

New natural products from terrestrial medicinal plants and marine algae

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Abstract: From the higher plants, our search yielded new steroidal and triterpenoidal saponins, sesquiterpenes and alkaloids. A triterpenoidal compound with a novel carbon skeleton is also reported. From the marine algae, new sterols and acyclic diterpene alcohols with interesting bioactivity were isolated and characterised.

INTRODUCTION

Plants continue to provide a myriad of natural products which find extensive application in combating disease and fulfilling various other everyday needs. This paper describes the results of our current research on the isolation and structure elucidation of several new natural products isolated from terrestrial and marine plants. These have been achieved by the application of various chromatographic techniques and by the use of modern spectroscopic studies like 1D-NMR, 2D-NMR, MS, UV and IR as well as simple chemical reactions.

Terrestrial Plants

Sesquiterpenes

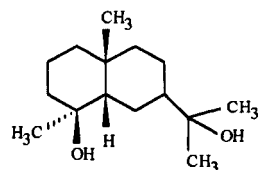
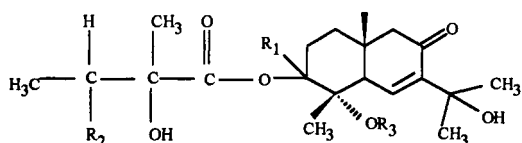
Five eudesmane sesquiterpenes **1**, **2**, **3**, **4** and **5** were isolated from *Pluchea arguta* Boiss (Compositae) syn. *Conyza odontophylla*. **1** and **2** showed antibacterial activity against *Shigella boydii*, *Staphylococcus aureus*, *Klebsiella pneumoniae* and *Escherichia coli* whereas **4** showed this activity against *Klebsiella ozaenae*, *Proteus vulgaris*, *S. pyogenes* and *B. anthracis* (1)

Triterpenoidal compound

Peradione **6a** is a new triterpene with a novel carbon skeleton isolated from the hexane extract of *Perovska abrotanoides* Kerel (Labiatae). A possible biogenetic pathway is suggested (2). Earlier we had isolated perovskone, the first member of this new class of terpenes - for which we suggested the name perovskane (3). The biogenesis of **6a** is assumed to proceed from a precursor of icetexone and geranyl pyrophosphate **6b** as in perovskone; but in case of peradione **6a**, a C-C bond formation takes place between C-12 and C-25 instead of C-11 and C-26.

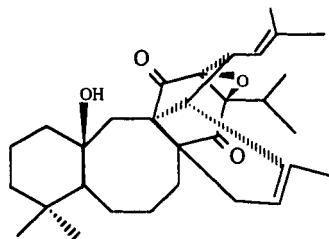
Triterpenoidal Saponins

Guaianin M, **7** and Guaianin N, **8** are triterpenoidal saponins isolated from *Guaiacum officinale* (Zygophyllaceae). They both exhibited toxicity in Brine Shrimp Lethality bioassay. **7** showed antibacterial activity against gram positive *Shigella flaxneiri*, *Klebsiella ozaenae* and gram negative *Corynebacterium xerosis*, whereas **8** showed antibacterial activity against *Pseudomonas pseudomaliae* only (4). Saponins **9**, **10** and **11** were isolated from the ethanolic extract of the roots of *Symphytum officinale* L. (Boraginaceae) commonly known as "Comfrey" which is widely distributed in North Asia, England and Europe and is abundantly found in Turkey. Compound **9** is a monodesmosidic triglycoside having oleanolic acid as aglycone (5). Compounds **10** and **11** are bidesmosidic saponins. On acid hydrolysis **10** and **11** yielded hederagenin as the aglycone. Symphytoxin A, **12**, a saponin isolated earlier from this plant exhibited hypotensive activity in anaesthetized rat (6). Compound **13**, also a saponin, is isolated from *Castanospermum australe* (Fabaceae) (also known as Moreton Bay chestnut or

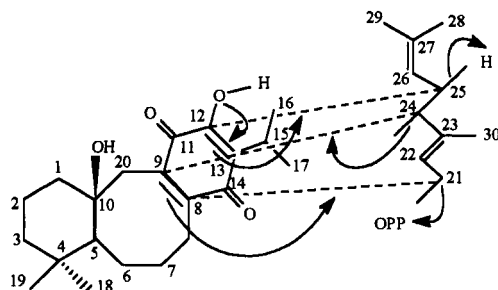


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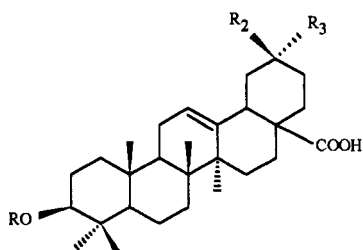
	R ₁	R ₂	R ₃
1	αH	Cl	Ac
2	βH	Cl	Ac
3	αH	OH	H
4	αH	Cl	H



