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Structure and Absolute Configuration of Sugetriol[1]

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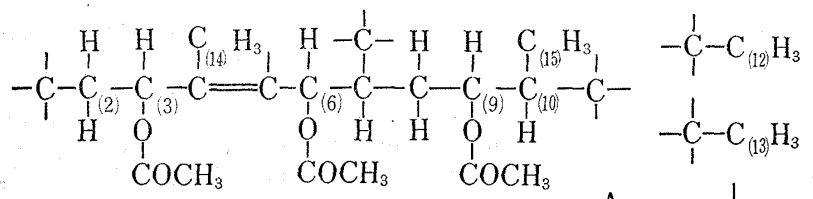
The sesquiterpenoid sugetriol, the triacetate of which was isolated from nutgrass, *Cyperus rotundus* (Cyperaceae), has been shown by spectral and degradative studies to be I.

During our recent study on the constituents of the tuber of nutgrass, *Cyperus rotundus* Linné (Cyperaceae), of Japanese origin, we have hitherto isolated the sesquiterpenoids, cyperene, β-selinene,[3] α-cyperone, cyperotundone,[4] patchoulenone,[3] cyperolone,[5] cyperol, isocyperol,[6] and sugeonol.[7] In addition, there has been obtained a new sesquiterpenic trialcohol which we have called sugetriol. It is the purpose of this report to present the results leading to the selection of formula I as the representation of the structure and absolute configuration of sugetriol.[8]

Sugetriol is naturally present as the triacetate (II), in which the presence of three secondary acetoxyl groups is indicated by infrared bands (1736 and 1235 cm^{-1}) and especially by nuclear magnetic resonance (NMR) signals originating from three acetoxyl methyls (1.95, 1.98, and 2.11 ppm) and three hydrogens on carbons bearing the acetoxyls (4.63, 5.48, and 5.83 ppm). The NMR spectrum also shows the presence of a secondary methyl (0.88 ppm), two tertiary methyls (0.91 and 1.06 ppm), and a tetrasubstituted ethylenic linkage with a methyl on it (1.66 ppm).

The NMR spectrum of the triacetate (II) was then analyzed with the aid of decoupling experiments. The chemical shifts and coupling constants thus determined for all protons are tabulated in Table I. These data leads to the conclusion that all the functions are linked as indicated in the partial structure A. Since the formula A contains more than 21 carbon atoms required from the molecular formula, some of them should be overlapped. However,



A

—C— denotes a quaternary carbon atom

1) This paper constitutes Part XXIX in the series on Sesquiterpenoids. Preceding paper, Part XXVIII: H. Hikino, Y. Hikino, K. Agatsuma, and T. Takemoto, *Chem. Pharm. Bull.* (Tokyo), **16**, 1779 (1968).
2) Location: *Kita-4-bancho, Sendai.*
3) H. Hikino, K. Aota, and T. Takemoto, unpublished data.
4) H. Hikino, K. Aota, and T. Takemoto, *Chem. Pharm. Bull.* (Tokyo), **13**, 628 (1965); **14**, 890 (1966).
5) H. Hikino, K. Aota, Y. Maebayashi, and T. Takemoto, *Chem. Pharm. Bull.* (Tokyo), **14**, 1439 (1966); **15**, 1349 (1967).
6) H. Hikino, K. Aota, and T. Takemoto, *Chem. Pharm. Bull.* (Tokyo), **15**, 1929 (1967).
7) H. Hikino, K. Aota, and T. Takemoto, *Chem. Pharm. Bull.* (Tokyo), **16**, 52 (1968).
8) Part of the material here described was first presented in preliminary form, H. Hikino, K. Aota, and T. Takemoto, *Chem. Pharm. Bull.* (Tokyo), **15**, 1433 (1967).

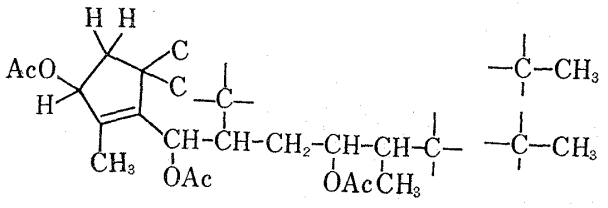
Table I. NMR Data from Sugetriol Triacetate (100 Mcps, $CDCl_3$)

