

STUDIES ON THE CHEMICAL CONSTITUENTS
OF
THE SEEDS OF *VIGNA UNGUICULATA* (LINN.)
WALP SUBSP. *UNGUICULATA*
AND
THE ROOTS OF *SYMPHYTUM OFFICINALE*
LINN.

THESIS SUBMITTED

FOR

THE FULFILMENT OF THE DEGREE OF
DOCTOR OF PHILOSOPHY

BY

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To God belongeth
The dominion
Of the heavens
And the earth;
And God hath power
Over all things.¹⁸⁹

Behold ! In the creation
Of the heavens and the earth,
And the alternation
Of Night and Day,-
There are indeed Signs
For men of understanding,-¹⁹⁰

Men who celebrate
The praises of God,
Standing, sitting,
And lying down on their sides,
And contemplate
The (wonders of) creation

In the heavens and the earth,
(With the thought):
"Our Lord! not for naught
Hast Thou created (all) this !
Glory to Thee ! Give us
Salvation from the Penalty
Of the Fire."¹⁹¹

Al-Quraan
Al-i-Imran,
Sūra III 189-191

Translated
by
Abdullah Yusuf Ali

**DEDICATED TO
MY LOVING PARENTS,
BROTHERS, SISTERS
AND
MY WIFE
DR. FARYAL VALI MOHAMMED**

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SUMMARY

The work embodied in the present thesis is presented in two parts. **Part I** describes the isolation and structure elucidation of the chemical constituents of *Vigna unguiculata* subsp. *unguiculata* belonging to the family Papilionaceae.

Part II deals with the isolation and structure elucidation of saponins and alkaloids from *Symphytum officinale* L. belonging to the family Boraginaceae. A brief review of the biosynthesis of saponins and triterpenoids leading to triterpenoidal saponins is also included.

