder, mp 190–193°, [α] _D ²² -8.7° (MeOH, c 0.5), IR, PMR, CMR, C ₄₉ H ₇₈ O ₁₉ · 3H ₂ O (EA).		Takabe et al., 1985
69	<i>Thladiantha dubia</i> (Cucurbitaceae) (tubers)	Dubioside A (160)	Quillaic acid (15) 2 gal---glcUA (3 β -OH) 2 rha---ara (28-COOH)	methyl ester: amorphous powder, mp 210–215° (dec.), [α] _D ²⁵ - 31.9° (MeOH, c 2.7), FAB-MS [1139 (M + Na) ⁺], PMR, CMR, C ₅₄ H ₈₄ O ₂₄ · 3H ₂ O (EA).		Nagao, Okabe, Mihashi, & Yamauchi, 1989
		Dubioside B (161)	Quillaic acid (15) 2 gal---glcUA (3 β -OH) 4 xyl---rha---ara (28-COOH)	methyl ester: fine needles (MeOH), mp 225–226°, [α] _D ²⁴ - 26.1° (MeOH, c 1.0), FAB-MS [1271 (M + Na) ⁺], PMR, CMR, C ₅₉ H ₉₂ O ₂₈ · 3H ₂ O (EA).		Nagao et al., 1989
		Dubioside C (162)	Quillaic acid (15) 2 gal---glcUA (3 β -OH) 3 xyl---xyl---rha---ara (28-COOH)	methyl ester: fine needles (MeOH), mp 229–231°, [α] _D ²⁴ - 27.6° (70% MeOH, c 0.8), FAB- MS [1403 (M + Na) ⁺], PMR, CMR, C ₆₄ H ₁₀₀ O ₃₂ · 2H ₂ O (EA).		Nagao et al., 1989
70	<i>T. hookeri</i> var. <i>pentadactyla</i> (tubers)	Thladioside-H1 (163)	Gypsogenin (5) 2 gal---glcUA (3 β -OH) 3 xyl---xyl---rha---ara (28-COOH)	white powder, [α] _D ²² +3.8° (H ₂ O, c 0.89), IR, PMR, CMR, C ₆₃ H ₉₈ O ₃₁ · 2H ₂ O (EA).		Nie et al., 1989
71	<i>Tragopogon porrifolius</i> (Compositae) (roots)	Tragopogonsaponin B (164)	Echinocystic acid (3) glcUA (3 β -OH) xyl (28-COOH) 12 CO-CH=CH-CH ₂ -OH	methyl ester: amorphous powder, [α] _D ²⁵ +24.9° (MeOH, c 1.27), UV, FAB-MS [963 (M + Na) ⁺], PMR, CMR, C ₅₁ H ₇₂ O ₁₆ · 3H ₂ O (EA).		Warashina et al., 1991
		Tragopogonsaponin C (165)	Echinocystic acid (3) glcUA (3 β -OH) xyl (28-COOH) 12 CO-CH=CH-CH ₂ -OH 3 OMe	methyl ester: amorphous powder, [α] _D ²⁵ +24.3° (MeOH, c 0.9), UV, FAB-MS [993 (M + Na) ⁺], PMR, CMR, 2D NMR (NOES), C ₅₂ H ₇₄ O ₁₇ · 2H ₂ O (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, [α] _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 · 3H ₂ O (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, [α] _D ²⁵ +7.3° (MeOH, c 1.1), UV, FAB-MS [1155 (M+Na) ⁺], PMR, CMR, C ₅₈ H ₈₄ O ₂₂ · 7/2H ₂ O (EA).	Warashina et al., 1991
Tragopogonsaponin F (168)	Echinocystic acid (3) glcUA (3β-OH) glc---xyl (28-COOH) ₂ 4 CO-CH=CH- $\varnothing$ ---OH ₃ OMe	methyl ester: amorphous powder, [α] _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 · 4H ₂ O (EA).	Warashina et al., 1991
Tragopogonsaponin G (169)	Echinocystic acid (3) glcUA (3β-OH) glc---xyl (28-COOH) ₂ 4 CO-CH ₂ -CH ₂ - $\varnothing$ ---OH ₃ OMe	methyl ester: amorphous powder, [α] _D ²⁵ -11.7° (MeOH, c 0.95), UV, FAB-MS [1127 (M+Na) ⁺], PMR, CMR, C ₅₇ H ₈₄ O ₂₁ · 3H ₂ O (EA).	Warashina et al., 1991
Tragopogonsaponin H (170)	Echinocystic acid (3) glcUA (3β-OH) glc---ara (28-COOH) ₂ 4 CO-CH ₂ -CH ₂ - $\varnothing$ ---OH ₃ OMe	methyl ester: amorphous powder, [α] _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 · 5/2H ₂ O (EA).	Warashina et al., 1991
Tragopogonsaponin I (171)	Echinocystic acid (3) glcUA (3β-OH) glc---ara (28-COOH) ₂ 4 CO-CH ₂ -CH ₂ - $\varnothing$ ---OH ₃ OMe	methyl ester: amorphous powder, FAB-MS [1127 (M+Na) ⁺], PMR, CMR.	Warashina et al., 1991
Tragopogonsaponin J (172)	Echinocystic acid (3) glcUA (3β-OH) 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) glc---xyl (28-COOH) ₂ 4 CO-CH=CH- $\varnothing$ ---Oglc ₃ OMe	methyl ester: amorphous powder, [α] _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 · 6H ₂ O (EA).	Warashina et al., 1991

