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Saponin and Sapogenol. II.[1] Seeds Sapogenols of *Thea sinensis* L. (2). Theasapogenol A

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The structure of theasapogenol A, one of seeds sapogenols of *Thea sinensis* L. has been established as 3β,16α,21β,22α,23,28-hexahydroxy-olean-12-ene (II), and some additional investigations on the oxide ring formation between C-21 and C-16 of barringtogenol C (I) and II have been summarized. In addition, the evidence concerning to the anisotropic effect caused by the trityl function has been presented.

As described in the preceding paper[1], the structure of barringtogenol C has been revised as 3β,16α,21β,22α,28-pentahydroxy-olean-12-ene (I). In the present paper, we describe the full account of the study on theasapogenol A which leads the structure expressed by 3β,16α,21β,22α,23,28-hexahydroxy-olean-12-ene (II).[3]

Theasapogenol A (II), $C_{30}H_{50}O_6$, mp 301—303°, $[\alpha]_D$ +14° (pyridine), possesses hydroxyl function and olefin moiety as revealed by its infrared (IR) absorption bands at 3356 and 1639 cm^{-1}. Upon mild acetylation, it afforded a tetraacetate (III), $C_{30}H_{46}O_2(OCOCH_3)_4$, mp 225—228°, and a pentaacetate (IV), $C_{30}H_{45}O(OCOCH_3)_5$, mp 174—178°, which in turn gave a pentaacetyl-monoketone (V), $C_{30}H_{43}O(OCOCH_3)_5$, mp 264—266°, on chromium trioxide-pyridine complex oxidation. Under more forced condition, on the other hand, II furnished a hexaacetate (VI), $C_{30}H_{44}(OCOCH_3)_6$, mp 134—135°, which regenerated II on alkaline hydrolysis. The IR spectra of V(KBr) and VI(CCl_4), indicating absorption bands at 1751, 1725, 1245 cm^{-1} and 1747, 1244, 1227 cm^{-1}, disclose that both V and VI possess no free hydroxyl. It is therefore deduced that theasapogenol A is a hexahydroxy triterpenoid whose hydroxyls are the only oxygen functions in its chemical structure.

The nuclear magnetic resonance (NMR) spectrum (Table I) of the pentaacetate (IV) in comparison with barringtogenol C tetraacetate (VIII)[1] clearly demonstrates that theasapogenol A is expressed by a structure having one more primary carbinol function and one less tertiary methyl as compared with barringtogenol C. Thus, six tertiary methyls are shown as singlets at 9.16(3H), 9.10(6H), 9.00(3H), 8.94(3H) and 8.56τ(3H), while signals due to two acetylated primary carbinol methylenes are observed at 6.09, 6.29(1H each, AB quartet, J=11.6 cps) and 6.33τ(2H, broad singlet). In addition, five hydrogens are exhibited among the signals in the lower region: that is, an AB quartet (J=10 cps) at 4.48 and 4.59τ assignable to the *trans*-diaxial carbinyl hydrogens of the acetylated α-glycol at C-21 and C-22, a multiplet at 4.63τ due to the olefinic hydrogen at C-12, a quartet at 5.20τ (J=9.6 and 6.1 cps)[4] indicating a characteristic feature of C-3α axial hydrogen of triterpenoid sapogenol, and a multiplet at 5.81τ with a small half-band width (8.7 cps) ascribable to the hydrogen on the carbon (C-16) bearing axial hydroxyl.

As is shown in the NMR spectrum, the tetraacetate (III) carries two free hydroxyls, the one axial (probably at C-16) whose carbinyl hydrogen appearing at 5.85τ (as multiplet) and

1) Part I: I. Yosioka, T. Nishimura, A. Matsuda, and I. Kitagawa, *Chem. Pharm. Bull.* (Tokyo), **18**, 1610 (1970).
2) Location: *Toneyama, Toyonaka, Osaka.*
3) I. Yosioka, T. Nishimura, A. Matsuda, and I. Kitagawa, *Tetrahedron Letters*, **1966**, 5979 (preliminary report on the structure).
4) Observed as a quartet at 100 Mc, however usually shown as a triplet-like signal at 60 Mc.

Table I. The NMR Data given in τ Values (at 60 Mc, J Value in the Parenthesis is in cps)[a]

Compound	C-3H[b]	C-16H	C-21H	C-22H	C-23H$_2$	C-28H$_2$	C-12H[c]	lowest CH$_3$	Others
III[d]	5.25 (t.l)	5.85 (m.)	6.06 (d., 10)[e]	4.82 (d., 10)[e]	6.13, 6.33 (ABq., 11)	6.37 (br.s.)	4.68	8.62	
VIII[1]	5.45 (t.l)	5.77 (m.)	4.40, 4.54 (2H, ABq.,10)		—	6.30 (br.s.)	4.60	8.53	9.10(4 Me), 9.03(1 Me), 8.93(1 Me), 8.53(1 Me)
IV[d]	5.20 (q.,9.6 & 6.1)	5.81 (m.)	4.48, 4.59 (2H, ABq.,10)		6.09, 6.29 (ABq.,11.6)	6.33 (br.s.)	4.63	8.56	9.16(1 Me), 9.10(2 Me), 9.00(1 Me), 8.94(1 Me), 8.56 (1 Me)
V	5.16 (t.l)	—	4.41, 4.77 (2H, ABq.,11)		6.16 (br.s.)	5.50, 5.78 (ABq.,11)	4.48	8.74	
IX	5.18 (t.l)	5.74 (m.)	6.39 (s.)	4.7[f] (s.)	6.17[g]	5.90, 6.16 (ABq.,12)	4.7[f]	8.46	
XIII	5.16 (t.l)	—	6.72 (d.,10)	4.81 (d.,10)	6.14 (4H, br. s.)		4.56	8.72	4.22, 4.37 (ABq., 11): C–15H, C–16H
XIV	5.2[f]	—	4.57, 5.17 (2H, ABq., 10)		6.10, 6.22 (2H, ABq.,11) 6.20(2H, br. s.)		4.56	8.72	4.20, 4.34 (ABq., 11): C–15H, C-16H
XIX	6.5[f]	5.80 (m.)	4.44, 4.54 (2H, ABq.,10)		6.45 (br.s.)	6.30 (br.s.)	4.61	8.50 or 8.52[h]	
XX	6.4[f]	5.15 (m.)	4.40 (d.,11)	6.15 (d.,11)	6.45 (2H, br.s.) 6.39, 6.62 (2H, ABq.,11)		4.70	8.52 or 8.55[h]	
XXI[d]	6.6[f]	6.31 (t.,7)	4.90 (d.,8)	6.05 (d.,8)	6.54, 6.63 (ABq.,11)	6.04 (br.s.)	4.75	8.79	
XXXI	5.50 (t.l)	5.12 (m.)	4.25 (d.,10)	6.51 (d.,10)	—	6.20 (d.,11) 6,89 (d.,11)	4.73	8.56	4.88, 5.29(d. each, 6): –OCH$_2$O–
XXXII[d]	5.51 (q.,9 & 7)	4.14 (m.)	4.49 (d.,11)	6.50 (d.,11)	—	6.14 (d.,11) 6.83 (d.,11)	4.65	8.71	4.86, 5.31(d. each, 6): –OCH$_2$O–

a) br.s.=broad singlet, d.=doublet, m.=multiplet q.=quartet, s.=singlet, t.=triplet, t.l=triplet like
b) See the footnote 4).
c) All the signals were observed as multiplets.
d) measured at 100 Mc
e) The assignment was confirmed by the decoupling experiment.
f) Undefined signal due to the overlapping.
g) The center of the signal was taken, as the exact coupling constant was not obtained due to the overlapping.
h) Overlapped by the methyl signal of acetonide group.