Chemical shifts (δ: ppm from TMS)		Apparent coupling constants (J: cps)	
δ_2 = *ca.* 1.4	$\delta_{8'}$ = *ca.* 1.8	$J_{2,2'}$ = ?	$J_{7,8'}$ = 3
$\delta_{2'}$ = *ca.* 1.6	δ_9 = 4.66	$J_{2,3}$ = 7	$J_{8,8'}$ = ?
δ_3 = 5.91	δ_{10} = *ca.* 2.2	$J_{2',3}$ = 7	$J_{8,9}$ = 7
δ_{14} = 1.65	δ_{15} = 0.87	$J_{3,14}$ = 1	$J_{8',9}$ = 10
δ_6 = 5.57	δ_{12} = 1.06	$J_{6,14}$ = 1	$J_{9,10}$ = 10
δ_7 = 2.33	δ_{13} = 0.89	$J_{6,7}$ = 6	$J_{10,15}$ = 6
δ_8 = *ca.* 1.8		$J_{7,8}$ = 3	

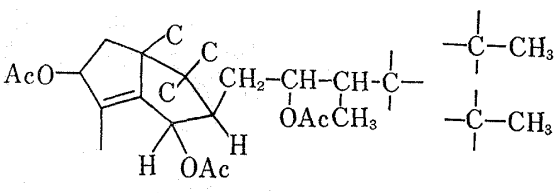
all 21 carbon atoms in the molecule must be included in the formula A without omission. Likewise, all 30 hydrogen atoms in the molecule have been already allocated in the formula A.

Complete hydrolysis of the triacetate (II) yielded the free tri-alcohol, sugetriol (I), $C_{15}H_{24}O_3$, which on acetylation regenerated the original triacetate (II). When the triacetate (II) was submitted to partial hydrolysis to give the triol 6,9-diacetate (III) and the triol 9-acetate (IV). These assignments were accomplished by the NMR spectra which showed that the C-3 hydrogen signal of the former (III) was shifted upfield (+0.99 ppm) as compared with that of the triacetate (II), the acetoxyl group at C-3 being hydrolyzed first, and the C-3 and C-6 hydrogen signals of the latter (IV) were similarly shifted to higher field (+0.91 and *ca.* +0.72 ppm, respectively) as compared with those of the triacetate (II), the acetoxyl group on C-6 being hydrolyzed next.

The line position of the C-3 hydrogen signal (5.80 ppm) in the NMR spectrum of the triacetate (II) is lower than that expected for a hydrogen simply on an acetoxyl-bearing carbon, and suggests the carbinyl hydrogen to be next to an ethylene bond. In confirmation, on oxidation with chromium trioxide-pyridine complex the triol diacetate (III) afforded the keto-diol diacetate (V), of which spectral properties (244 mμ, 1714 and 1674 cm^{-1}) showed the presence of a cyclopentenone moiety indicating the C-3 carbon to be oriented at an α-position to the ethylenic linkage and further involved in a five membered ring. This finding leads to the extension of the formula A to the partial formula B.



