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New Diterpenes from *Alpinia galanga* WILD.

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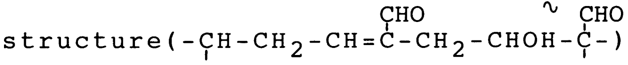
Two new skeleton diterpenes(galanal A and B) and a new labdane type diterpene were isolated from the seeds of *Alpinia galanga* WILD.(Zingiberaceae) with (E)-8, 17-epoxy-labd-12-ene-15, 16-dial and their structures were established by the spectral evidences.

The rhizomes of *A. galanga* has been used for flavouring foods in the preparation of meat dishes and curries.[1)] In our previous paper,[2)]the anti-tumour substance and pungent principle were isolated from the rhizomes and the seeds of *A. galanga*. Continuing with our work on phytochemical constituents of *A. galanga*, two new skeleton diterpenes(**1** and **2**)[3)] and a new labdane type diterpen(**3**) have been isolated along with (E)-8 ,17-epoxy-labd-12-ene-15,16-dial(**4**). Only a few instances have been reported on the isolation of diterpenes from Zingiberaceous plant.[4,5)] In the present paper, the authors wish to report on the structural elucidation of new diterpenes.

The seeds of *A. galanga* commercially purchased were extracted with methanol and the methanolic extracts were shaken with n-hexane after addition of water. Chromatographic purification of the n-hexane soluble fraction furnished compound **1**-**4**.

Compound **1**, named as galanal A, was obtained as colorless needles, mp 167.0-169.0 °C, molecular formula, $C_{20}H_{30}O_3$ based on high resolution MS(318.2214). ^{1}H-NMR($CDCl_3$), IR($CHCl_3$), and UV(EtOH) spectra indicated the presence of dialdehyde, that is, one was a normal aldehyde(δ10.10; 1710 cm^{-1}), the other was an unsaturated aldehyde(δ9.38; 1685 cm^{-1}; 232 nm, ε7600). Then the presence of a secondary hydroxyl group was indicated by the IR(3620 cm^{-1})

and ^{1}H-NMR(δ4.06). The remaining ^{1}H-NMR signals of three quarternary methyl (δ0.77, 0.80, and 0.88) and the ^{13}C-NMR(Table 1) signals were readily accommodated to a labdane skeleton and were similar to published data.[6)] The relationship between two aldehyde groups and a secondary hydroxyl group of 1 was established as shown in partial structure



$(-\underset{|}{C}H-CH_2-CH=\overset{CHO}{\overset{|}{C}}-CH_2-CHOH-\underset{|}{\overset{CHO}{\overset{|}{C}}}-)$

by detailed double resonance experiments and correlation spectrum in NMR, compared with those of 5 which was afforded by oxidation of 1 with PCC. ^{1}H-NMR data were shown in Table 2. To combine this partial structure in a labdane skeleton, ring C was considered to be present as a seven-membered ring. The presence of a seven-membered ring can be also explained satisfactorily by the NMR(Table 2) and IR spectra(1700 cm^{-1}) of 5.

The relative configuration of B/C ring junction and a hydroxyl group was determined by NOE experiments of 1 and 5. Irradiation of H-20 and H-9 in 5 caused 7 and 12% increase in the integrated intensity of H-17 and H-14 , respectively. Therefore the ring junction was concluded to be trans. Furthermore 4% NOE was observed between the protons at C-15 and C-17 in 1, indicating the relative configuration of a hydroxyl group was to be α.

Compound 2, named as galanal B, was obtained as colorless needles, mp 134.0-134.5 °C, molecular formula, $C_{20}H_{30}O_3$(318.2213) and was considered to be closely related structure to 1 by spectral data. Compound 1 and 2 were proved to be an epimer with respect to a hydroxyl group by oxidation of 2 with PCC which afforded the same compound to 5 in all respects. 5% NOE was observed between the protons at C-9 and C-15 in 2, indicating the relative configuration of a hydroxyl group was to be β.

Compound 3 was obtained as an unstable colorless oil and a major diterpene, molecular formula, $C_{20}H_{30}O_2$(302.2238), $[\alpha]_D$ +15.8°. The spectral data was completely identical with labda-8(17), 12-diene-15, 16-dial(6: $[\alpha]_D$ -15.0°) except for the optical rotation, which was isolated from Alpinia speciosa in our privious communication.[7)] To determine the absolute structure, Octant rule was applied to the compound 7(Chart 2) which was afforded by ozonolysis of 3. The CD spectrum of 7 showed the negative Cotton effect(289 nm, Δε=-2.79, c=0.18, EtOH). Therefore the absolute structure of 3 was determined as shown in Chart 1 and that of 6 isolated from A. speciosa was also concluded as shown in Chart 1.[8)]

Table 1. ^{13}C-NMR Chemical Shifts of 1-5(100MHz in $CDCl_3$)

No.	1	2	3(6)	4	5
1	38.6	38.9	39.2 a)	39.6	38.9
2	18.5 a)	18.7	19.3	18.4	18.6 a)
3	41.7	41.7	42.0	42.0	41.6
4	33.4	33.4	33.6	33.6	33.4
5	53.6 b)	55.5 a)	55.4 b)	52.8	51.7
6	18.6 a)	19.1	24.1	20.0	18.8 a)
7	28.5	34.5	39.3 a)	39.6	35.4
8	55.5	55.4	148.0	57.6	66.3
9	55.8 b)	55.6 a)	56.5 b)	55.2	55.5
10	38.5	39.0	39.6	40.0	37.7
11	23.6	24.1	24.7	22.4	26.6
12	156.1	157.7	159.8	161.2	153.4
13	142.3	140.8	134.7	136.0	135.4
14	27.7	28.7	37.8	36.0	31.6
15	71.3	78.7	197.1	198.0	206.2
16	193.3	193.5	193.4	194.0	191.7
17	206.5	208.1	107.8	48.8	200.0
18	33.2	33.3	33.6	33.6	33.3
19	21.3	21.4	21.7	21.6	21.3
20	16.6	15.9	14.4	14.8	15.5

a) and b) Tentative.

