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Contribution from Indian laboratories to the chemistry of plant products

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Abstract. The review describes chemical work carried out in India on plant products highlighting only those compounds which have novel structural patterns and/or significant biological activity. Contributions mainly in the areas of oxygen heterocycles, terpenoids and alkaloids are discussed.

Keywords. Plant products; oxygen heterocycles; terpenoids; alkaloids

1. Introduction

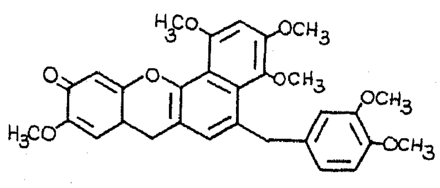
Organic chemists in India have contributed in an impressive measure to the chemistry of plant products during the past fifty years, a period coeval with the life of the Indian Academy of Sciences. Situated as it is in the tropical and sub-tropical belts of the world, India is endowed with a profusion of plant life, numbering some twenty thousand species of flowering plants, some of which have been in use through the ages for medicinal purposes. It was natural that the chemical investigation of plants became a major area of interest to organic chemists in India. Indeed the amount of chemical work on plants is prodigious and the number of compounds isolated from plants is very large. In this brief review it will only be possible to deal with some of these compounds which have an element of novelty or biological activity and whose structures have been elucidated entirely in this country. There are three major areas in which significant contributions have been made in India *viz* oxygen heterocycles, terpenoids and alkaloids and an attempt will be made to highlight these contributions.

2. Oxygen heterocycles

The late Professor T R Seshadri, working first at Andhra University and later at Delhi University published 1130 papers, most of these on oxygen heterocycles, during a research career spanning forty years. He isolated a large number of flavanoid pigments of Indian plants, both aglycones and glycosides and determined their structures. He carried out extensive synthetic studies to prove the structures assigned on the basis of degradation. In this connection he evolved methods for hydroxylation as well as for removal of hydroxyl groups, methods for partial methylation and demethylation. From flavones and flavanols the methods were extended to isoflavones, chalcones, aurones, isoflavanones, xanthones and anthraquinones. Methods for the total synthesis of compounds containing C-methyl and C-phenyl groups, furan and chromone rings were also developed. Many other groups of oxygen heterocycles, such as flavandiols, coumarins, halocoumarins, 3- and 4-phenylcoumarins as well as flavanolignans, C-glycosides and neoflavanoids were studied by him. His work on gossypol, the pigment from cotton seed oil served to clear up the confusion which surrounded its structure. Among other complex structures, he solved the structures of santalin A (1) and santalin-B, pigments isolated from *Pterocarpus santalinus* Linn. f. A detailed account of Seshadri's work is presented in a memoir, together with important references (Baker and Rangaswamy 1979).

The late Prof. K Venkataraman, first at the Bombay University Department of Chemical Technology and later at the National Chemical Laboratory, Poona, besides being a leading authority on synthetic dyes contributed extensively to the chemistry of oxygen heterocycles by his work on plant pigments. He elucidated the structures of several of these, such as calycopterin from *Calycopteris floribunda* Lam (Shah and Venkataraman 1942), artocarpin (Dave *et al* 1962) from *Artocarpus integrifolia* Linn. f. and pinoquercetin and pinomyrcetin (Kurth *et al* 1956; Mani *et al* 1956) from *Pinus ponderosa*. Considerable work was carried out on morellin (2), the complex pigment from *Garcinia morella* Desr. whose structure was ultimately solved by x-ray analysis (Kartha *et al* 1963; Madhavan Nair and Venkataraman 1964) as was also that of xanthochymol (Karanjgaokar *et al* 1973; Blount and Williams 1976; Venkatswamy *et al* 1975) from *Garcinia xanthochymus* Hook. f. It is of interest that cambogin (Rogers and Pai, Private Communication) from *Garcinia cambogia* Desr. is enantiomeric with isoxanthochymol. Among unusual flavanoids isolated by his group are chaplashin from *Artocarpus chaplasha* Roxb. and cyclointegrin (3) from *Artocarpus integer* Thunb. Venkataraman contributed greatly in developing methods for the synthesis of flavones and isoflavones. The Baker-Venkataraman transformation provides a convenient route to flavones (Mahal and Venkataraman 1934). The direct conversion of chalcones to flavones was achieved by the use of selenium dioxide (Mahal *et al* 1936). Ethylorthoformate was used for the direct synthesis of isoflavones from desoxybenzoins (Kagal *et al* 1956).

