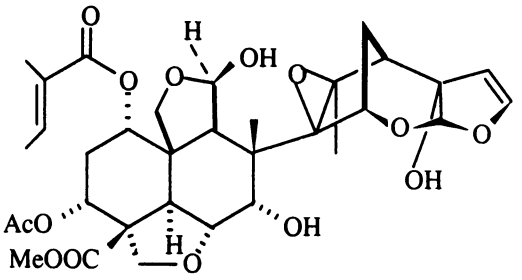

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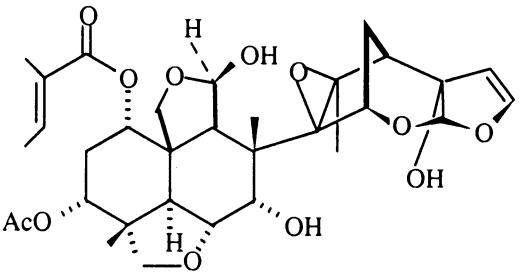
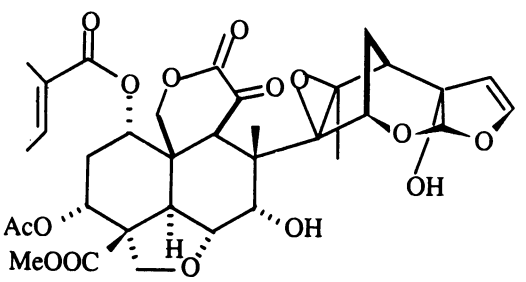


(I)



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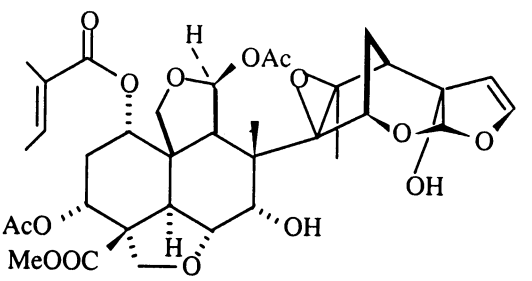

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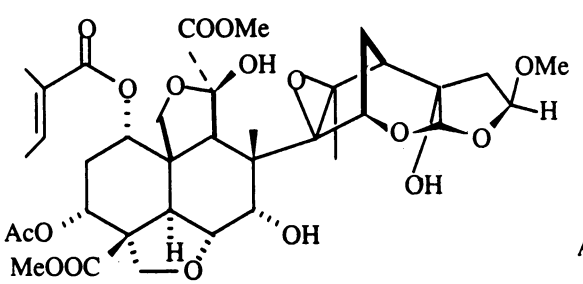

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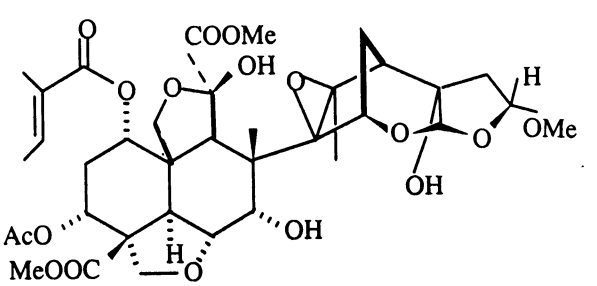


(21)

Fig. 2.3b. Azadirachtins.

3. Ryania

A review on Ryania is given by Crosby [9]. The Casida group utilizing radial TLC and preparative HPLC were able to isolate 10 out of 11 compounds, identified earlier and provided a procedure for monitoring different lots of plant samples [10].

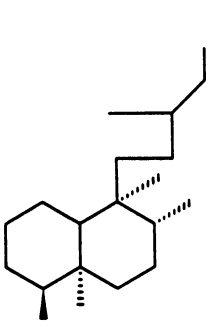
The most active components of *Ryania speciosi* plant are Ryanodine (22) and its di-dehydro derivative (23). A pyridine-3-carboxylate analogue (24) of ryanodine showed little activity but its degradation products ryanodol (25) and di-dehydro ryanodol (26) were found to have good knock down property. A total synthesis of ryanodol has been reported [11].

