SOME RECENT CHEMISTRY OF INDIAN RUTACEAE*

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Chemistry of five plants of the Rutaceae family, namely Clausena heptaphylla Wt. & Arn., Clausena indica Oliv., Murraya exotica Linn., Murraya koenigii Spreng., and Vepris bilocularis Engler, has been reviewed. The structures of some new carbazole alkaloids, terpenes, flavonoids and coumarins have been discussed.

The Rutaceae family comprises of one hundred fifty genera and more than about nine hundred species[1]. Many of the chemical constituents and especially the alkaloids are known to possess useful pharmacological properties. A wide variety of structurally different alkaloids are known to be present in the Rutaceae family e.g. alkaloids belonging to the quinoline, furoquinoline, pyrrolidine, quinazoline, protoberberine, imidazole, oxazole and aporphine types have been obtained[2,3]. A number of alkaloids which are carbazole derivatives have been isolated in recent years and appear to be limited to the Rutaceae family[4]. The present review describes some of the work carried out on the Rutaceae family in our laboratories.

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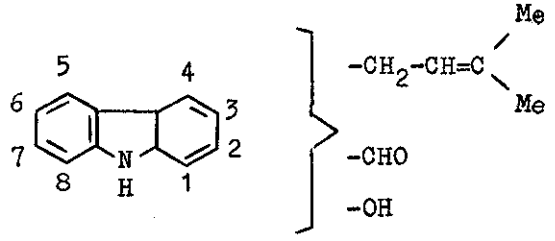
* Contribution No.409 from CIBA-GEIGY Research Centre. This review is based on the Professor K. Venkataraman endowment lecture given on behalf of the University of Bombay on 20th December, 1974.

Carbazole alkaloids

The oil obtained by hexane extraction of the roots of Clausena heptaphylla Wt. & Arn. on chromatographic separation gave a weakly basic alkaloid in about 0.004% yield designated as heptaphylline[5,6]. Heptaphylline, $C_{18}H_{17}NO_2$ showed in the UV λ_{max} 234, 278, 298 and 346 nm (log ε, 4.42, 4.53, 4.58 and 4.09) and IR ν_{max} 3300 (OH or NH), 2740, 1640 (chelated CHO or >C=O) and 1618, 1590 (aromatic) cm^{-1}. A deep blue ferric colour indicated the presence of a hydroxyl group. The presence of a formyl group was indicated from the formation of a red crystalline dinitrophenylhydrazone and the singlet at 9.9 ppm. in its NMR spectrum. Heptaphylline gave a green colour reaction with conc. H_2SO_4 and HNO_3 characteristic of carbazoles. Its NMR spectrum showed two methyl singlets at δ 1.66 and 1.83, a benzylic methylene doublet at 3.6 (J = 6 Hz), a broad triplet due to a vinyl proton at 5.35 (J = 6 Hz), all indicative of an isopentenyl chain, a chelated hydroxyl at 11.7 (exchanged by addition of D_2O), and imine (10.3) functions. The aromatic part of the spectrum between δ 7.1 - 8.3 indicated a total of five protons. The sharp singlet at 8.25 suggested no ortho or meta coupling with one of the aromatic protons. A partial structure(1) could therefore be written for heptaphylline. On treatment with polyphosphoric acid heptaphylline afforded an isomeric product cycloheptaphylline, the NMR spectrum of which showed a sharp singlet at 1.42 due to gem dimethyl groups and two sets of triplets at 2.0 and 2.95 (J = 7 Hz) due to Ar-CH_2-CH_2- grouping. While there was no change in the UV spectrum, the IR spectrum showed

ν_{max} 3280 (NH), 1670 (unchelated -CHO) cm^{-1}. This clearly showed that the hydroxyl should be placed adjacent to the dimethyl allyl group. Depending on the placement of the formyl group at the 1,2,3 or 4 positions of the carbazole ring, four structures could be written



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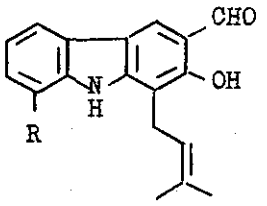
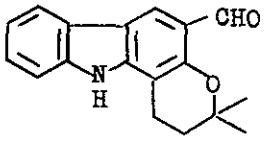