Of the interesting results obtained in the field of oxygen heterocycles from other laboratories may be mentioned the isolation of echioidinin (Govindachari *et al* 1965a), wightin (Govindachari *et al* 1965b) and serpylline (Govindachari *et al* 1968) which gave respectively the unusual 2'-, 2',3'- and 2',3',4'-oxygenation pattern in the B-ring. Wedelolactone (4) the first representative of the class of coumarano-coumarins was isolated from the medicinal plant *Wedelia calendulaceae* Less and the structures proved



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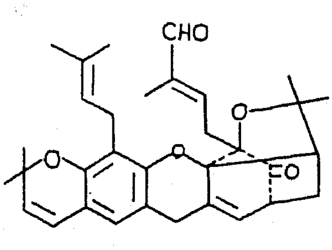

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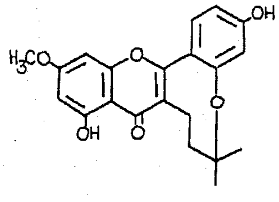

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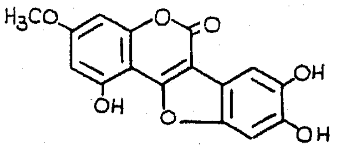

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by degradation and synthesis on classical lines (Govindachari *et al* 1956, 1957; Bowyer *et al* 1957).

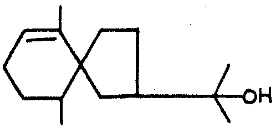
3. Terpenoids

One of the earliest to work on plant products in India was Sir John Lionol Simonson (Jones 1958), who served at the Presidency College, Madras, the Indian Institute of Science, Bangalore, and the Forest Research Institute, Dehra Dun before returning to England. His finding that Δ^3-carene was the major constituent of Indian turpentine and his isolation of longifolene from *Pinus longifolia* Roxb were important contributions. In England he became one of the leading organic chemists of his generation recognised for his extensive work on the chemistry of terpenoids.

Thanks to the work of schools led by Prof. S C Bhattacharyya and Dr Sukh Dev, the output of work done in India in the field of terpenoids is both notable and extensive. A large number of the economically important essential oils and resin exudates have been examined by these groups in the past three decades. Several hundred new compounds belonging to the sesqui-, di- and triterpenoid classes have been isolated, many of them are of novel types and their structures elucidated.

From fungus-infected agarwood, *Aquillaria agallocha* Roxb. agarospirol (5) α- and β-agarofurans and dihydroagrospirol were isolated and structurally characterised (Maheshwari *et al* 1963). Costus root oil (*Saussurea lappa* C B Clarke) has been intensively studied and several sesquiterpenes with the germacrane skeletons have been isolated and characterised. Typical studies are the structure elucidation of dehydrocostus lactone (Mathur *et al* 1965) and the study of the transformation products of costunolide (Joshi *et al* 1966; Hiremath *et al* 1968). (+)-Junenol, canarone and epikhusinol were isolated from the Indian black dammar resin (Hinge *et al* 1965). The structure of bergamotene (6), a novel sesquiterpene, was determined (Kulkarni *et al* 1966). The constituents of North Indian vetiver oil were shown to be distinctly different from those of the oil obtained from other parts of the country, which contain essentially α- and β-vetivones and related compounds. The former is conspicuous by the presence of many antipodal cadinenic and eudesmanic compounds. The major constituent is khusinol (Kalsi *et al* 1963; Kartha *et al* 1963; Rao *et al* 1963; Kelly and Eber 1972). Another constituent is khusiol (7) which is perhaps a precursor of the zizaene type of sesquiterpenes (Ganguly *et al* 1978).

Many novel results have been obtained by Sukh Dev and his collaborators in the field of terpenoids. From *Cedrus deodara* Roxb. several hydrocarbons and alcohols such as α- and β-himachalenes (Joseph and Sukh Dev 1968), himachalol (Bisarya and Sukh Dev 1968a) and allohimachalol (Bisarya and Sukh Dev 1968b) were isolated and their structures established.



