

ANGELIKOREANOL, A NEW SESQUITERPENE KETO-ALCOHOL
FROM ANGELICA KOREANA MAX.

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From the ether extract of the crude drug "Korean Qianhu (韓國羌活)", the dried root of Angelica koreana Max., a new sesquiterpene keto-alcohol, named angelikoreanol (I), was isolated and its structure was determined as formula I. The present communication concerns the evidence of the proposed structure of this compound.

The compound I is crystallized from ethanol in colorless plates, mp. 157-158°, $[\alpha]_D +132.2^\circ$ (C=1.2 in CHCl_3), and was assigned to molecular formula $\text{C}_{15}\text{H}_{20}\text{O}_3$ on the basis of analytical and mass spectral data. It gradually becomes deep yellow during storage, transforming into resinous substance. The compound gives positive reaction towards carbonyl reagent and was characterized as an α,β -unsaturated ketone on the basis of the infrared (IR) absorption at 1640 cm^{-1} which shifts to 1680 cm^{-1} when I is subjected to catalytic hydrogenation.

The IR absorption at 3300 cm^{-1} and signal at $\tau 6.52$ due to a deuterium exchangeable proton in the NMR spectrum of I indicate the presence of a hydroxyl group. Upon acetylation with acetic anhydride and pyridine, however, I exhibited a strong green fluorescence continuing about for half an

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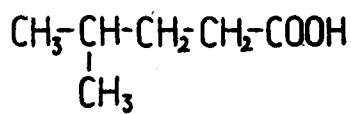
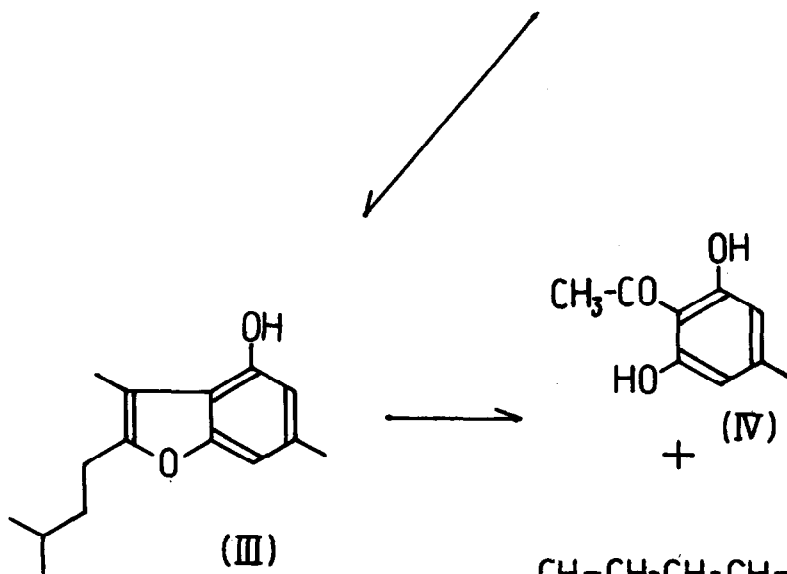
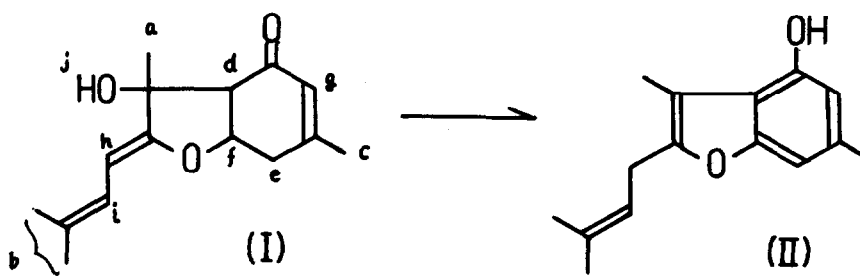
hour under ordinary light resulting in the formation of a yellow resinous substance which seemed a dehydration product, suggesting that anhydro derivative of I may be formed upon the treatment with dehydrating agents.

To prepare, therefore, the anhydro derivative (II) attempts were made under various conditions and it was found that II was formed in fairly good yield when I was treated with p-toluene sulfonic acid in anhydrous benzene at a room temperature until the fluorescence almost disappeared. Although the compound II, mp. 105-106°, optically inactive, was assigned to molecular formula $C_{15}H_{18}O_2$ which is consistent with the composition of the expected anhydro derivative, it exhibits IR absorption at 3200 cm^{-1} corresponding to hydroxyl group, and was characterized as a phenol from the fact that it gives positive reaction towards $FeCl_3$ test solution and Gibb's reagent and it affords monomethyl ether upon the treatment with diazomethane.

On the other hand, II gives negative reaction towards carbonyl reagent and exhibits no absorption band corresponding to carbonyl group in the IR spectrum. The NMR spectrum of II shows a series of signals which is typical of isopentenyl group $CH_3-C(CH_3)=CH-CH_2-$, i.e. a singlet at $\tau 8.25$ (6H, splitting due to long range coupling with a olefinic proton), a doublet at $\tau 6.62$ (2H $J=7\text{Hz}$) and a triplet at $\tau 4.67$ (1H $J=7\text{Hz}$, splitting due to long range coupling with methyl protons). Further signals, two singlets at $\tau 7.67$ and $\tau 7.63$ (protons of 2 methyl groups), a broad singlet at $\tau 5.13$ (a proton of phenolic hydroxyl group) and a pair of doublets at $\tau 3.67$ and $\tau 3.20$ ($J=1\text{Hz}$, 2 aromatic protons) are observed.

These findings indicate that II was formed from I not only by dehydration but by followed aromatization giving rise to a phenol function from a ketone group. On hydrogenation over Adams catalyst in ethanol II took up 1 mole of hydrogen to afford dihydro derivative (III), $C_{15}H_{20}O_2$, mp. 95-96°.

Ozonolysis of III led to the formation of p-acetophenone (IV), identified by the IR and NMR spectrometric comparison as well as mixed melting point examination with the authentic sample, together with 4-methyl-n-valeric acid identified as its p-phenylphenacyl ester. On the basis of this evi-



dence the structure of III was established as formula III, 2-(3-methylbutyl)-3,6-dimethyl-4-hydroxybenzofuran, and then taking into consideration the fact that the NMR spectrum of II indicated the presence of isopentenyl group, the structure of II was elucidated as formula II.

Thus, the structure of I which may give rise to II upon dehydration and aromatization can be represented as formula I. The NMR data of I are also in accord with the proposed structure and can be assigned as follows:

H _a	sharp singlet	τ8.38 (3H)
H _b	2 singlets*	τ8.28 and 8.22 (3H X 2)
H _c	singlet*	τ8.00 (3H)
H _d	doublet	τ7.35 (1H J=7Hz)
H _e	doublet	τ7.28 (2H J=7Hz)
H _f	quartet	τ5.15 (1H J=7Hz)
H _g	broad singlet*	τ4.05 (1H)
H _h	doublet	τ4.67 (1H J=11.5Hz)
H _i	broad doublet*	τ4.00 (1H J=11.5Hz)
H _j	sharp singlet	τ6.52 (1H disappears with D ₂ O)

* splitting due to long range coupling J=nearly 1Hz

Double resonance experiments supplied further evidence for the partial structure $\text{—CH—CH—CH}_2\text{—}$, i.e. the quartet at τ5.15 became clear singlet when both H_d at τ7.35 and H_e at τ7.28 were irradiated at the same time, on the other hand both the doublets at τ7.35 and τ7.28 became singlet when H_f was irradiated.

The elucidation of stereochemistry will be reported later.

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