2: R = H

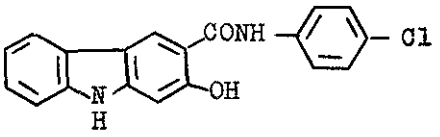
11: R = OH



3

for heptaphylline. A unique structure(2)was chosen on the basis of its UV spectrum which closely resembles the spectrum of 3-formyl carbazole. Cycloheptaphylline should then be(3). For the synthesis of 2, we wished to use the commercially available 2-hydroxy-carbazole-3-carboxylic acid from which Naphtol AS-LB is manufactured and its structure is assumed to be(4)[7]. The Kolbe reaction of 2-hydroxy carbazole has been assumed to give aboout 80% of 2-hydroxy carbazole-3-carboxylic acid and 10-20% of 2-hydroxy carbazole-1-

carboxylic acid. However, there is no evidence for the orientation of the carboxy group in these compounds. The hydrolysed acid of a commercial sample of Naphtol AS-LB showed in the aromatic region of its NMR spectrum two doublets at 8.05 (J = 9 Hz) and 6.75



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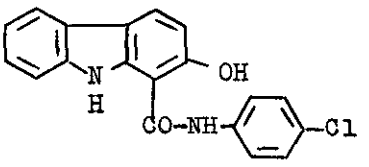

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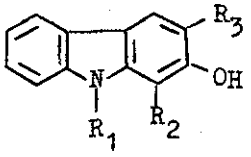
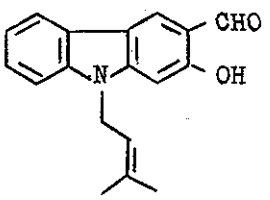
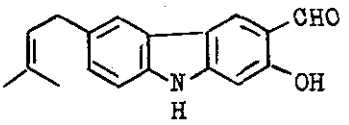
(J = 9 Hz) integrating for one proton each. Decoupling experiments showed them to be mutually coupled and should therefore be attributed to two ortho protons. The carboxylic acid should then be constituted as 2-hydroxycarbazole-1-carboxylic acid and the structure of Naphtol AS-LB should be revised to 5[8,9]. Vilsmeier-Haak reaction of 2-hydroxycarbazole with N-methyl formanilide and phosphorous oxychloride led to a mixture of 2-hydroxycarbazole-1-carbaldehyde (6), 2-hydroxycarbazole-3-carbaldehyde (7) and the compound (8). Heptaphylline (2) was synthesized in poor yield by the reaction of 7 with 3,3-dimethyl allyl bromide[10]. Treatment of (7) with 2-methyl-3-buten-2-ol in presence of BF_3-etherate led to a mixture of (2), (9) and (10). The structure proofs were based on analytical and spectral data[6]. Heptazoline (11) and heptazolidine (12) are reported to be isolated from the bark of Clausena heptaphylla Wt. & Arn.[11,12]







6 : R_1, R_3 = H
R_2 = CHO

7 : R_1, R_2 = H
R_3 = CHO

8 : R_2, R_3 = H
R_1 = CHO

9

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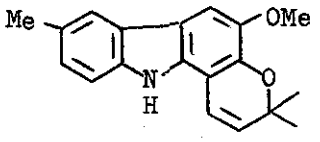

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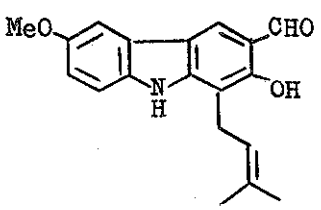
Chromatographic separation of the hexane extract of the roots of another related species, Clausena indica oliv. afforded a bright yellow substance m.p. 173°, $C_{19}H_{19}NO_3$[13]. It gave a blue-green ferric colouration and its UV spectrum resembled that of heptaphylline indicating a 3-formyl carbazole. Its NMR spectrum showed the following signals: 11.7 (s, OH, exchanges with D_2O), 9.9 (s, CHO), 8.15 (br, NH), 7.92 (s, 1H), 6.9-7.5 (m, 3H), 5.3 (t, J = 8 Hz, 1H), 3.9 (s, 3H, OMe), 3.6 (d, J = 8 Hz), 1.88 (br s, -Me on a double bond), 1.75 (br s, 3 H, -Me on a double bond). The compound on heating with formic acid gave an isomeric cyclised product which showed a similar UV spectrum. The new alkaloid should therefore be a derivative of heptaphylline , having a methoxyl substituent in one of the four positions of the unsubstituted benzene ring. The chemical shifts of the four aromatic protons