Continued overleaf

Table 1—Continued

No.	Source (family, part)	Saponin (No.)	Structure	Structural and spectral data	Bioactivity	Reference
72	<i>T. pratensis</i> (whole plants)	Tragopogonsaponin O (174)	Echinocystic acid (3) glcUA (3 β -OH) 3 glc---xyl (28-COOH) 12 CO-CH ₂ -CH ₂ -O---Oglc 4	methyl ester: amorphous powder, [α] _D ²⁵ 0° (MeOH, c 0.4), UV, FAB-MS [1289 (M+Na) ⁺], PMR, CMR, 2D NMR (NOEDS), C ₆₃ H ₉₄ O ₂₆ · 11/2H ₂ O (EA).		Warashina et al., 1991
		Tragopogonsaponin P (175)	Echinocystic acid (3) glcUA (3 β -OH) 3 glc---ara (28-COOH) 12 CO-CH ₂ -CH ₂ -O---Oglc 4	methyl ester: amorphous powder, [α] _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 · 11/2H ₂ O (EA).		Warashina et al., 1991
		Tragopogonsaponin R (176)	Echinocystic acid (3) glcUA (3 β -OH) 3 glc---ara (28-COOH) 12 CO-CH ₂ -CH ₂ -O---Oglc 3 OMe	methyl ester: amorphous powder, [α] _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 · 9/2H ₂ O (EA).		Warashina et al., 1991
		Tragopogonoside A (177)	Echinocystic acid (3) glcUA (3 β -OH) xyl (28-COOH)	methyl ester: amorphous powder, [α] _D ²⁴ -21.9° (MeOH, c 0.48), FAB-MS [817 (M+Na) ⁺], PMR, CMR, 2D NMR (NOES), C ₄₂ H ₆₆ O ₁₄ · 3/2H ₂ O (EA).		Miyase et al., 1992
		Tragopogonoside C (178)	Echinocystic acid (3) gal---glcUA (3 β -OH) xyl (28-COOH) 2	methyl ester: amorphous powder, [α] _D ²⁴ -16.3° (MeOH, c 1.63), FAB-MS [979 (M+Na) ⁺], PMR, CMR, 2D NMR (NOES), C ₄₃ H ₇₆ O ₁₉ · 7/2H ₂ O (EA).		Miyase et al., 1992
		Tragopogonoside D (179)	Echinocystic acid (3) glcUA (3 β -OH) 3 glc---xyl (28-COOH)	methyl ester: amorphous powder, [α] _D ²³ -27.8° (MeOH, c 0.45), FAB-MS [979 (M+Na) ⁺], PMR, CMR, 2D NMR (NOES), C ₄₃ H ₇₆ O ₁₉ · 7/2H ₂ O (EA).		Miyase et al., 1992
		Tragopogonoside E (180)	Echinocystic acid (3) gal---glcUA (3 β -OH) 3 glc---xyl (28-COOH)	methyl ester: amorphous powder, [α] _D ²⁴ -22.9° (MeOH, c 0.35), FAB-MS [1141 (M+Na) ⁺], PMR, CMR, C ₅₄ H ₈₆ O ₂₄ · 11/2H ₂ O (EA).		Miyase et al., 1992
		Tragopogonoside F (181)	Echinocystic acid (3) gal---glcUA (3 β -OH) 3 glc---xyl (28-COOH) 12 CO-CH=CH-O---OH 4	methyl ester: amorphous powder, [α] _D ²⁴ +1.3° (MeOH, c 1.16), UV, FAB-MS [1288 (M+Na) ⁺], PMR, CMR.		Miyase et al., 1992

