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Labdane and Bisnorlabdane Type Diterpenes from *Alpinia speciosa* K. SCHUM.

Two new diterpenes were isolated from the rhizomes of *Alpinia speciosa* K. SCHUM. (Zingiberaceae) and their structures were established by the spectral evidences as I and II. The latter has an unusual bisnorlabdane carbon skeleton. It is the first example that diterpenes were obtained from Alpinia genus.

Keywords——Zingiberaceae; *Alpinia speciosa* K. SCHUM.; diterpene; bisnorditerpene; labdane; labda-8(17),12-diene-15,16-dial; 15,16-bisnorlabda-8(17),11-dien-13-one; ^{13}C-NMR

The seeds of *Alpinia speciosa* have been used as an aromatic stomachic in Japan, but none of their active constituents has so far been characterized.[1] In the course of our extensive studies on the Zingiberaceous plant having pharmacological activities against excised ileum of guinea pigs,[2] we isolated two new diterpenes from this plant. Only a few instances have been recorded of the isolation of diterpenes from Zingiberaceous plant.[3]

The fresh rhizomes of the plant were extracted with methanol, and the aqueous methanolic extracts were shaken with petroleum ether. Chromatographic purification of the petroleum ether soluble fraction furnished compound (I) and (II).

Compound (I) obtained as an unstable oil, $C_{20}H_{30}O_2$(M$^+$: 302.226, Calcd: 302.225), $[\alpha]_D^{25}$ $-15°$ (c=0.04, EtOH), showed the UV absorption maxima at 235 and 292 (infl.) nm (ε=8900 and 340, EtOH) and IR bands at 1729 and 1680 cm^{-1} (liquid film). The ^{1}H-NMR spectrum

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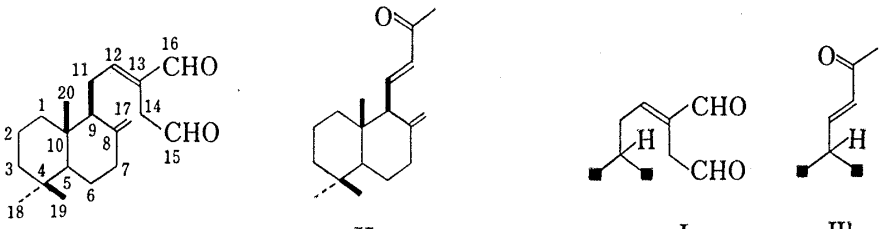

I II Ia IIb

Chart 1

($CDCl_3$) revealed an allylic methylene (δ 3.40, 2H, br s), an olefinic proton (δ 6.70, 1H, br t, J=7 Hz) and two aldehyde proton signals (δ 9.36, 1H, s and 9.56, 1H, br s). The above spectral data presented a close similarity to those observed in (E)-8β,17-epoxylabd-12-ene-15,16-dial (III),[3a] and linaridial,[4] suggesting the presence of a partial structure (Ia). ^{1}H-NMR decoupling experiment gave convincing proof of Ia.

The remaining ^{1}H-NMR signals of three quarternary methyl (δ 0.76, 0.84 and 0.90) and exo-methylene suggested that the compound (I) possesses a labdane skeleton. This was supported by the appearance of a characteristic mass fragment at m/e 137 (100%).[5] The ^{13}C-NMR signals of I showed a close similarity with those of III (Table I). Accordingly, the structure of this compound could be illustrated as formula (I) including the relative configuration.

The molecular formula of compound (II), $C_{18}H_{28}O$, mp 145.5—146.0°, $[\alpha]_D^{25}$ +4.5° (c=0.3, $CHCl_3$), was confirmed by high resolution mass spectrometry (M^+: 260.214, Calcd: 260.214), indicating that this should be an unusual bisnorditerpene. The ^{1}H-NMR spectrum ($CDCl_3$) (three quarternary methyl signals: δ 0.92 (3H), 0.94 (6H); exo-methylene signals: δ 4.20, d, J=2Hz, 4.80, d, J=2 Hz) as well as the mass spectrum (m/e 137, 31%) suggested that II also possesses the bicyclic carbon skeleton of labdane.

