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THE CONSTITUTION OF ADUNCIN, A SESQUITERPENE RELATED TO PICROTOXININ, FOUND IN *DENDROBIUM ADUNCUM*

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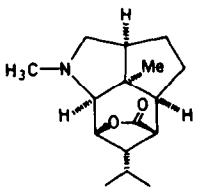
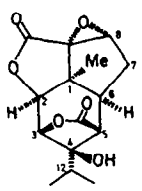
Key Word Index—*Dendrobium aduncum*; Orchidaceae; sesquiterpene; aduncin; 4-hydroxy-6-deoxydihydropicrotoxinin.

Fifteen alkaloids of the dendrobine (**1**) type have hitherto been isolated from various *Dendrobium* species [1]. They are structurally and biogenetically related to the sesquiterpenes of the picrotoxane group [2]. We now report the constitution of aducin (**2**) the first sesquiterpene of this group isolated from a *Dendrobium* species.

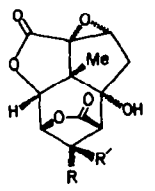


1

Spectrochemical and elemental analyses show aduncin (**2**) to have the molecular formula $C_{15}H_{18}O_6$. From the similarities between the spectral properties (IR, NMR, and CD) of aduncin and those of α- and β-dihydropicrotoxinin (**3** and **4**), derived from picrotoxinin, aduncin is assigned the structure **2**.



2



3: R = -CH(Me)$_2$, R' = -H
4: R = -H, R' = -CH(Me)$_2$

The location of the hydroxyl group in aduncin (**2**) is evident from its NMR spectrum (see Table 1). In aduncin (**2**) as well as in α-dihydropicrotoxinin (**3**) H-3 appears as a doublet of doublets. In the case of aduncin (**2**), however, the splitting is due to coupling to H-2 and H-5, whereas in α-dihydropicrotoxinin it is due to coupling to H-2 and H-4 as demonstrated by double resonance experiments. A long range coupling between H-3 and H-5 has also been observed in some other compounds of the picrotoxane group [3]–[6]. In β-dihydropicrotoxinin (**4**) H-3 appears as a doublet due to coupling to H-2 while H-5 appears as a singlet. Although no coupling to H-4 is shown by H-3 or H-5 in **4**, H-4 is coupled to H-12 and represented by a distinct doublet which cannot be seen in the NMR spectrum of **2**. These results indicate that aduncin (**2**) is 4-hydroxy-6-deoxydihydropicrotoxinin.

The configuration at C-4 is not yet known, but since all 4-hydroxylated compounds of the picrotoxane group of known stereochemistry have the 4R configuration [2], aduncin is proposed to have structure **2**. Although alkaloids have been reported to occur in *D. aduncum* [7], we were not able to detect any.

EXPERIMENTAL

Mp's are corrected. NMR spectra were measured on a Varian XL-100 spectrometer, CD spectra on a Jasco J-40 spectropolarimeter and MS on a Varian MAT 311 instrument. Elemental analyses were carried out at Alfred Bernhardt, Mikroanalytisches Laboratorium, Elbach über Engelskirchen, Germany.

Plant material. Dendrobium aduncum Wall. was delivered from Chandra Orchid & Bulb Nurseries, 8 1/2 Miles P.O. Kalimpong, West Bengal, India.

Isolation of **2**. Fresh plants of *Dendrobium aduncum* Wall. (2.8 kg) were extracted with MeOH (12 l). The extract was concentrated to 0.7 l, washed with CCl_4 (5 × 100 ml), concentrated to 0.3 l and diluted with water (0.4 l). The aqueous solution was extracted with butanol (6 × 100 ml). Concentration of the combined butanolic extracts gave a syrup from which **2** (115 mg) slowly crystallised.