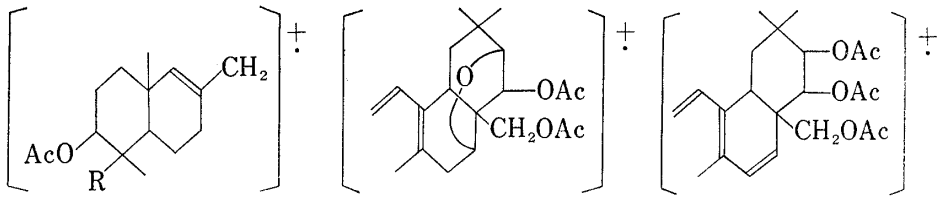
the other equatorial (probably at C-21, one of the α-glycol moiety) whose based hydrogen at 6.06τ (duoblet, J=10 cps) respectively. To elucidate the correlation of these two hydroxyls, the tetraacetate (III) was treated with phosphorus oxychloride in pyridine at reflux similarly as in barringtogenol C triacetate (VII),[1] and it was found that the product is in fact an anhydro-tetraacetate (IX), $C_{30}H_{44}O(OCOCH_3)_4$, (M^+: 656 m/e), mp 188—193°, on the basis of the NMR analysis analogously made as for barringtogenol D triacetate (X).[1] The essential characteristic is the fact that the signals predictable to hydrogens at C-21 and C-22 are observed as two singlets respectively at 6.39 and *ca.* 4.7τ and this supports to assume the chemical environment of rings D and E in the anhydro-tetraacetate (IX) being quite resembled to that of barringtogenol D triacetate. An anhydro-derivative (XI), $C_{30}H_{48}O_5$, mp 307—312°, prepared by alkaline hydrolysis of IX, was also obtainable by acid treatment (for instance, refluxing in ethanolic hydrogen chloride) although the yield was rather low under the latter condition.

Meanwhile, treatment of the tetraacetate (III) with thionyl chloride in pyridine at 30° yielded another dehydrated derivative (XIII), $C_{30}H_{44}O(OCOCH_3)_4$, mp 194—198°, as a sole

product. As clarified by the NMR spectral inspection, the dehydrated tetraacetate (XIII) lacks the axial secondary hydroxyl at C-16 and instead possesses one newly formed olefinic double bond, which is observed as an AB quartet at 4.22 and 4.37 τ (J=11 cps) assignable to two adjacent olefinic hydrogens (at C-15, -16). On similar treatment with thionyl chloride in pyridine, theasapogenol A pentaacetate (IV) afforded a dehydrated pentaacetate (XIV), $C_{30}H_{43}(OCOCH_3)_5$, mp 216—219°, which was likewise derived from the above tetraacetate (XIII) through the ordinary acetylation.

The observations so far point out that the partial structures around rings D and E of barringtogenol C(I) and theasapogenol A are quite alike.

The location of the second primary carbinol in theasapogenol A was first inferred mass spectroscopically. Thus, the comparison between mass numbers of two fragment peaks, the one at 307 m/e[5] in the mass spectrum of IX and the other at 249 m/e of barringtogenol C derivative (XV)[1] and both predictable respectively to the ions (a) and (b) deriving from rings A and B,[1,6] demonstrates that the additional primary carbinol function of theasapogenol A is allocated in either ring A or B.

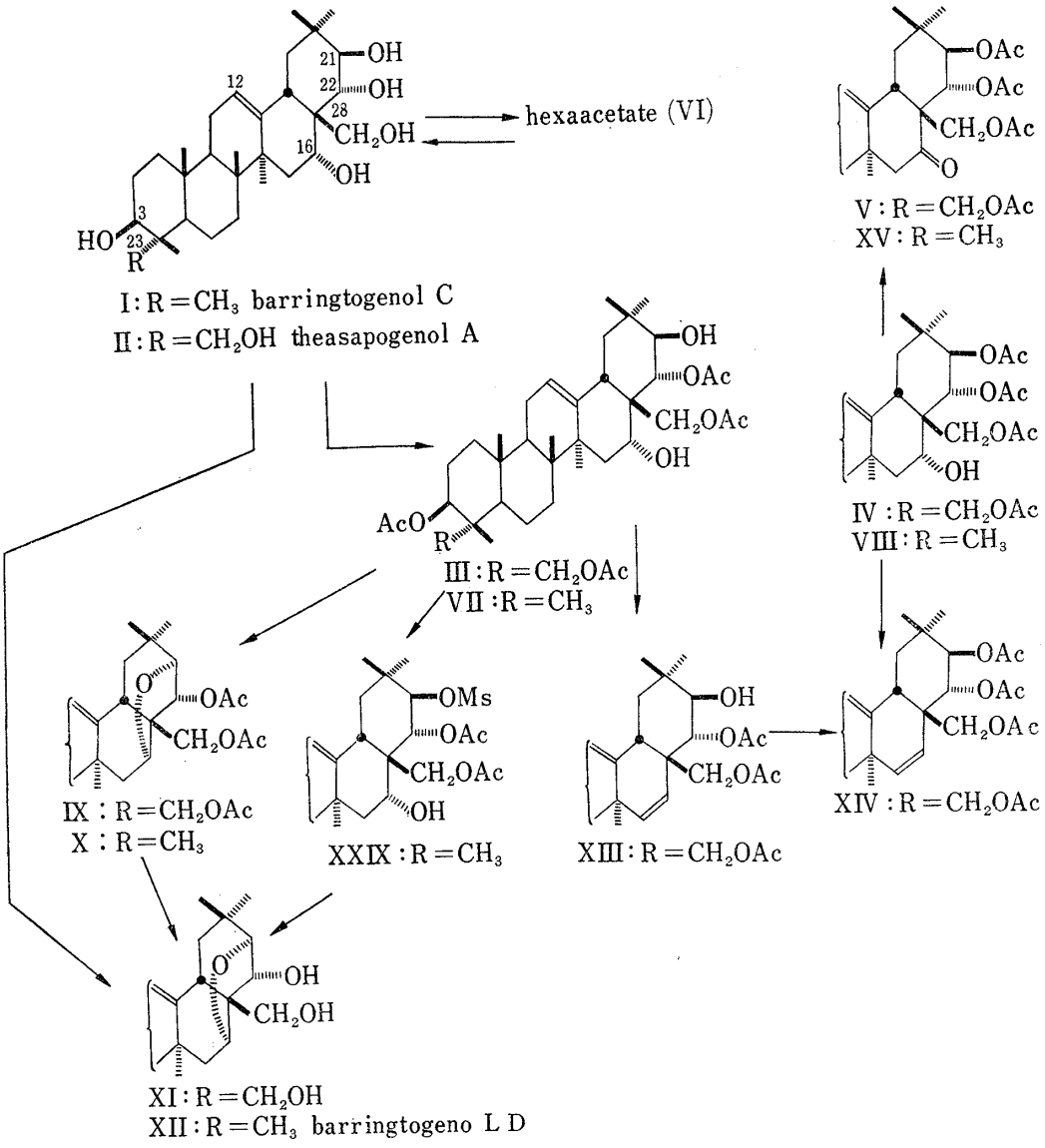


(a) R=CH_2OAc: 307 m/e
(b) R=CH_3: 249 m/e
(c) 348 m/e
(d) 390 m/e

Next, the location at C-23 is rationalized by the following evidence. Acetonide formation of theasapogenol A(II) with the aid of 2,2-dimethoxypropane and p-toluenesulfonic acid in acetone furnished a mixture of a monoacetonide (XVI), $C_{33}H_{54}O_6$, mp 299—301°, and two isomeric diacetonides, $C_{36}H_{58}O_6$, XVII (major), mp 256—258°, and XVIII, mp 277—280°, whose separation was achieved by alumina column chromatography. The elucidation of the acetonide linkage was made on the basis of the NMR data of the acetyl derivatives of these acetonides: triacetyl-monoacetonide (XIX), $C_{39}H_{60}O_9$, mp 234—235.5°, monoacetyl-diacetonide (XX), $C_{38}H_{60}O_7$, mp 254—257°, and diacetyl-diacetonide (XXI), $C_{40}H_{62}O_8$ (amorphous). The noteworthy matter to point out is that the hydroxyls at C-3 of all the acetonides are participating in the dioxane ring formation. All the signals due to C-3α hydrogens in XIX, XX, and XXI are found in the higher region around 6.4—6.6 τ, whereas the methylene hydrogens of the second primary carbinol functions are observed at around 6.4—6.6 τ, about 0.2—0.3 τ in the higher field as compared with those signals of III and IV (at 6.1—6.3 τ). The findings demonstrate that the second primary carbinol moiety of theasapogenol A is located in the proximity of C-3 hydroxyl being able for acetonide formation, *i.e.* either at C-23 (α-equatorial) or at C-24 (β-axial). The preference of the former position is based on the chemical shifts at 6.13, 6.33 τ and 6.09, 6.29 τ[7] of the AB quartet signals ascribed to the methylene hydrogens of the acetylated primary carbinol functions in III and IV. The structure II is consequently put forward for theasapogenol A. To substantiate the formulation including the carbon framework, the derivation from theasapogenol A (II) leading to barringtogenol C (I) was accomplished.

