Treatment of acetate **1a** with p.toluen sulfonic acid in acetone afforded an alcohol **2** which showed absorption at 207 nm (ε 4100) in the ultraviolet and 3400, 1735 and 1640 cm^{-1} in the infrared spectrum indicating the presence of an unsaturated alcohol group. The NMR-spectrum of this compound showed the low field singlet of a new exocyclic methylene group (4.98), and a triplet (4.28, J = 7), due to a methine proton on the carbon atom bearing an allylic hydroxyl group.

Compound **2** oxidated with Jones reagent gave the conjugated ketone **2a** ν_{max} 1695 cm^{-1}; this compound showed UV absorption at 225 nm (ε 6000) for the αβ unsaturated ketone. The NMR-spectrum of **2a** shows 2 signals at 4.96 and 5.07 for the exocyclic methylene conjugated with the ketone group.

Reduction of ketone **2a** with aluminium amalgam yielded a dihydroderivative **3** which does not show high absorption at 207 nm in the UV. Its IR-spectrum has a band at 1690 cm^{-1}. The NMR-spectrum of **3** does not show the low field 2 signals (4.96, 5.07) of the exocyclic methylene protons of **2a**, a doublet observed (J = 7.5 Hz) centered at 1.22 corresponds to a secondary methyl group α to the ketone.

The IR-spectrum of **3** indicate that the ketonic group is found as a substituent in an 8-membered ring, this fact indicates that the exocyclic methylene group in ceralbol is attached to C-3 and therefore the epoxy group is linked at C-7 and C-8.

Ceroplastol I (**4**), whose molecular structure and absolute configuration have been determined by X-ray method, was correlated with ceralbol (**1**) in the following manner:

Ceroplastol I (**4**) was oxidated with CrO_3/Py yielding the aldehyde (**4a**) and, after a selective epoxidation of the double bond between C_7–C_8 of this compound with 3 chloroperbenzoic acid in benzene, afforded the epoxide aldehyde that was identical with the aldehyde obtained from natural ceralbol (**1b**).

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1 Contribution No. 465 from Instituto de Quimica de la Universidad Nacional Autonoma de Mexico.
2 This work was supported by a grant from Syntex laboratories, S.A., Mexico, D.F.
3 T. Rios and F. Colunga, Chem. Ind. *1965*, 1184.
4 T. Rios and L. Quijano, Tetrahedron Lett. *1969*, 1317.
5 T. Rios and F. Gomez, Tetrahedron Lett. *1969*, 2929.
6 T. Rios, L. Quijano and J. Calderon, J. chem. Soc. chem. Commun. *1974*, 728.
7 R. Veloz, L. Quijano, J. Calderon and T. Rios, J. chem. Soc. chem. Commun. *1975*, 191.

Structure and stereochemistry of attenuol, a new lignan from *Knema attenuata* (Wall.) Warb.[1]

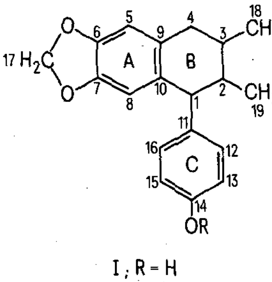
B.S. Joshi, K.R. Ravindranath and N. Viswanathan[2]

Ciba-Geigy Research Centre, Goregaon, Bombay 400063 (India), 31 May 1977

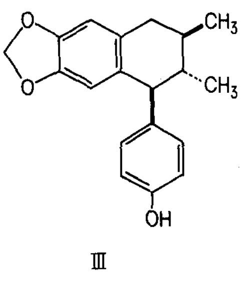
Summary. A new lignan attenuol has been isolated from the bark of *Knema attenuata* (Wall.) Warb. Its structure (I) is deduced on the basis of analytical and spectral data. The compound has been assigned the absolute configuration as 2S,3R-dimethyl-1S-(p-hydroxyphenyl)-6,7-methylenedioxytetralin (**III**).