B

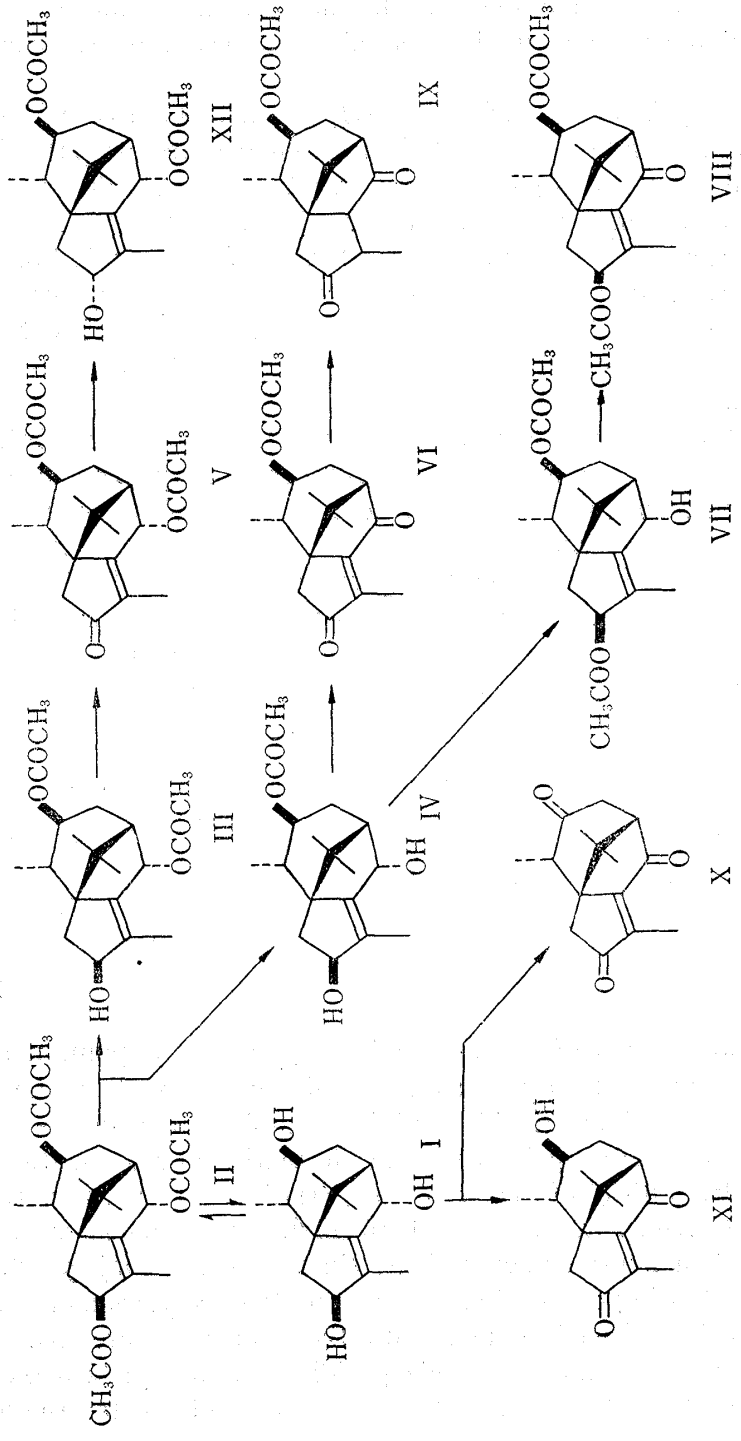


C

The lower field position of the C-6 hydrogen signal (5.46 ppm) in the spectrum of the triacetate (II) also implies the hydrogen to be allylic. In reality, the triol 9-acetate (IV) was oxidized with chromium trioxide-pyridine complex to yield the enedione (VI), whose ultraviolet absorption at 268 mμ indicated the formation of a 2-ene-1,4-dione chromophore. The infrared spectrum (CCl_4) of the enedione (VI) discloses bands in the ketonic carbonyl stretching vibration region at 1719 and 1715 cm^{-1}, which demonstrate that both carbonyl groups are situated in five-membered rings, since they are conjugated. This was further supported by the following observations. Thus partial acetylation of the triol 9-acetate (IV) gave the triol 3,9-diacetate (VII) along with the triol triacetate (II). The triol diacetate (VII) on oxidation with chromium trioxide-pyridine complex yielded the keto-diol diacetate (VIII), whose spectral data(255 mμ, 1722 and 1670 cm^{-1}) indicated the formation of a cisoid

α,β-unsaturated five-membered ring ketone system. Furthermore, in the enedione (VI), it was predicted that the ethylene bond between the carbonyl groups was reduced readily by zinc–acetic acid treatment which, in fact, converted the acetoxy–enedione (VI) into the acetoxy–dione (IX), 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 demonstrate that the C–6 carbon is also oriented in a five-membered ring, and are, therefore, compatible with the conversion of the part-structure shown in B to that shown in C.

Oxidation of sugetriol with chromium trioxide–pyridine complex gave, together with the diketo–alcohol (XI), the triketone (X) whose infrared spectrum (CCl_4) exhibited bands at 1720 and 1715 cm^{-1} indicating the formation of a cyclohexanone rather than a cyclopentanone system. This fact revealed the C–9 carbon to be located in a six-membered ring.

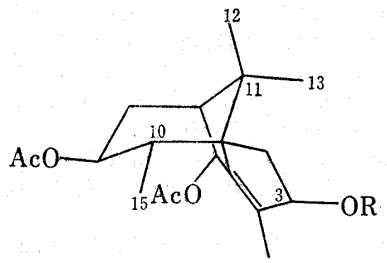


Therefore, sugetriol is represented by the structure I but exclusive of stereochemistry which remains to be established.