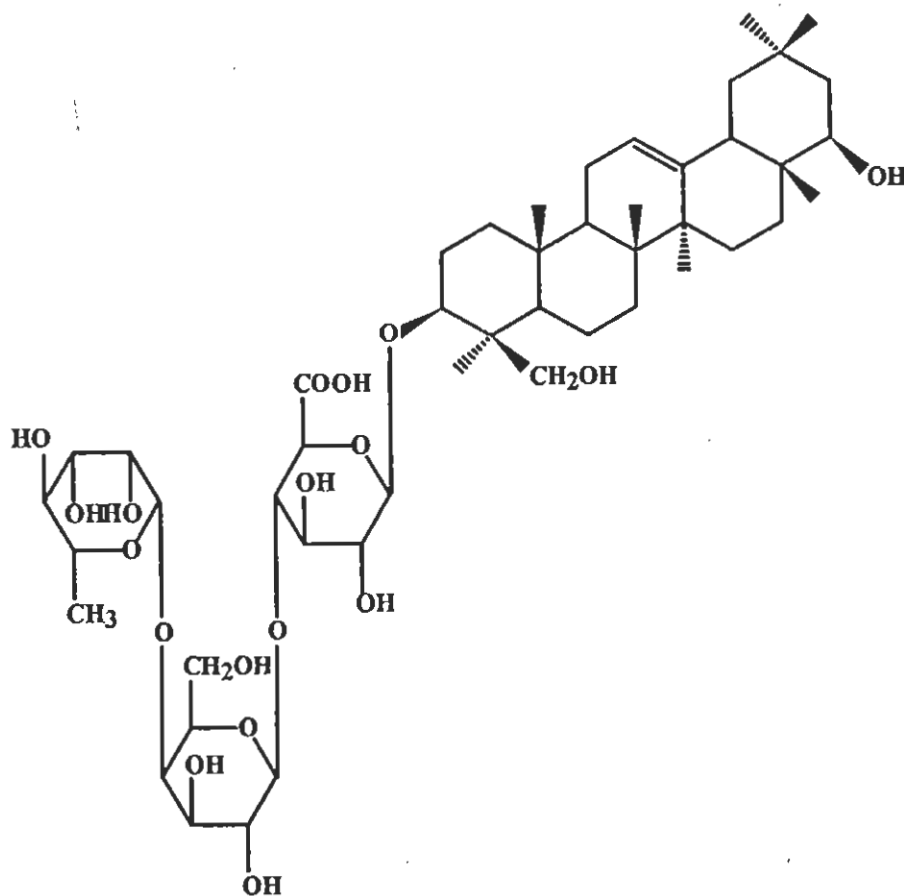
PART I

The introduction of **Part I** provides a review of the earlier contribution made in the chemistry and pharmacology of the plant *Vigna unguiculata* subsp. *unguiculata*. Studies undertaken on the chemical constituents of *Vigna unguiculata* subsp. *unguiculata* have resulted in the isolation of one new saponin which was named as vignalin (1). The aglycone part of this saponin belongs to the oleanane series of triterpenoids and identified as soyasapogenol B. Beside saponin 1, cycloartenol (2), stigmasterol (3), oleanolic acid acetate (4) and sitosterol β -D-glycoside (5) were also isolated for the first time from this plant. Compound 1-5 were isolated from the column chromatography of the methanolic extract of the seeds of *V. unguiculata* subsp. *unguiculata*.

SAPONIN A (1)

(3-O-[α -L-rhamnopyranosyl-(1 \rightarrow 4)- β -D-galactopyranosyl-(1 \rightarrow 4)- β -D-glucuronopyranosyl]-soyasapogenol B.

J. Nat. Prod., **58** (7), 1070 (1995).



SAPONIN A (1)

The **Part II** of the thesis deals with the isolation and structural elucidation of three new pentacyclic bidesmosidic triterpenoidal saponins named as saponin I (9), saponin J (10) and saponin K (11)

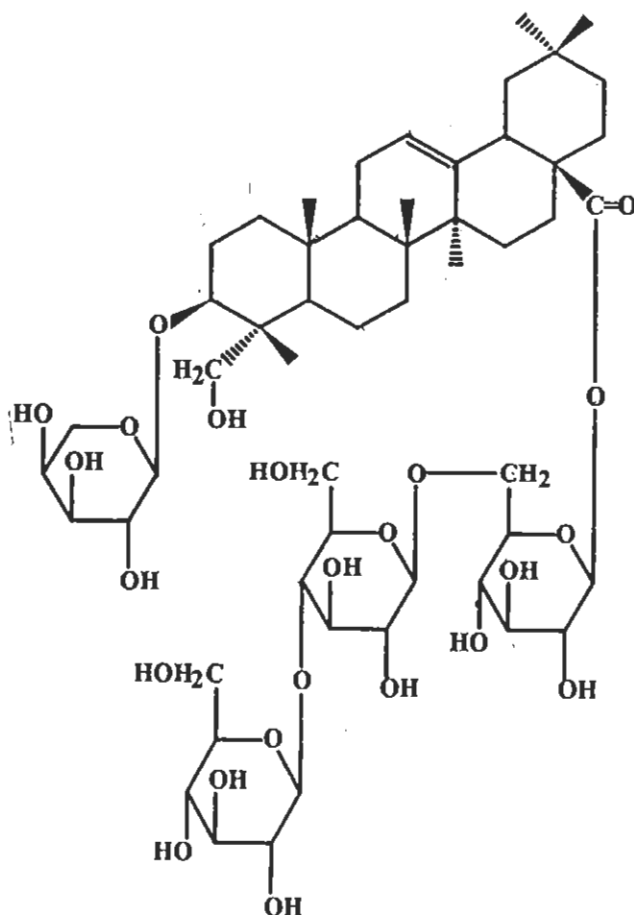
isolated from the roots of *Symphytum officinale* L. (Boraginaceae). The aglycone of all the above three saponins is hederagenin. Two pyrrolizidine alkaloids L (12) (Otosenine) and M (13) (seneciophylline) were also isolated from ethanolic extract of the roots of *S. officinale* L. Alkaloid L (12) and M (13) have already been reported earlier but isolated for the first time from this plant.

