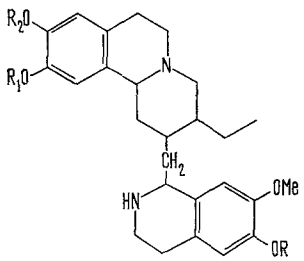
line with 1:1 hydrochloric acid under reflux. The alternative structure Ia or Ib is therefore assigned to the new base with our preference for Ia because of the expected preferential demethylation at the electron-rich position 7 rather than at 6.

AL 60, mp 160–162°, $[\alpha]_D \pm 0°$ ($CHCl_3$), was previously isolated[5] from the chloroform solution of the total crude bases by repeated and successive removal of impurities by dilution with ether, concentration and precipitation with light petroleum. It was subsequently proved to be a mixture of at least 3 components by TLC over silica gel using chloroform:methanol (85:15) as developing solvent.

After several chromatographic separations and crystallisations, the constituents[7] were eventually identified as psychotrine, cephaeline and demethylcephaeline. The



Ia, R=R1=H, R2=Me
b, R=R2=H, R1=Me
c, R=H, R1=R2=Me
d, R=R1=R2=Me

reason why they eluded detection so far was that the almost zero specific rotation recorded in the presence of adhering impurity which was too difficult to remove misled us to assume the compounds to be racemic in nature. However, to the best of our knowledge, no work has so far been reported on the effect of the constituents of AL 60 on blood pressure though scanty reports are traceable on such effect of emetine[8] and *O*-methylpsychotrine[9].

Résumé. A partir de l'écorce de la tige d'*Alangium lamarckii* Thw., une base, $C_{27}H_{36}N_2O_4$ (p.f. 147–149°, $[\alpha]_D - 53,5°$) ainsi que de la céphaeline, psychotrine, desméthylpsychotrine et tubulosine ont été isolées. Cette nouvelle base est identifiée comme déméthylcéphaeline, montrant que le principe hypotendu AL 60, précédemment obtenu de la même provenance est un mélange de psychotrine, de céphaeline et de déméthylcéphaeline.

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Indian Institute of Experimental Medicine, Calcutta 32 (India), 9 March 1970.

[7] The proportions of psychotrine and cephaeline, the major constituents, varied somewhat on the extent of preliminary purification.

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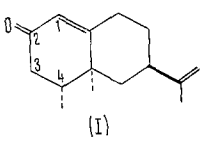
Conformation of Nootkatone

Nootkatone, originally isolated from a heartwood of *Chamaecyparis nootkatensis*, was reported[1] to exhibit $[\alpha]_D + 195.5°$. The same ketone was isolated from *Citrus paradisi* and the structure was confirmed as (I) on the basis of IR- and NMR-spectra, ORD curve and chemical degradation[2]. The total synthesis of (I) was recently



(I)

accomplished[3,4]. We have now attempted to clarify the preferred conformation of nootkatone by a combination of CD curve and NMR-spectrum measurements at various temperature.

Nootkatone (I) may take 3 possible conformations: Ia, Ib and Ic, as shown in Figure 1. The back octant rule is applied to transoid α,β-unsaturated ketone, and the sign of the Cotton effect is predicted from the octant

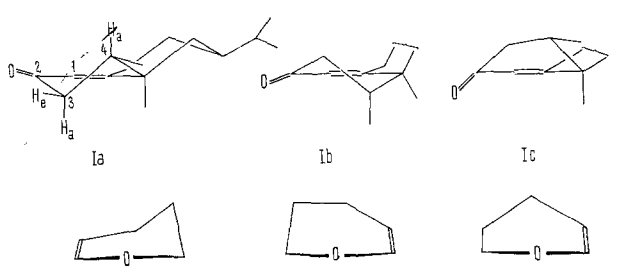


Fig. 1. Possible conformations of nootkatone and the octant projection diagram.

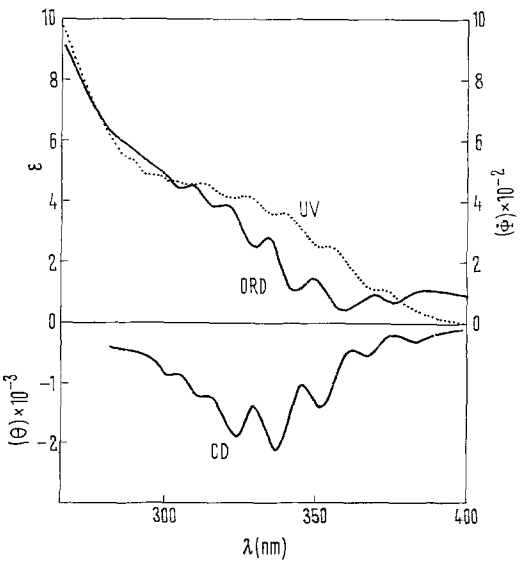


Fig. 2. ORD, UV- and CD-curves of nootkatone in isooctane at 25 °C.