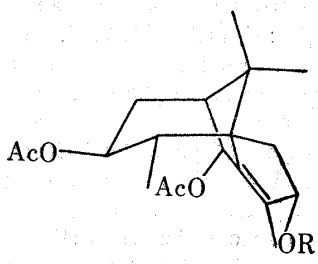
Close similarity of the circular dichroism curve ($[\theta]_{324}$ -69×10^2) of the enone (V) to that ($[\theta]_{314}$ -54×10^2) of cyperotundone (XV) showed that the configuration of the C–11 carbon bridge of sugetriol is the same (*i.e.*, β) as that of cyperotundone (XV), whose absolute stereochemistry is known.[4] 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 spectra of the derivatives (II—V), the C–12 methyl protons appear at 1.05—1.08 ppm and the C–13 methyl protons at 0.82—0.89 ppm, whereas the C–15 methyl protons occur at 0.69—0.88 ppm, the high field of the last resonances indicates that the C–10 methyl group is situated in the α–configuration.[4,9] The signals due to the C–9 hydrogens of the derivatives (II—VI) are sextets whose coupling constants (10, 10, and 7 cps) reveal the configuration of the C–9 oxygen functions as being β.[9] Judging by inspection of the Dreiding models and from a Karplus type relation between the coupling constants and the dihedral angles between vicinal protons, it is expected that the coupling constant between the C–6α and the C–7 hydrogens is very small, while that between the C–6β and the C–7 hydrogens is fairly large.[7] In agreement with this view, Nerali, *et al.*[10] have recently reported that the NMR signal of the C–6α hydrogen in the cyperene skeleton appears as a singlet. In the derivatives (II—V), the C–6 hydrogen signals occur as slightly multiplying doublets with the coupling constants 6 cps which show the C–6 oxygen functions to be located in the α–configuration. The coupling constants (7 cps) of the slightly multiplying triplets arising from the C–3 hydrogens of the derivatives (II—IV) did not permit the assignment of the configuration of the C–3 oxygen functions. Therefore, determination of the configuration at C–3 was accomplished by the following evidence. Thus the ketone (V) was reduced with sodium borohydride to give the epimeric alcohol (XII). In the NMR spectra, the C–15 methyl proton signal (0.94 ppm) of the epimeric

Table II. NMR Data from Sugetriol Derivatives (CCl_4)

Compounds	Functions at C–3 on the cyperene skeleton	Chemical shifts of the methyl protons (ppm from TMS)		
		C–12 (11β)	C–13 (11α)	C–15 (10α)
Cyperene (XIV)	none	0.94	0.75	0.80
Sugetriol 6,9–diacetate (III)	β–OH	1.06	0.89	0.81
Sugetriol triacetate (II)	β–$OCOCH_3$	1.06	0.88	0.88
3–*epi*–Sugetriol 6,9–diacetate (XII)	α–OH	1.04	0.73	0.94
3–*epi*–Sugetriol triacetate (XIII)	α–$OCOCH_3$	1.07	0.79	0.90



III : R=H
II : R=Ac

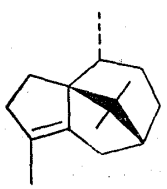


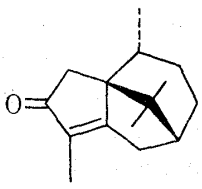
XII : R=H
XIII : R=Ac

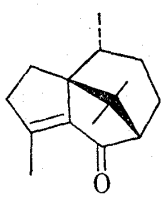
9) H. Hikino, K. Ito, K. Aota, and T. Takemoto, *Chem. Pharm. Bull.* (Tokyo), **16**, 43 (1968).
10) S.B. Nerali and K.K. Chakravarti, *Tetrahedron Letters*, **1967**, 2447.

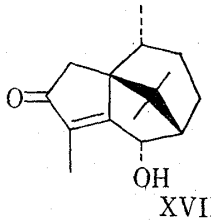
alcohol (XII) is shifted to lower field as compared with those (0.81 and 0.80 ppm) of the original alcohol (III) and cyperene (XIV), while the C–13 methyl proton signal (0.89 ppm) of the alcohol (III) shows downward shift as compared with those (0.73 and 0.75 ppm) of its epimer (XII) and cyperene (XIV). The acetylation shifts observed are very small in these cases (Table II). These observations indicate that the newly formed C–3 hydroxyl of the epimeric alcohol (XII) 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. This conclusion was further supported by the following evidence. Thus it was found that the triol diacetate (III) is more laevorotatory ($\Delta[M]_D$ −49°) than its 3–epimer (XII), a fact which on application to Mills' rule shows the configuration of the C–3 hydroxyl group of sugetriol to be *S*. On the basis of the above results, the absolute stereochemistry of sugetriol is 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 degree of oxidation, *i.e.*, cyperene (XIV), cyperotundone (XV), patchoulenone (XVI), sugeonol (XVII), and sugetriol (I).


