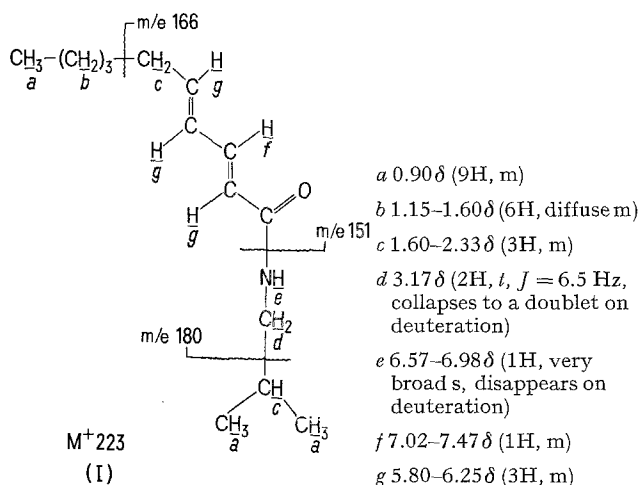


sorbic chromophore^{3,4}. The IR-spectrum showed the presence of a secondary amide, with an α , β -unsaturated conjugated diene system [$\nu_{\max}^{\text{Nujol}}$: 3300 cm^{-1} ($-\text{NH}-$), 1630 cm^{-1} (conjugated carbonyl), 1665 cm^{-1} (conjugated double bond)]. The presence of absorption bands at 849 and 878 cm^{-1} and a very strong one at 998 cm^{-1} , indicated that the α , β -unsaturated conjugated diene system had a *trans-trans*-configuration⁴.

At this stage, the physical and spectral properties of our compound appeared to be similar to those of *N*-isobutyldeca-*trans-2-trans-4*-dienamide (I), a constituent of pellitorine³, which had been previously isolated from some other *Piper* species by ATAL⁵. Since an authentic sample of this compound was not available, we had to

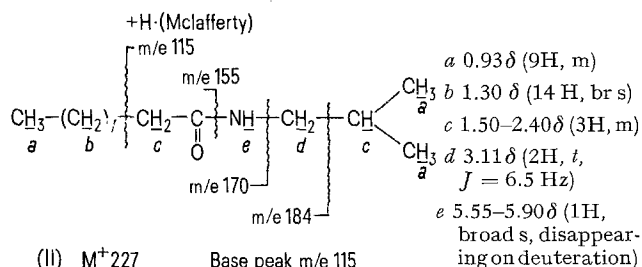


undertake detailed spectral and chemical studies in order to confirm its structure. Our investigations, which provide additional information about this compound, are reported in the present communication.

The 60 MHz NMR-spectrum (CDCl_3) of the amide, was consistent with structure (I).

On hydrogenation over ADAM's catalyst, (I) afforded a tetrahydroderivative (II), mp 40°, $\text{C}_{14}\text{H}_{29}\text{ON}$ ($M^+ 227$). (II) lacked the bands due to olefinic unsaturation at 1665, 998 and 878 cm^{-1} in its IR-spectrum (Nujol), the amide carbonyl band now appearing at 1655 cm^{-1} . The 60 MHz NMR-spectrum (CDCl_3) and the mass spectral fragmentation pattern of the tetrahydro-compound were consistent with its formulation as *N*-isobutyldecanamide (II).

Hydrolysis of (II) with concentrated hydrochloric acid in a sealed tube furnished decanoic acid and isobutylamine hydrochloride, mp 165°. *N*-isobutyldecanamide was synthesized from decanoyl chloride and isobutylamine in presence of 10% aqueous sodium hydroxide and found to be identical on comparison (mp, mmp, co-TLC, superimposable IR-spectra) with the tetrahydroderivative (II).



On the basis of the above spectral and chemical observations, the original compound could be assigned a structure (I). The structural assignment was in conformity with its mass spectral fragmentation pattern, the diagnostic peaks appearing at m/e 223 (M^+), 180 ($M-\text{C}_3\text{H}_7$), 166 ($M-\text{C}_4\text{H}_9$), 152, 151 ($M-\text{C}_4\text{H}_9\text{NH}$) (base peak), 96, 95 and 81. The NMR and mass spectra of (I) and its tetrahydroderivative (II), as well as the synthesis of the latter, have not been reported previously, and provide additional information about these compounds⁶.

Zusammenfassung. Spektroskopische Strukturaufklärung eines Inhaltsstoffes (Alkaloid) aus *Piper sylvaticum* Roxb. mit teils synthetischer Beweisführung.

A. BANERJI, R. N. REJ and P. C. GHOSH

Department of Chemistry,
 University College of Science,
 Calcutta 9 (India),
 13 June 1973.

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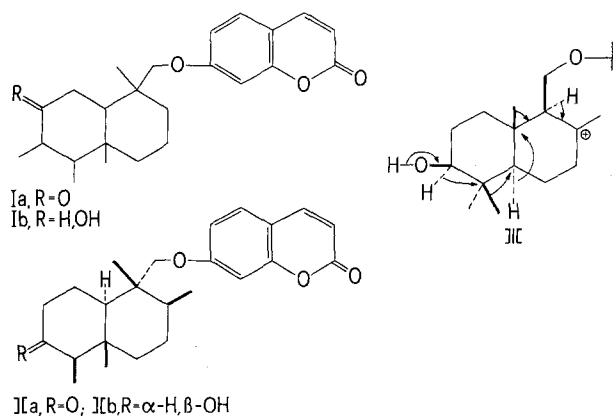
⁶ Acknowledgment. The authors thank Professor (Mrs.) A. CHATTERJEE, University of Calcutta, for laboratory facilities and helpful discussions; and Dr. NITYA NAND, CDRI, Lucknow, and Dr. S. C. PAKRASHI, I.I.E.M., Calcutta, for spectral measurements.