SAPONIN I (9)

3-O-[α -L-arabinopyranosyl]-hederagenin-28-O-[β -D-glucopyranosyl-(1 \rightarrow 4)- β -D-glucopyranosyl-(1 \rightarrow 6)- β -D-glucopyranosyl] ester.

(1-6) (1-4)

Phytochemistry, 36 (2), 439 (1994).

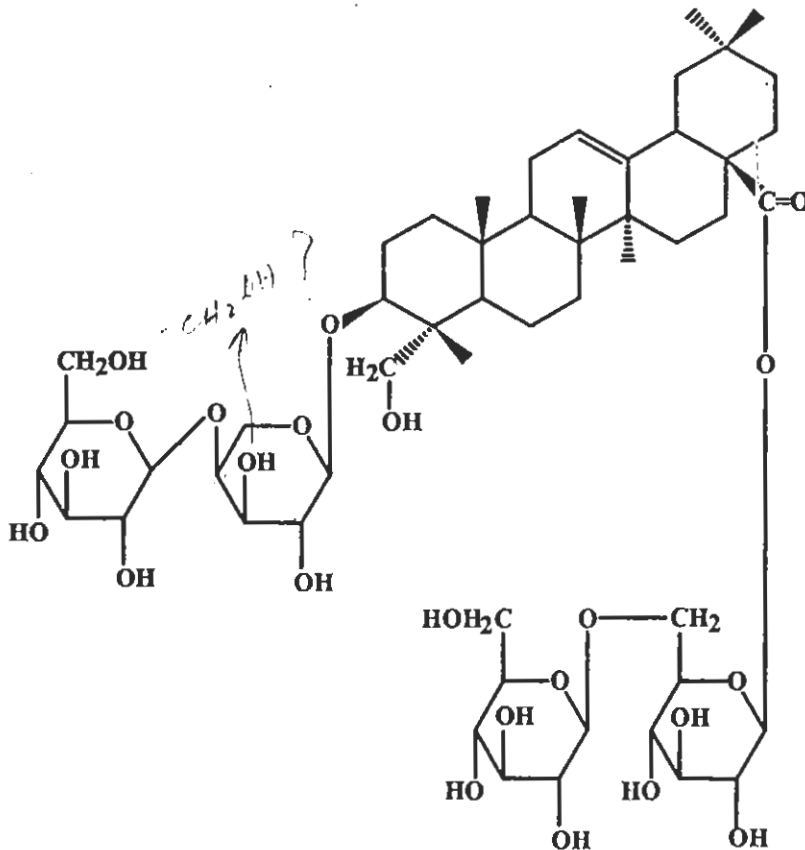


SAPONIN I (9)

SAPONIN J (10)

3-O-[β -D-glucopyranosyl-(1 \rightarrow 4)- α -L-arabinopyranosyl]-hederagenin-28-O-[β -D-glucopyranosyl-(1 \rightarrow 6)- β -D-glucopyranosyl] ester.

Planta Med., 59, 462 (1993).