appearing at 7.92 (s, C-4), 7.45 (d, J = 2 Hz, C-3), 7.3 (d, J = 7.5 Hz, C-8) and 7.0 (d,d; J = 7.5, 2 Hz, C-7) suggested that the new alkaloid could be constituted as 6-methoxy-heptaphylline (13). The cyclised product should then be 14. This was confirmed by the conversion of (14) by Huang-Minlon reduction to dihydrokoenimbine (15), which was obtained by hydrogenation of koenimbine, isolated from



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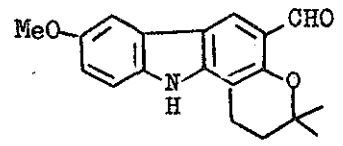

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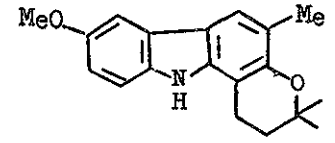
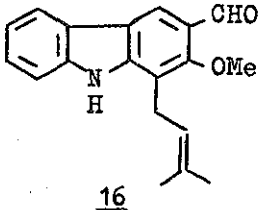


15

Murraya koenigii[14]. Another minor alkaloid (0.001%) $C_{19}H_{19}NO_2$ designated as indizoline has been isolated from the roots of Clausena indica Oliv.[15] Its IR spectrum showed the presence of an unchelated aldehyde group (1660 cm^{-1}) and the NMR spectrum indicated a γ,γ-dimethylallyl group. The presence of a methoxyl group (3.29) and an aldehydic group (10.3) was also evident. The NH proton appeared as a broad signal at 8.8 and the C-4 proton ortho to the aldehydic group was a singlet deshielded at 8.4. The quartet at 8.02 (1H, J = 2 and 7 Hz) could be attributed to the C-5 proton. Indizoline was different when compared with heptaphylline-2-methyl ether (16). Its UV spectrum showed a

hyperchromic shift of the maximum at 275 nm and the Huang-Minlon reduction product of indizoline closely resembled the spectrum of 1-methoxycarbazole and 1-methoxy-3-hydroxy-methylcarbazole. On the basis of this data indizoline was formulated as (17) and the Huang-Minlon reduction product as (18). The structure was confirmed by



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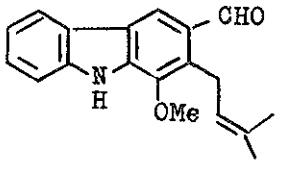

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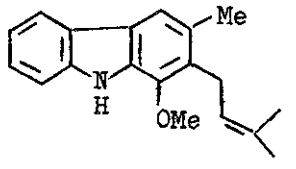
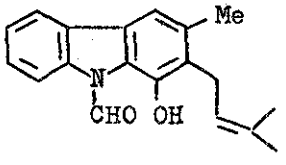


18

an unambiguous synthesis of 18. 1-Hydroxy-3-methylcarbazole was N-formylated and C-alkylated with 2-methyl-3-buten-2-ol in the presence of BF_3-ether to give a mixture of (19) and (20). Structure (19) was assigned on the basis of its cyclisation to give the dimethylchromene (21). The compound (19) on methylation and acid hydrolysis gave (18) identical with the product obtained from indizoline.