73	<i>Ullucus tuberosus</i> (Basellaceae) (tubers)	Tragopogonoside G (182)	Echinocystic acid (3) 2 gal---glcUA (3 β -OH) xyl (28-COOH) 12 4 CO-CH=CH- $\emptyset$ ---OH	methylester: amorphous powder, FAB-MS [1125 (M+Na) ⁺], PMR, CMR.	Miyase et al., 1992
		Tragopogonoside H (183)	Echinocystic acid (3) 2 gal---glcUA (3 β -OH) xyl (28-COOH) 12 4 CO-CH=CH- $\emptyset$ ---OH 13 OMe	methylester: amorphous powder, FAB-MS [1153 (M+Na) ⁺], PMR, CMR.	Miyase et al., 1992
		Tuberoside B (184)	Oleanolic acid (11) 2 xyl---glcUA (3 β -OH) 14 glc glc (28-COOH)	sodium/choline salt: microcrystalline white powder, mp 203–206°, FAB-MS [1111 (M+Na+H) ⁺ , 1087 (M) ⁻], PMR, CMR, 2D NMR (COSY, HMQC, HMBC, ROESY), C ₅₃ H ₈₄ O ₂₃ Na (pos. HR-FAB- MS).	Espada et al., 1996
		Tuberoside C (185)	Hederagenin (7) 2 xyl---glcUA (3 β -OH) 14 glc glc (28-COOH)	sodium/choline salt: FAB-MS [1149 (M+Na+Na) ⁺], PMR, CMR, C ₅₃ H ₈₃ O ₂₄ Na ₂ (pos. HR- FAB-MS).	Espada et al., 1996
					Continued overleaf

Table 1—Continued

No.	Source (family, part)	Saponin (No.)	Structure	Structural and spectral data	Bioactivity	Reference
74	<i>Vaccaria segetalis</i> (Caryophyllaceae)	Vaccegoside B (186)	Gypsoenin (5) gal---glcUA (3 β -OH) 3/ \ 6 gal ara 4 3 xyl---rha---fuc (28-COOH)			Baeva, Karryev, & Abubakirov, 1975
		Vaccegoside C (187)	Gypsoenin (5) gal---glcUA (3 β -OH) 3/ \ 4 \ 6 gal xyl ara 3 4 3 rha---xyl---rha---fuc (28-COOH) 4 qui			Baeva, Karryev, & Abubakirov, 1976
75	<i>Viscaria viscosa</i> (Caryophyllaceae)	Viscoside (188)	Gypsoenin (5) 2 3 xyl---gal---glcUA (3 β -OH) 2/ \ 4 xyl gal 2 2 glc---rha---fuc (28-COOH)			Bukharov, Chirva, & Bukharova, 1975
76	<i>Ximenia americana</i> (Olacaceae) (roots)	(189)	Oleanolic acid (11) 2 3 rha---galUA---glcUA (3 β -OH) gle (28-COOH)			Agostino, Biagi, Simone, & Pizza, 1994
77	<i>Zanha africana</i> (Sapindaceae) (root barks)	Zanhasaponin A (190)	Zanhic acid (19) glcUA (3 β -OH) 2 rha---rha (28-COOH)	crystals, mp 245–247°, [α] _D ²⁰ -9° (MeOH, c 0.1), CMR.	anti-inflammatory activity	Cuellar et al., 1997
		Zanhasaponin B (191)	Zanhic acid (19) glcUA (3 β -OH) 2 2 xyl---rha---rha (28-COOH)	amorphous, mp 258–260°, [α] _D ²⁰ +6° (MeOH, c 0.1), CMR.	anti-inflammatory activity	Cuellar et al., 1997
		Zanhasaponin C (192)	Zanhic acid (19) glcUA (3 β -OH) 3 2 2 xyl---xyl---rha---rha (28-COOH)	amorphous, mp 260–262°, [α] _D ²⁰ +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 widely 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, ^1H - ^{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-Zsilavec, 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 (Higuchi, 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 (Ohtani, 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 H₂O 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