5) A significant fragment peak with the same mass number was also seen in case of XIV.
6) H. Budzikiewicz, J.M. Wilson, and C. Djerassi, *J. Am. Chem. Soc.*, **85**, 3688 (1963).
7) A. Gaudemer, J. Polonsky, and E. Wenkert, *Bull. Soc. Chim. France*, **1964**, 407.

Tritylation of theasapogenol A (II) with trityl chloride in pyridine yielded a mixture of 23-O- and 28-O-trityl derivatives and 23,28-di-O-trityl derivatives. Since the separation of two monotrityl derivatives was hardly attained (even by thin-layer chromatography (TLC)), the mixture was acetylated with acetic anhydride and pyridine under heating and separated by preparative TLC to afford 28-O-trityl pentaacetate (XXII, with lower *Rf* value), $C_{59}H_{74}O_{11}$, mp 213—217°, anddesired 23-O-trityl pentaacetate (XXIII), $C_{59}H_{74}O_{11}$, mp 246—248°. The respective location of the trityl functions in XXII and XXIII was confirmed by preparing XXII from theasapogenol A 3,23-acetonide (XVI) through the following sequence. Tritylation of the monoacetonide (XVI) gave 28-O-trityl monoacetonide (XXIV), $C_{52}H_{68}O_6$, 177—182°, the acetonide bonding of which was then cleaved by treatment with 1% methanolic hydrogen chloride giving 28-O-trityltheasapogenol A (XXV), $C_{49}H_{64}O_9$, mp 193—197°. A fully acetylated derivative of the latter was found identical (mixed mp, IR, and TLC) with above XXII, thus determining the location of the trityl functions in XXII and XXIII. Therefore, the acetate aiming at barringtogenol C is the one (XXIII) with higher *Rf* value. Treatment of XXIII with aqueous acetic acid on a boiling water-bath followed by chromium trioxide-pyridine oxidation, afforded two products. The one with lower *Rf* value on TLC, exhibiting positive Zimmermann color test and IR absorption band (in CCl_4) at 1708 cm^{-1} of six-membered carbonyl, is assigned structure XXVI, which



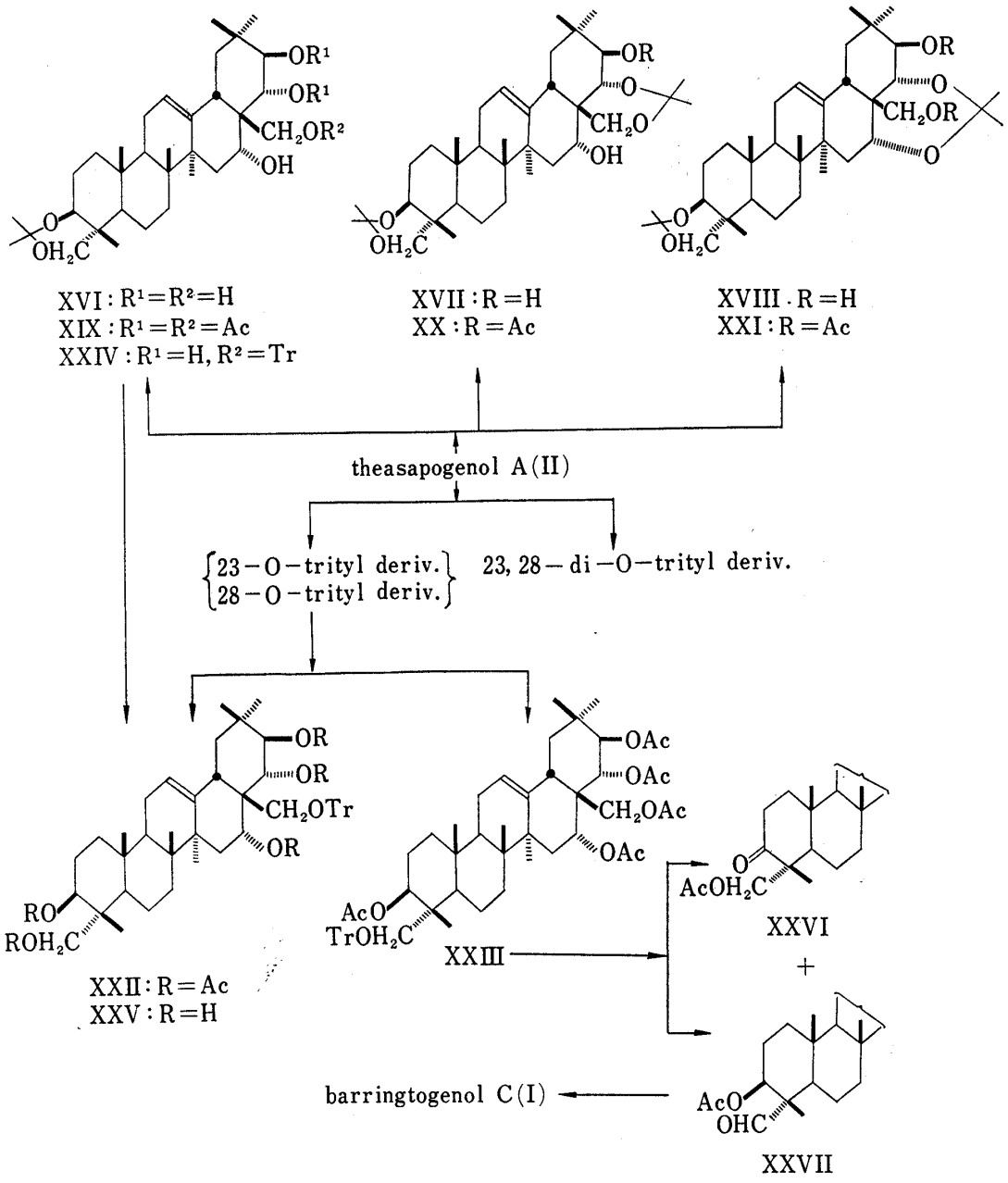


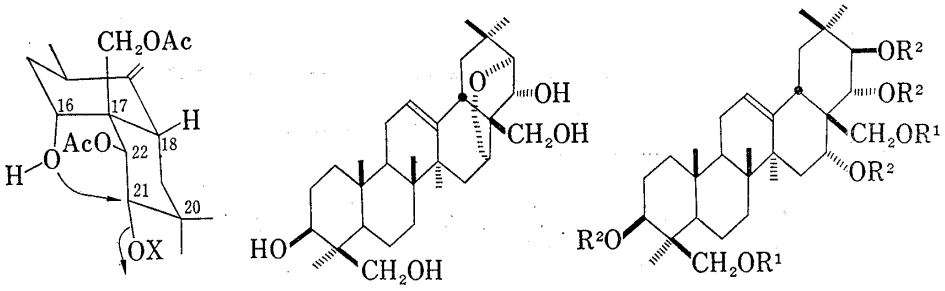
Chart 1

probably was derived *via* acetyl migration (C-3 OH→C-23 OH)[8] during the detritylation procedure and successive oxidation of the resulted C-3 hydroxyl. The other product having higher *Rf* value shows an aldehydic C–H stretching absorption band at 2720 cm^{-1} in its IR spectrum (CCl_4) and is expressed as XXVII, which was then subjected to Huang–Minlon reduction giving a product of melting at 277—282°. The final product was found identical with barringtogenol C (I) in all respects (mixed mp, IR, and TLC), thus concluding that theasapogenol A is assigned the structure, 3β,16α,21β,22α,23,28-hexahydroxy-olean-12-ene (II).

