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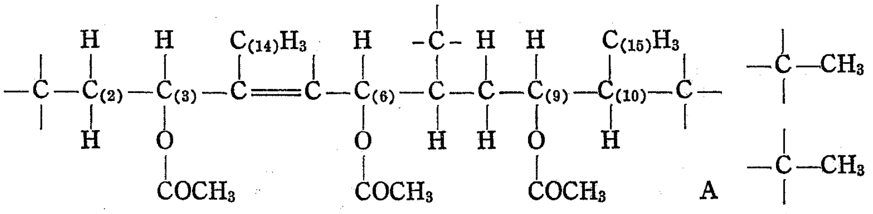
Structure of Sugetriol

From the tuber of nutgrass (*Cyperus rotundus* LINNÉ) of Japanese origin, a new sesquiterpenoid triol has been isolated for which the name sugetriol is proposed. In the present communication the authors wish to provide evidence for its constitution as shown in formula I.

Sugetriol is naturally present as the triacetate (Ⅱ), $C_{21}H_{30}O_6$, m.p. 132°, $[\alpha]_D$ +60.5°.[*1] The presence of three secondary acetoxyl groups is indicated by infrared bands (KBr) at 1736 and 1235 cm^{-1} and especially by nuclear magnetic resonance (NMR) signals at 1.95, 1.98, 2.11 (3H each), 4.63, 5.48, and 5.83 (1H each). The NMR spectrum also shows the presence of a secondary methyl (0.88), two tertiary methyls (0.91 and 1.06), and a tetra-substituted ethylenic bond with a methyl on it (1.66). The extensive NMDR experiments revealed that the above functions are linked as indicated in the part structure A.



A

Coupling constants, J.
(Apparent values in c.p.s.)

$J_{2,3}=7$ $J_{6,7}=6$ $J_{8',9}=10$
$J_{2',3}=7$ $J_{7,8}=3$ $J_{9,10}=10$
$J_{3,14}=1$ $J_{7,8'}=3$ $J_{10,15}=6$
$J_{6,14}=1$ $J_{8,9}=7$

Complete hydrolysis of the triacetate (Ⅱ) yielded sugetriol (I), $C_{15}H_{24}O_3$, m.p. 221～222°, $[\alpha]_D$ +62.4°(EtOH). While partial hydrolysis gave the triol 6,9-diacetate (Ⅲ) and the triol 9-acetate (Ⅳ), these assignments being accomplished by the NMR spectra which showed that the C_3 hydrogen signal of the former (Ⅲ) was shifted upfield (+0.99 p.p.m.), and the C_3 and C_6 hydrogen signals ($CHCl_3$) of the latter (Ⅳ) were similarly shifted to higher fields as compared with those of the triacetate (Ⅱ).

On oxidation with chromium trioxide-pyridine complex the triol diacetate (Ⅲ) afforded the keto-diol diacetate (Ⅴ), of which spectral properties ($\nu_{max}^{CCl_4}$ 1714, 1674 cm^{-1}, λ_{max}^{EtOH} 244 mμ (log ε 4.32)) showed the presence of a cyclopentenone moiety indicating the C_3 to be located in a five-membered ring.

