1678 cm^{-1} (C=O); 1589 and 1580 cm^{-1} (C=C aromatic); 1330 cm^{-1}, 1170 cm^{-1}, 810 cm^{-1} and 695 cm^{-1} identical to that of anthraquinone with additional bands at 720 cm^{-1} and 730 cm^{-1} due to $-(CH_2)_4-$ and a broad absorption at 3450 cm^{-1} (OH), indicating the presence of other aliphatic components.

To ensure that the anthraquinone was not a contaminant, all solvents used were carefully purified and all apparatus and filter papers were washed with purified solvent before use. The possibility that the anthraquinone was being leached from the inner tissues by the chloroform extraction was tested by dipping the grass leaves for ten seconds whilst ensuring that the cut ends did not come into contact with the solvent. This is the accepted procedure for removal of surface waxes[3] and the anthraquinone was found in this extract.

Anthraquinone has been isolated from the heartwood *Quebrachia lorentzii*[4] but its presence in a cuticular leaf wax has not been reported previously. Our present finding and the occurrence of aromatic hydrocarbons[5] in banana leaf suggest that aromatic compounds may play an important role in the leaf metabolism. It has been widely accepted that cuticular waxes prevent UV-radiation damage within the leaf and these aromatic substances may be the UV shielding components. An alternative role for anthraquinone relates to the protection of the leaf from insect attack. 5-Hydroxy 1,4 naphthaquinone from the tree *Carya ovata* deters the beetle *Scolytus multistriatus* from feeding[6] and NORRIS[7] has suggested that compounds with the necessary redox potential could enter the exposed chemoreceptors of the beetle and block its oxidative metabolic mechanisms. It may be that anthraquinone can also act as an insect repellent. We have failed to find anthraquinone in a number of dicotyledons and intend to compare their insect deterrent capabilities with that of *Lolium perenne* L.

Résumé. L'anthraquinone a été extrait pour la première fois de la cire cuticulaire d'une plante, le *Lolium perenne* L. Son identité a été confirmée par la spectrométrie de masse, la chromatographie en phase gaseuse et sur lames minces, la spectrométrie infrarouge et ultraviolette et sa fonction dans la cire est discutée.

J. E. ALLEBONE, R. J. HAMILTON, T. A. BRYCE and W. KELLY

Liverpool Polytechnic, Chemistry Department, Byrom Street, Liverpool L3 3AF (England), and Unilever Research Laboratory, Colworth House, Sharnbrook, Bedford (England), 14 July 1970.

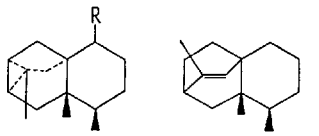
[3] S. J. PURDY and E. V. TRUTER, Proc. R. Soc., London, Ser. B *158*, 536 (1963).
[4] K. S. KIRBY and T. WHITE, Biochem. J. *60*, 582 (1955).
[5] B. NAGY, V. MODZELESKI and SISTER M. T. J. MURPHY, Phytochemistry *4*, 945 (1965).
[6] B. L. GILBERT, J. E. BAKER and D. M. NORRIS, J. Insect Physiol. *13*, 1453 (1967).
[7] D. M. NORRIS, Nature, Lond. *222*, 1263 (1969).

A Novel Tetracyclic Sesquiterpene from the Oil of Orejuela of *Cymbopetalum penduliforum* (Dunal)

'Orejuelas', the dried petals of *Cymbopetalum penduliforum* (Dunal) Baill. (Amonaceae), are well known in many parts of Central America and are used in Guatemala for flavoring pinol and other beverages[1]. Our interest in sesquiterpenes led us to examine the fragrant constituents of the petals. A literature search revealed the only species in this family that had been studied was *Anoma senegalensis*[2].