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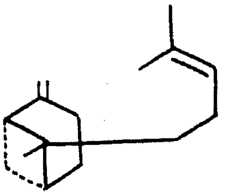

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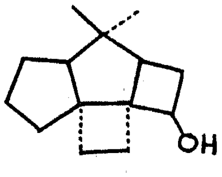

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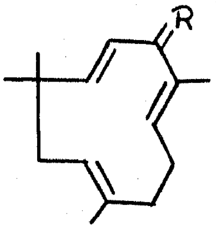
Humulene (8), zerumbone (9), caryophyllene and curcumene were some of the constituents of *Zingiber zerumbut* Smith and all aspects of the structures of the first two compounds were settled (Damodaran and Sukh Dev 1968). The fascinating transformations undergone by the tricyclic longifolene molecule have been the subject of intensive study by Sukh Dev and his group who have also studied in detail the chemistry of isolongifoline (Sukh Dev 1981).

The structures of ishwarone (10) and ishwarane (11) which are rare tetracyclic sesquiterpenes with a novel skeleton were elucidated by Govindachari and coworkers (Govindachari *et al* 1970; Führer *et al* 1970). A number of germacranolides were isolated from *Tithonia tagetiflora* Dept. of which tagitinin F (12) displayed significant anti-cancer activity (Pal *et al* 1976, 1977). Several diterpenes have been isolated from *Coleus forskohliü* Brig. of which the most interesting is coleonol (13) with pronounced hypotensive activity (Bhat *et al* 1977; Tandon *et al* 1977, 1978; Jauhari *et al* 1978). The resin exudate of *Commiphora mukul* (Hook. ex Stocks) has been submitted to detailed chemical examination by Sukh Dev and coworkers. A variety of compounds such as long chain alcohols, lignans, diterpenes and steroids have been isolated and characterised (Patil *et al* 1972, 1973; Prasad and Sukh Dev 1976). There are about ten steroids of which Z and E guggulusterones (14) have marked lipid lowering activity.

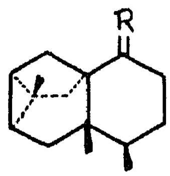
Hardwickiic acid (15) is the first simple member of the rearranged labdanes (Misra *et al* 1968).

Cheilanthatriol (16) from the fern *Cheilanthes farinosa* Kaulf. belongs to the rare group of sesterterpenoids (Khan *et al* 1971). Typical of the large number of triterpenoids characterised are the 19-oxygenated oleonane arjunic acid from *Terminalia arjuna* W and A (Row *et al* 1970), the hopane mollugogenol-A from *Molluga hirta* Roxb. (Chakrabarti 1969), and the ursane, lantic acid from *Lantana vamara* Linn. (Barua *et al* 1972).

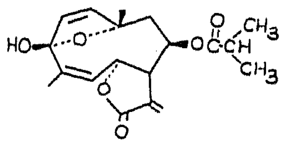
Litsomentol (17) is the simplest member of the cucurbitacin group (Govindachari *et al* 1971) and is exceedingly toxic. Nimbin (18) isolated from the oil of neem



8 $R = CH_2$
9 $R = O$



10 $R = O$
11 $R = CH_2$



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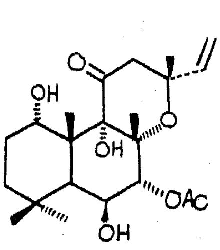

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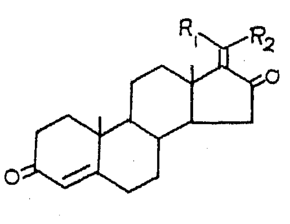
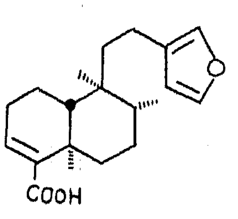


14 Z $R_1 = H; R_2 = CH_3$
E $R_1 = CH_3; R_2 = H$



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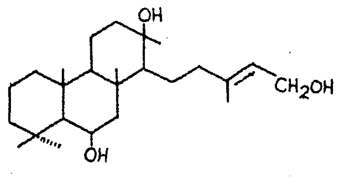