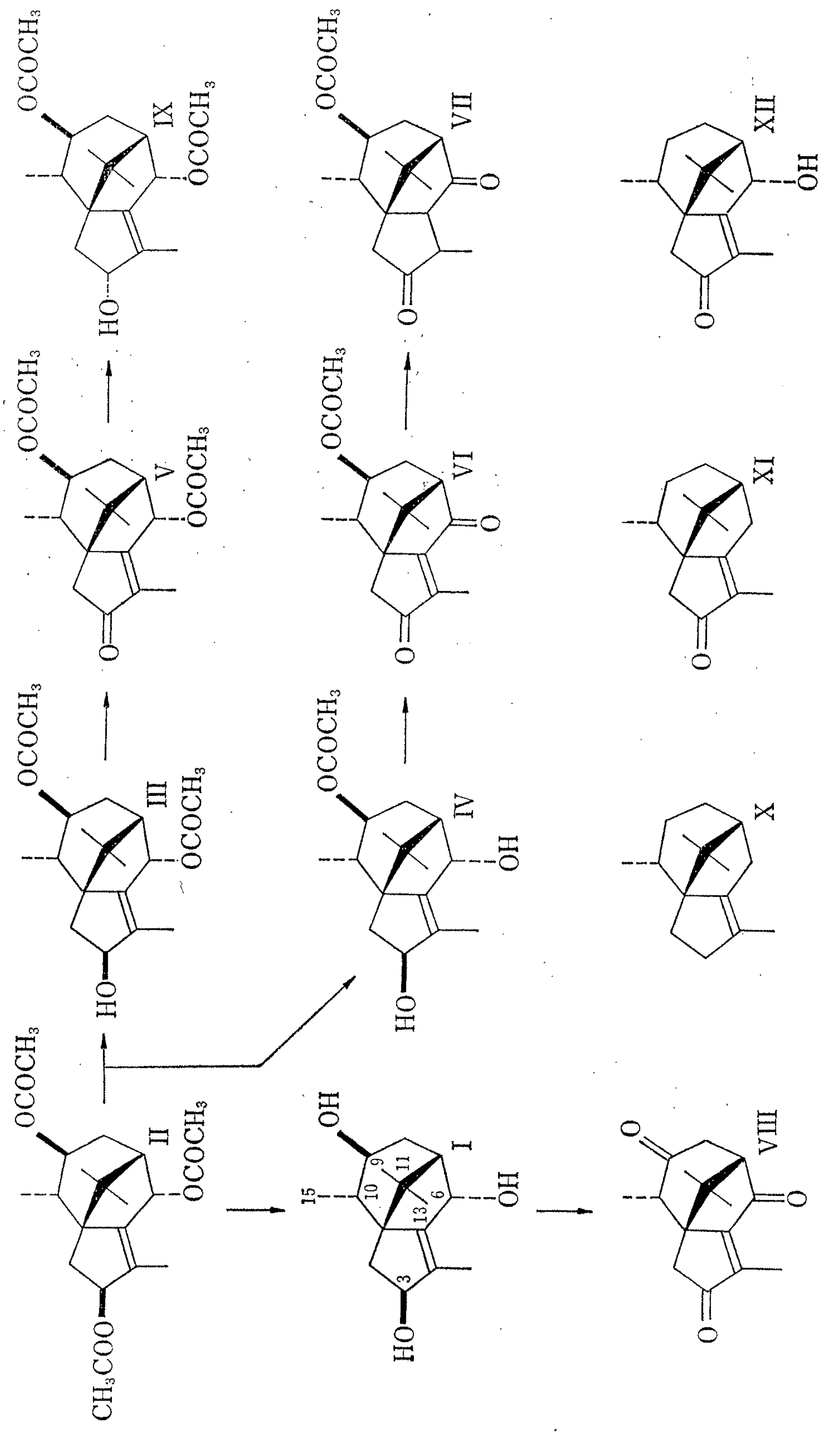
The triol monoacetate (Ⅳ) was oxidized with chromium trioxide-pyridine complex to yield the ene-dione (Ⅵ), λ_{max}^{EtOH} 268 mμ (log ε 4.46). The infrared spectrum (CCl_4) of the ene-dione (Ⅵ) disclosed bands in the ketonic C=O stretching vibration region at 1719 and 1715 cm^{-1}, both attributed to α,β-unsaturated five-membered ring ketones. The ene-dione (Ⅵ) was reduced with zinc and acetic acid to give the acetoxy-dione (Ⅶ), which showed in the infrared (CCl_4) a band at 1745 cm^{-1} associated with an acetoxyl and cyclopentanones but no band attributable to a cyclohexanone. These observations demonstrated that the C_6 is also oriented in a five-membered ring.

Oxidation of sugetriol with chromium trioxide-pyridine complex gave the triketone (Ⅷ) whose infrared spectrum (CCl_4) exhibited bands at 1720 and 1715 cm^{-1} indicating the formation of a cyclohexanone but a cyclopentanone system. This fact revealed the C_9 to be situated in a six-membered ring.

Therefore, sugetriol is represented by the structure I but exclusive of stereochemistry.