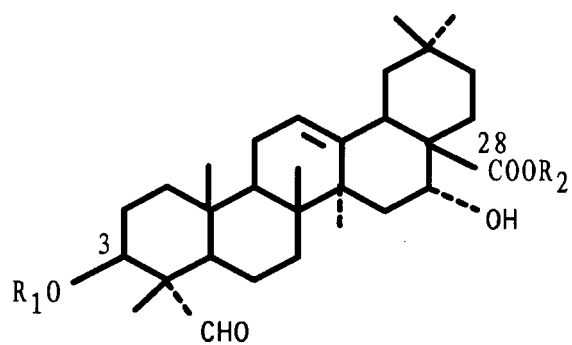
Since 1985 six enzymes have been used in enzymatic hydrolysis of GOTCAB. Using cellulase followed by methylation with CH₂N₂, aster saponin Hc methyl ester (**50**) liberated its 3-prosapogenins and 28-prosapogenins (Tanaka, Nagao, Okabe, & Yamauchi, 1990); with the same cellulase lucyoside N (**104**) 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 mono-saccharide 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 P₁ (**133**) to produce aglycones (Paphassarang, Raymaud, Lussignol, & Becchi, 1989; Paphassarang, Raymaud, Lussignol, & Cabalion, 1990). On enzymatic hydrolysis with crude hesperidinase talinumside I (**156**) and thaladioside-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
	2	2 4 3
193	glcUA----gal 3 xyl	fuc----rha----xyl----api(f) 3 glc
	2	
194	glcUA----gal 3 xyl	H
		2 4 3
195*		(α and β) fuc----rha----xyl----api(f) 3 glc

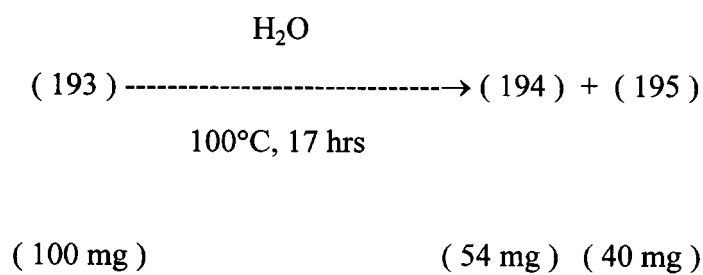
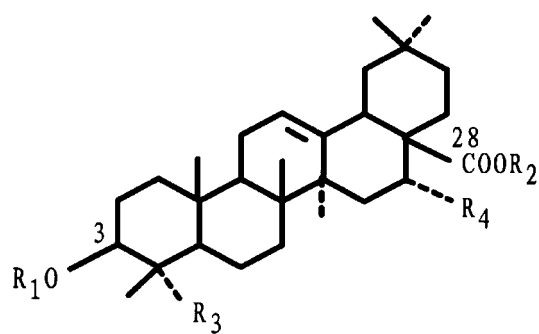


Fig. 2. Hydrothermolysis of DS-2 (193) by mere heating with water solution (*indicates 28-oligosaccharides).



	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).

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

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 GOT-CAB:

(1) Structures of aglycones were elucidated with PMR, CMR, distortionless enhancement by polarization transfer (DEPT), ^1H – ^1H shift correlation spectroscopy (^1H – ^1H COSY or COSY), total correlation spectroscopy (TOCSY), ^1H -detected heteronuclear multiple bond coherence spectrum (HMBC), ^1H 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, ^1H – ^{13}C COSY, ^1H – ^{13}C relayed COSY, ^1H -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-pro-

sapogenins 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 *downshift* from 71.6–78.4 to 81.8–90.5 ppm. Meantime C_2 and C_4 *upshift* about 0.0–2.0 ppm, and C_{23} , C_{24} *downshift* 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 *upshift* 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 *downshift* 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 *upshift* about 1.1–7.9 ppm; but C_6 *downshift* 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 *downshift* from 29.9 to 182.2, 38.8 to 53.6 ppm, respectively. C_3 , C_5 , and C_{24} δ values *upshift* about 2.9–4.3 ppm; but C_6 *downshift* 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 *downshift* 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 *upshift* about 3.0–4.9 ppm, but C_{18} and C_{22} *downshift* 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 *downshift* from 26.3–28.2 to 69.6–71.5 ppm; and C_1 , C_{23} , C_{24} and C_{25} δ values *downshift* 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 *downshift* 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 *downshift* 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 *downshift* from 23.6–23.8 to 73.9–74.8 ppm; and C_{15} , C_{17} , and C_{21} δ values *downshift* about 1.7–8.4 ppm (Nie et al., 1984; Warashima et al., 1991). When C_{19} – αH was replaced with OH, C_{19} δ values *downshift* from 46.2 to 81.2 ppm; and C_{16} , C_{18} , C_{20} and C_{30} δ values *downshift* about 1.5–5.0 ppm, but C_{21} and C_{29} *upshift* 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 *downshift* from 33.7–34.2 to 72.2–72.4 ppm; and C_{17} , C_{20} , and C_{22} δ values *downshift* about 2.2–8.6 ppm, but C_{29} and C_{30} *upshift* 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

