Tetrahedron Letters No.28, pp. 2375-2377, 1969. Pergamon Press. Printed in Great Britain.

EXTRACTIVE COMPONENTS FROM THE WOOD OF TAIWANIA CRYPTOMERIOIDES HAYATA : THREE NEW SESQUITERPENE ALCOHOLS, MUUROLANE-3-ENE-9β-OL-2-ONE, MUUROLANE-2α,9β-DIOL-3-ENE, AND MUUROLANE-2β,9β-DIOL-3-ENE

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(Received in Japan 14 April 1969; received in UK for publication 12 May 1969)

In our previous paper(1), we have described isolation of nine crystalline compounds, A, B, C, D, E, F, G, H, and I, from the acetone soluble fraction of wood of Taiwania cryptomerioides Hayata by alumina column chromatography using various combination of n-hexane, benzene, and ethylacetate as eluents. Identification of Compound F as cadinane-3-ene-9α-ol-2-one has been reported(2).

Rechromatography of the n-hexane eluent(1) on neutral alumina, yielded pure A, B, and the tenth new Compound J on successive elution with n-hexane-benzene (1:1) solvent system for A, benzene for B, and benzene-ethylacetate (9:1) solvent system for J.

The following experimental evidences support that Compound A, B, and J are muurolane-3-ene-9β-ol-2-one, muurolane-2α,9β-diol-3-ene, and muurolane-2β,9β-diol-3-ene, respectively.

Compound J (Ia) was crystallized from ethylacetate in colorless plates, mp. 168-170°C,$[\alpha]_D^{18}$-111° (C 1.00 in MeOH), $C_{15}H_{26}O_2$* (M^+ ion m/e 238). It exhibits IR absorption bands at 3360 (-OH), 1360 and 1370 ($-CH(CH_3)_2$), 1670 and 872 cm^{-1} (CH_3-C=CH-). The NMR spectrum shows at $\tau^{CDCl_3}_{ppm}$ 9.09 and 9.12 (6 H, a pair of doublets, J=6.5 cps, $-CH(CH_3)_2$), 8.75 (3 H, s., $CH_3C(OH)$=), 8.14 (3 H, broad s., CH_3-C=CH), 5.91 (1 H, broad s., $W_{\frac{1}{2}}$: 5 cps, HC(OH)=), 4.04 (1 H, broad d., J=6 cps. CH_3C=C-H), 8.87 (2 H, s., -OH, disappeared on D_2O addition). Treating with acetic anhydride in pyridine, Compound J gave monoacetate (Ib), mp. 128-130° (νmax 3520, 1710 cm^{-1}), and shows the chemical shift of hydrogen attached at carbon atom carring acetate group undergoing downfield to $\tau_{\mathrm{ppm}}^{\mathrm{CDCl}_3}$ 4.83 ($W_{\frac{1}{2}}$: 6 cps). The oxygen atoms of Compound J, therefore, exist as one secondary and one tertiary hydroxyls.

Compound A (II) was crystallized from n-hexane in colorless plates, mp. 126-127°C, $[\alpha]_D^{27}$ -104°C (C 1.00 in EtOH), $C_{15}H_{24}O_2$*, 2,4-dinitrophenylhydrazone : mp. 150-152°C. It exhibits IR absorption bands at 3410 (-OH), 1380 and 1370 ($-CH(CH_3)_2$), 1660 and 1675 ($-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-C=CH-$), 1425 ($-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-CH_2-$), and 1640 and 840 cm^{-1} ($CH_3C=CH-$). The UV absorption $\lambda_{\mathrm{max}}^{\mathrm{MeOH}}$ 241 $\mathrm{m}\mu$(log ε 3.95), indicates an α,β-unsaturated ketone with two alkyl substituents. The NMR spectrum shows at $\tau_{\mathrm{ppm}}^{\mathrm{CDCl}_3}$ 9.11 (6 H, d, J=6.6 cps, $-CH(CH_3)_2$), 8.82 (3 H, s., $CH_3C(OH)=$), 8.20 (3 H, broad s., $CH_3-C=CH$), 3.09 (1 H, broad d., J=6.3 cps, $-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-C=CH-$).

Compound B (IIIa) was crystallized from ethylacetate in colorless needles, mp. 206-207°, $[\alpha]_D^{27}$ -47.7 (C 1.00 in EtOH), $C_{15}H_{26}O_2$ (M^+ ion m/e 238). It exhibits IR absorption bands at 3410 (-OH), 1365 and 1380 ($-CH(CH_3)_2$), 1670 and 840 cm^{-1} ($CH_3C=CH-$). The NMR spectrum shows at $\tau_{\mathrm{ppm}}^{\mathrm{CDCl}_3}$ 9.11 and 9.17 (6 H, a pair of doublets, J=6.5 cps, $-CH(CH_3)_2$), 8.80 (3 H, s., $CH_3C(OH)=$), 8.25 (3 H, broad s., $CH_3-C=CH$), 5.96 (1 H, broad s., $W_{\frac{1}{2}}$ = 13 cps $HC(OH)=$), 4.33 (1 H, broad doublets, J=6.1 cps, $CH_3C=C-H$). Monoacetate (IIIb) was obtained by treating compound B with acetic anhydride in pyridine, mp. 54-56° (ν max 3430, 1730 cm^{-1}). The hydrogen attached at carbon atom carring acetate group shifts downfield to $\tau_{\mathrm{ppm}}^{\mathrm{CDCl}_3}$ 4.67 ($W_{\frac{1}{2}}$: 15 cps). Again, Compound B contains one secondary and one tertiary hydroxyls.

Compound J, on chromic acid oxidation in acetic acid(3), gave an α,β-unsaturated ketone identical with Compound A, When subjected to reduction by $NaBH_4$ in aqueous methanol, Compound A yielded Compound B as a sole product.

Since $W_{\frac{1}{2}}$ of α-hydrogens in Compounds J and B are 5 cps and 13 cps, (6 cps and 15 cps for monoacetates), respectively, the secondary hydroxyl group of Compound J is axial and Compound B is equatorial.

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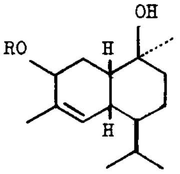
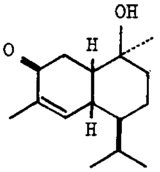
* All gave satisfactory analytical data.

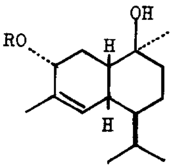
Selenium dioxide oxidation(4) of T-muurolol(5) in boiling ethanol for six hours followed by chromatographic separation on neutral alumina gave two crystalline products, muurolane-3-ene-9β-ol-2-one and muurolane-2α,9β-diol-3-ene. IR and NMR spectra as well as mixed fusion confirmed that these were identical with Compound A and Compound J, respectively.



I



II



III

Ia R = H
b R = Ac

IIIa R = H
b R = Ac

Acknowledgement

We are indebted to professor T. Kubota (Osaka City University), Dr. Y. Hirose (The Institute of Food Chemistry, Osaka) and Dr. T. Toda (Tohoku University) for the measurement of NMR, MS and elementary analysis, and to the chemical Research Center under the project CRC-5703 financial support.

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