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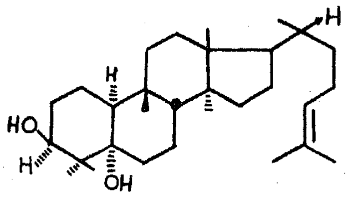

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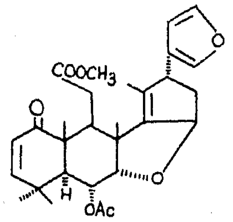

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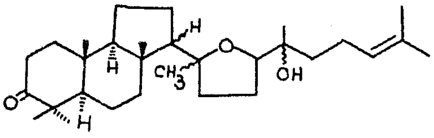

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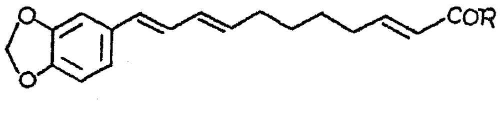
(*Azadirachta indica* A. Juss) represents one of the early examples of a novel type of tetranorterpenoid (Narayanan *et al* 1964).

Malabaricol (19) isolated from *Ailanthus malabarica* DC represents a new fundamental type of triterpene not encountered before (Chawla and Sukh Dev 1967; Sobti and Sukh Dev 1968).

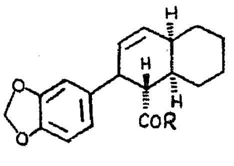
4. Alkaloids

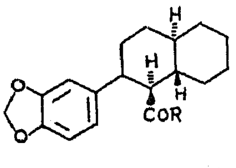
The great pioneer in the chemical work on plants in India was certainly Prof. S Siddiqui (now settled in Pakistan) who worked at the Tibbia College of Unani Medicine and later at the Board of Scientific and Industrial Research, Delhi. He isolated conessine, conessimine, conessidine from *Holarrhena antidysentrica* Wall. whose bark is used in India for treatment of dysentery (Siddiqui and Pillay 1932, 1934). His work on *Rawvolfia serpentina* Benth ex Kurz whose roots had been used in North India as a sedative led to the isolation of ajmaline, ajmalinine and serpentine (Siddiqui and Siddiqui 1931, 1932, 1935). Siddiqui's publications along with the clinical work of Vakil on *Rawvolfia serpentina* extracts led to a close examination of the plant resulting in the isolation of reserpine, the active principle of the plant with marked hypotensive and sedative activities. These findings created a worldwide interest in the search for medicinal agents from plants, after the Second World War, leading to the isolation of thousands of new compounds of a wide diversity and the development of new techniques of isolation and structure determination. This was the single big factor which enriched organic chemistry in the post-war years.

The medicinal importance of the genus *Piper* has led to the examination of several of its species. Joshi and coworkers isolated from *Piper trichostachyon* C. Dc. four new alkaloids, piperstachine (20), cyclostachine-A (21), cyclostachine-B (22), and cyclopiperstachine (23). The structures were elucidated by a combination of chemical and spectroscopic methods and confirmed by syntheses (Joshi *et al* 1975a; Viswanathan *et al* 1975). Confirmation of the structures of cyclostachine-A was obtained by x-ray analysis (Joshi *et al* 1975b). Cyclostachine A and B evidently arise by an internal Diel-



20 R = $NHCH_2CH(CH_3)_2$
24 R = –N□





21 R = –N□
23 R = $-NHCH_2CH(CH_3)_2$

22 R = –N□

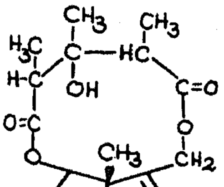
Alder reaction of the amide (24) and cyclopiperstachine from piperstachine. The *cyclo* compounds are not artefacts but exist in the plant. The genus *Crotalaria* is known to produce macrocyclic ester alkaloids incorporating a pyrolizidine system. Atal *et al* have investigated a large number of plants of the genus and isolated over a dozen new alkaloids. Cromadurine (25) is a typical alkaloid of this group (Rao *et al* 1975). The genus *Ancistrocladaceae* is represented only by one species in India, *Ancistrocladus heyneanus* Wall. A novel group of isoquinoline alkaloids have been isolated from this species. The major alkaloid ancistrocladine has been assigned the structure and stereochemistry depicted in 26. These alkaloids are unique in being the only isoquinoline alkaloids arising from acetate units instead of the usual aromatic amino acids. The chemistry of this group has been reviewed (Govindachari and Parthasarathy 1977).