As was discussed in the preceding[1] and present papers, the oxide ring formation between C-21 and C-16 has been playing an important role in the structure elucidation of barringotgenol C (I) and theasapogenol A (II). Therefore, some additional examination in this connection have been performed are given below.

8) *a*) J. Wicha and E. Caspi, *Canad. J. Chem.*, **45**, 707 (1967); *b*) T. Kubota, F. Tonami, and H. Hinoh, *Tetrahedron Letters*, **1966**, 701.

Anhydro-theasapogenol A (XI) was prepared by refluxing theasapogenol A in ethanolic hydrogen chloride similarly as in case of aescigenin (XXVIII)[9] and barringtogenol D (XII).[1,10] On treatment with phosphorus oxychloride in pyridine, barringtogenol C triacetate (VII)[1] and theasapogenol A tetraacetate (III) yielded the anhydrotriacetate (X)[1] and the anhydrotetraacetate (IX) respectively in the excellent yields (—88%). Moreover, 21-O-mesyl derivative (XXIX), $C_{37}H_{58}O_{10}S$, mp 156—158°, prepared from VII furnished barringtogenol D (XII) readily upon $LiAlH_4$ reduction (at room temp. in ether) instead of 21-desoxy-barringtogenol C. Assuming the intramolecular S_{N2} type reaction mechanism as depicted in Fig. 1 (X=$POCl_2$, Ms), the β-equatorial orientation of C-210H in III is reasonably understood.



XXVIII: aescigenin

XXXIII: $R^1=R^2=H$ protoaescigenin
XXXIV: $R^1=Tr, R^2=Ac$

Fig. 1

It has been reported however on B-norcoprostane derivatives by Goto[11] in 1960 that the oxide derivative (1) was prepared either from (2) (49% yield) and (3) (21%) under heating with benzenesulfonic acid in pyridine or from (4) (10%) by heating with pyridine only, although the yields were rather low as compared with the present case. The decision based only on the reaction mechanism (Fig. 1) seem inadequate to eliminate C-21α axial hydroxyl assignment for III. Yet, since the S_{N1} type mechanism could not be excluded in case of B-norcoprostane derivatives, the conclusion giving the C-21β orientation for III appears more probable even on the basis of the mechanism.

On the other hand, Gillis and Beck reported[12] the tetrahydrofuran ring formation from 1,4-diol by heating in dimethylsulfoxide (DMSO). Since two hydroxyls at C-21 and C-16 of barringtogenol C (I) are composing 1,4-diol moiety, the reaction was undertaken. Upon heating in anhydrous DMSO (oil bath temp., 150—160°) for 8 hours, I furnished two products in 30% yield. The major one (20%) was found identical with barringtogenol D (XII) as expected, while the minor one (10%) having higher *Rf* value on TLC was found a new dioxane derivative and is now expressed as XXX based on the following data. Thus, the dioxane derivative (XXX), $C_{31}H_{50}O_5$, mp 267.5—269°, exhibits IR absorption bands at 3460 and 3410 cm^{-1} (OH) and resulted I easily on heating in ethanolic hydrogen chloride, which suggests that XXX retains the carbon skeleton of I. Acetylation of XXX with acetic anhydride and pyridine at room temperature afforded a diacetate (XXXI), $C_{31}H_{48}O_3(OCOCH_3)_2$, mp 307—313°, whereas the acetylation under heating with acetic anhydride and anhydrous sodium acetate gave a triacetate (XXXII), $C_{31}H_{47}O_2(OCOCH_3)_3$, mp 281—283°, which lacks free hydroxyl as revealed by its IR spectrum. It is therefore deduced that amoung the initial five hydroxyls of I two are blocked in XXX. As disclosed by the NMR analysis of

9) *a*) For the structure see: I. Yosioka, T. Nishimura, A. Matsuda, K. Imai, and I. Kitagawa, *Tetrahedron Letters*, **1967**, 637, and the literatures cited therein. *b*) R. Kuhn and I. Loew, *Ann.*, **669**, 183 (1963).
10) A.K. Barua and P. Chakrabarti, *Tetrahedron*, **21**, 381 (1965).
11) T. Goto, *J. Am. Chem. Soc.*, **82**, 2005 (1960).
12) B.T. Gillis and P.E. Beck, *J. Org. Chem.*, **28**, 1388 (1963).

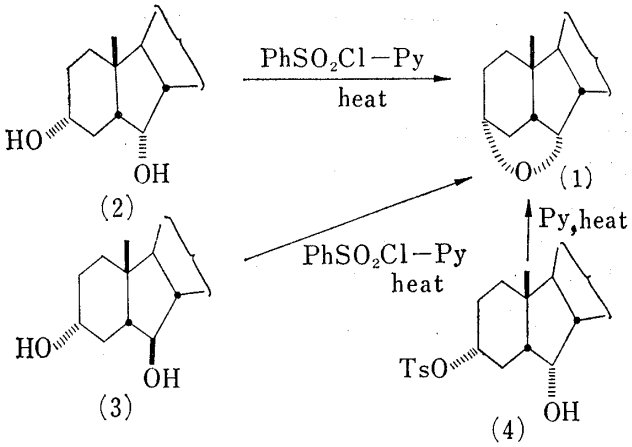


Chart 2

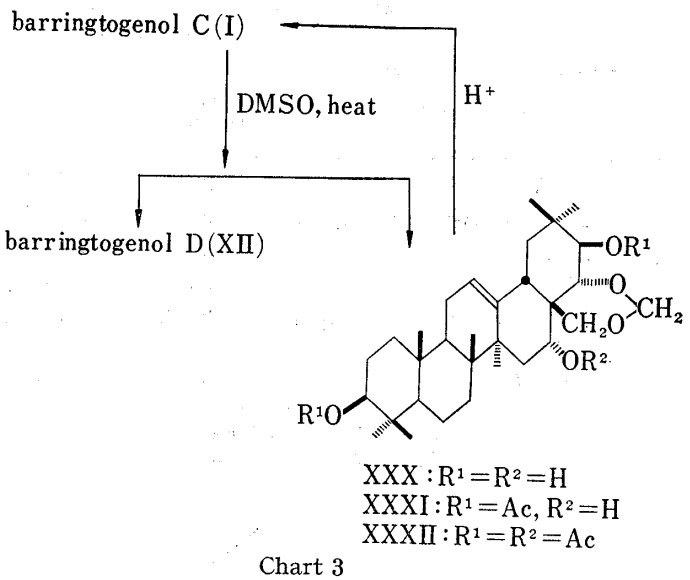


Chart 3

XXXI and XXXII (Table I): C-22H at 6.51 τ (doublet, J=11 cps) and C-28H_2 at 6.20 and 6.89 τ (d. each, J=11) in XXXI; C-22H at 6.50 τ (d., J=11) and C-28H_2 at 6.14 and 6.83 τ (d., each, J=11) in XXXII, two hydroxyls blocked are one of α-glycolic hydroxyls and the primary carbinol. Furthermore, a significant feature in the NMR spectra of these two acetates, XXXI and XXXII, is that both spectra show the new AB quartet signals respectively at 4.88 and 5.29 τ (2H) (XXXI), and 4.86 and 5.31 τ (2H) (XXXII) which are predictable to the hydrogens of methylene attached by two oxygen functions and in addition it is of note to mention that the signals due to C-16H are appearing in the downfield: at 5.12 τ (multiplet) in XXXI and at 4.14 τ (m.) in XXXII, which are comparable with the findings in case of the 22,28-acetonide derivatives (for instance, XX).[13] These observations are in accordance with the formulation XXX for the dioxane derivative, in which two hydroxyls at C-22 and C-28 are linked by a methylene bridge. The ready regeneration of I from XXX with the acid treatment also corroborates the presentation. It follows that the dioxane compound (XXX) was resulted by a reaction between I and formaldehyde, which has been known to occur in the reaction with DMSO under the thermal condition.[14] The favored 22,28-acetonide (XVII) formation in case of theasapogenol A as described above is also consistent with the dioxane ring constructed with C-22 and C-28 hydroxyls in XXX.