Characterisation of **2**. Recrystallisation of **2** from MeOH gave needles mp 298–300°; $[\alpha]_{578}^{24}$ − 5.8° (*c* 0.4, Me_2CO). CD, nm (Δε): $\lambda_{extrema}$ (MeOH) 228 (−2.8). IR: ν_{max} (KBr) 3490(*m*), 3080(*w*), 1795(*s*), 1760(*s*) cm^{-1}. Ms, *m/e* (rel. intensity): 294 (M^+, 6), 161(10), 149(14), 147(12), 139(60), 137(11), 135(12), 133(11), 112(12), 109(11), 107(12), 105(13), 97(12), 95(19), 93(14),

Table 1. ^{1}H NMR shifts (δ) of **2**, **3** and **4** in pyridine-d_5

	Me-1	H-2	H-3	H-4	H-5	H-6	H-7α	H-7β	H-8	H-12	Me-12
Aduncin (2)	1.40 *s*	4.93 *d* $J = 3.5$	5.15 *d of d* $J_1 = 0.8$ $J_2 = 3.5$		2.89 *d of d* $J_1 = 0.8$ $J_2 = 5.6$	2.05–2.64	2.19 *d of d* $J_1 = 7.0$ $J_2 = 15$	2.50 *d of d* $J_1 = 3.2$ $J_2 = 15$	4.20 *d* $J = 3.2$	1.50–1.95	1.15 *d* $J = 6$ 1.21 *d* $J = 6$
α-dihydro-picrotoxinin (3)	1.53 *s*	4.88 *d* $J = 3.3$	5.10 *d of d* $J_1 = 3.3$ $J_2 = 5.0$	1.85–2.55	2.97 *d* $J = 4.5$		2.25 *d* $J = 15$	3.15 *d of d* $J_1 = 3.5$ $J_2 = 15$	4.06 *d* $J = 3.5$	1.85–2.55	0.99 *d* $J = 6$ 1.14 *d* $J = 6$
β-dihydro-picrotoxinin (4)	1.53 *s*	4.81 *d* $J = 3.6$	5.13 *d* $J = 3.6$	2.31 *d* $J = 8$	2.92 *s*		2.37 *d* $J = 15$	3.08 *d of d* $J_1 = 3.5$ $J_2 = 15$	4.09 *d* $J = 3.5$	1.45–1.90	0.90 *d* $J = 6$ 0.93 *d* $J = 6$

91(26), 81(10), 79(23), 77(21), 71(36), 69(13), 67(15), 65(17), 55(33), 53(15), 51(10), 44(61), 43(100). (Found: C 61.4; H 6.13; O 32.5. $C_{15}H_{18}O_6$ requires: C 61.2; H 6.16; O 32.6).

α-Dihydropicrotoxinin (**3**). Picrotoxinin was hydrogenated as described by Mercer and Robertson [8] giving **3**, mp 253–254°; $[\alpha]_{578}^{23}$ − 5° (*c* 0.5, Me_2CO). CD, nm ($\Delta\epsilon$): $\lambda_{extrema}$ (methanol) 228 (−3.7). IR: ν_{max} (KBr) 3540(*m*), 3470(*m*), 3050(*w*), 1797(*s*), 1775(*s*) cm^{-1}.

β-Dihydropicrotoxinin (**4**). Picrotoxinin was hydrogenated and the product isolated as described by O'Donnell *et al.* [9] giving **4**, mp 255–257°C; $[\alpha]_D^{23}$ − 24° (*c* 1.0, Me_2CO).

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3β-BROMO-8-EPICAPARRAPI OXIDE, THE MAJOR METABOLITE OF *LAURENCIA OBTUSA*

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Key Word Index—*Laurencia obtusa*; Rhodomelaceae; brominated sesquiterpene; 3β-bromo-8-epicaparrapi oxide.

Investigations of marine red algae of the genus *Laurencia* (Rhodomelaceae, Rhodophyceae) have resulted in the structural elucidation of many interesting halogenated metabolites [1]. Some recent studies on *Laurencia* metabolites have focused on the possible biosynthetic relationship between the more common halogenated chamigrene derivatives and brominated monocyclofarnesol derivatives [2, 3]. Howard and Fenical [2] have described the structural elucidations of α-snyderol (**1**) and β-snyderol (**2**). α-Snyderol (**1**) was obtained from a sample of *L. obtusa* which was collected in Tossa de Mar, Spain. I wish to report the isolation and identification of 3β-bromo-8-epicaparrapi oxide (**3**), which was the major lipid-soluble metabolite of *L. obtusa* (Huds.) Lamouroux collected from the English Channel.

* The major portion of this research was performed at the University Chemical Laboratory, Cambridge University, Lensfield Road, Cambridge.