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TWO NOVEL HUMULENOIDS FROM TORILIS SCABRA D.C.

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Two humulene type sesquiterpnoids were isolated from Torilis scabra D.C. and their structures were determined by X-ray analysis.

Torilis scabra D.C.(Japanese name "O-yabujirami"; Umberifellae) is a biennial and wildly distributing only in Japan and south Korea. From the fruits, caucalol diacetate and apocaucalol diacetate were isolated by Mitsui[1)] and the structure of the former was determined by Sasaki and co-workers[2)] as indicated in Chart 1. In the course of our study on a chinese crude drug "She-Hunzi", we have reported the isolation of germacrene, eudesmane, oppositane, and the novel cycloeudesmane type sesquiterpenoids from Torilis japonica D.C.(Japanese name "Yabujirami").[3)] In this paper, we present the isolation of two novel humulenoids from T. scabra.

The fresh fruits of T. scabra were extracted in the same manner,[3)] and the hexane extract was chromatographed on silica gel repeatedly to afford compound 1 and 2.[4)] Compound 1($C_{17}H_{28}O_3$) was an acetyl ester of sesquiterpene from NMR spectra [^{1}H-;2.03 3H,s: ^{13}C-;170.4 (s)]. Compound 2($C_{15}H_{26}O_2$) was assigned as a monodeacetyl derivative of 1 because base catalyzed hydrolysis of 1 gave 2.

Compound 2 was converted to a p-bromobenzoyl ester(3), and the CD spectra of 3 showed the negative Cotton curve (max 246 nm; Δε=-13.6 in EtOH). The absolute configulation of 3 recrystalized from pet. ether (Mp. 175-179°C) was determined by X-ray method using bromine as an anomalous scatterer as illustrated in Fig. 1.

Crystal data: $C_{22}H_{29}O_3Br$, orthorhombic, $P2_12_12_1$; Z=4, a=8.435, b=40.229, c=6.239 (Å). A total of 1451 reflections were recorded using a Philips four-cir-

1: R=Ac
2: R=H
3: R=p-Br-C_6H_4-CO

Caucalol diacetate

Chart 1.

cle diffractometer with graphite-monochromated Cu-Kα radiation. The structure was solved by heavy atom method. Block-matrix least-squares refinement with anisotropic temperature factors for non-hydrogen atoms, and isotropic temperature factors for hydrogen atoms converged to a conventional R-value of 0.06.

Although the conformation of 3 in the solution was not clear, S configuration at C1 position, the coupling constant of the C1 proton (J=10 Hz), and the negative Cotton curve exhibit that the conformation aruond the allylic position of 3 should be shown as 4. The chiroptical method for determining the absolute configulation of allylic alcohol by Harada$^{5)}$ is applicable to that of eleven-membered ring.

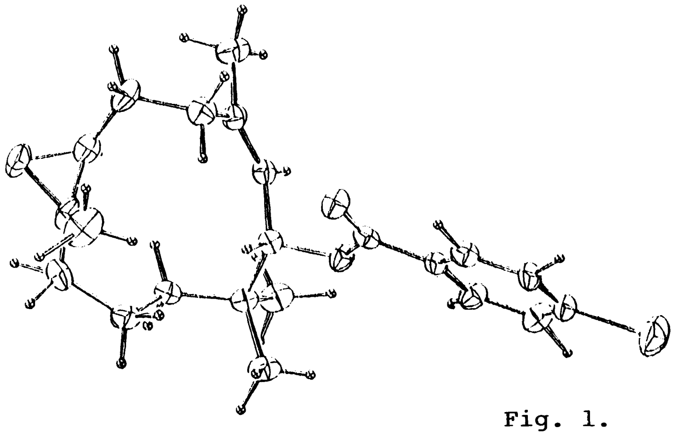
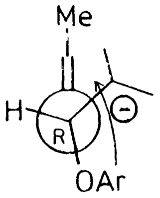


Fig. 1.



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4) Compound 1 $[\alpha]_D$ +21.4^o(c 0.36,CHCl$_3$). Mp 125-130^{o}C. IR (CCl$_4$): 3000, 2970, 2930, 2870, 1730, 1655. ^{1}H-NMR (CDCl$_3$): 0.86(3H,s), 0.94(3H,s), 1.36(3H,s), 1.82(3H,s), 2.03(3H,s), 2.84(1H,dd,J=4,11 Hz), 5.28(1H,d,J=10 Hz), 5.54(1H, d,J=10 Hz). ^{13}C-NMR (CDCl$_3$): 16.66(q), 19.72(t), 21.16(q), 22.72(q), 23.01 (q), 24.04(q), 25.02(t), 29.12(t), 37.02(s), 37.59(t), 38.69(t), 60.60(s), 60.60(d), 73.40(d), 122.58(d), 140.86(s), 170.44(s).
Compound 2 $[\alpha]_D$ +30.9^o(c 0.22,CHCl$_3$). Mp 125-130^{o}C. IR (CCl$_4$): 3630, 2940, 2920, 2870, 1660, ^{1}H-NMR (CDCl$_3$): 0.88(3H,s), 0.98(3H,s), 1.32(3H,s), 1.84 (3H,s), 2.87(1H,dd,J=4,11 Hz), 4.30(1H,d,J=11 Hz), 5.41(1H,br-d,J=11 Hz). ^{13}C-NMR (CDCl$_3$): 16.55(q), 19.66(t), 22.89(q), 22.89(q), 25.02(q), 25.02(t), 28.71(t), 37.42(s), 37.54(t), 39.03(t), 60.54(s), 60.54(d), 70.86(d), 126.90 (d),138.03(s).

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