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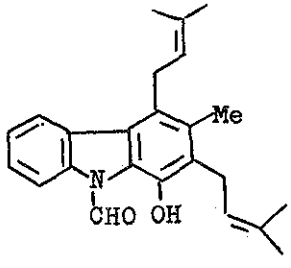

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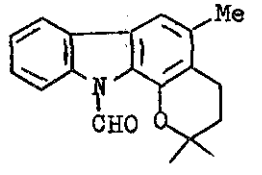
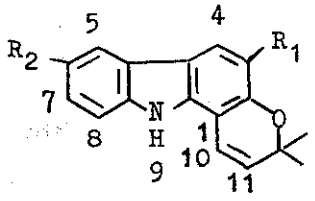
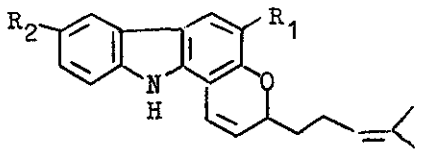


21

From the leaves of Murraya koenigii Spreng. Chakraborty et al. had reported the isolation of the carbazole alkaloids girinimbine, mahanimbine and murrayacine. Girinimbine and murrayacine were formulated by them as (22) and (23) respectively[16,17,18]. Narasimhan et al. formulated mahanimbine as (24)[13], and Dutta and Quassim proposed the structure (25) for girinimbine[19]. We have established the structures of girinimbine, mahanimbine and two new alkaloids designed as isomahanimbine and koenimbidine.[20]





22 : R_1 = H; R_2 = Me

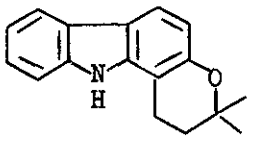
23 : R_1 = H; R_2 = CHO

25 : R_1 = Me; R_2 = H

28 : R_1 = CHO; R_2 = H

24 : R_1 = Me; R_2 = H

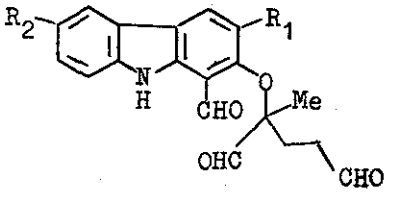
30 : R_1 = H; R_2 = Me

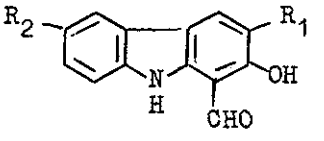


29

Mahanimbine on ozonolysis gave a phenolic aldehyde having a UV spectrum typical of 1-formylcarbazole. The aldehyde on decarbonylation was identified from its m.m.p., TLC and IR spectrum as 2-hydroxy-3-methylcarbazole which was synthesized by Huang-Minlon reduction of 2-hydroxycarbazole-3-carbaldehyde (7). A neutral compound

obtained in the ozonolysis of mahanimbine has been assigned the structure (26) on the basis of spectral data. This confirms the structure of mahanimbine as (24), and the phenolic aldehyde as (27). Since the ozonolysis of girinimbine gave a phenolic aldehyde identical with (27), the alkaloid should have the structure (25) and not (22). The structure (23) for murrayacine[18,21] was based on the LAH reduction of its dihydroderivative to give a compound identical with dihydrogirinimbine. The structure of murrayacine therefore appeared to be (28). However the m.p. 176° reported for



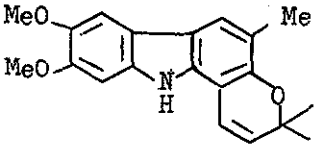


26 : R_1 = Me; R_2 = H

32 : R_1 = H; R_2 = Me

27 : R_1 = Me; R_2 = H

31 : R_1 = H; R_2 = Me



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dihydromurrayacine differs from that of cycloheptaphylline (3) m.p. 250°. With a view to ascertain the correctness of the

structure (3) assigned to cycloheptaphylline, it was decarbonylated to give (29) m.p. 178°. This was identical with the synthetic compound obtained by reaction of 2-hydroxycarbazole with 2-methyl-3-buten-2-ol and cyclisation with formic acid. The structure of murrayacine and its dihydro derivative therefore needs to be reinvestigated.