The compound (II) showed the UV absorption maxima at 224 and 280 (infl.) nm (ε= 21500 and 370, EtOH) corresponding to an α,β-unsaturated ketone. The intensity of the former is unusually high. These facts coupled with the IR ($CDCl_3$, 1665 cm^{-1}), ^{1}H-NMR spectra (δ 2.23 (3H, s), 6.02 (1H, d, J=16 Hz), 6.80 (1H, d.d, J=16 Hz, 10 Hz)) and ^{1}H-NMR decoupling experiment provided conclusive proof of the side chain (IIb). Consequently, the structure could be illustrated as formula (II). The relative configuration of II has been assumed on comparision of its ^{13}C-NMR signals with those of III (Table I).

Table I. ^{13}C-NMR Chemical Shifts (δ, ppm, $CDCl_3$) of I, II, III

No.	I	II	III	No.	I	II	III
1	39.2(t)[a]	36.6(t)[a]	39.6	11	24.7(t)	146.5(d)	22.4
2	19.3(t)	19.0(t)	18.4	12	159.8(d)	133.5(d)	161.2
3	42.0)t)	42.0(t)	42.0	13	134.7(s)	197.9(s)	136.0
4	33.6(s)	33.6(s)	33.6	14	37.8(t)	27.2(q)	36.0
5	55.4(d)[a]	54.4(d)	52.8	15	197.1(d)	—	198.0
6	24.1(t)	23.2(t)	20.0	16	193.4(d)	—	194.0
7	39.3(t)[a]	40.9(t)[a]	39.6	17	107.8(t)	108.6(t)	48.8
8	148.0(s)	148.5(s)	57.6	18	33.6(q)	33.6(q)	33.6
9	56.5(d)[a]	60.8(d)	55.2	19	21.7(q)	21.9(q)	21.6
10	39.6(s)	39.3(s)	40.0	20	14.4(q)	15.1(q)	14.8

a) Tentative.

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The unusual bisnorditerpene skeleton[6] of II might be biogenetically derived from manool on oxidation of the vinyl group to an aldehyde followed by retroaldol condensation.

The pharmacological activities of these diterpenes (I) and (II) are still under investigation.

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The Chemical Transformation of Gardnerine to 2-Acylindole Alkaloid "Ochropine"

The absolute configuration and the geometry of ethylidene group of the 2-acylindole alkaloid "Ochropine" have been confirmed by the chemical transformation starting from "Gardnerine" whose absolute configuration is known.

Keywords——ochropine; gardnerine; absolute configuration; chemical transformation; ring opening reaction; 2-acylindole alkaloids; indole alkaloid

The 2-acylindole alkaloid, ochropine **1**, was isolated from *Ochrosia poweri* Bailey (Apocynaceae) by Doy and Moore in Australia in 1962.[1] From the chemical and physical studies, the structure **1** was posturated to ochropine in 1964.[2]

In this communication, we wish to report the chemical conversion to ochropine from gardnerine **2** which is a main alkaloid of *Gardneria nutans* Sieb. *et* Zucc. (Loganiaceae).[3,4] It should be stressed that this forms the first correlation of ochropine with the other natural indole alkaloids whose absolute configurations are known.

Thus, the primary alcohol group of Na-methylgardnerine **3** obtained from Na-methylgardnerine acetate[5] was oxidized to Na-methylgardneral **4** (mp 198°, in 76% yield) using N-chlorosuccinimide, Me_2S and Et_3N by Corey method.[6] Compound **4** was isomerized to Na-methyl-epi-gardnerinal **5** (mp 204°) by treatment with alumina or sodium hydroxide in methyl alcohol at 80°. The nuclear magnetic resonance (NMR) spectra of the both aldehydes **4** and **5** revealed the aldehyde protons at δ 9.07 and 9.56. In the former case the aldehyde group was shown to be shielded with indole skeleton. Normal (**6**, mp 267°) and epi-(**7**, mp 248°) oxime derivatives formed the both aldehydes were refluxed with acetic anhydride for 15 minutes under Ar atmosphere. The resulting nitriles **8** (mp 285°, δ 1.63 C=CHC$\underline{H}_3$) and **9** (mp 238°, δ 1.74 C=CHC$\underline{H}_3$) were obtained in the pure states with moderate yields by each

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