From *Tiliacora racemosa* colebr (*Menispermaceae*) a number of *bis*-bensylisoquinoline alkaloids were isolated, which are unique in having the isoquinoline moieties joined through a diphenyl unit and not through a diphenyl ether unit as is common. Essential features of the structures of tiliacorine and accompanying alkaloids were established by degradation and synthesis (Anjaneyalu *et al* 1969, 1971). More recently the position of the phenolic hydroxyl group was determined (Shamma *et al* 1976).

The absolute configuration depicted in 27 was derived using biosynthesis as a tool (Bhakuni *et al* 1978).

More than a dozen alkaloids have been isolated by Bhakuni and coworkers from *Cocculus laurifolius* DC and their structures elucidated (Uprety and Bhakuni 1975; Bhakuni *et al* 1976). Of these isococculidine (28) is a neuromuscular blocking agent. Six bases of the *bis*-benzylisoquinoline type were isolated from *Cocculus pendulus* Forsk and characterised (Bhakuni and Joshi 1975) of which cocculinine (29) displayed anti-cancer activity.

From the leaves of *Murraya koenigii* Spreng, used as a flavouring material for many items of food, almost thirty alkaloids belonging to the carbazole group have been isolated. Chakraborty and coworkers were the first to report the isolation of the alkaloids girinimbine, mahanimbine, and murrayacine. Subsequently, a number of other alkaloids were isolated in other laboratories and there is confusion due to the multiplicity of names given to the same alkaloid. Mahanimbine was correctly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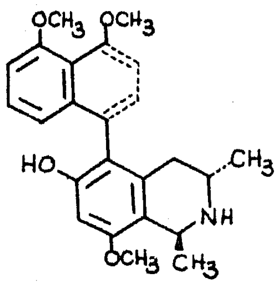
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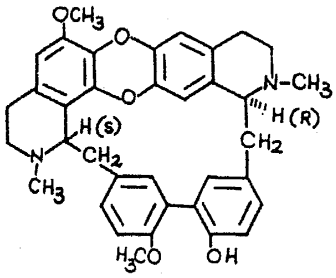
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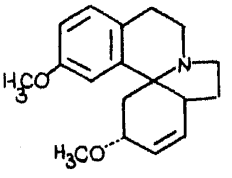
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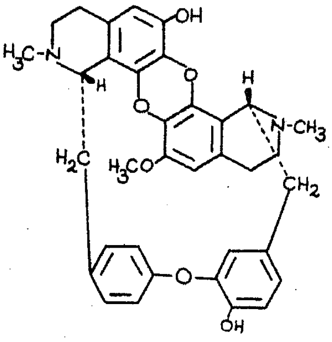
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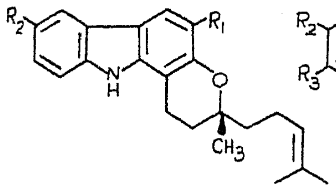
formulated as 30 (Narasimhan *et al* 1968), girinimbine as 31 (Dutta and Quassim 1969), murrayacine as 32 (Chakraborty *et al* 1971), koenimbine as 33 (Kureel *et al* 1969; Joshi *et al* 1970), koenimbidine as 34 (Narasimhan *et al* 1968), isomahanimbine as a position isomer of mahanimbine with the structure 35, mahanine (Narasimhan *et al* 1970) was formulated as 36.

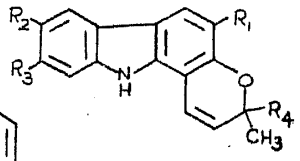
Among the more complex alkaloids, cyclomahanimbine appears correctly constituted as 37 (Bandaranayake *et al* 1974). An x-ray study of murrayazoline (mahanimbidine) has confirmed the structure as 38 (Bordner *et al* 1972).

The chemistry of carbazole alkaloids from *M. koenigii*, as well as from other plants of the Rutaceae, has been the subject of two recent reviews (Chakraborty 1977; Joshi 1975).