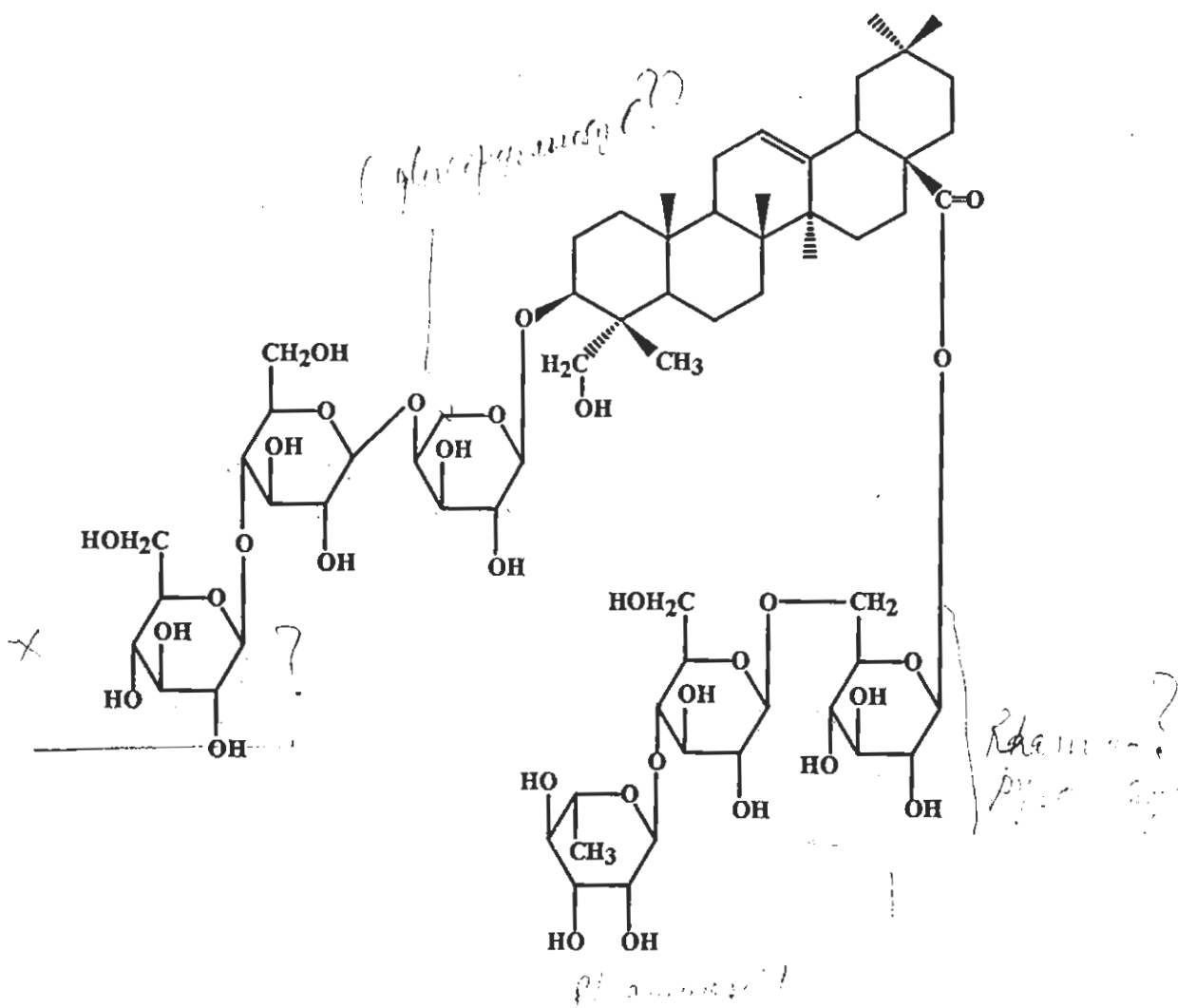
SAPONIN J (10)

SAPONIN K (11)

3-O-[β -D-glucopyranosyl-(1 \rightarrow 4)- β -D-glucopyranosyl-(1 \rightarrow 4)- α -L-arabinopyranosyl]-hederagenin 28-O-[α -L-rhamnopyranosyl-(1 \rightarrow 4)- β -D-glucopyranosyl] ester.

pyranosyl-(1→6)-β-D-glucopyranosyl] ester. The prosapogenin 11a of this saponin is also a new compound.

Phytochemistry, 40 (1), 213 (1995).