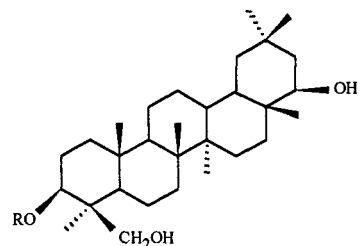
6a



6b

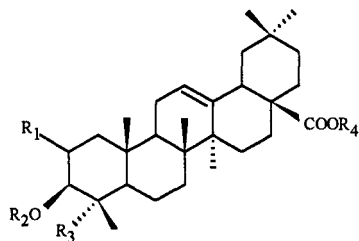


	R ₁	R ₂	R ₃
7	Glc $\xrightarrow{1 \rightarrow 4}$ Ara	=CH ₂	
8	Glc $\xrightarrow{1 \rightarrow 4}$ Ara	Me	Me

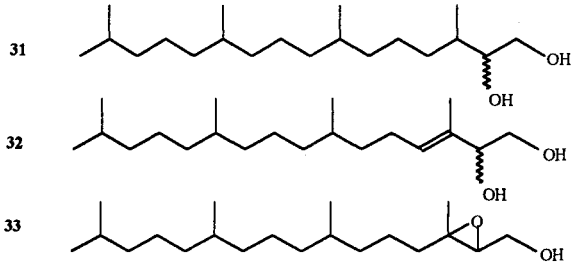
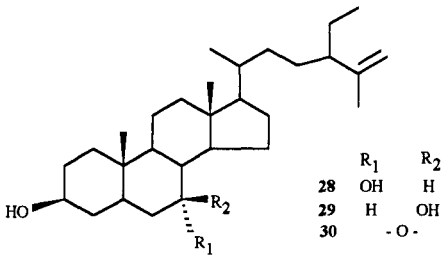
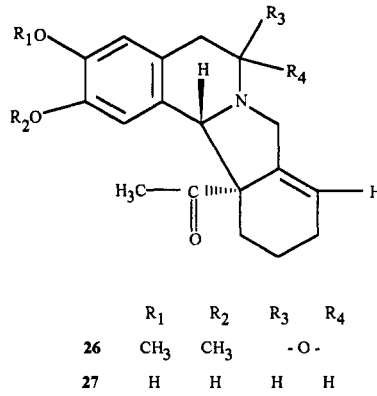
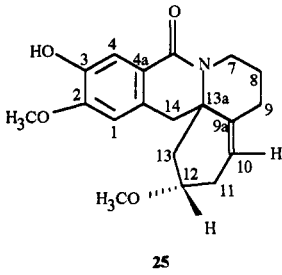
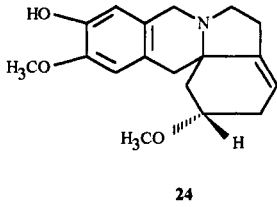
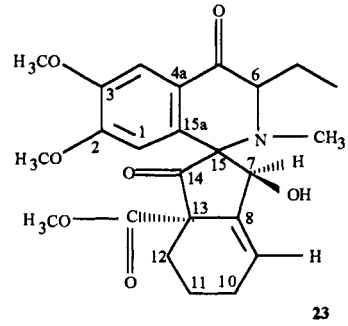
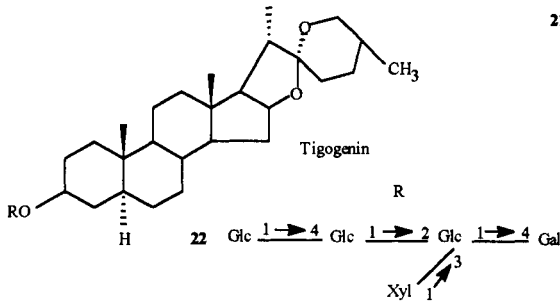
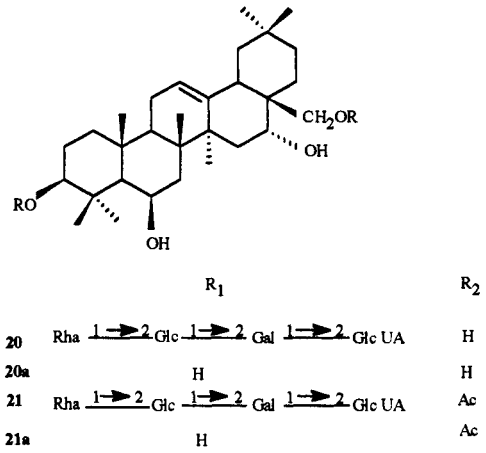
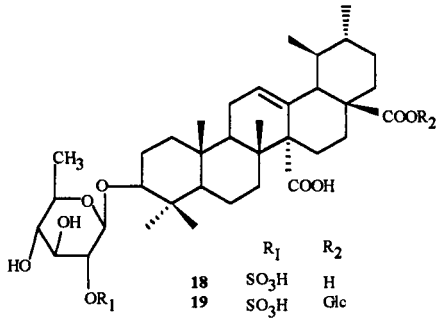