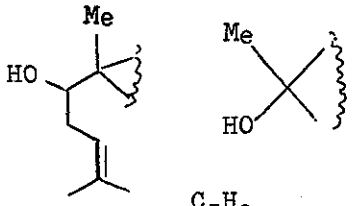
Isomahanimbine $C_{23}H_{25}NO$ resembled closely mahanimbine in its UV spectrum and on reduction with Pd-C it gave a tetrahydro derivative, the UV spectrum of which was similar to 2-methoxy-carbazole. The NMR spectrum of isomahanimbine revealed the attachment of a geranyl side chain oxidatively cyclized as in mahanimbine. A downfield shift of the C-10 proton by about 0.6 ppm in the N-methyl derivatives of a number of compounds where the Δ^3-pyran is angularly fused to the carbazole nucleus appeared to be of diagnostic value in determining the attachment of the pyran ring. N-Methylisomahanimbine showed a similar shift of the C-10 proton. The C-3 and C-4 protons formed an AB quartet at 6.7 and 7.7 (J = 8.5 Hz) and the C-5 proton appeared as a slightly broad singlet at 7.68. The C-7 and C-8 protons formed an AB spectrum having signals at 7.05 (J = 8 Hz and 1 Hz) and 7.15 (J = 8 Hz). These data indicated structure (30) for isomahanimbine. The ozonolysis of (30) gave phenolic and neutral aldehydes which could be constituted as (31) and (32) respectively.

Koenimbidine (koenigicine[22], koenidine[14]) $C_{20}H_{21}NO_3$ on catalytic reduction formed a dihydro-derivative by reduction of

the 2,2-dimethylchromene double bond. NMR spectrum revealed the presence of an aromatic methyl and two methoxyl groups. Three aromatic singlet protons at 7.53, 7.4 and 6.9 could be ascribed to the C-4, C-5 and C-8 protons. Koenimbidine has been constituted as (33).

Terpenoids

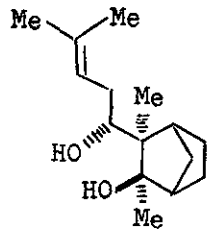
A new sesquiterpene named clausantalene has been isolated from the roots of Clausena indica Oliv.[23]. It analysed for $C_{15}H_{26}O_2$, m.p. 114°, $[\alpha]_D$ + 27.7° and in the IR spectrum indicated the presence of hydroxyl groups (3380 cm^{-1}). Its mass spectrum showed a negligible molecular ion peak at m/e 238 and a base peak at m/e 220 ($M^+ - H_2O$). The other fragment ions at m/e 177 (220 - C_3H_7) and m/e 151 (220 - C_5H_9) suggested the presence of an isopentenyl side chain. This was confirmed by its NMR spectrum. Hydrogenation of clausantalene gave a dihydroderivative by reduction of the isopentenyl double bond. On the basis of the NMR spectrum and double irradiation experiments, a partial structure (34) was suggested for the sesquiterpene. Clausantalene should therefore belong to the sesquicarane, bergamotane or β-santalane types. An X-ray crystallographic analysis of the sesquiterpene carried out by Dr. D.J. Williams at the Imperial College, London, showed it to be a new β-santalane derivative (35).



C_5H_8

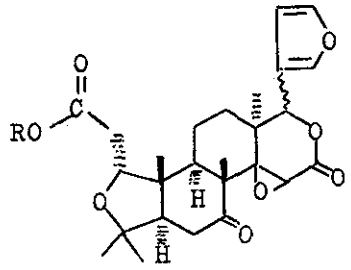
(bicyclic)

34



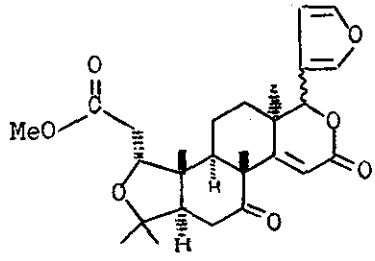
35

From the roots of Vepris bilocularis Engler, a new bitter principle $C_{27}H_{34}O_8$ named veprisone was isolated[24]. The presence of a furan ring was suggested from its UV and IR spectra. An ester and/or lactone band at 1740 cm^{-1} and six membered ketone band at 1710 cm^{-1} were also present. Veprisone was characterised by the formation of an oxime and semicarbazone. On the basis of the spectral data and degradation studies, veprisone has been