¹³C-NMR chemical shifts of GOTCAB aglycone moieties in C₃D₃N

	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 ^{de}
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	24.2	24.2	24.3	23.9	23.9	23.9	24.0	24.1	24.3	24.3	23.8	23.8	23.8	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	2																	

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 ⁱ	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 ^j															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

^aFree aglycones. ^bAglycones of 3-prosapogenins. ^cAglycones of 28-prosapogenins. ^dAglycones of 3,28-saponins. ^eThe solvent was not indicated in the literature. ^fData measured in CDCl₃. ^gData measured in CD₃OD:C₅D₅N(3:2). ^hData measured in CD₃OD:AcOD. ⁱIt linked in C-28 or C-30 COOH. ^jIt was 23.3 in the literature (Li et al., 1994), but we corrected it as 33.3 compared with relative data in the literature. ^kIt 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). ^lOriginal data were four digits, and now we changed these data to three digits for being identical. ^mIt showed C-30 COOMe.

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

shift from 28.0–28.1 to 64.4–64.5 ppm; and C₄ δ values downshift about 2.9–4.3 ppm and C₃, C₅, C₂₄ upshift about 3.0–8.0 ppm (Nie et al., 1984; Amimoto et al., 1993). When C₂₄– β CH₃ was replaced with CH₂OH, C₂₄ δ values downshift from 16.8 to 63.3 ppm; and C₄ δ values downshift about 5.1 ppm and C₂₃ upshift about 4.6 ppm (Nie et al., 1984; Amimoto et al., 1993).

4.2.2. ¹³C 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
¹³C-NMR chemical shifts of GOTC/AB monosaccharide moieties and their derivatives with different glycosidic and acyl linkages in C₃D₃N

	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
glc	free	4-osidic	4-acyl				
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 ₃ COO			171.5				
CH ₃ COO			20.9				
Ref.	Nie et al., 1984	Paphassarang et al., 1990 ^f	Tan et al., 1996 ^f				
28-glc	free	2-osidic	6-osidic	2,6-osidic			
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 ^g	Morita et al., 1986	Nagao and Okabe, 1992 ^e			
gal	free	4-osidic					
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					

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 ₃ COO		170.2			
CH ₃ COO		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	
28-ara	free	2-osidic	2-acyl	3-osidic-2-acyl	
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	
ara	free	4-osidic	2-osidic- α -OMe	2-osidic- β -OMe	2-osidic (f)
1	106.5	104.3	103.6	101.1	106.3
2	71.3	72.0	76.8	78.7	88.2
3	74.5	73.1	74.2	69.1	77.0
4	69.0	77.4	69.2	70.6	84.8
5	67.0	65.4	65.9	63.5	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	Higuchi et al., 1988
28-xyI	free	2-osidic	2-acyl	2-acyl-3-osidic	2,3-osidic
1	96.2	95.1	93.6	93.5	94.0
2	73.6	75.9	73.6	71.1	74.8
3	78.1	77.0	76.1	85.5	79.5
4	70.8	70.6	71.0	69.4	68.3
5	67.6	66.9	68.0	67.1	65.2
Ref.	Nagao et al., 1991 ^e	Shao et al., 1996	Warashina et al., 1991	Warashina et al., 1991	Nagao et al., 1993 ^e
				Miyase et al., 1992	

	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						

^aData measured in CD₃OD. ^bData measured in CD₃OD-AcOD. ^cData measured in DMSO-d₆. ^dData measured in C₃D₈N-D₂O. ^eThe solvent was not indicated in the literature. ^fOriginal 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 ¹³C 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.

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