R

14	Rha $\xrightarrow{1 \rightarrow 4}$ Gal $\xrightarrow{1 \rightarrow 4}$ GlcUA
15	Rha $\xrightarrow{1 \rightarrow 3}$ Gal $\xrightarrow{1 \rightarrow 2}$ GlcUA
16	Rha $\xrightarrow{1 \rightarrow 2}$ Gal $\xrightarrow{1 \rightarrow 4}$ GlcUA
17	Rha $\xrightarrow{1 \rightarrow 2}$ GlcUA $\xrightarrow{4 \rightarrow 1}$ Gal



	R ₁	R ₂	R ₃	R ₄
9	H	Glc $\xrightarrow{1 \rightarrow 4}$ Ara	CH ₃	H
10	H	Ara	CH ₂ OH	Glc $\xrightarrow{1 \rightarrow 4}$ Glc $\xrightarrow{1 \rightarrow 6}$ Glc
11	H	Glc $\xrightarrow{1 \rightarrow 4}$ Ara	CH ₂ OH	Rha $\xrightarrow{1 \rightarrow 4}$ Glc $\xrightarrow{1 \rightarrow 6}$ Glc
12	H	Glc $\xrightarrow{1 \rightarrow 2}$ Ara	CH ₂ OH	H
13	OH	4-deoxy - β - L - threo hex 4-eno- pyranosid - uronic acid	CH ₂ OH	CH ₃



black beans). It is a large tree, native of Queensland, Australia and is cultivated in the gardens of Pakistan (7). Vignalin **14** is a monodesmosidic triglycoside isolated from the n-butanol soluble fraction of the edible seeds of *Vigna unguiculata* (L.) Walp. subsp *unguiculata* (Papilionaceae) (8). The aglycone of **14** is soyasapogenol B. Compound **15**, **16** and **17** designated as Cicerin A, B and C, respectively were isolated from the seeds of *Cicer arietinum* (Leguminaceae) (common name is chick peas or gram seeds). This constitutes one of the major foods in Pakistan (9). **18** and **19** were isolated from *Zygophyllum propinquum* Decne, (*Zygophyllaceae*) syn. *Z. coccineum* L. Both of these contain a -SO₃H group linked to the C-2 oxygen of the β-D-quinovoside moiety (10). Macrophyllucin, **20** and macrophyllucin **21** have been isolated from the methanolic extract of the whole plant, *Primula macrophylla* D. Don (*Primulaceae*), syn. *P. stuartii* Wall. The farina on the leaves is locally used in Pakistan and Afghanistan for the treatment of eye diseases. **20a** and **21a** are new triterpenoidal aglycones obtained on hydrolysis of **20** and **21** respectively (11).

Steroidal Saponin

Diurnoside **22** is a spirostanol pentaglycoside isolated from the n-butanol soluble fraction of the fresh leaves of *Cestrum diurnum* (*Solanaceae*). Tigogenin is the aglycone. **22** exhibited toxicity in the BSL bioassay with LD₅₀=110.069 ppm (12). This species is cultivated in Pakistan for its fragrant flowers. It is indigenous to South America and the West Indies.

Alkaloids

Cohirsitine **23**, cohirsitinine **24**, cohirsinine **25**, jamtinine **26** and haiderine **27** are isoquinoline alkaloids isolated from *Cocculus hirsutus* (L.) Diels (*Menispermaceae*). Its various parts are known for their medicinal properties in the indigenous system of medicine (13).

Marine Algae

Pakistan has a rich algal flora in the coastal and inshore waters of northern Arabian Sea. Seaweeds are the prime source for sterols in the marine environment. In order to elucidate the pattern of sterol composition, a chemical investigation of different species of chlorophyta occurring around the Karachi coast has been initiated.

Sterols

Decortinol **28**, isodecortinol **29** and decortinone **30** have been isolated from the ethyl acetate soluble portion of the extract of a green alga *Codium decorticum* (*Cordiaceae*) (14).

Acyclic Diterpene Alcohols

31, **32** and **33** are isolated from the siphonaceous green seaweeds *C. decorticum*, *Coulerpa taxifolia* and *Valoniopsis pachynema*, respectively. The three alcohols displayed strong toxicity (LC₅₀<1000 ppm) (15) at all the concentrations in BSL bioassay.

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