XIV


XV


XVI


XVII

Experimental[11]

Isolation of Sugetriol Triacetate——The crude drug "Kō-bushi," the dried rhizomes of *Cyperus rotundus* Linné (Japanese name: Hama-suge), was steam-distilled to give the essential oil as a pale brown liquid in 0.6% yield.[4]

The oil was chromatographed on alumina. After percolation of ketone fractions with benzene, successive elution with the same solvent afforded acetate fractions which were combined and rechromatographed on silica gel. When eluted with benzene, a crystalline substance was obtained immediately after the elution of sugeonyl acetate.[7] The substance on crystallization from light petroleum yielded sugetriol triacetate (II) as colorless needles, mp 132°, $[\alpha]_D$ +60.6° (c=5.2). *Anal.* Calcd. for $C_{21}H_{30}O_6$: C, 66.64; H,7.99. Found: C, 66.62; H, 7.89. IR (KBr) cm^{-1}: 1736, 1235 (acetoxyl). NMR: doublet (3H) at 0.88 (J=6, C<u>H</u>$_3$–CH〈), singlet (3H) at 0.91 (C<u>H</u>$_3$–C〈), singlet (3H) at 1.06 (C<u>H</u>$_3$–C〈), triplet (3H) at 1.66 (J=1, C<u>H</u>$_3$–C=C〈), three singlets (3H each) at 1.95, 1.98, 2.11 (C<u>H</u>$_3$–CO–O–), sextet (1H) at 4.63 (J_1=J_2=10, J_3=7, –CH_2–C<u>H</u>(OCOCH_3)–CH〈), doublet (1H) at 5.48 (J=6, 〉C=C–C<u>H</u>(OCOCH_3)–CH〈), triplet (1H) at 5.83 (J=7, –CH_2–C<u>H</u>(OCOCH_3)–CH〈), NMR ($CDCl_3$, 100 Mcps): described previously (Table I).

Complete Hydrolysis of Sugetriol Triacetate——The triacetate (II) (86 mg) was treated 1 hr at room temperature with ethanolic NaOH solution (5%; 2.0 ml). The mixture was concentrated, diluted with H_2O, and extracted by AcOEt. Removal of the AcOEt gave a crude product (51 mg) which was crystallized from AcOEt to afford sugetriol (I) as colorless needles, mp 221—222°, $[\alpha]_D$ +62.4° (c=3.5, EtOH). *Anal.* Calcd. for $C_{15}H_{24}O_3$: C, 71.39; H, 9.59. Found: C, 71.08; H, 9.61. IR (KBr) cm^{-1}: 3420 (hydroxyl).

Acetylation of Sugetriol——Sugetriol (11 mg) in pyridine (0.5 ml) was allowed to stand overnight at room temperature with Ac_2O (0.3 ml). Extraction into ether and crystallization from light petroleum gave the triacetate (II) as colorless needles, mp 132°, identified in the usual criteria.

Partial Hydrolysis of Sugetriol Triacetate——The triacetate (II) (196 mg) and NaOH (20 mg) in EtOH (6.5 ml) were stirred 30 min at room temperature. After isolation, the product (165 mg) was placed on a silica gel column (5 g).

Elution with benzene–AcOEt (5:1) gave a product (90 mg) which was distilled under reduced pressure to yield sugetriol 6,9–diacetate (III) as a colorless oil, $[\alpha]_D$ +55.0° (c=5.3). *Anal.* Calcd. for $C_{19}H_{28}O_5$:

11) Melting points are uncorrected. Specific rotations were measured in $CHCl_3$ solution unless otherwise stated. UV spectra were recorded using EtOH as solvent. NMR spectra were determined at 60 Mcps in CCl_4 solution unless specified to the contrary. Chemical shifts are given in ppm units from Me_4Si as internal reference and coupling constants (J) in cps units. Signals are expressed without fine splittings.

C, 67.83; H, 8.39. Found: C, 67.71; H, 8.21. IR (CCl_4)cm^{-1}: 3660, 3470 (hydroxyl), 1738, 1238 (acetoxyl), NMR: doublet (3H) at 0.81 (J=6, C$\underline{H}_3$–CH<), singlet (3H) at 0.89 (C$\underline{H}_3$–C<), singlet (3H) at 1.06 (C$\underline{H}_3$–C<), singlet (3H) at 1.72 (C$\underline{H}_3$–C=C<), two singlets (3H each) at 1.97, 2.12 (C$\underline{H}_3$–CO–O–), sextet (1H) at 4.57 (J_1=J_2=10, J_3=7, –CH_2–C$\underline{H}$(OCOCH_3)–CH<), triplet (1H) at 4.84 (J=6, –CH_2–C$\underline{H}$(OH)–C=C<), doublet (1H) at 5.46 (J=6, >C=C–C$\underline{H}$(OCOCH_3)–CH<).