From a petroleum ether extract of the petals we have isolated[3] a tetracyclic sesquiterpene hydrocarbon **1** consisting of about 60% of the steam volatile portion of the extract. Elemental analysis indicated an empirical formula of $C_{15}H_{24}$[4]. High resolution mass spectral data confirmed the formula. An intense molecular ion $[M]^+$ 204 and a base peak at $[M\text{-}15]^+$ 189 were observed[5] suggestive of a polycyclic sesquiterpene structure[6]. The NMR-spectrum[7] showed absorptions at 0.8 (s, 3H), 1.15 (s, 3H), 0.7 (d, 3H), and 0.45 ppm (m, 1H) among others. No vinyl protons were detected. From these data we concluded that **1** contained at least 2 tertiary methyl groups, 1 secondary methyl group and 1 cyclopropyl proton. The IR-spectrum[8] showed absorptions characteristic of a saturated hydrocarbon. No UV-absorption above 220 nm was observed. Chemical evidence toward unraveling the structure of **1** supported spectral data. The compound was resistant to catalytic hydrogenation, could not be oxidized by perbenzoic acid and showed a faint yellow color with tetranitromethane[9]. The existence of a carbon-carbon double bond was ruled out by the spectral and chemical evidence. Thus **1** contained 4 rings of which at least one must be cyclopropyl.

When **1** was refluxed with cupric acetate in glacial acetic acid isomerization occurred to produce compound **2**. Preparative gas liquid chromatography (GLC) was used to purify the material. Mass spectral analysis indicated



1:R=H_2
3:R=O

2

[1] R. F. DAWSON, private communication.
[2] A. MACKIE and N. GHATGE, J. Sci. Food Agric. *9*, 88 (1958); Chem. Abstracts *52*, 12104f (1958).
[3] A. F and M 500 gas chromatograph was used for preparative vapor phase chromatography. The column was a quarter-inch O.D. copper tubing, 12 feet long, packed with 10% FFAP on Chromosorb G, 60–80 mesh. The column was maintained at 190° with a helium flow rate of 50 cm^3 per min.
[4] The analyses were performed by Galbraith Laboratories, Inc., Knoxville (Tennessee, USA).
[5] Mass spectra were obtained on the CEC 21-104 instrument.
[6] L. SMEDMAN and E. ZAUARIN, Tetrahedron Lett. *1968*, 3833.
[7] The NMR-spectra were determined on Varian A-60A and HR-100 spectrometers using carbontetrachloride as solvent and TMS as the internal standard.
[8] The IR-spectra were recorded as thin films on a Perkin-Elmer 621.
[9] L. F. FIESER and M. FIESER, *Reagents for Organic Synthesis* (J. Wiley Inc., New York 1967).

a formula of $C_{15}H_{24}$ and a relatively small peak for $[M-15]^+$ 189. The IR-spectrum showed a typical carbon-carbon double bond absorption. The NMR-spectrum of this compound was compared with **1**. There were distinguishing differences. The multiplet at δ 0.45 present in **1** had disappeared, the singlet at δ 1.15 became a doublet at δ 1.73 (J = 1.5 Hz) and a vinyl proton was noted [δ 5.62 (m, J = 1.5 Hz)]. The rest of the NMR-spectrum was relatively unchanged.

Since cupric acetate is known to cause isomerization in tricyclene systems[6,10], we concluded from the spectral data that the 3 membered ring in **1** had been opened to form a tricyclic sesquiterpene. This same compound was formed by reaction of **1** with gaseous HCl in ether followed by dehydrohalogenation.

While this work was in progress GOVINDACHARI et al.[11,12] reported the isolation of a tetracyclic sesquiterpenone, ishwarone **3** and ishwarane, from *Aristolochia indica* (Aristolochiaceae). The stereochemistry has been recently proven[13]. During their structural elucidation of ishwarone the authors formed isoishwarane **2**. From their NMR-data we suspected our tricyclic sesquiterpene to be identical to isoishwarane. An authentic sample of **2** has superimposable IR-, NMR-mass spectra, and retention time on GLC.

The spectral data reported for ishwarane is identical with our tetracyclic sesquiterpene from the oil of orejuela. Therefore the identity of these compounds was unambiguously established.

Résumé. De l'éther de pétrole extrait de l'huile de l'Orejula (*Cymbopetalum penduliforum* Dunal, Baill) fut examiné pour son contenu en terpènes. On a isolé les sesquiterpènes tétracycliques (ishwarone). L'évidence chimique et spectral appuie la constitution chimique et sa conversion à isoishwarone.

L. C. TENG and J. F. DEBARDELEBEN[14]

Philip Morris Research Center, P.O. Box 30, Richmond (Virginia 23206, USA), 6 June 1970.