36 : R = Me

40 : R = H



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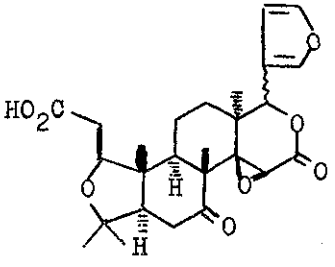
constituted as methyl epi-isoobacunoate (36). Reduction of veprisone with HI-acetic acid gave a deoxy-acid which on treatment with

diazomethane gave deoxyveprisone (37), indicating an epoxy ring in an environment probably identical as in limonin. Hydrolysis of veprisone with methanolic KOH gave a carboxylic acid identical with isoobacunoic acid (38). Mild alkaline hydrolysis of obacunoic acid (39) affords epi-isoobacunoic acid (40) which is transformed under vigorous conditions to give (38). Similarly, veprisone (36) on brief treatment with $Ba(OH)_2$ gave (40). Meerwein-Pondorf reduction of (36) gave isopropyl epi-isoobacunolate (41) identical with an authentic sample[25,26].



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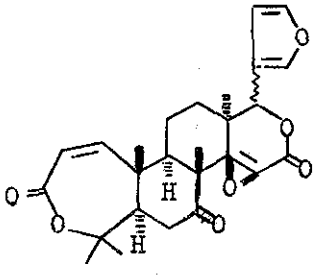

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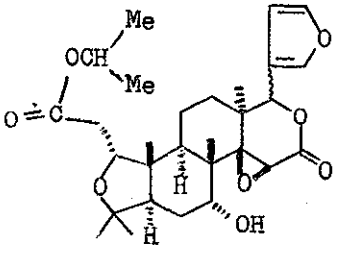
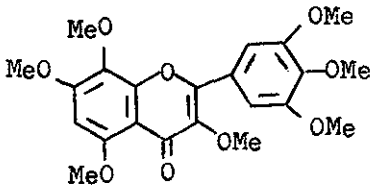


41

Flavonoids

From the leaves of a related species Murraya exotica Linn. which is an ornamental plant, two new flavones have been isolated.

One of these has been characterised as hibiscetinheptamethyl ether (42) and the other designated exoticin has been shown to have the structure 43[17,18].



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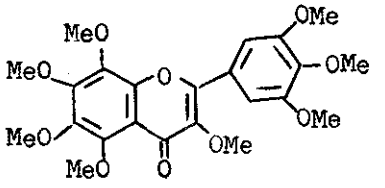

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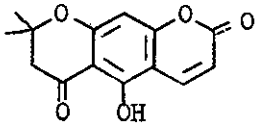
Coumarins

Many coumarins are found to occur in the Rutaceae family. From the hexane extract of the roots of Clausena heptaphylla Wt. & Arn. two new coumarins $C_{14}H_{12}O_5$ and $C_{19}H_{20}O_5$ designated as clausenin and clausenidin respectively were isolated[29,30]. Both the compounds contain one chelated phenolic hydroxyl group. These formed the monomethyl ether and p-toluenesulphonate derivatives. The UV spectra of these derivatives resembled the spectrum xanthoxyletin. Alkaline hydrolysis of clausenin and clausenidin gave the corresponding coumaric acids from which it is clear that both the compounds contain the coumarin nucleus. Clausenin on KOH fusion gave phloroglucinol. Its NMR spectrum showed two sets of doublets at 6.1 and 8.0 (J = 10 Hz) attributed to the C-3, C-4 protons of the coumarin. A six proton singlet at 1.5 indicated a gem-dimethyl group, a two proton singlet at 2.8 could be assigned to a methylene group adjacent to a carbonyl and the sharp peak at 6.3 should be due to an aromatic

proton. These data suggested two alternative structures (44) or (45) for clausenin. Unambiguous synthesis of these two coumarins proved



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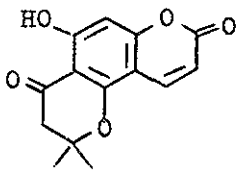

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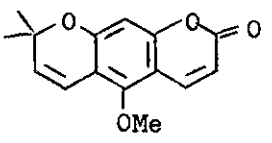

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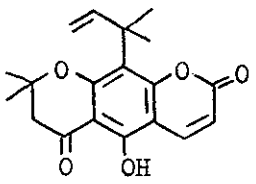
that clausenin should have the linear structure (44)[31]. 5,7-Dihydroxy-2,2-dimethyl chroman-4-one on condensation with ethyl propiolate gave a mixture of two isomeric compounds $C_{15}H_{12}O_5$, (A) m.p. 156° and (B) m.p. 220°. The compound (A) on methylation, subsequent reduction of the methyl ether with $NaBH_4$ and dehydration gave xanthoxyletin which is proven to have the structure (46). The compound (B) which has the structure (45), by a similar series of reactions gave the angular coumarin alloxanthoxyletin.