Elution with benzene–AcOEt (2:1) gave a product (70 mg) which on distillation under diminished pressure furnished sugetriol 9-acetate (IV) as a colorless oil, $[\alpha]_D$ +22.5° (c=7.0). *Anal.* Calcd. for $C_{17}H_{26}O_4$: C, 69.36; H, 8.90. Found: C, 69.20; H, 8.84. IR ($CHCl_3$) cm^{-1}: 3630, 3470 (hydroxyl), 1730 (acetoxyl), NMR ($CHCl_3$): doublet (3H) at 0.76 (J=7, C$\underline{H}_3$–CH<), singlet (3H) at 0.82 (C$\underline{H}_3$–C<), singlet (3H) at 1.05 (C$\underline{H}_3$–C<), singlet (3H) at 1.80 (unresolved, C$\underline{H}_3$–C=C<), singlet (3H) at 2.03 (C$\underline{H}_3$–CO–O–), sextet ?[12] (1H) at *ca.* 4.64[12] (–CH_2–C$\underline{H}$(OCOCH_3)–CH<), doublet (1H) at *ca.* 4.73[12] (J=5, >C=C–C$\underline{H}$(OH)–CH<), triplet (1H) at 4.89 (J=7, –CH_2–C$\underline{H}$(OH)–C=C<).

Oxidation of Sugetriol 6,9-Diacetate with Chromium Trioxide-Pyridine Complex——The triol diacetate (III) (26 mg) in pyridine (0.5 ml) was added to CrO_3 (32 mg) in pyridine (0.3 ml) and let stand 5 hr at room temperature. The oxidation product (22 mg) isolated in the usual manner was crystallized from ether to give the keto-diol diacetate (V) as colorless needles, mp 156—156.5°, CD (c=0.058, dioxane): $[\theta]_{324}$ −6900. *Anal.* Calcd. for $C_{19}H_{26}O_5$: C, 68.24; H, 7.84. Found: C, 67.97; H, 8.14. UV λ_{max}^{EtOH} mμ (log ε): 244 (4.32). IR (CCl_4) cm^{-1}: 1740, 1230 (acetoxyl), 1714, 1674 (cyclopentenone), 1417 (methylene adjacent to carbonyl), NMR: doublet (3H) at 0.69 (J=6, C$\underline{H}_3$–CH<), singlet (3H) at 0.85 (C$\underline{H}_3$–C<), singlet (3H) at 1.18 (C$\underline{H}_3$–C<), singlet (3H) at 1.75 (unresolved, C$\underline{H}_3$–C=C<), two singlets (3H each) at 1.97, 2.18 (C$\underline{H}_3$–CO–O–), sextet (1H) at 4.55 (J_1=J_2=10, J_3=7, –CH_2–C$\underline{H}$(OCOCH_3)–CH<), doublet (1H) at 5.64 (J=6, >C=C–C$\underline{H}$(OCOCH_3)–CH<).

Oxidation of Sugetriol 9-Acetate with Chromium Trioxide-Pyridine Complex——The triol monoacetate (IV) (20 mg) in pyridine (1.2 ml) was added to CrO_3 (39 mg) in pyridine (0.3 ml) and set aside overnight at room temperature. Upon isolation, the product (19 mg) was crystallized from ether to yield the diketo-ol acetate (VI) as pale yellow needles, mp 117 —118°, $[\alpha]_D$ −97.7° (c=5.7), CD (c=0.056, dioxane): $[\theta]_{401}$ −3260, $[\theta]_{353}$ +1890. *Anal.* Calcd. for $C_{17}H_{24}O_4$: C, 69.83; H, 8.27. Found: C, 69.74; H, 8.19. UV λ_{max}^{EtOH} mμ (log ε): 268 (4.46). IR (CCl_4) cm^{-1}: 1847, 1227 (acetoxyl), 1719, 1715 (cyclopentenone, 2-methylene-cyclopentanone), 1413 (methylene α to carbonyl). NMR ($CHCl_3$): doublet (3H) at 0.72 (J=6, C$\underline{H}_3$–CH<), singlet (3H) at 0.90 (C$\underline{H}_3$–C<), singlet (3H) at 1.24 (C$\underline{H}_3$–C<), singlet (6H) at 2.06 (C$\underline{H}_3$–C=C<, C$\underline{H}_3$–CO–O–), sextet (1H) at 4.49 (J_1=J_2=10, J_3=7, –CH_2–C$\underline{H}$(OCOCH_3)–CH<).