[*1] Analytical values are in agreement with the molecular formulae indicated. Specific rotations were measured in $CHCl_3$ solution unless otherwise stated. NMR spectra were recorded at 60 Mc. in CCl_4 solution unless noted to the contrary, and chemical shifts are given in p.p.m. downfield from internal Me_4Si.

Close similarity of the circular dichroism curve ($[\theta]_{324}$ -69×10^2) of the enone (V) to that ($[\theta]_{314}$ -54×10^2) of cyperotundone (XI) showed that the configuration of the C-11 carbon bridge of sugetriol is the same (*i.e.*, β) as that of cyperotundone (XI), whose absolute stereochemistry is known.[1] To establish the configurations of the substituents at C-10, C-9, C-6, and C-3, the NMR spectra of the triol derivatives were taken into consideration. Thus, in the derivatives (II~V), the C-15 methyl protons occur at 0.69~0.88; the high field of the resonances indicates that the C-10 methyl group is situated in the α-configuration.[1,2] The signals due to the C-9 hydrogens of the derivatives (II~VI) are sextets



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[1] H. Hikino, K. Aota, T. Takemoto: This Bulletin, **13**, 628 (1965); **14**, 890 (1966).
[2] H. Hikino, K. Ito, K. Aota, T. Takemoto: *Ibid.*, in press.

whose coupling constants ($J_1=J_2=10$, and $J_3=7$ c.p.s.) reveal the configuration of the C-9 oxygen functions as being β.[2] The C-6 hydrogen signals of the derivatives (Ⅱ～Ⅴ) appear as slightly multiplying doublets with the coupling constants 6 c.p.s. which show the C-6 oxygen functions to be α-oriented.[3] The ketone (Ⅴ) was reduced with sodium borohydride to give the epimeric alcohol (Ⅸ). In the NMR spectra, the C-15 proton signal (0.94) of the epimeric alcohol (Ⅸ) is shifted to lower field as compared with those (0.81 and 0.80) of the original alcohol (Ⅲ) and cyperene (Ⅹ), while the C-13 proton signal (0.89) of the alcohol (Ⅲ) shows downward shift as compared with those (0.73 and 0.75) of its epimer (Ⅸ) and cyperene (Ⅹ). These observations indicate that the C-3 hydroxyl of the epimeric alcohol (Ⅸ) is closely located to the C-10α methyl and, therefore, α-situated, and likewise, the C-3 hydroxyl of the original alcohol (Ⅲ) is closely oriented to the C-11α methyl and, therefore, β-situated.

The absolute stereochemistry of sugetriol is consequently elucidated as shown in formula I.

It is of interest to note that the Japanese nutgrass oil contains a series of substances having the isopatchoulane skeleton and with different degrees of oxidation, *i.e.*, cyperene (Ⅹ),[4] cyperotundone (Ⅺ),[1] sugeonol (Ⅻ),[3] and sugetriol (I).

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[3] H. Hikino, K. Aota, T. Takemoto: This Bulletin, in press.

[4] *Idem.*: Unpublished data.

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Comparative Study on the Sapogenin Constituents of Five Primulaceous Plants

Some kinds of roots belonging to *Primula* genus (Primulaceae) have long been familiar as valuable expectorants. Especially in Europe, the roots and rhizomes of *Primula elatior* L. SCHREBER and *P. veris* L. em. HUDSON (*P. officinalis* L. HILL) have often been used as well as the other vegetable expectorants such as Senega roots.[1] Among several kinds of the root constituents, the saponin has been believed responsible for the physiological activity[2] although the conclusive work in this line is still lacking, and this appears why saponins and sapogenins originated from these European *Primulaceous* plants (including also *P. vulgaris* HUDS.) have been investigated extensively by Tschesche and coworkers and other groups.[1,3]

In connection with the effort to find rich saponin source expecting its biological activity at the same time, we have first attempted a comparative study on saponin and sapogenin constituents of *Primulaceous* plants which are easily available in this country.

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[1] R. Tschesche, F. Ziegler: Liebig's Ann., **674**, 185 (1964), and literatures cited therein.

[2] R. Tschesche, G. Wulff: Planta Medica, **12**, 272 (1964).

[3] R. Tschesche, B. T. Tjoa, G. Wulff: Liebig's Ann., **696**, 160 (1966), and literatures cited therein.