During the course of the investigation presented above, it has been noticed that a trityl function induced at C-23 or C-28 primary carbinol exhibits distinct shielding effect on a tertiary methyl group nearby, which may be of use to delineate the location of the primary carbinol tritylated and/or the stereochemical environment in the proximity, and hence is briefly summarized below.

All the tertiary methyl signals of the derivatives described in this and the preceding[1] papers are found below 9.2 τ, while a compound tritylated at C-23 or C-28 shows one C-methyl signal observed in the upfield region as given in Table II. A trityl group at C-28 primary carbinol is giving rise to more marked shielding effect than the one at C-23. To explain the anisotropic effect of the trityl function, the depictions, (A)—(D) (Fig. 2), based on the

13) Deshielded by a neighboring oxygen function of the dioxane ring. The subject will be discussed in more detail in the forthcoming paper (I. Yosioka, *et al.*, to be published). *cf.* *a*) ref. 1); *b*) T. Hayashi, C. Koshiro, T. Adachi, I. Yosioka, and I. Kitagawa, *Tetrahedron Letters*, **1967**, 2353; *c*) I. Yosioka, I. Kitagawa, T. Hino, A. Matsuda, and Y. Nakagawa, *Chem. Pharm. Bull.* (Tokyo), **16**, 190 (1968).

14) *a*) V.J. Traynelis and W.L. Hergenrother, *J. Org. Chem.*, **29**, 221 (1964); *b*) W.H.W. Lunn, *J. Org. Chem.*, **30**, 2925 (1965).

Table II. Methyl Signal given in τ Value[a] (Number in Parenthesis implies the Number of Methyl included)

Compound	Position of trityl group	
XXIV	28	**9.54**(1), 9.12(1), 9.02(1), 8.99(1), 8.91(1), 8.60(or 8.52(1))[b]
28-O-Trityl-barringtogenol C	28	**9.53**(1), 9.21(1), 9.14(1), 9.09(1), 9.01(2), 8.63(1)
XXV	28	**9.68**(1), 9.17(1), 9.05(1), 9.03(1), 8.73(2)
XXIII	23	**9.39**(1), 9.11(1), 9.04(2), 8.92(1), 8.61(1)
23,28-Di-O-tritylteasapogenol A tetraacetate	23, 28	**9.72**(1), **9.41**(1), 9.08(1), 9.04(1), 8.72(1), 8.68(1)
XXXIV	24, 28	**9.85**(1), **9.63**(1), 9.08(1), 8.86(1), 8.77(2)

a) all signlets Gothic denotes the shielded methyl
b) indistinguishable from the acetonide methyl

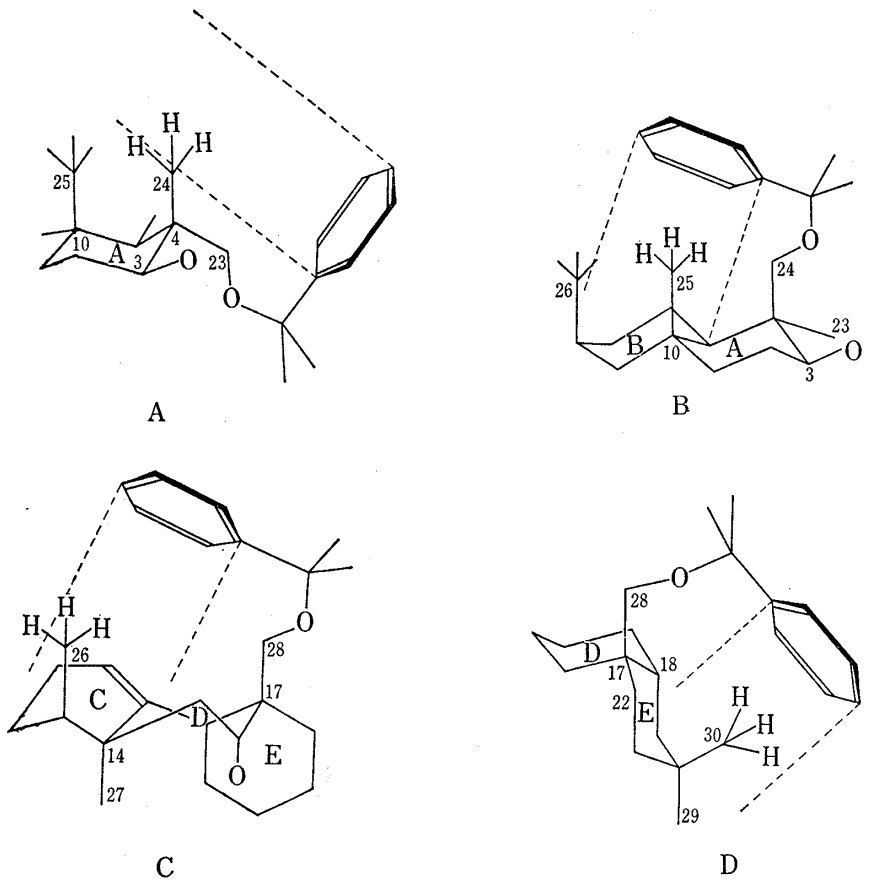


Fig. 2. Only One Benzene Ring of Trityl Function is depicted in Each Figure

Dreiding model may be pertinent.[15] Thus, in the solution, the trityl (=Tr) group is expected rotating freely around Tr–O bond unless steric obstruction existed otherwise. Moreover, in the whole system $\geqslant C–CH_2–O–Tr$, the similar rotations as well are anticipated around two single bonds: $\geqslant C–CH_2$ and $CH_2–O$. Provided that the preferred conformation between C–C bond in the triterpenoid carbon skeleton (*e.g.* $C_{(4)}–C_{(3)}$ and $C_{(4)}–C_{(5)}$ bonds in Fig. 2 (A)) and $CH_2–O$ bond (*e.g.* $C_{(23)}H_2–O$ bond in Fig. 2 (A)) is skew form rather than eclipsed, the depictions above are delivered as the ones of possibilities. Fig. 2 (A) demonstrates that

15) A kind of shielding cone with hollow due to the anisotropy caused by benzene rings rotating around Tr-O axis is presumed.

the trityl function inserted at C-23 is causing anisotropic effect upon 24-CH_3, whereas in Fig. 2 (B) 25-CH_3 is involved in the shielding cone of the trityl group attached to C-24 primary carbinol. In case of the trityl group at C-28 primary carbinol, two possibilities are considered. Although the decisive conclusion could not be made, Fig. 2 (C) explains shielded 26-CH_3, while Fig. 2 (D) reasons the shielding effect occurring upon 30-CH_3 (where $C_{(28)}H_2$–O and $C_{(17)}$–$C_{(22)}$ bonds are close to the eclipsed conformation). The magnitude of the upfield shifting of the methyl signals is estimated on the basis of the geometry: spacial situation of CH_3 group in the conical shielding zone brought out by the rotating trityl group and the distance between CH_3 and the trityl function. Examination using the Dreiding model in conjunction with the above consideration reveals that 24-O-trityl group is expected to cause the most significant shielding effect upon CH_3 group (25-CH_3 in this case) as compared with 23- and 28-O-trityl groups. In fact, 24,28-di-O-trityl-protoaescigenin tetraacetate (XXXIV) synthesized from protoaescigenin (XXXIII),[9a] exhibits remarkably shielded two methyl signals as expected at 9.85 and 9.63 τ (3H each, singlet) (Table II), the former assignable to 25-CH_3 and the latter to 26-CH_3 or 30-CH_3.