Partial Acetylation of Sugetriol 9-Acetate——The triol monoacetate (IV) (76 mg) in pyridine (0.6 ml) was treated with Ac_2O (0.3 ml) at room temperature for 45 min. TLC indicated that the starting diol (IV) had just been exhausted at this time. After isolation, the product (79 mg) was chromatographed on silica gel (2 g).

Elution with benzene gave sugetriol triacetate (II) (32 mg), identified by the usual criteria.

Successive elution with benzene–AcOEt (5:1) afforded crystalline fractions (36 mg) which were crystallized from ether to yield sugetriol 3,9-diacetate (VII) as colorless needles, mp 140—140.5°, $[\alpha]_D$ +44.7 (c=4.2). *Anal.* Calcd. for $C_{19}H_{28}O_5$: C, 67.83; H, 8.39. Found: C, 68.15; H, 8.39. IR (CCl_4) cm^{-1}: 3650, 3525 (hydroxyl), 1738, 1233 (acetoxyl). NMR: doublet (3H) at 0.82 (J=6, C$\underline{H}_3$–CH<), singlet (3H) at 0.82 (C$\underline{H}_3$–C<), singlet (3H) at 1.03 (C$\underline{H}_3$–C<), singlet (3H) at 1.73 (unresolved, C$\underline{H}_3$–C=C<), singlet (6H) at 2.01 (C$\underline{H}_3$–CO–O–), sextet ?[12] (1H) at *ca.* 4.62[12] (–CH_2–CH(OCOCH_3)–CH<), doublet (1H) at *ca.* 4.69[12] (J=*ca.* 6,[12] >C=C–C$\underline{H}$(OH)–CH<), triplet (1H) at 5.80 (J=7, –CH_2–C$\underline{H}$(OCOCH_3)–C=C<).

Oxidation of Sugetriol 3,9-Diacetate with Chromium Trioxide-Pyridine Complex——The triol diacetate (VII) (42 mg) in pyridine (1.2 ml) was added to CrO_3 (56 mg) in pyridine (0.4 ml) and let stand at room temperature for 4 hr. The reaction mixture was dissolved in dil. HCl and extracted with ether to give a product (39 mg) which on distillation under reduced pressure afforded the keto-diol diacetate (VIII) as a colorless oil, CD (c=0.057, dioxane): $[\theta]_{341}$ −2100. *Anal.* Calcd. for $C_{19}H_{26}O_5$: C, 68.24; H, 7.84. Found: C, 68.15; H, 7.78. UV λ_{max}^{EtOH} mμ (log ε): 255 (4.03). IR (CCl_4) cm^{-1}: 1730, 1228 (acetoxyl), 1722, 1670 (2-methylene-cyclopentanone). NMR: doublet (3H) at 0.88 (J=7, C$\underline{H}_3$–CH<), singlet (3H) at 0.95 (C$\underline{H}_3$–C<), singlet (3H) at 1.10 (C$\underline{H}_3$–C<), singlet (6H) at 1.98 (C$\underline{H}_3$–CO–O–), singlet (3H) at 2.04 (C$\underline{H}_3$–C=C<), sextet (1H) at 4.35 (J_1=J_2=10, J_3=7, >CH–C$\underline{H}$(OCOCH_3)–CH_2–), triplet (1H) at 5.87 (J=8, –CH_2–C$\underline{H}$(OCOCH_3)–C=C<).

Reduction of the Diketo-ol Acetate with Zinc and Acetic Acid——The diketo-ol acetate (VI) (10 mg) was dissolved in AcOH (0.5 ml) and Zn powder (0.1 g) added. The mixture was heated at 90° for 1 hr. Isolation of the neutral product in the usual way gave the dione (IX) as a colorless oil, IR (CCl_4) cm^{-1}: 1745, 1737 (cyclopentanones, acetoxyl), 1412 (methylene adjacent to carbonyl), 1232 (acetoxyl).

Oxidation of Sugetriol with Chromium Trioxide-Pyridine Complex——The triol (I) (90 mg) in pyridine (1.5 ml) was added to CrO_3 (313 mg) in pyridine (1 ml) and the mixture let stand 2 days at room temperature. The oxidation product (33 mg) isolated in the customary manner was chromatographed over silica gel (1 g).

12) Overlapping of the signals does not permit exact determination.

