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A NEW SKELETON SESQUITERPENOID FROM ALPINIA JAPONICA (THUNB.) MIQ.

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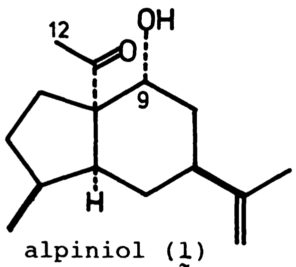
A new skeleton sesquiterpenoid (alpiniol) was isolated from Alpinia japonica (THUNB.) MIQ. and the structure was determined by X-ray analysis.

Seeds of Alpinia japonica (THUNB.) MIQ. (Zingiberaceae) have been used as an aromatic stomachic under the name, "Izu-shukusha", in Japan. From the seeds, several flavonoids (alpinon, izalpinin, kumatakenin and rhamnocitrin) and monoterpenes (camphor and cineole) were isolated by Kimura and co-workers,[1)] and from the rhizome, several sesquiterpenoids (4α-hydroxydihydroagarofuran, 3α,4α-oxidoagarofuran, α-agarofuran and β-eudesmol) by Itokawa et al.[2)] In this paper, isolation of a sesquiterpenoid, alpiniol with a new skeleton from the same source will be reported.

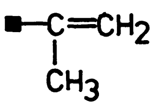
Fresh rhizome of A. japonica was treated in the same manner as described in the previous paper.[2)] The chloroform-soluble fraction was subjected to HPLC on silica gel and silver nitrate-coated silica gel to afford compounds 1 and 2.[3)]

The spectral data suggested the presence of partial structures A and B in compound 1 ($C_{15}H_{24}O_2$). Partial structure A was deduced from ^{1}H-NMR and IR spectra giving signals corresponding to a methyl group (singlet, δ1.74) and an exo-methylene group (each singlet, δ4.71 and 4.73). Partial structure B contained a methylketone group as evidenced by the ^{1}H-, ^{13}C-NMR and MS spectra and a secondary hydroxyl group as shown by IR band at 3630 cm^{-1}, a carbamate resonance signal at δ8.31 on addition of trichloroacetylisocyanate(TAI)[4)] and the low field shift (-1.28) of H9 signal with TAI. The location of the secondary hydroxyl group was suggested by ^{1}H-NMR solvent effect[5)] ($CDCl_3$ - benzene-d_6: H9, +0.35 ; C-12 methyl, +0.16).

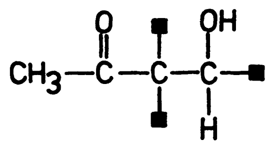
The above data suggest a few possible structures for the alpiniol, of which the structure shown below was proved by X-ray analysis.



alpiniol (1)



A

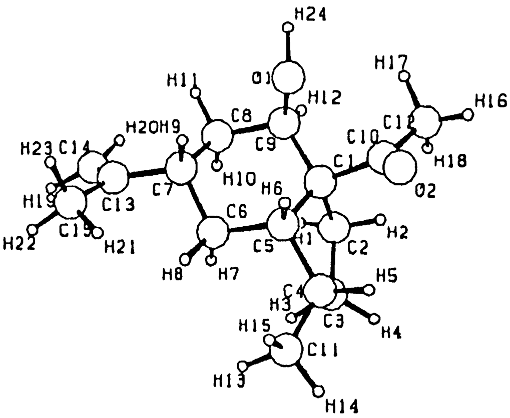


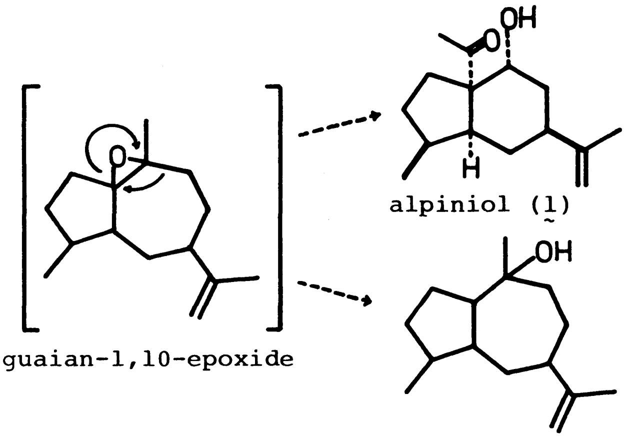
B

Crystalographical data: $C_{15}H_{24}O_2$, orthorhombic, $P2_12_12_1$; Z=4, a=7.887, b=28.945, c=6.155(Å). A total of 1124 reflections were recorded on a Philips fourcircle diffractometer with graphite-monochromated Cu-Kα radiation. The final R value was 0.08.

Compound 2 was identified as pogostol by comparison of the IR- and ^{1}H-NMR spectral data with those of an authentic sample provided by Hikino.[6)]

Biogenetically, alpiniol and pogostol may be considered to be derived from guaian-1,10-epoxide through a rearrangement, as illustrated below.





guaian-1,10-epoxide

alpiniol (1)

pogostol (2)

We wish to thank Prof. H. Hikino, Pharmaceutical Institute, Tohoku University, for spectral data of an authentic sample of pogostol.

References

1) Y. Kimura and M. Hoshi, Yakugaku Zasshi, 57, 147 (1937); Y. Kimura and M. Hoshi, ibid., 55, 1101 (1935); Y. Kimura, M. Takido, and S. Takahashi, ibid., 87, 1132 (1967); Y. Kimura and M. Hoshi, ibid., 53, 794 (1933).

2) H. Itokawa, K. Watanabe, S. Mihashi, and Y. Iitaka, Chem. Pharm. Bull., 28, 681 (1980).

3) Alpiniol $[\alpha]_D$-12.7°(c 0.35,$CHCl_3$). Mp 115-118 °C. IR(CCl_4): 3630, 3500, 3080, 2950, 2880, 1705, 1645, 1455, 1375, 1350, 1170, 890. ^{1}H-NMR($CDCl_3$): 0.91(3H, d, J=7 Hz), 1.74(3H, s), 2.22(3H, s), 4.13(1H, brs), 4.71(1H, s), 4.73(1H, s). ^{13}C-NMR($CDCl_3$): 15.22(q), 21.05(q), 25.77(q), 28.02(t), 28.71(t), 29.87(t), 35.23(t), 36.21(d), 36.67(d), 40.42(d), 64.12(s), 70.57(d), 108.57(t), 149.85(s), 213.16(s).

Pogostol $[\alpha]_D$-18.9°(c 0.40,$CHCl_3$). IR(neat): 3400, 3070, 2950, 2880, 1643 ,1453, 1376, 1104, 885. ^{1}H-NMR(CCl_4): 0.89(3H, d, J=6 Hz), 1.12(3H, s), 1.67(3H, s), 4.53(1H, brs), 4.61(1H, brs). ^{13}C-NMR($CDCl_3$): 16.14(q), 19.89(q),26.12(t), 28.54(t×2), 29.69(q), 31.07(t), 36.04(t), 38.86(d), 45.78(d), 46.07(d), 55.29(d), 74.84(s), 107.65(t), 152.33(s).

4) V. W. Goodlett, Anal. Chem., 37, 431 (1965).

5) D. H. Williams and N. P. Bhacca, Tetrehedron, 21, 2021 (1965); D. H. Williams, Tetrahedron Lett., 1965, 2305.

6) H. Hikino, K. Ito, and T. Takemoto, Chem. Pharm. Bull., 16, 1608 (1968).

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