The details of the study on the other seeds sapogenols of *Thea sinensis* L. designated theasapogenol E,[16] dihydropriverogenin A (=camelliagenin A, theasapogenol D,[17] and camelliagenin C (=theasapogenol C[17]) will be reported in our forthcoming paper.

Experimental[18]

Theasapogenol A (II)——Theasapogenol A was obtained by alumina column chromatography of the crude sapogenol mixture prepared from seeds saponin of *Thea sinensis* L. as described in the preceding paper.[1] Analytical sample of theasapogenol A was prepared by alkaline hydrolysis of IV. A solution of IV (44 mg) in 5% KOH–MeOH (3 ml) was refluxed for 1.5 hr, treated as usual, and recrystallized twice from aq. EtOH giving colorless needles of theasapogenol A (II) (15 mg), mp 301—303°, $[\alpha]_D$ +14° (c=0.51, pyridine). *Anal.* Calcd. for $C_{30}H_{50}O_6$: C, 71.11; H, 9.95. Found: C, 71.29; H, 9.91. IR ν_{max}^{KBr} cm^{-1}: 3356 (OH), 1639 (C=C).

3,22,23,28-Tetra-O-acetyl- and 3,21,22,23,28-Penta-O-acetyl-theasapogenol A (III and IV)——a) A solution of theasapogenol A (II) (1 g) in pyridine (100 ml)–Ac_2O (25 ml) was kept at 0° for 21 hr, and worked up in a usual manner affording a crude product (1.23 g), which was chromatographed on silicic acid (Mallinckrodt, 25 g) eluting with $CHCl_3$ and $CHCl_3$–MeOH (98:2). The product (256 mg) from the former eluate gave IV, while the latter (493 mg) yielded III.

b) Acetylation of theasapogenol A (II) (129 mg) with pyridine (12 ml) and Ac_2O (3 ml) at room temperature for 2 overnights, followed by silicic acid chromatography gave III (113 mg) (from $CHCl_3$–MeOH (99:1) eluate). Analytical sample of III was given by recrystallization with ether–*n*-hexane, mp 225—228°, $[\alpha]_D$ +18° (c=1.02, $CHCl_3$). *Anal.* Calcd. for $C_{38}H_{58}O_{10}$: C, 67.63; H, 8.66. Found: C, 67.37; H, 8.50. IR ν_{max}^{KBr} cm^{-1}: 3413 (OH), 1733, 1241 ($OCOCH_3$). IV, recrystallized with EtOH–*n*-hexane and then with aq. EtOH, mp 174—178°, $[\alpha]_D$ +29° (c=1.05, $CHCl_3$). *Anal.* Calcd. for $C_{40}H_{60}O_{11}$: C, 67.01; H, 8.43. Found: C, 66.73; H, 8.25. IR ν_{max}^{KBr} cm^{-1}: 3472 (OH), 1742, 1242 ($OCOCH_3$).

Oxidation of IV giving V——To a solution of IV (71 mg) in pyridine (2 ml) was added pyridine-CrO_3 complex (1 ml-100 mg) under ice-cooling and the total mixture was stirred at r.t. for 8 hr, treated as usual. The crude product (67 mg) was purified by passing through a short column of alumina (Woelm, neutral, grade I, 500 mg) using benzene and $CHCl_3$. The eluate was recrystallized with EtOH and then with MeOH giving colorless needles of V, mp 264—266°, $[\alpha]_D$ −30° (c=0.62, $CHCl_3$). *Anal.* Calcd. for $C_{40}H_{58}O_{11}$: C, 67.21; H, 8.18. Found: C, 67.28; H, 8.06. IR (grating) ν_{max}^{KBr} cm^{-1}: 1751, 1245 ($OCOCH_3$), 1725 (shoulder) (CO), no hydroxyl.

3,16,21,22,23,28-Hexa-O-acetyl-theasapogenol A (VI)——A mixture of theasapogenol A (308 mg) in pyridine (0.7 ml) and Ac_2O (7 ml) was refluxed in an oil bath for 4 hr, worked up as usual. Purification by

16) I. Yosioka, A. Matsuda, T. Nishimura, and I. Kitagawa, *Chem. Ind.* (London), **1966**, 2202.
17) I. Yosioka, T. Nishimura, N. Watani, and I. Kitagawa, *Tetrahedron Letters*, **1967**, 5343.
18) Melting points were taken on the Yanagimoto Micromelting-point Apparatus (a hot stage type) and the Ishii Highmelting-point Apparatus (a capillary type) and recorded as read. Specific rotations were measured with the Rex Photoelectric Polarimeter NEP-2 (l=1 dm), the IR spectra were taken with the Hitachi EPI-2 and EPI-S2 Spectrophotometer, the NMR spectra were with the Hitachi–Perkin Elmer H-60 NMR Spectrometer and the Varian HA-100 Spectrometer (tetramethylsilane as the internal standard), and the Mass spectra with the Hitachi RMU-6D Spectrometer. TLC plates were developed by spraying 1% Ce $(SO_4)_2$/10% H_2SO_4 solution followed by heating.

preparative TLC (Camag D-5, $CHCl_3$–AcOEt (10:2)) of the crude product gave VI (313 mg), which was recrystallized with benzene–petr. ether and then benzene–*n*-hexane. mp 134—135° (sinter at 129°). *Anal.* Calcd. for $C_{42}H_{62}O_{12}$: C, 66.46; H, 8.23. Found: C, 66.13; H, 8.15. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1747, 1244, 1227 ($OCOCH_3$), no hydroxyl.

16,21-Anhydro-3,22,23,28-tetra-O-acetyl-theasapogenol A (IX)——A pyridine solution (15 ml) of III (311 mg) was added with $POCl_3$ (1 ml), refluxed in an oil bath for 2 hr, and treated in a usual manner. After benzene solution of the product (299 mg) was passed through a short column of alumina (Woelm), the eluate was dissolved in petr. ether to remove insolubilities. The petr. ether solution gave colorless crystals (221 mg) on standing. From the mother layer, additional crop (45 mg) was obtained by preparative TLC (Camag D-5, $CHCl_3$–AcOEt (6:1)) followed by recrystallization with aq. MeOH. Further recrystallization of the combined crystals with *n*-hexane yielded IX of melting at 188—193°. *Anal.* Calcd. for $C_{38}H_{56}O_9$: C, 69.48; H, 8.59. Found: C, 69.48; H, 8.57. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1750, 1238 ($OCOCH_3$). Mass Spectrum *m/e* (relative peak intensity, assignment): 656 (2, M^+), 596 (7, M^+-AcOH), 536 (7, M^+-2AcOH), 476 (2, M^+-3AcOH), 348 (71, c), 307 (5, a), 288 (59, c-AcOH), 228 (100, c-2AcOH), 215 (79, c-AcOH-CH_2OAc), 187 (46, a-2AcOH).

16,21-Anhydro-theasapogenol A (XI)——a) From IX: Refluxing (1 hr) a solution of IX (221 mg) in 1% KOH–MeOH (30 ml) yielded a crude product (157 mg), which upon recrystallization with $CHCl_3$–MeOH gave colorless needles (145 mg). Further recrystallization with AcOEt–MeOH gave XI, mp 303—311°, $[\alpha]_D$ +58° (c=1.05, $CHCl_3$). *Anal.* Calcd. for $C_{30}H_{48}O_5$: C, 73.73; H, 9.90. Found: C, 73.83; H, 9.83. IR ν_{max}^{KBr} cm^{-1}: 3389 (OH), 1631 (C=C).

b) From Theasapogenol A (II): A suspension of II (1 g) in EtOH (40 ml) and 6N HCl (40 ml) was refluxed 1 hr. After removing the unchanged II (469 mg) by filtration, the filtrate was concentrated under reduced pressure to a half-volume and diluted with water to give a precipitate (464 mg). The product was chromatographed on alumina (Woelm, 33 g). The eluates with $CHCl_3$–MeOH (97:3—95:5) gave 72 mg of XI and successive eluates with $CHCl_3$–MeOH (50:50) and MeOH recovered theasapogenol A (II) (219 mg). XI thus obtained here was recrystallized with $CHCl_3$–MeOH giving fine needles (31 mg) of mp 307—312°, which was identified with XI obtained from IX by mixed mp, IR (KBr), and TLC.