Elution with benzene–AcOEt (5:1) gave a product (27 mg) which on crystallization from ether yielded the trione (X) as pale yellow needles, mp 99.5—100.5°, $[\alpha]_D$ −167° (c=3.4), CD (c=0.063, dioxane): $[\theta]_{405}$ −3100, $[\theta]_{334}$ −4700. *Anal.* Calcd. for $C_{15}H_{18}O_3$: C, 73.14; H, 7.37. Found: C, 73.01; H, 7.32. UV λ_{max}^{EtOH} mμ (log ε): 269 (4.51). IR (CCl_4) cm^{-1}: 1720 (2-methylene-cyclopentanone), 1715 (cyclopentenone, cyclohexanone), 1411 (methylene α to carbonyl). NMR: doublet (3H) at 0.90 (J=7, C<u>H</u>$_3$–CH<), singlet (3H) at 1.03 (C<u>H</u>$_3$–C<), singlet (3H) at 1.27 (C<u>H</u>$_3$–C<), singlet (3H) at 2.05 (C<u>H</u>$_3$–CO–O–).

Successive elution with the same solvent afforded the diketo-ol (XI) as a colorless oil (6 mg). IR (CCl_4) cm^{-1}: 3448 (hydroxyl), 1719, 1713 (2-methylene-cyclopentanone, cyclopentenone), 1413 (methylene next to carbonyl), NMR ($CHCl_3$): doublet (3H) at 0.83 (J=7, C<u>H</u>$_3$–CH<), singlet (3H) at 0.88 (C<u>H</u>$_3$–C<), singlet (3H) at 1.22 (C<u>H</u>$_3$–C<), singlet (3H) at 2.03 (C<u>H</u>$_3$–C=C<), sextet (1H) at 4.33 (J_1=J_2=10, J_3=7, –CH_2–C<u>H</u>(OH)–CH<).

Reduction of the Keto-diol Diacetate with Sodium Borohydride——The ketodiol diacetate (V) (56 mg) in MeOH (2 ml) was stirred with an excess of $NaBH_4$ at room temperature for 2 hr. Isolation in the usual manner gave the 3-*epi*-triol 6,9-diacetate (XII) (56 mg) as a colorless oil, $[\alpha]_D$ +69.5° (c=5.0). IR ($CHCl_3$) cm^{-1}: 3640, 3470 (hydroxyl), 1723 (acetoxyl). NMR: singlet (3H) at 0.73 (C<u>H</u>$_3$–C<), doublet (3H) at 0.94 (J=7, C<u>H</u>$_3$–CH<), singlet (3H)at 1.04 (C<u>H</u>$_3$–CH<), singlet (3H) at 1.73 (C<u>H</u>$_3$–C=C<), singlet (3H) at 1.95 (C<u>H</u>$_3$–CO–O–), singelt (3H) at 2.21 (C<u>H</u>$_3$–CO–O–), doublet ?[12] (1H) at *ca.* 4.5 (J=8, –CH_2–C<u>H</u>(OH)–C=C<), sextet (1H) at 4.68 (J_1=J_2=10, J_3=7, –CH_2–C<u>H</u>($OCOCH_3$)–CH<), doublet (1H) at 5.25 (J=6, >C=C–C<u>H</u>–($OCOCH_3$)–CH<).

Acetylation of 3-*epi*-Sugetriol 6,9-Diacetate——3-*epi*-Sugetriol 6,9-diacetate (XII) (34 mg) in pyridine (0.8 ml) was set aside overnight at room temperature with Ac_2O (0.3 ml). Dilution with water and extraction with ether gave 3-*epi*-sugetriol triacetate (XIII) as a colorless oil, $[\alpha]_D$ +64.7° (c=3.1). IR (CCl_4) cm^{-1}: 1738, 1247 (acetoxyl). NMR: singlet (3H) at 0.79 (C<u>H</u>$_3$–C<), doublet (3H) at 0.90 (J=7, C<u>H</u>$_3$–CH<), singlet (3H) at 1.07 (C<u>H</u>$_3$–C<), singlet (3H) at 1.75 (C<u>H</u>$_3$–C=C<), singlet (6H) at 1.98 (C<u>H</u>$_3$–CO–O–), singlet (3H) at 2.14 (C<u>H</u>$_3$–CO–O–), sextet (1H) at 4.72 (J_1=J_2=10, J_3=7, –CH_2–C<u>H</u>($OCOCH_3$)–CH<), doublet (1H) at 5.37 (J=6, >C=C<u>H</u>($OCOCH_3$)–CH<), doublet (1H) at 5.43 (J=7, –CH_2–C<u>H</u>($OCOCH_3$)–C=C<).

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