The most potent compound is polygodial (41) which can kill the fungi like *Saccharomyces cerevisiae* within 10 min at a concentration of 50 g/ml. It inhibits germination in rice and promotes root elongation. Other analogues exhibit similar type of PGR activity. Muzigadial (42) at 5 ppm acts as an effective helicocide against *Binmphalaria pfeiffer* and *B. glabratus*, the casual organisms of schistosomes and bilharzia. It also exhibits piscicidal and molluscicidal activity [Kubo and Nakanishi, 20]. It was observed that the activity was species-specific and analogue dependent.

ii) Clerodanes [Hanson, 21; Vadar, 22].

Clerodane belongs to a group of diterpenes having general structure (43). Till date more than 500 clerodanes have been isolated from numerous species of many plant families, micro-organisms and marine fauna. These compounds exhibit broad spectrum of biocidal activity such as antimicrobial, piscicidal; antipeptic-ulcer and as insect antifeedant. SAR studies on these compounds indicate that their activity is reduced if a) α-hydroxyl at C-2 is epimerised or acetylated or b) the ester groups are hydrolysed and c) the stereochemistry of epoxide is altered.

Further studies on ajugarin (44) indicated that the ajugarin analogues (44a, 44b and 44c) showed similar antifeedant activity but 44d & 44e were inactive. Pickett *et al.* (1987) [23] showed that 44a was inactive against aphids but active as antifeedant against the diamond-back moth, *Plutella xylostella* at 250 ppm.



(43)

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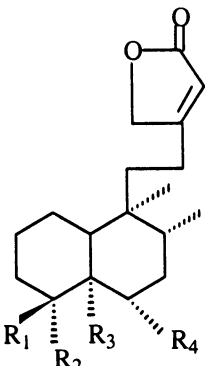
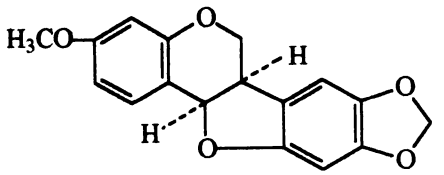


(44)

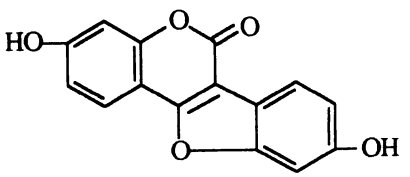
	R_1	R_2	R_3	R_4
a,	CH_2	O	OAc	OAc
b,	CH_2	O	OAc	OH
c,	CH_2OH	OH	OAc	OAc
d,	H	$COOCH_3$	H	OAc
e,	CH_2	O	H	OAc

iii) Chromenes

Chromenes (benzopyrans) and benzofurans of diverse structures were isolated from many species of higher plants such as Asteraceae. The biological activities along with chemical configurations of 167 isolated compounds have been reviewed by Proksch *et al.* [24]. Chromene derivatives, the precocene I and II (45a, 45b) isolated by Bowers and co-workers [25] from the plant *Ageratum honstonianum* prevent juvenile hormone synthesis. The desert sunflowers of the genus *Encelia* (Asteraceae) contain three major acetyl chromenes like encecalin (46a), demethylencecalin (46b), and demethoxyencecalin (46c) possessing antifeedant activity. In another experiment, the isolates of four tarweed *Hemizonia fitchii* A. Gray (Asteraceae) comprising some volatile compounds (46a, 46b) and 6-vinyl-7-methoxy 2,2-dimethylchromene (47) were found to reduce the population of *Culex pipiens*.



(83)



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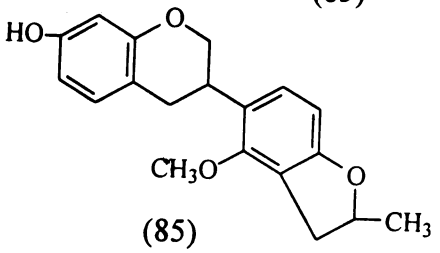

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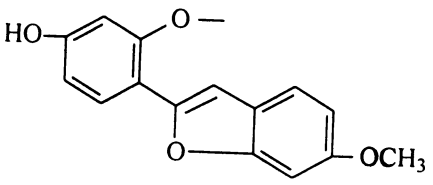


(86)

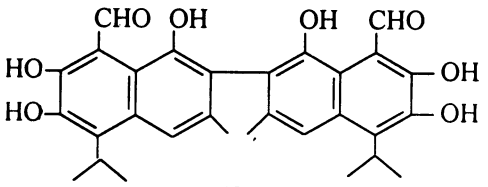
Phytoalexins derived from Solanaceae are classified into three categories :

a) The terpenoid — derived from acetate-mevalonate pathway.