NMR spectrum of clausenidin showed that it contains an α,α-dimethylallyl group. There are numerous coumarins which contain the γ,γ-dimethylallyl chain but perhaps this is the first example of a coumarin bearing an α,α-dimethylallyl grouping. On the basis of the spectral data clausenidin could be constituted as (47) or (48).



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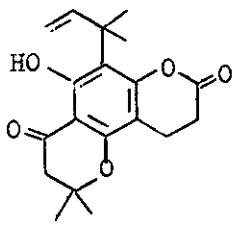

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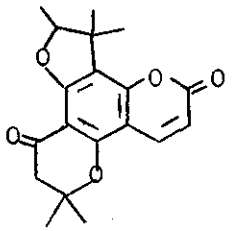

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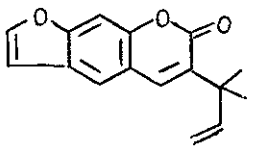
A choice between the two structures was arrived at on the basis of nucleur overhauser effect (NOE) studies[32]. An increase in the integrated intensity and height of the olefinic proton H-4 on double irradiation of the methoxyl group in clausenidin monomethyl ether could be rationalised on the basis of structure (47). Clausenidin (47) on treatment with sulphuric acid gave (49) and on heating with $AlCl_3$, the compound (45), by opening of the pyrone ring and recyclisation involving a rearrangement. Clausenin and clausenidin-monomethyl ethers have been synthesised[33].

From the roots of Clausena indica Oliv. the known coumarins imperatorin, phellopterin, chalepensin (50) and chalepin (51) were isolated[34]. On heating (50) with HCl or $AlCl_3$ in benzene a rearrangement product was obtained which has been formulated as 52[35,36].



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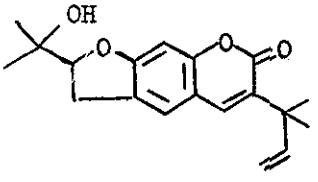

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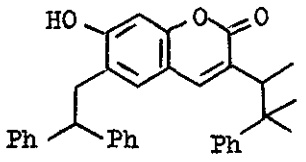

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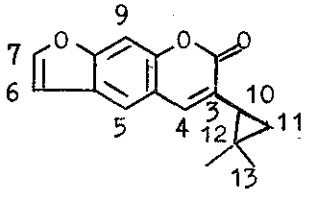
A new coumarin, $C_{16}H_{14}O_3$ designated as clausindine[37] has also been isolated from Clausena indica Oliv. Its UV spectrum indicated it to be a linear-furanocoumarin which was supported by its NMR spectrum showing the α and β furan protons at 7.6 and 6.8 respectively. The aromatic protons at 7.58 and 7.4 could be assigned to the C-5 and C-9 protons. The attachment of a 5-carbon unit (C_5H_9) in the form of gem-dimethylcyclopropane grouping at C-3 of the furanocoumarin could also be deduced from its NMR spectrum. A singlet at 7.35 showed the C-4 proton. The methyl singlets at 0.9 and 1.3 together with the methylene multiplet at 0.8 and the triplet at 1.9 (7.5 Hz) indicated the dimethylcyclopropane ring. These assignments were confirmed by double resonance experiments and on the basis of this evidence clausindine could be formulated as (53). Clausindine on hydrogenation afforded the dihydroderivative



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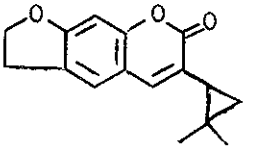

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(54) and its structure was confirmed by an unambiguous synthesis of (54). This is probably the first example of a coumarin having the isoprenoid unit attached to the aromatic nucleus in the form of a gem-dimethylcyclopropane grouping[38].

ACKNOWLEDGEMENT : The author is grateful to Dr. T.R.Govindachari for his interest and the University of Bombay for their invitation to present this work.

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Received, 16th July, 1975