From the leaves of *Tylophora asthmatica* Wright et Arn used in folk medicine as a cure for asthma, several phenanthroindolzidine alkaloids, the first of this type to be discovered, tylophorine (39), tylophorinine (40), tylophorinidine (41), d-isotylocrebrine (42) and the seco-alkaloid septicine (43) as well as quaternary alkaloids have been isolated. All aspects of the structure and stereochemistry of these alkaloids have been established. Three recent reviews give a detailed account of the chemistry of this group (Góvindachari and Viswanathan 1978; Wiegrebe 1972; Gellert 1982). All the phenanthroindolizidine alkaloids show significant anti-cancer activity.

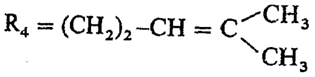
The alkaloids venenatine and isovenenatine (echitovenine) were first isolated from *Alstonia venenata RBr.* and assigned structures (44) and (45) on the basis of degradation studies. In an admirable thorough study of all parts of *A. venenata*, Chatterjee *et al* have reported the isolation of over twenty new alkaloids. The alkaloids belong to the class of yohimbine, aspirdofractinine and vincadifformine types. The occurrence of the

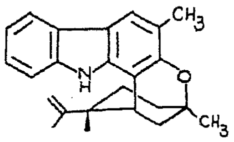




30 $R_1 = CH_3$; $R_2 = H$
35 $R_1 = H$; $R_2 = CH_3$

31 $R_1 = R_4 = CH_3$; $R_2 = R_3 = H$
32 $R_1 = CHO$; $R_2 = R_3 = H$; $R_4 = CH_3$
33 $R_1 = R_4 = CH_3$; $R_3 = H$; $R_2 = OCH_3$
34 $R_1 = CH_3$; $R_4 = CH_3$; $R_2 = R_3 = OCH_3$
36 $R_1 = CH_3$; $R_2 = H$; $R_3 = OH$


$$R_4 = (CH_2)_2\text{-}CH = C\begin{matrix}\diagup CH_3 \\ \diagdown CH_3\end{matrix}$$



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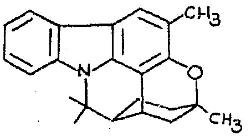

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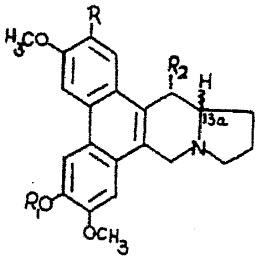
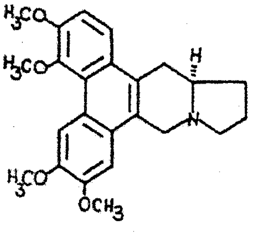


39 R = OCH_3; β-H at 13a
$R_1 = CH_3$; $R_2 = OH$

40 R = H; α-H at 13a
$R_1 = CH_3$; $R_2 = OH$

41 R = H; β-H at 13a
$R_1 = H$; $R_2 = OH$



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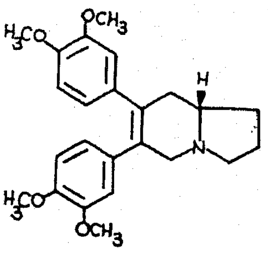
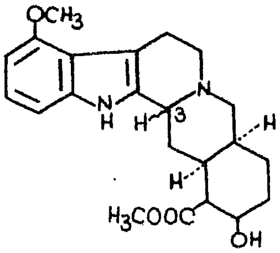
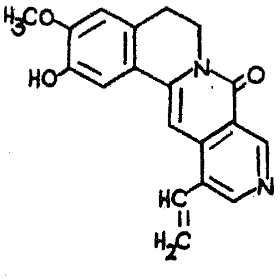


43

monoterpenoid alkaloid venoterpine is of great biogenetic significance. The chemistry of the alkaloids of *A. venenata* is the subject of a recent review (Chatterjee *et al* 1978). During the past three decades Prof. (Mrs) Chatterjee and coworkers have investigated over a hundred species of plants, mostly belonging to the *Apocyanaceae* and isolated over fifty alkaloids of the indole group in which most fall into well-recognised categories, some like noreline and grandifoline are of immense complexity whose structures could be solved only by x-ray analysis and multi-national effort.