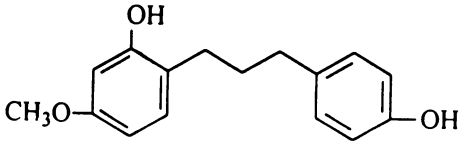
b) Phenyl propanoid — from shikimic acid pathway.

c) The acetylenes — from acetate-malonate pathway.

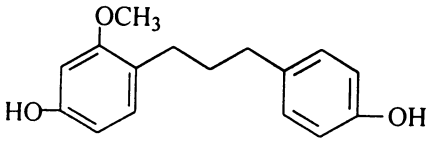
A large number of acetylene and polyacetylene phytoalexins possessing good fungicidal activity have been found in vegetables. The most important antifungal compound with broad spectrum activity is gossypol (87) and its analogues, and broussonin A & B (88a, 88b).



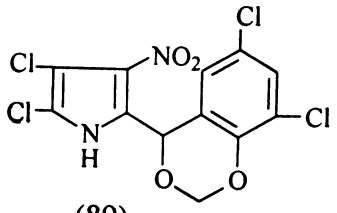
(87)



(88a)



(88b)



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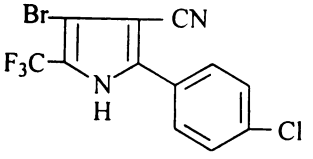

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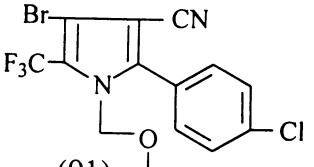
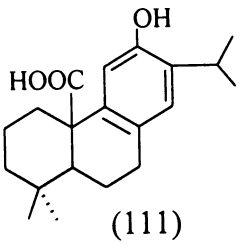


(91)

Pyrrolnitrin (105) isolated from *Pseudomonas pyrrocinia* is found very active as fungicide. But its less active synthetic analogue fenpiclonil (112) which controls snow mould and bunt and was reported in 1988 [53].



(111)

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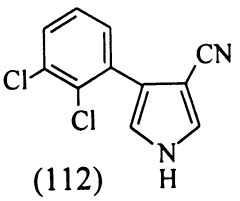

(112)

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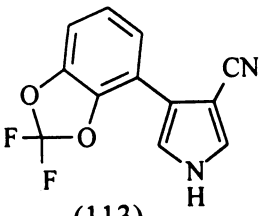
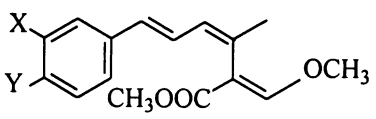


(113)

Later on the Ciba company developed a more active derivative CGA-173506 (113) to use as an antifungal seed dressing agent in USA under the trade name Saphire.

The β-methoxyacrylates

The synthetic analogues with fungicidal activity were prepared based on natural products strobilurin A (106) and oudemansin A (107) having low acute toxicity to mammals. A few synthetic strobilurin analogues (114a, 114b, 114c, 114f, 114h) were prepared which can control a large number of fungal parasites especially on rice, vegetables and fruit crops [54].

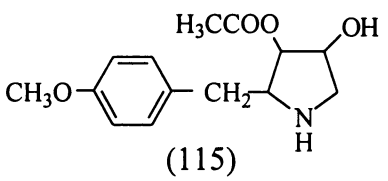


(114)

a, X = Y = H
b, X = OCH_3; Y = Cl
c, X = H; Y = OCH_3
f, X = OH; Y = H
h, X = OCH_3; Y = H

Hadacidin

A novel compound WL 87353 (108b) derived from natural product hadacidin (108a) was reported to be effective as post harvest treatment against downy mildew disease of vine [55].



(115)

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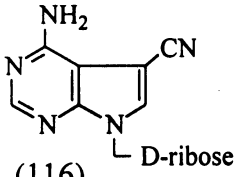

(116)

Thiolutin

The natural product thiolutin (109) of the pyrrothine family, obtained from *Streptomyces* paved way for the synthesis of analogues which are effective as fungicides and bactericides. The compound thiolutin effectively controls black rot and fire blight of apples, tobacco and wilt on tomatoes. The optimised synthetic analogues showed good activity against many fungi [55].

Griseofulvin

Griseofulvin (110) was first isolated from *Penicillium griseofulvum*. It is used for the control of