Table 2. ^{1}H-NMR Chemical Shifts of 1, 2, and 5(400MHz in $CDCl_3$)

H	1	2	3
9	1.61(d,10.3Hz)	1.47(d,10.3Hz)	2.34(dd,2.2,12.0Hz)
11α	2.80(m)	3.12(ddddd,0.9,1.8,4.5, 10.3,17.2Hz)	2.86(dddd,2.1,2.2,6.3,20.6Hz)
β	2.49(dd,8.3,18.6Hz)	2.55(dd,8.5,17.2Hz)	2.99(dddd,3.0,3.5,12.0,20.6Hz)
12	6.89(dd,2.2,8.3Hz)	7.04(dd,4.5,8.5Hz)	6.87(ddd,2.5,3.0,6.3Hz)
14α	2.60-2.70(m)	2.92(ddd,0.9,9.0,16.4Hz)	3.68(dddd,2.1,2.5,3.5,14.1Hz)
β		2.67(ddd,1.8,1.8,16.4Hz)	3.53(d,14.1Hz)
15	4.06(dd,2.9,8.9Hz)	3.54(dd,1.8,9.0Hz)	
16	9.38(s)	9.40(s)	9.40(s)
17	10.10(s)	10.20(s)	9.86(s)
18	0.80(s) a)	0.77(s) a)	0.81(s) a)
19	0.88(s) a)	0.86(s) a)	0.90(s) a)
20	0.77(s)	0.78(s)	0.77(s)

a) The assignments may be reversed.

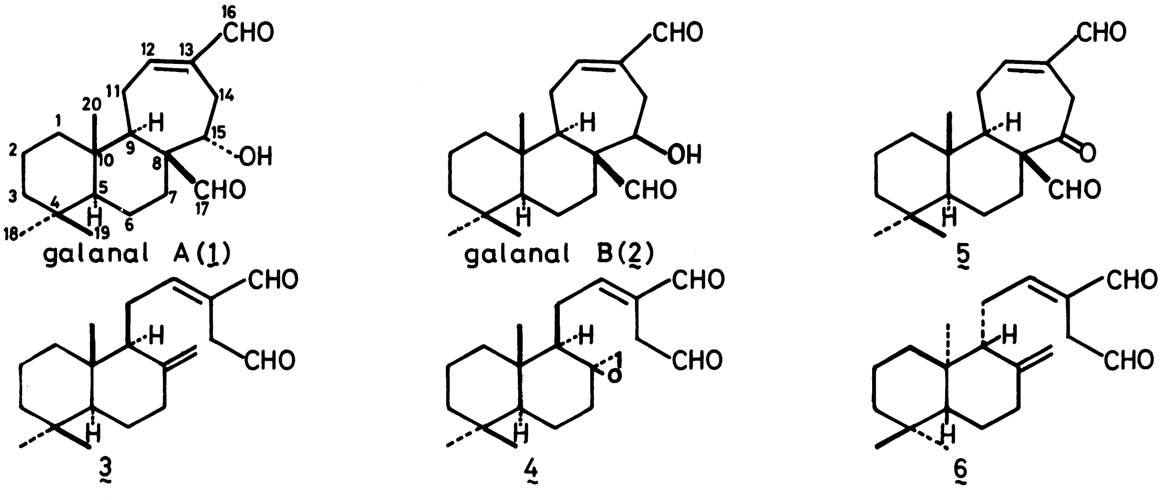
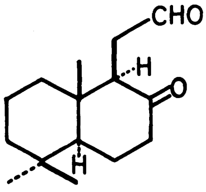


Chart 1.

Compound 4 was completely identical with (E)-8 , 17-epoxy-labd-12-ene-15, 16-dial4) which was a antifungal labdane dialdehyde.9)

In view point of biogenesis, galanal A and B were considered to be derived by ring closure following the cleavage of epoxide of 4.



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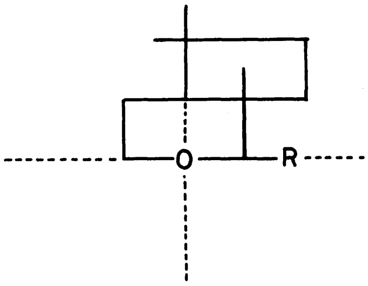

Chart 2.

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3) galanal A: $[\alpha]_D$ -44.0°(c 0.1, $CHCl_3$). IR($CHCl_3$): 3620, 2940, 1710, 1685, 1640, 1460, 1445, 1390, 1370, 1165, 1055.
galanal B: $[\alpha]_D$ -48.0°(c 0.1, $CHCl_3$). IR($CHCl_3$): 3610, 2950, 1710, 1680, 1650, 1460, 1440, 1390, 1370, 1160, 1085, 1050. UV(EtOH): 236 nm, ε 8000.

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