44 C_3-β-H
45 C_3-α-H



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Pakrashi's work on *Alangium lammerckii* Thev. besides furnishing several bases of the emetine type has also yielded some alkaloids of novel structures like alangimarine (46) (Pakrashi *et al* 1980) which are 10-azaberberines.

5. Biosynthetic and tissue culture studies on alkaloids

Excellent work has been done for the first time in India, on the biosynthesis of several important alkaloids by Bhakuni and Kapil at the Central Drug Research Institute, Lucknow, Specific incorporation of (+)-reticuline (47) into boldine (48) was demonstrated in *Litsea glutinosa.* The evidence supports the direct oxidative coupling of (+)-reticuline to isoboldine (49) which in turn was a specific precursor for boldine (Bhakuni and Kapil 1974).

The biosynthesis of papaverine (Uprety *et al* 1975), of the *bis*-benzylisoquinoline alkaloid cocsulinin (Bhakuni *et al* 1978) of the abnormal Erythrina alkaloids cocculidine and cocculine (Bhakuni and Singh 1978), the morphinandienone alkaloid sebiferine (Bhakuni *et al* 1978) and several others have all been worked out by Bhakuni and coworkers.

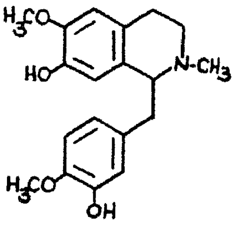
Very interesting tissue culture studies on alkaloid-bearing plants such as *Atropa belladonna* and *Tylophora asthmatica* have been carried out by Chadha *et al* at Bhabha Atomic Research Centre, Bombay, which shed light on the stage of formation of alkaloids in these plants (Eapen *et al* 1978; Benjamin *et al* 1979).

6. Miscellaneous

Extensive contributions have been made in India in the field of lignans and glycosides. From the reputed medicinal plant *Picrorhiza kurrooa* Benth two C_9 iridoid glycosides picroside (50) and kutkoside (51) were isolated and their structures determined. These compounds are claimed to have hepatoprotective properties (Singh and Rastogi 1972; Rastogi *et al* 1949, 1959).

The cardiac glycoside peruvoside (52) isolated from *Thevetia nerifolia* Juss (Rangaswamy and Venkat Rao 1959; Bisset *et al* 1962) has been shown to be superior to diosgenin and has been marketed in Europe under the name 'Encordin'.

There has been a decline in the investigation of plant products during the past decade and the emphasis has shifted to organic chemical synthesis. However, there is still plenty of scope for work on plant products, using newer techniques of isolation, as well



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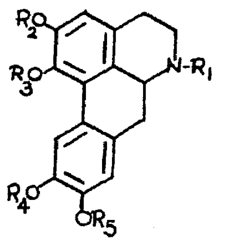
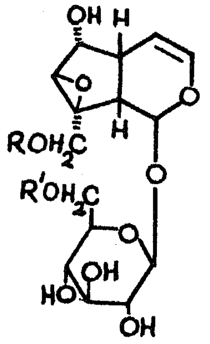
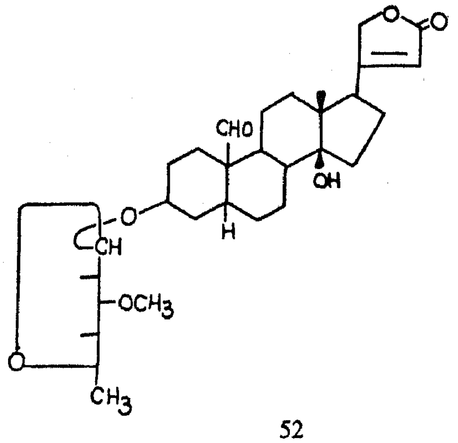


48 $R_1 = R_3 = R_4 = CH_3$
$R_2 = R_5 = H$

49 $R_1 = R_2 = R_4 = CH_3$
$R_3 = R_5 = H$



50 R = H; R′ = cinnamoyl
51 R = Vanilloyl; R′ = H



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as newer analytical methods in structure elucidation. While x-ray analysis can lead to rapid unravelling of structure, it will not contribute to the enrichment of organic chemistry and will serve to dry up the contributions received from the chemical investigation of plant products.

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