The Terpenoid Parts of Kamolone and Kamolol of *Ferula penninervis*

The importance of biogenetic theory in terpene structure elucidation has been amply demonstrated¹. We have recently applied the principles embodied in this theory to arrive at and establish the structure of reportedly unidentified sesquiterpene from *Citrus sinensis*, as 5 β , 7 β , 10 α -selina-3,11-diene². This note reports on the revised structures of kamolone and kamolol, the sesquiterpenoid coumarins of *Ferula penninervis* Rgl. et Schmalh., which on the basis of extensive spectral and chemical degradation studies have been formulated³ as (Ia) and (Ib) respectively. Subsequently, mass spectral fragmentation studies have been reported⁴ in support of these structures.

Although the terpenoid parts of structures (Ia) and (Ib) are dissectable into isoprene units, nevertheless it is difficult to envisage their derivation from farnesyl pyrophosphate, the bonafide precursor of sesquiterpenes, by means of accepted mechanistic operations enunciated in the biogenetic isoprene rule^{5,6}. A biogenetically more correct formulation of terpenoid moieties of kamolone and kamolol would be the structural variants represented in (IIa) and (IIb) respectively, which can be conceived as derivable from farnesyl pyrophosphate by oxidative cyclisation to an intermediate cation (III) involving drimane skeleton, followed by a 'friedo' rearrangement and finally deprotonation. The new structures (IIa) and

(IIb) are fully consistent with all the reported spectral (Figure) and chemical data^{3,4}. It is to be noted that kamolone bears the same relationship to kamolol as friedelin to friedelenol, the latter two co-occurring in *Clusea rosea*⁷. Finally, it remains to be stressed that the stereochemical details may be as indicated by (IIa) and (IIb) or their mirror images.



Zusammenfassung. Neue Strukturvorschläge für den terpenoiden Teil zweier Inhaltsstoffe aus *Ferula penninervis*.

S. K. PAKNIKAR and J. K. KIRTANY

Department of Chemistry,
Centre of Post-graduate Instruction and Research,
University of Bombay,
18th June Road,
Panaji (Goa, India),
15 August 1973.

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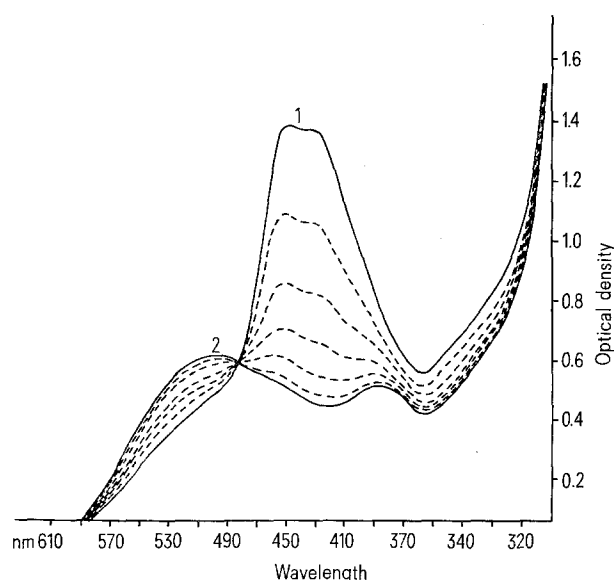
Occurrence and Characterization of a Labile Xanthommatin Precursor in some Invertebrates

In a previous paper¹ we reported that a labile yellow pigment was detected, by extraction at low temperature, in the eyes of *Octopus vulgaris* and *Sepia officinalis*. When left standing this pigment is rapidly converted into dihydroxanthommatin and by subsequent air oxidation into xanthommatin.

In this paper we intend to examine the eyes and skin of *Loligo vulgaris*, *Sepia officinalis*, *Octopus vulgaris*, the eyes of *Homarus gammarus* and, in addition, the heads of *Musca domestica* and *Apis mellifera*. In all these animal species the presence of xanthommatin was known². All results are reported in Table I.

The animals were frozen to death and the structures containing the photoreceptors were carefully separated from animals and potterized at -5°C in acetone. After several washings with acetone, at low temperature, the materials were extracted with buthanol-acetic acid-0.5N HCl (60:15:25 v/v) and were examined spectrophotometrically (Figure).

The UV-spectrum of crude extract from the eyes of *Octopus* displayed absorption maxima at 450 and 430 nm. In all the cases reported in Table I, it is possible to note the presence of the labile pigment with UV-maxima at 450 and 430 nm. It is noteworthy that the spectrophotometric curves of the extracts from the eyes of *Homarus* and heads of *Musca* and *Apis* are not so well defined, owing to the presence of impurities³.



Absorption spectra of the labile pigment in buthanol-acetic acid, 0.5N HCl (60:15:25) (curve 1) and its spectrophotometric transformation into dihydroxanthommatin (curve 2).

Table I. Composition of extracts in buthanol-acetic acid-HCl 0.5 N (60:15:25 vv) at -5°C

<i>Octopus</i>	eyes	labile pigment, ommin
	skin	
<i>Sepia</i>	eyes	labile pigment, ommin
	skin	
<i>Loligo</i>	eyes	labile pigment, ommin
	skin	
<i>Homarus</i>	eyes	labile pigment, ommin
<i>Apis</i>	heads	labile pigment, ommin
<i>Musca</i>	heads	labile pigment, little xanthommatin

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