16(15)-Anhydro-3,22,23,28-tetra-O-acetyl-theasapogenol A (XIII)——To an ice-cooled solution of III (174 mg) in anhydrous pyridine (15 ml) was added $SOCl_2$ (0.5 ml) and the total mixture was let stand at 12—14° for 2 days. Since checking by TLC disclosed that most of the starting compound was unchanged, the mixture was kept at 30° for further 19 hr. After working up in a usual manner, the product was purified by using charcoal (EtOH as solvent), recrystallized from EtOH–*n*-hexane to give XIII, mp 194—198°, $[\alpha]_D$ +23° (c=1.03, $CHCl_3$). *Anal.* Calcd. for $C_{38}H_{56}O_9$: C, 69.48; H, 8.59. Found: C, 69.22; H, 8.67. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3550 (OH), 1747, 1240 ($OCOCH_3$).

16(15)-Anhydro-3,21,22,23,28-penta-O-acetyl-theasapogenol A (XIV)——a) From IV: A solution of IV (100 mg) in pyridine (5 ml) was treated with $SOCl_2$ (1 ml), let stand at r.t. for 2 days, and treated as usual. After passing through a short alumina (Woelm) column in benzene solution, the product was crystallized from *n*-hexane giving colorless needles (65 mg). Subsequent recrystallization with ether–*n*-hexane and then with aq. EtOH furnished XIV, mp 216—219°. *Anal.* Calcd. for $C_{40}H_{58}O_{10}$: C, 68.74; H, 8.37. Found: C, 68.76; H, 8.25. IR ν_{max}^{KBr} cm^{-1}: 1742, 1237 ($OCOCH_3$). Mass Spectrum *m/e* (relative peak intensity, assignment): 698 (M^+), 638 (15, M^+-AcOH), 578 (7, M^+-2AcOH), 518 (5, M^+-3AcOH), 390 (16, d), 307 (42, a), 270 (38, d-2AcOH), 257 (52, d-AcOH-CH_2OAc), 247 (27, a-AcOH), 215 (69, d-AcOH-CH_2OAc-CH_2CO), 197 (100, d-2AcOH-CH_2OAc), 187 (47, a-2AcOH).

b) From XIII: Acetylation of XIII (5 mg) with pyridine (0.5 mg)–Ac_2O (0.3 ml) by keeping at r.t. for 3 days yielded a product, which was identical with XIV obtained above by TLC (Camag D-5, $CHCl_3$ and benzene–MeOH (40:1)).

Acetonide Derivatives, XVI, XVII, and XVIII, from Theasapogenol A (II)——A suspension of II (500 mg) in dry acetone (150 ml) containing 2,2-dimethoxypropane (1 ml) and *p*-TsOH·H_2O (150 mg) was kept stirring at r.t. After 1.5 hr, the mixture turned semitransparent, and after 3 hr, it was noticed that only a small amount of II remained as the insolubility. After 4 hr, the mixture was treated with pyridine (1 ml) and unreacted II (11 mg) was recovered by filtration. Evaporation of the solvent under reduced pressure followed by dilution with water and usual treatment as described in the preceding paper,[1] gave a crude product (566 mg). Benzene soluble portion of the crude product was then chromatographed on alumina (Merck, standard, 30 g) developing with i) benzene–$CHCl_3$ (2:1), ii) $CHCl_3$, iii) $CHCl_3$–MeOH (99.7:0.3), iv) $CHCl_3$–MeOH (98:2—97:3), and v) $CHCl_3$–MeOH (80:20). The eluates from i) and ii) gave XVII (276 mg). XVIII (71 mg) was obtained from iii). Fractions from iv) afforded XVI (63 mg after recrystallization with EtOH–*n*-hexane and then with acetone). From the eluates of v), theasapogenol A was recovered (totally 52 mg). Analytical sample of XVI was obtained by recrystallization with EtOH–*n*-hexane as colorless needles, mp 299—301°, $[\alpha]_D$ +27° (c=1.0, dioxane). *Anal.* Calcd. for $C_{33}H_{54}O_6$: C, 72.49; H, 9.96. Found: C, 72.40; H, 10.13. IR ν_{max}^{KBr} cm^{-1}: 3367 (OH), 1629 (C=C).

Analytical sample of XVII was prepared by further TLC separation (Merck, aluminum oxide G, $CHCl_3$–MeOH (100:1)) followed by recrystallization with ether–*n*-hexane and then with ether–petr. ether, giving crystals of melting at 256—258°. *Anal.* Calcd. for $C_{36}H_{58}O_6 \cdot \frac{1}{2}H_2O$: C, 71.48; H, 10.00. Found: C, 71.53; H, 9.95.

Further recrystallization with acetone–*n*-hexane gave analytical sample of XVIII, mp 277—280°, $[\alpha]_D$ −7° (c=1.0, $CHCl_3$). *Anal.* Calcd. for $C_{36}H_{58}O_6$: C, 73.68; H, 9.96. Found: C, 73.61; H, 9.79.

Acetylation of XVI, XVII, and XVIII yielding XIX, XX and XXI——a) Acetylation of XVI (60 mg) with pyridine (5 ml) and Ac_2O (2 ml) by keeping at 23° for 63 hr, followed by usual treatment furnished a crude product (67 mg), which was purified by alumina (Merck, neutral, 1.5 g) column chromatography developing with benzene and benzene–$CHCl_3$ (9:1). Most of XIX was eluted out with benzene. Recrystallization with ether–*n*-hexane and then with acetone–*n*-hexane gave colorless needles of XIX, mp 234—235.5°, $[\alpha]_D$ +15° (c=1.04, $CHCl_3$). *Anal.* Calcd. for $C_{39}H_{60}O_9$: C, 69.61; H, 8.99. Found: C, 69.31; H, 8.79. IR ν_{max}^{KBr} cm^{-1}: 3448 (OH), 1739, 1250 ($OCOCH_3$).

b) Acetylation (at 35°, 22 hr) of XVII (128 mg) with pyridine (5 ml) and Ac_2O (3 ml) and recrystallization (twice) with aq. EtOH gave the acetate (91 mg), which was further recrystallized with ether–petr. ether giving XX, mp 254—257° (If the temperature was raised rapidly, the sample melted once around 175—185°, and resolidified above 185°). *Anal.* Calcd. for $C_{38}H_{60}O_7$: C, 72.57; H, 9.62. Found: C, 72.21; H, 9.58.

c) XVIII (71 mg) was treated with pyridine (0.3 ml) and Ac_2O (3 ml) by refluxing for 2 hr. After treating with additional pyridine (3 ml) the mixture was poured into ice–water, worked up in a usual manner. Purification of the crude product by preparative TLC (Merck, aluminum oxide G, $CHCl_3$–MeOH (100:1—100:0.5) furnished an amorphous product (56 mg). Although the product showed single spot on TLC using various solvent systems, its crystallization was without success. *Anal.* Calcd. for $C_{40}H_{62}O_8$: C, 71.61; H, 9.32. Found: C, 71.31; H, 9.28. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1742, 1234 ($OCOCH_3$), no hydroxyl.

