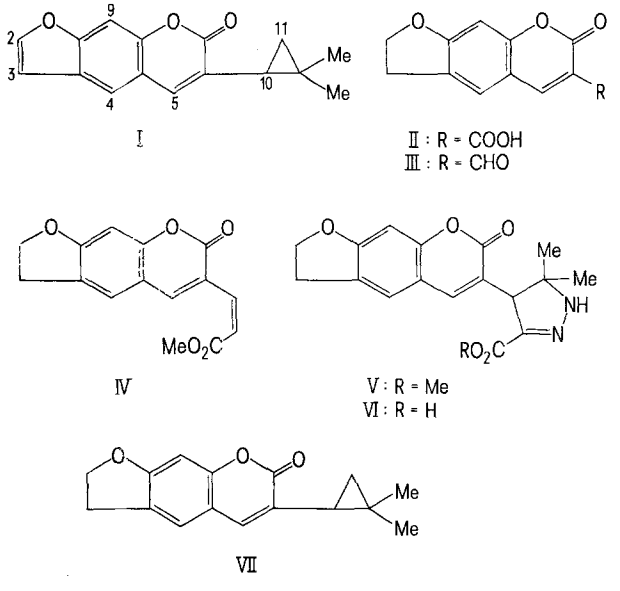
## Structure of Clausindine, a New Coumarin from *Clausena indica* Oliv.

Isolation of the alkaloid 6-methoxyheptaphylline[1] and some furanocoumarins[2] from the roots of *Clausena indica* Oliv. has been recorded earlier. We wish to report the structure determination of a coumarin designated clausindine (I), $C_{16}H_{14}O_3$; $M^+$ 254, mp 128° isolated from the roots of the same plant. It showed UV $\lambda_{max}^{EtOH}$ 248, 303 and 332 nm (log $\varepsilon$ 4.3, 4.1 and 4.0) and IR $\nu_{max}^{nujol}$ 1720, 1620 and 1580 $cm^{-1}$ bands characteristic of linear furanocoumarins. Its NMR-spectrum (100 MHz) showed the furan protons at $\delta$ 7.6 and 6.8 [d, 2 Hz each; C(2)- and C(3)-H] and the aromatic protons at $\delta$ 7.58 [C(4)-H] and 7.4 [C(9)-H]. The C(3)-proton showed ortho coupling and also long range coupling[3] with C(9)-H as shown by double resonance experiments. By irradiation of the proton at C(3), both the C(2)-H and C(9)-H were affected and irradiation of the C(9)-H at $\delta$ 7.4 affected only C(3)-H at $\delta$ 6.8. The attachment of a 5 carbon unit at C(6) of the furanocoumarin nucleus was deduced from the singlet C(5)-proton appearing at $\delta$ 7.35[4]. That the side chain consists of a gem-dimethylcyclopropane grouping was evident from the NMR-spectrum and also the base peak at *m/e* 199 by the loss of a $C_4H_7$ unit from the molecular ion. The methyl groups appeared as singlets at $\delta$ 0.9 and 1.3 and the C(10)-proton as a slightly split (< 1 Hz) triplet at $\delta$ 1.9 (6.5 Hz) and the C(11)-methylene protons of the cyclopropane at $\delta$ 0.8 (2 H; m). Irradiation at $\delta$ 1.9 affected the methylene protons as well as the C(5)-proton. Irradiation at $\delta$ 7.35 resulted in a sharp triplet at $\delta$ 1.9. Since the amount of clausindine was too small for degradation studies, confirmation of the structure was obtained by synthesis.




Dihydropsoralene-3-carboxylic acid (II), mp 246° obtained by the condensation of 6-hydroxy-5-formylcoumaran[5] with malonic acid was converted to the acid chloride and reduced to the corresponding aldehyde (III), mp 200°. Wittig reaction with carbomethoxymethylene triphenylphosphorane[6] provided the olefinic ester (IV) which on cycloaddition with diazopropane gave the pyrazoline (V), mp 242° (NH, 3340 $cm^{-1}$)[7]. The ester (V) was hydrolyzed to give the carboxylic acid (VI) mp 185° which was pyrolyzed by heating with copper bronze and quinoline. Separation of the reaction mixture on thick layer silica gel gave (VII), mp 200° identical with dihydroclausindine obtained by mild reduction of (I) with 10% Pd/C. Clausindine is probably the first example wherein the ubiquitous isoprenoid unit is attached to the aromatic nucleus as a gem-dimethylcyclopropane grouping.

*Zusammenfassung.* Es wurde mit Clausindin ein neuartiges, Gemdimethylcyclopropan-Ring enthaltendes Cumarin aus den Wurzeln von *Clausena indica* Oliv. isoliert. Die Struktur (I) ist auf Grund spektraler Daten und der Synthese von Dihydroclausindin aufgeklärt worden.

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## Isolation of N-Isobutyl Deca-*trans*-2-*trans*-4-Dienamide from *Piper sylvaticum* Roxb.

The seeds of *Piper sylvaticum* Roxb. are often used as an effective drug in the treatment of asthma and chronic bronchitis in the Indian Ayurvedic system of medicine[1]. Investigation of the petrol (bp 60–80°) extract of its seeds has resulted in the isolation of a number of compounds. The characterisation of two of these, viz. 4',7-dimethoxy-5-hydroxy flavone and sylvatine, a new alkamide, has been previously described by us[2]. The present paper deals with the characterisation of a third compound (I) isolated from the petrol extract by chromatography over silica gel using petrol:benzene (1:1) as eluent. This compound, mp 75°, $[\alpha]_D$ 0°, was difficultly crystallisable as it was highly soluble in all organic solvents. It was extremely unstable in the solid state, decomposing within a few hours to a reddish gum on exposure to air, and hence had to be stored in sealed evacuated tubes. Its molecular formula was confirmed by analysis and mass spectrometry ($M^+$ 223) as $C_{14}H_{25}ON$. The UV-spectrum of the compound ($\lambda_{max}^{EtOH}$: 257 nm: log $\varepsilon$: 4.53) indicated a

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