By hexane extraction of the bark of *Knema attenuata* (Wall.) Warb. (Myristicaceae), collected at the Khandala Ghats, we isolated attenuol $C_{19}H_{20}O_3$ (**I**), as colourless needles m.p. 160–1 °C $[\alpha]_D^{25\,°C}$–20.52° (C, 1.16, $CHCl_3$), ν_{max} (KBr), 3400, 2970, 1600 cm^{-1} and λ_{max} (EtOH), 223 (sh), 287 and 294 (sh) nm (log ε, 4.16, 3.69 and 3.63). In its NMR-spectrum ($CDCl_3$, 100 MHz), it exhibited signals at δ 0.9 (3H, d, J = 6 Hz, $-\overset{|}{C}H-CH_3$), 1.1 (3H, d, J = 6 Hz, $-\overset{|}{C}H-CH_3$) 1.2–1.8 (2H, m, H-2, H-3), 2.7 (2H, m, Ar–CH_2), 3.42 (1H, d, J = 10 Hz, H-1), 5.05 (1H, exchanged with D_2O, Ar-*OH*), 5.81 (2H, s, O-CH_2-O), 6.15 (1H, s, H-8), 6.55 (1H, s, H-5), 6.75 (2H, d, J = 9 Hz, H-13, H-15), 6.98 (2H, d, J = 9 Hz, H-12, H-16) in accordance with the unique structure (**I**). The natural abundance Fourier transform ^{13}C-NMR-spectrum of attenuol was in conformity with the proposed structure showing the following chemical shifts (in ppm in $CDCl_3$ at 25.155 MHz vs. tetramethylsilane; assignments are tentative) C-14, 153.1 (s); C-6, C-7, 145.5, 145.3 (s); C-11, 139.0 (s); C-10, 133.8 (s); C-12, C-16, 130.5 (d); C-9, 130.1 (s); C-13, C-15, 115.2 (d); C-5, 109.7 (d); C-8, 107.6 (d); C-17, 100.4 (t); C-1, 54.1 (d); C-2, 44.0 (d); C-3, 39.5 (d); C-4, 35.5 (t); C-19, C-18, 19.9, 17.1 (q each).

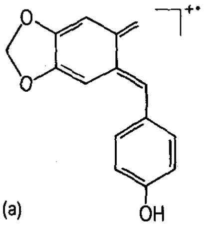
Attenuol afforded a monoacetate (**II**), m.p. 110–1 °C, and its analytical and spectral data supported this formulation. The stereochemistry of attenuol could be derived from its ORD curve (figure) which showed a negative first Cotton effect indicating that the aryl group (ring C) should have a β-configuration[3]. The C-1, C-2 hydrogens are trans to each other as seen by the large coupling[4,5] (J = 10 Hz) of H-1.



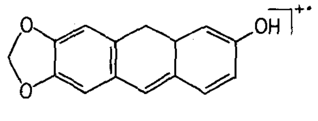
I; R = H
II; R = $COCH_3$



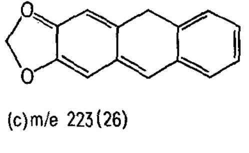
III



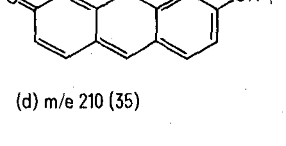
(a) m/e 240 (44)



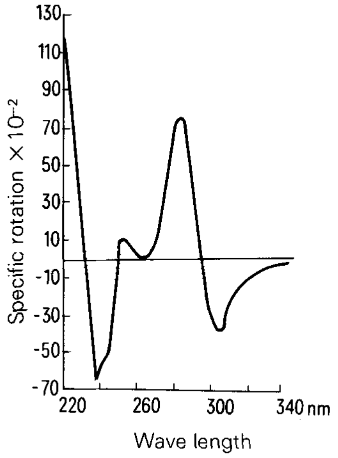
(b)



(c) m/e 223 (26)



(d) m/e 210 (35)



Optical rotatory dispersion curve (in ethanol) of attenuol (I).

From the generalized observations of Swan and Klyne[6] on the stereochemistry of 1-aryl tetralins, since attenuol shows the molecular amplitude $(a \times 10^{-2})$ of −347°, the substituents of ring B should be 1S, 2S and 3R. Thus the new lignan should have the stereostructure (III) in which H-2 and H-3 are trans to each other. All the substituents in ring B are pseudo-equatorial.

In its mass spectrum attenuol (I) showed the molecular ion peak at m/e 296 (58%) and a prominent fragment arizing from reverse Diels-Alder reaction of ring B[7] giving the ion (a) followed by cycloaddition to the ion (b). Other fragments which could be attributed to the ions (c) and (d) are also observed.

