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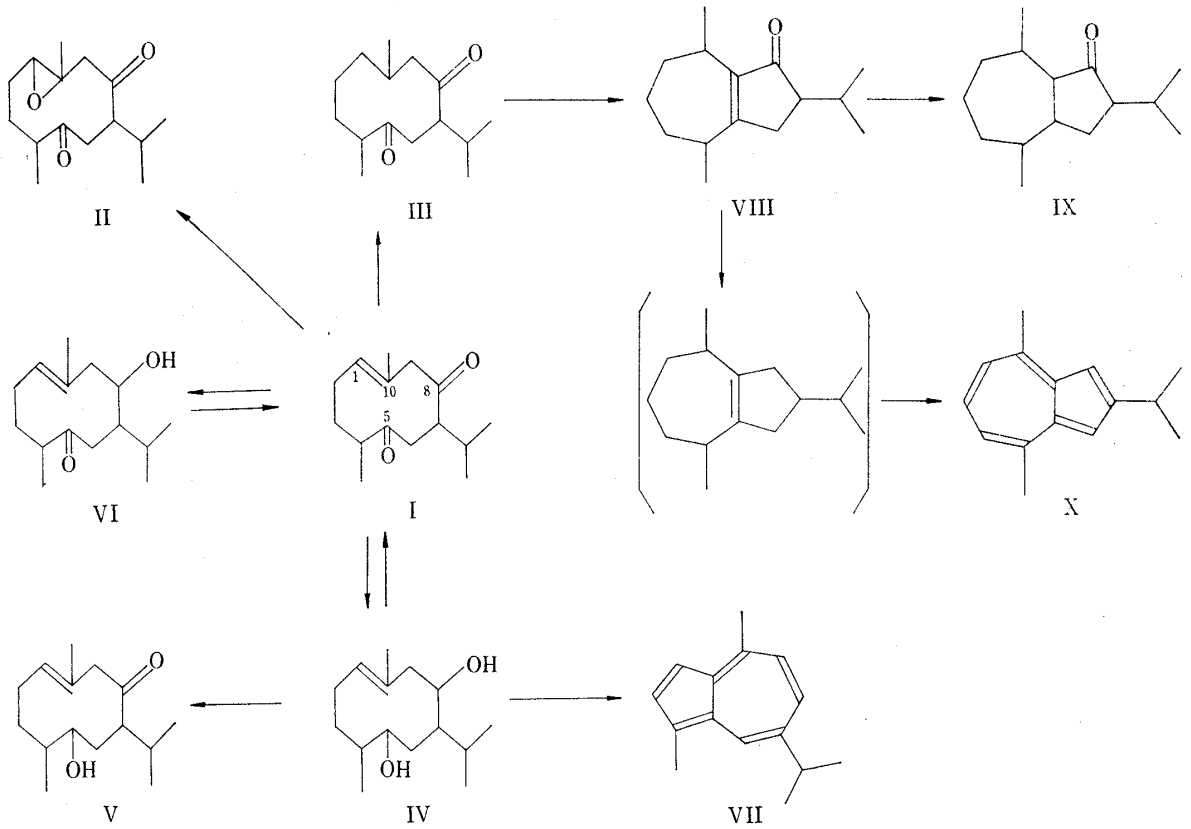
Structure of Curdione

This paper describes evidence leading to the constitution I for a new sesquiterpenoid diketone, curdione, which the authors have recently isolated from the rhizome of zedoary (*Curcuma zedoaria* Roscoe).

Curdione, $C_{15}H_{24}O_2$, m.p. 61.5~62°, $[\alpha]_D$ +25.6°,*1 has infrared bands (KBr) at 1704 (carbonyl in a six-membered or larger ring) and 1416 cm^{-1} (methylene α to carbonyl). The nuclear magnetic resonance (NMR) spectrum shows the presence of a vinyl methyl (8.40 τ) and a vinyl hydrogen (4.91 τ) next to a methylene as well as three secondary methyls (9.14, 9.08, 9.05 τ). Peracid oxidation gave two saturated epimeric monoepoxides (II), the epoxide A, $C_{15}H_{24}O_3$, m.p. 118~119.5°, $[\alpha]_D$ +106°, and the epoxide B, $C_{15}H_{24}O_3$, m.p. 129~130°, $[\alpha]_D$ −109°, and hydrogenation afforded the saturated dihydrocurdione (III), $C_{15}H_{26}O_2$, m.p. 65.5~66°, $[\alpha]_D$ −32.9°, IR (KBr) : $\nu_{C=O}$ 1701 cm^{-1}. These results show curdione to be mono-unsaturated.