[10] U. R. NAYAK and S. DEV, Tetrahedron Lett. *1963*, 243.
[11] A. K. GANGULY, K. W. GOPINATH, T. R. GOVINDACHARI, K. NAGNARAJAN, B. R. PAI and P. C. PARTHASARATHY, Tetrahedron Lett. *1969*, 133.
[12] T. R. GOVINDACHARI, P. A. MOHAMED and P. C. PARTHASARATHY, Tetrahedron *26*, 615 (1970).
[13] T. R. GOVINDACHARI, K. NAGARAJAN and P. C. PARTHASARATHY, Chem. Commun. *1969*, 823.
[14] The authors are grateful to Dr. F. WILL, Mr. W. F. KUHN and Mr. G. VILCINS for their valuable analytical data and to Dr. R. F. DAWSON for the oil of orejuela and Dr. P. C. PARTHASARATHY for the authentic sample of isoishwarane. We wish to thank Professors A. BURGER and N. H. CROMWELL for helpful discussions.

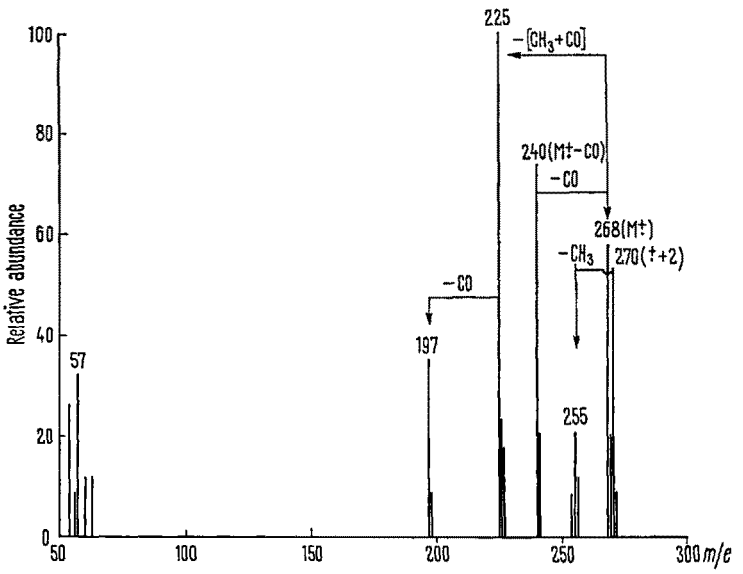
Isolation and Characterization of Hallachrome, a Red Pigment from the Sea Worm *Hallaparthenopeia*[1]

Hallachrome is a red pigment occurring in the epidermal epithelial cells of *Halla parthenopeia*[2], a rare polychaete found chiefly in the Bay of Naples. Controversial publications on this pigment, which was originally thought[3] to have the structure of 2,3-dihydroindole-5,6-quinone-2-carboxylic acid, have appeared in the literature[4–9].

Being so fortunate as to have access at the Zoological Station of Naples to a number of specimens of *Halla parthenopeia*, we took the opportunity to examine Hallachrome anew. Considering the discrepancies in the literature and the reported instability of Hallachrome, our attention was initially directed to find the mildest conditions for the extraction of the natural form of the pigment. To achieve this purpose, pieces of living worms were plunged into different solvents and the resulting extracts were analyzed at regular intervals by TLC on silica (F_{254}, Merck), using as eluents chloroform-ethanol 95:5, v/v) and *n*-butanol-acetic acid-water (60:20:20, v/v).

By this procedure it was found that the red pigment could be selectively extracted without modification with chloroform at room temperature. Consequently, the following procedure was developed for the isolation of Hallachrome in almost quantitative amount: 8 living specimens of *Halla parthenopeia*, between 20 and 30 cm in length, were plunged into chloroform (100 ml) and after 30 min the resulting red extract was decanted and the worms re-extracted a few times until the chloroform assumed a pale pink colour. The combined extracts were filtered and, after addition of benzene (15 ml), were concentrated under reduced pressure to a volume of about 10 ml. The solution was then chromatographed on a 3×40 cm polyamide column (Macherey, Nagel and Co.), using C_6H_6-$CHCl_3$ (20:80, v/v) as the eluent. On concentration to a small volume and standing overnight at 4 °C, the red band gave 68 mg of Hallachrome, as deep-red prisms, mp 224–226° (dec), slightly soluble in ethanol, insoluble in water and in aqueous sodium bicarbonate.

The purified pigment showed no optical activity and displayed absorption maxima



Mass spectrum of Hallachrome.