Closely related lignans of this type have been isolated from plants belonging to the Myristicaceae family, e.g. otobain and otobaphenol from *Myristica otoba*[8]. Biogenetically it is well known that such lignans are formed by the dimerization of C_6-C_3 precursors (generally cinnamyl alcohols).

It is of interest to note that attenuol is the only example of a 1-aryl lignan in which the ring C contains only 1 oxygen substituent.

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[3] W. Klyne, R. Stevenson and R.J. Swan, J. chem. Soc. *1966,* 893.

[4] R. Wallace, A.L. Porte and R. Hodges, J. chem. Soc. *1963,* 1445.

[5] S.T. Murphy, E. Ritchie and W.C. Taylor, Austr. J. Chem. *28,* 81 (1975).

[6] R.J. Swan and W. Klyne, Chem. Ind. *1965,* 1218.

[7] A. Pelter, J. chem. Soc. (c) *1968,* 74.

[8] F. Kohen, I. Maclean and R. Stevenson, J. chem. Soc. (c) *1966,* 1775.

A new alarm pheromone (2-decen-1-yl-acetate) isolated from the stings of *Apis dorsata* and *Apis florea* (Hymenoptera: Apidae)

H.J. Veith, J. Weiss[1] and N. Koeniger[1]

Institut für Organische Chemie und Biochemie der Technischen Hochschule, D-6100 Darmstadt (Federal Republic of Germany), and Institut für Bienenkunde an der Universität Frankfurt, D-6370 Oberursel/Ts. (Federal Republic of Germany),

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Summary. From sting extracts of *Apis dorsata* and *A. florea,* a substance was isolated which is active in alarm behaviour of both of these species but not of *A. mellifera* and *A. cerana.* The active substance was identified as 2-decen-1-yl-acetate.

Isopentyl acetate has been isolated from the sting apparatus of honey bee workers in 1962[2]. This pheromone evokes a typical alarm behaviour from bees guarding the entrance of their hive. Morse et al. found that also the stings of *A. dorsata, A. cerana* and *A. florea* contain isopentyl acetate[3]. However, comparative tests showed that a freshly prepared sting apparatus of *A. florea* is longer effective than one of *A. mellifera* and *A. cerana* although the latters have more isopentyl acetate in their stings. A fraction – containing no isopentyl acetate – isolated from the sting extracts of *A. dorsata* and *A. florea* was active in the bioassays of both of these species but not of *A. mellifera* and *A. cerana*[4]. In this communication the analysis of the active compound is reported.

Material and methods. A. mellifera was of the carnica-race, *A. dorsata, A. cerana* and *A. florea* originated from Sri Lanka (Anuradhapura and Kandy). These species were kept in tropical flight-rooms; thus we always could work with freshly prepared material. For preparation the bees were caused to sting into a soft piece of leather, stings were plucked with forceps and dropped into a centrifuge tube immersed in dry ice. To the stings (100 per tube and species) 1 ml of n-pentane was added, tube removed from dry ice, the contents macerated and centrifuged briefly.

The products were analyzed by GC-MS; gas chromatograph Perkin-Elmer F20 equipped with a 3.5 m glass column, 0.1% Carbowax 20 M on glass beads (60–80 mesh), column temperature programmed from 70 °C to 200 °C (20 °C/min). The gas chromatograph was coupled to a Varian-Mat CH4-B mass spectrometer which was connected to a Varian-Mat SS100 MS data system.

Results and discussion. The sting extracts of *A. dorsata* and *A. florea* mainly contain the esters of acetic acid with higher alcohols. In the mass spectra of acetates, the base peak is due to the acetylium ion (m/e 43). The ion at m/e 61 results from a double hydrogen transfer and corresponds to the protonated acetic acid[5]. The mass spectra of acetates with higher alcohols exhibit no molecular ion peak under electron impact conditions. Mass highest peaks are recorded for the ions $M-60^+$ and $M-42^+$ e.g. elimination of acetic acid and ketene from the molecular ion.

In the gas chromatograms of the sting extracts of *A. dorsata* and *A. florea,* 2 peaks are registered with higher intensities, besides the peak for isopentyl acetate. The compound with longer retention time could be identified as 2-decen-1-yl-acetate[6]. The retention time and the mass spectrum was identical with that of a synthetic product (m/e 156 (M-42), 5%; m/e 138 (M-60), 9%; m/e 43, 100%). The synthetic sample was prepared by a Reformatzky reaction with ethyl-α-bromoacetate and caprylaldehyde[7], dehydration with