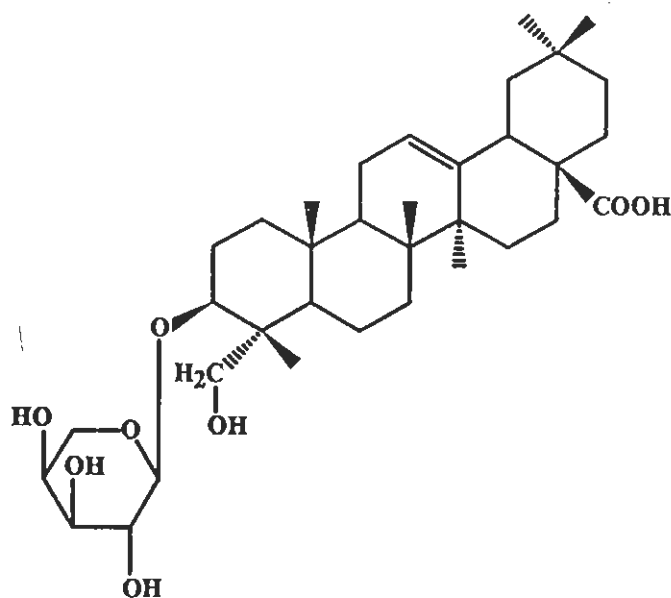
SAPONIN K (11)

In addition to these compounds, two pentacyclic monodesmosidic triterpenoidal saponin F (6) and saponin G (7) were also isolated and reported for the first time from this plant.

SAPONIN F (6)

3-O-[α -L-arabinopyranosyl]-hederagenin.

Fitoterapia, LXIV (5), 477 (1993).

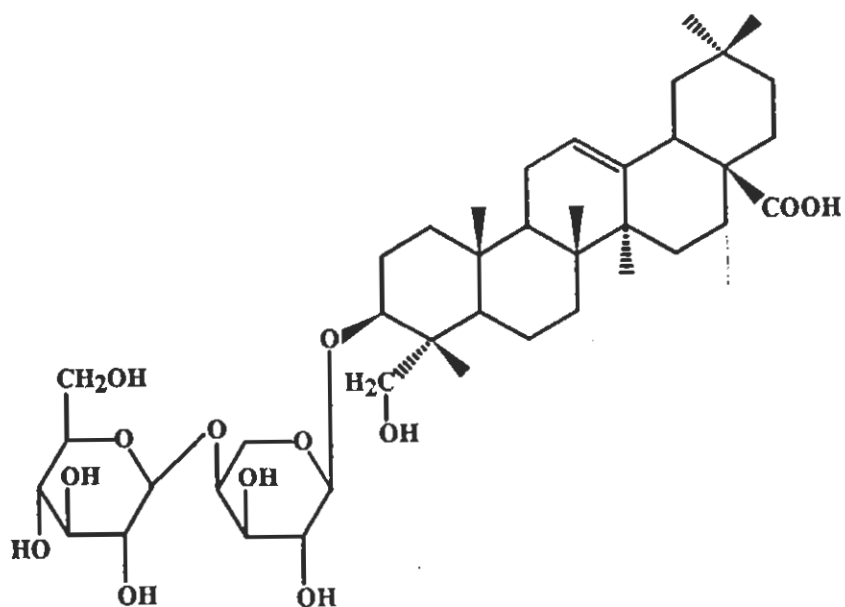


SAPONIN F (6)

SAPONIN G (7)

3-O-[β -D-glucopyranosyl-(1 \rightarrow 4)- α -L-arabinopyranosyl] hederagenin.

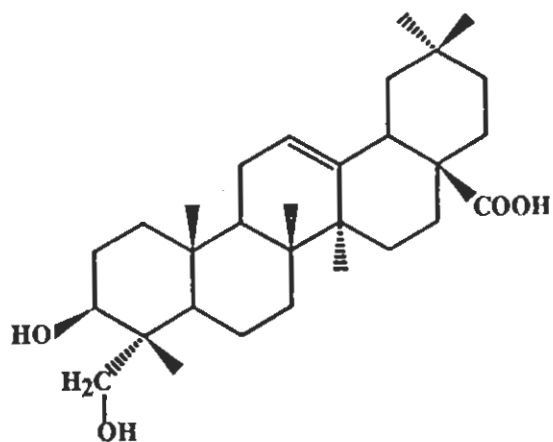
Fitoterapia, LXIV (5), 477 (1993).



