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Structure of Dendropanoxide, a new Triterpenoid from the Leaves of *Dendropanax trifidus* MAKINO

The isolation of friedelin, epifriedelinol, and a new triterpenoid, dendropanoxide (I), from the leaves of *Dendropanax trifidus*[1] MAKINO was reported previously[2] and structural elucidation[3] of (I) was carried out.

Benzene extract of the leaves was treated with boiling ethanol and the ethanol extract was extracted with petroleum ether to leave friedelin and epifriedelinol in the petroleum ether-insoluble residue. The petroleum ether extract was recrystallized from ethanol to long needles (I), m.p. 206~207°, $[\alpha]_D^{28}$ +68.4 (c=1.05, $CHCl_3$); mol. wt. (Rast Method), 430 (*Anal.* Calcd. for $C_{30}H_{50}O$: C, 84.44; H, 11.81. Found: C, 84.32; H, 12.04). (I) gave no color with tetranitromethane and its infrared spectra taken in KBr-disk and in carbon tetrachloride solution did not show the absorption of either OH, >C=C<, or >C=O. (I) is not acetylated with acetic anhydride in pyridine. Accordingly, (I) is considered to have no unsaturated bond and the oxygen is presumed to form an ether. The ether bond was not reduced by lithium aluminium hydride, either in ether or dioxane, and was stable against metallic lithium in ethylamine solution.

Cleavage of (I) with 0.6% sulfuric acid in dioxane (yield, 6% at 15~20°) or with 0.02% hydrogen chloride in ethanol (yield, 70% at 60~70°) gave crystals (II), m.p. 240~242°, $[\alpha]_D^{28}$ −39.4° (c=0.25, $CHCl_3$) (*Anal.* Calcd. for $C_{30}H_{50}O$: C, 84.44; H, 11.81. Found: C, 84.24; H, 12.03. IR λ_{max}^{KBr} cm^{-1}: 3480~3460, 1065, 1055, 1040, 988 (OH)).[4] Oxidation of (II) with CrO_3-pyridine complex yielded a ketone (IV), m.p. 250~252°, $[\alpha]_D^{28}$ −86.5° (c=0.73, $CHCl_3$) (*Anal.* Calcd. for $C_{30}H_{48}O$: C, 84.84; H, 11.39. Found: C, 84.61; H, 11.61). Heating of (I) with acetic acid containing hydrochloric acid (100:1) gave crystals (III), m.p. 284~287°; $[\alpha]_D^{28}$ −26.5° (c=0.98, $CHCl_3$) (*Anal.* Calcd. for $C_{32}H_{52}O_2$: C, 81.99; H, 11.18. Found: C, 82.24; H, 11.18. IR: ν_{C-O} 1255 cm^{-1} (acetate)).

From these properties, (II), (III), and (IV) are evidently respectively identical with alnus-5(10)-en-3ξ-ol,[5] alnus-5(10)-en-3ξ-yl acetate,[5] and alnus-5(10)-en-3-one.[5]

The conformation of (I) is considered to be identical with that of alnusenone, because of identity of (II) with an alnusenone derivative as was mentioned above, and the ether bond in (I) is presumed to be bridged between the positions 3 and 5 or between 3 and 10, since the double bond formed in (II) is found between 5 and 10. Possible spatial formula of (I) would accordingly be either one of (VII) to (XI).

Reduction of (I) with sodium acetate and zinc dust in acetic acid yielded a product (V), $[\alpha]_D^{28}$ −15.2° (c=0.98, $CHCl_3$) (*Anal.* Calcd. for $C_{30}H_{50}O$: C, 84.44; H, 11.81. Found: C, 84.21; H, 12.02) which is considered to be a mixture, as it starts to shrink at 213° before melting at 220°. (V) gave a yellow color with tetranitromethane and presence of hydroxyl was presumed from its infrared spectrum. Oxidation of (V) with CrO_3-pyridine complex gave a mixture (VI), m.p. 245~249°, $[\alpha]_D^{28}$ −65.1° (c=0.38, $CHCl_3$). Its infrared spectrum indicated the presence of a double bond and a carbonyl group in (VI). When gently heated with acetic acid containing conc. hydrochloric acid (40:1), (VI) gave a product which was

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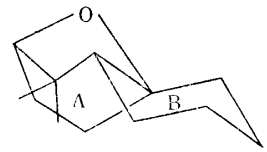
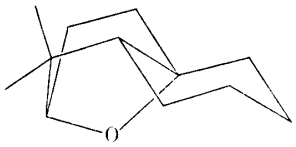
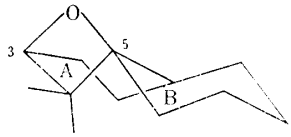


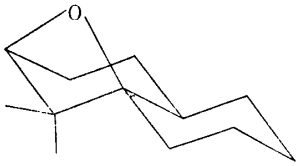
(VII)



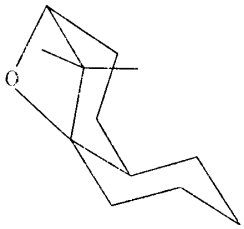
(VIII)



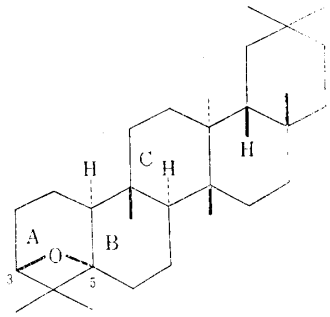
(IX)



(XI)



(X)



(I)

identified with (IV). By these reactions location of the hydroxyl group in (V) was ascertained to be at 3. Since the melting point and specific rotation of (V) correspond to the mixture of alnusenol and alnus-5(10)-en-3ξ-ol, and those of (VI) correspond to a mixture of alnusenone and alnus-5(10)-en-3-one, the double bond in (V) and (VI) is considered to be present respectively at 5—6 and 5—10. Accordingly, the ether in (I) is presumed to be at 3—5.

Henbest, *et al.* stated that the cleavage of 1—4 ether bond in 5,8α-epoxy-5α-ergosta-9,22-dien-3β-ol acetate[6] and 5,8α-epoxy-5α-ergost-22-en-3β-ol acetate[7] was completed in a few minutes by an acid and also that these compounds were not reduced with lithium aluminium hydride, whereas neither rapid cleavage of 1,3-epoxide bond of 3α,5α-epoxy-3α-cholestane[8] with acid nor reduction with lithium aluminium hydride takes place.

Taking these facts into consideration, (VII), (VIII), and (IX) can be excluded from the formulae proposed for the structure of (I). Furthermore, cleavage of the ether bond of (I) is regarded to proceed in the direction of *trans*-elimination, because of the formation of (II) in high yield with dilute hydrochloric acid. Consequently, the structure of (I) should be 3β,5β-epoxy-3β-alnusane.

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