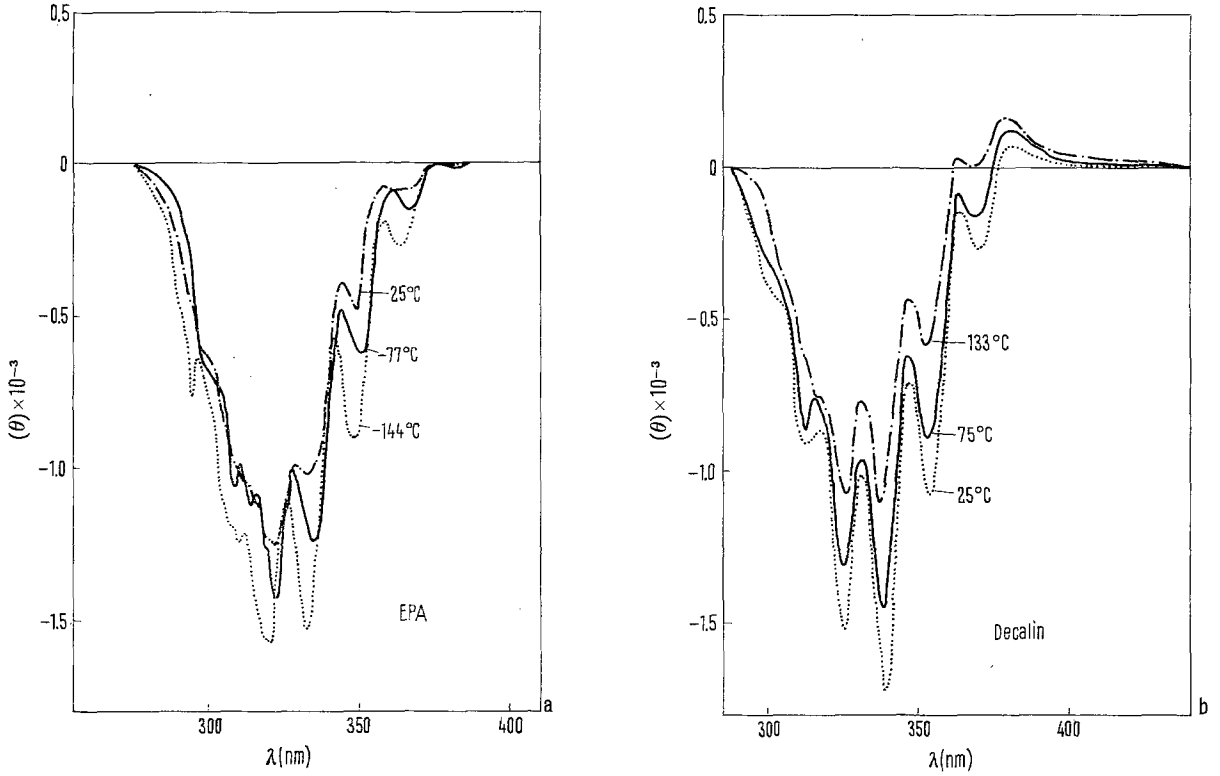


Fig. 3. Temperature-dependent curves of circular dichroism of nootkatone.

projection diagram to be negative to Ia, positive to Ib and positive to Ic, respectively.

Nootkatone (mp 39–40 °C; $[\alpha]_D^{20}$ + 208.9° (*c* 0.0012 in isooctane); λ_{max}^{EtOH} 237 nm, ε 16,000) was derived[5] from valencene by means of the tert-butyl chromate oxidation. The UV-, IR- and NMR-spectra data were in good accord with those of natural nootkatone. The ORD curve of nootkatone seems to exhibit the same Cotton effect as reported by MacLeod[2], as shown in Figure 2. However, the CD-curve was clearly negative. The preferred conformation of nootkatone is thus suggested to be Ia.

The CD-curve and the NMR-spectrum were then examined at various temperatures. The molecular ellipticity in the mixture of ether, isopentane, and alcohol (5:5:2 by volume) increased gradually with a change to lower temperature (Figure 3, a). On the other hand, the ellipticity decreased considerably upon changing the temperature from 25 °C to 133 °C in decalin (Figure 3, b). The observation on the temperature dependency of nootkatone indicates that conformer Ia is more stable at lower temperature.

The NMR-spectra at 50 °C and − 58 °C showed the same coupling constants: $J_{3a,3e} = 12$ Hz, $J_{4a,3e} = 5$ Hz, and $J_{1,3e} = 2$ Hz in the equatorial proton at C-3. The spectrum at 25 °C also gave the same values. This also supports the stability of conformer Ia.

The above observation on CD-curves and NMR-spectra establishes that the preferred conformation of nootkatone (I) is Ia.

Résumé. La conformation la plus fréquente de la nootkatone a été établie d'après la CD et la RMN mesurées à diverses températures.

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Department of Chemistry, Faculty of Science, Hiroshima University, Hiroshima (Japan), 2 April 1970.

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6 To whom all inquiries regarding to this report should be addressed.
7 The authors wish to express their gratitude to Dr. M. K. Veldhuis of U.S. Department of Agriculture for a gift of the authentic sample of nootkatone, and to Dr. E. von Rudloff of National Research Council of Canada for measurement of 100 MHz NMR-spectra.

Analyse électrophorétique des protéines caroténogènes de *Neurospora crassa*

La caroténogenèse de *Neurospora crassa* est un phénomène induit par la lumière[1]. L'utilisation d'inhibiteurs de la synthèse des protéines tels que cycloheximide et chloramphénicol a permis de montrer que les protéines caroténogènes induites par la lumière sont synthétisées en 6 h[2], à 4 °C ou en 1 h[3], à 20 °C. Une petite quantité de caroténoïdes est produite constitutivement, c'est-à-dire à l'obscurité[3].

Dans cette première étude, nous avons tenté de déterminer, par la méthode électrophorétique, le nombre de