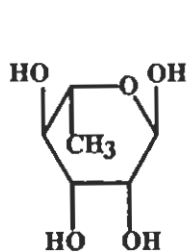
SAPONIN G (7)

SAPONIN H (8)

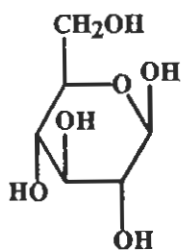
A minor saponin H (8) was also isolated. The aglycone of saponin H (8) is hederagenin and sugars were identified as arabinose, glucose and rhamnose. The complete structure elucidation of saponin H (8) is in progress.



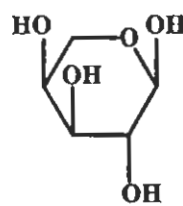
HEDERAGENIN



RHAMNOSE



GLUCOSE

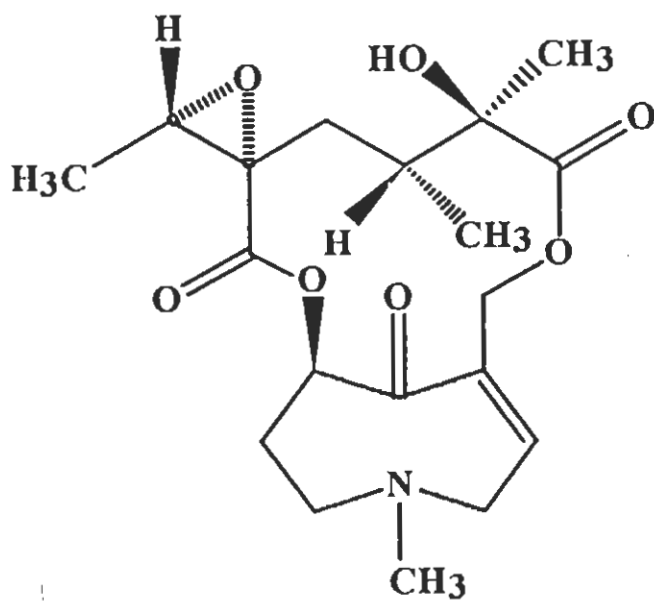


ARABINOSE

ALKALOID L (12)

Otosenine

(Manuscript under preparation).

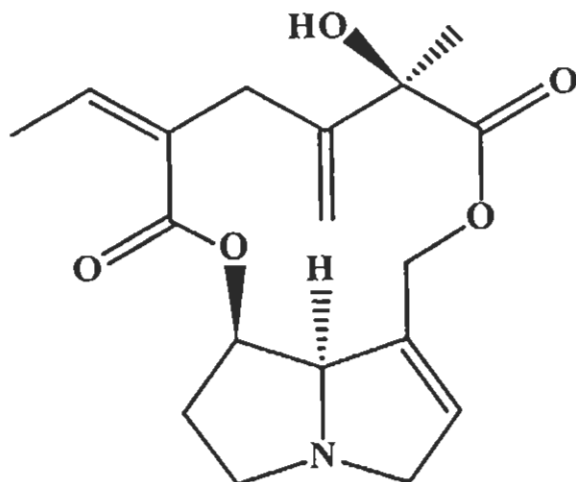


OTOSENINE (12)

ALKALOID M (13)

Seneciophylline

(Manuscript under preparation).



SENECIPHYLLINE (13)

Extensive spectroscopic techniques such as EIMS, FDMS, FABMS, HRMS, UV, IR, ^1H - and ^{13}C -NMR, 2D-NMR (COSY-45 $^\circ$, NOESY, HeteroCOSY, HMQC, HOHAHA 2 D *J*-resolved) and chemical reactions were employed to elucidate the structures of the compounds noted in **Part I** and **Part II**. DEPT experiments were also carried out to determine the multiplicities of the carbon atoms.