Reduction of curdione with lithium aluminum hydride furnished the diol (IV), $C_{15}H_{28}O_2$, m.p. 111~111.5°, $[\alpha]_D$ −17.3°, IR (KBr) : ν_{O-H} 3413 cm^{-1}, NMR (100 Mc., $CDCl_3$) : 1H quadruplet at 6.58 τ (J_1=8, J_2=9, H-C≤OH), 1H triplet at 5.90 τ (unresolved, J=4, H-C≤OH). The double resonance experiment shows the signal at 5.90 τ is coupled with



*1 Analytical values are in accord with the molecular formulae shown. Specific rotations refer to $CHCl_3$ solution. NMR spectra were determined at 60 Mc. in CCl_4 solution *vs.* $(CH_3)_4Si$ as internal standard unless specified to the contrary; coupling constants (J) are given in c.p.s.

a methylene (7.92 and 7.70 τ) adjacent to a quarternary carbon. The diol (Ⅳ) was oxidized with chromic acid to give the original dione, curdione, and the ketol (Ⅴ), $C_{15}H_{26}O_2$, m.p. 70~71°, $[\alpha]_D$ −303°, IR (CCl_4): ν_{O-H} 3410, $\nu_{C=O}$ 1688 cm^{-1}, NMR: 1H triplet at 6.78 τ (unresolved, J=11, H-C≤OH). Reduction of curdione with sodium borohydride afforded the other ketol (Ⅵ), $C_{15}H_{26}O_2$, $[\alpha]_D$ +74.5°, IR (liquid): ν_{O-H} 3500, $\nu_{C=O}$ 1696 cm^{-1}, NMR: 1H triplet at 5.88 τ (unresolved, J=4, H-C≤OH) which was regenerated to curdione on chromic acid oxidation. These observations indicate that curdione is a dione.

The presence of the above functions and the molecular formula require curdione to be a monocarbocyclic compound. When the diol (Ⅳ) was dehydrogenated with palladized charcoal guaiazulene (Ⅶ) was formed; a fact which confirmed that curdione has the germacrane skeleton.

Alkali treatment of the dihydro-derivative (Ⅲ) resulted in the aldol condensation to give the cyclopentenone (Ⅷ), $C_{15}H_{24}O$, UV λ_{max}^{EtOH} 243 mμ (ε 12500), IR (liquid): $\nu_{C=O}$ 1694, $\nu_{C=C}$ 1639 cm^{-1}, NMR: no vinyl hydrogen. The enone (Ⅷ) was hydrogenated to afford the cyclopentanone (Ⅸ), IR (liquid): $\nu_{C=O}$ 1733 cm^{-1}, while reduction with lithium aluminum hydride gave a hydrocarbon, NMR: no vinyl hydrogen, which on dehydrogenation with palladium-on-carbon furnished vetivazulene (Ⅹ). This series of reactions established the positions of the carbonyl groups of curdione being situated at C-5 and C-8 in the germacrane skeleton. From the ultraviolet (λ_{max}^{EtOH} 299 mμ (ε 250)) and NMR evidence, the only remaining functional group, the trisubstituted ethylenic linkage, must consequently be located at C-1:C-10 in curdione.

Curdione is thus elucidated to be as shown in formula Ⅰ.

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Pharmaceutical Institute,
Tohoku University School of Medicine,
Kita-4-bancho, Sendai

Hiroshi Hikino (ヒキノヒロシ)
Yojiro Sakurai (桜井洋二郎)
Hideji Takahashi (高橋秀次)
Tsunematsu Takemoto (竹本常松)

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Direct Analysis of Corticosteroids by Gas Chromatography as Trimethylsilyl Ethers of Methyloximes

In the gas chromatographic analysis of corticosteroids, it has been recognized that all of the known methods for preparing derivatives with favorable volatility, such as trimethylsilylation of a hydroxyl group[1] and a very recently reported methoxyimination of a carbonyl function,[2] do not prevent the 17β-side chains from undergoing pyrolytic cleavage. Therefore, the analysis of corticosteroids by gas chromatography has been carried out after their quantitative conversion to the corresponding 17-ketosteroids with some appropriate oxidant.[3] In this case, however, the presence of 17-ketosteroids in the original mixture interferes with the analysis of the corticosteroids.

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