Tritylation of Theasapogenol A (II) followed by Acetylation yielding XXII and XXIII——a) Tritylation of II: To a solution of II (150 mg) in dry pyridine (3 ml) was added trityl chloride (125 mg) and the mixture was refluxed for 30 min, poured into ice–water, and the resulted precipitate was collected by filtration and dried. Treatment of the crude product with acetone recovered II (21 mg) as the insolubility and the acetone soluble part was separated by preparative TLC (Merck HF_{254}, $CHCl_3$–MeOH (10:1)) giving 23,28-di-O-trityl-theasapogenol A (120 mg), and a mixture (94 mg) of 23-O- and 28-O-trityl-theasapogenol A. The former was further purified by preparative TLC (Merck, aluminum oxide H, $CHCl_3$), recrystallized from MeOH to afford an analytical sample of 23,28-di-O-trityl-theasapogenol A, mp 188—191°, $[\alpha]_D$ −18° (c=1.04, $CHCl_3$). *Anal.* Calcd. for $C_{68}H_{78}O_6$: C, 82.38: H, 7.93. Found: C, 82.11; H, 7.92.

The sample of 23,28-di-O-trityl-theasapogenol A tetraacetate for NMR (Table II) was prepared by refluxing (4 hr) a mixture of 23,28-di-O-trityl-theasapogenol A (101 mg) in pyridine (0.2 ml) and Ac_2O (2 ml), followed by preparative TLC separation (Camag D-5, $CHCl_3$).

b) Acetylation of the Mixture of 23-O-Trityl- and 28-O-Trityl-theasapogenol A: A solution of the mixture (94 mg) obtained in pyridine (0.3 ml) and Ac_2O (3 ml) was refluxed for 4 hr. The crude product was purified by TLC (Merck HF_{254}, $CHCl_3$–EtOAc (10:1)). The product (39 mg) having lower *Rf* value was further purified through silica gel (Merck, 2 g) column chromatography and recrystallized with aq. EtOH repeatedly, thus giving crystals of melting at 213—217°, which was found identical with XXII prepared from XXIV as described below. The other product (49 mg) with higher *Rf* value was recrystallized with aq. EtOH, and 95% EtOH to give fine plates (XXIII), mp 246—248°. *Anal.* Calcd. for $C_{59}H_{74}O_{11}$: C, 73.87; H, 7.78. Found: C, 73.71; H, 7.72.

Tritylation of Monoacetonide (XVI) giving XXIV——A mixture of monoacetonide (XVI) (550 mg) in pyridine (50 ml) and trityl chloride (2.2 g) was refluxed for 5 hr, poured into ice–water and the resulting oily product was extracted with ether. The extract was next chromatographed on alumina (Merck, standard, 75 g) developing with $CHCl_3$. The $CHCl_3$ eluate gave XXIV (445 mg). Analytical sample of XXIV was prepared by TLC separation (Merck HF_{254}, $CHCl_3$–MeOH (10:1) and (3:1)), followed by recrystallization with acetone–*n*-hexane and with benzene–EtOH (containing trace amount of pyridine). XXIV, mp 177—182°, $[\alpha]_D$ −19° (c=0.49, $CHCl_3$). *Anal.* Calcd. for $C_{52}H_{68}O_6$: C, 79.15; H, 8.69. Found: C, 78.89; H, 8.69. IR ν_{max}^{KBr} cm^{-1}: 3425 (OH), 705 (arom. CH).

28-O-Trityl-theasapogenol A (XXV) and Its Pentaacetate (XXII)——a) To a solution of XXIV (58 mg) in MeOH (2 ml) was added 5% HCl–MeOH (0.5 ml) and the total mixture was stirred at r.t. 3 min and treated with ice–water. The precipitate was filtered and purified by TLC (Merck HF_{254}, $CHCl_3$–MeOH (10:1)), yielding 37 mg of XXV, which was recrystallized with acetone–benzene and then with EtOH-*n*-hexane to furnish colorless fine needles of melting at 193—197°, $[\alpha]_D$ −12° (c=1.00, $CHCl_3$). *Anal.* Calcd. for $C_{49}H_{64}O_6$: C, 78.57; H, 8.61. Found: C, 78.20; H, 8.65. IR ν_{max}^{KBr} cm^{-1}: 3413 (OH), 704 (arom. CH).

b) Acetylation of XXV (57 mg) with pyridine (0.3 ml) and Ac_2O (3 ml) by refluxing 4.5 hr, followed by treatment with pyridine (3 ml) and then usual treatment gave a crude product, which was purified by TLC (Camag D-5, $CHCl_3$–EtOAc (10:1)) giving XXII (54 mg). Analytical sample (recryst. from aq. EtOH) melted at 213—217°. *Anal.* Calcd. for $C_{59}H_{74}O_{11}$: C, 73.87; H, 7.78. Found: C, 73.04; H, 7.70. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1744, 1242 ($OCOCH_3$), 699 (arom. CH), no hydroxyl.

Formation of Barringtogenol C (I) from XXIII——a) A solution of XXIII (97 mg) in AcOH (2.7 ml) and water (0.3 ml) was heated in a boiling water-bath for 2.5 hr. After distilling AcOH under reduced pressure, the mixture was added with EtOH and again evaporated under reduced pressure to remove AcOH. By repeating the procedure, AcOH was distilled off completely. The crude product was then chromatographed on silicic acid (Mallinckrodt, 4 g) and eluted with $CHCl_3$–MeOH (99:1) to afford colorless amorphous

product (54 mg). Pyridine solution (1.5 ml) of the product was treated with CrO_3–pyridine (150 mg–2 ml) complex and stirred for 80 min. The reaction mixture was diluted with ether, filtered to remove precipitate, washed with water, evaporated to dryness to give a product (51 mg), which was purified by TLC (Camag D-5, $CHCl_3$–AcOEt (5:1)) yielding XXVI (28 mg) (amorphous), with lower *Rf* value; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1748, 1248, 1227 ($OCOCH_3$), 1708 (CO) and XXVII (10 mg) (amorphous) having higher *Rf* value; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 2720, 1747, 1248, 1230 (CHO and $OCOCH_3$).

b) A solution of XXVII (10 mg) in EtOH (0.5 ml), diethyleneglycol (2.0 ml) and 80% hydrazine hydrate (0.5 ml) was refluxed for 30 min (bath temp. 130°). After adding KOH (0.2 g), the mixture was refluxed for further 20 min, and the condenser was fitted downward, and the bath temp. was raised to 200°. During the period, the excess hydrazine was distilled off. After refluxing 2 hr (bath temp. 227—228°) and additional 2 hr and 45 min (bath temp. 230—245°), the solution was poured into water and the colorless precipitate was collected by centrifugation, purified by TLC (Camag D-5, $CHCl_3$–MeOH (10:1)) and recrystallized with aq. EtOH furnishing crystals of melting at 277—282°. The product was identified with barringtogenol C (I) by mixed mp, IR (KBr), and TLC comparisons.

21-O-Mesyl-3,22,28-tri-O-acetyl-barringtogenol C (XXIX)——To an intensely cooled solution (−25°—−20°) of VII (200 mg) in dry pyridine (10 ml) was added pyridine solution (0.5 ml) containing CH_3SO_2Cl (200 mg). During the period of 8 hr monitoring by TLC, the temp. was raised gradually to −3°—+10°, and the mixture was treated in a usual manner giving a crude product (222 mg), which was chromatographed on silica gel, recrystallized with acetone–*n*-hexane to yield colorless needles (XXIX) of mp 156—158°. *Anal.* Calcd. for $C_{37}H_{58}O_{10}S$: C, 63.95; H, 8.41. Found: C, 64.40; H, 8.44. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3525, 3400 (OH), 1730, 1245 ($OCOCH_3$), 1338, 1171 (SO_2).

$LiAlH_4$ Reduction of XXIX yielding Barringtogenol D (XII)——Ten mg of XXIX in dry ether was treated with $LiAlH_4$ (10 mg) by stirring at r.t. for 2 hr, followed by usual treatment. The crude product was purified by TLC (Camag D-5, $CHCl_3$–MeOH (10:1)), recrystallized with AcOEt–MeOH to give colorless leaflets (3 mg), mp 304—312°, identical with barringtogenol D (XII) (mixed mp, IR (KBr), and TLC).

Treatment of Barringtogenol C (I) with DMSO giving Barringtogenol D (XII) and XXX——A solution of barringtogenol C (I) (2 g) in dry DMSO (50 ml) was refluxed in an oil bath (150—160°) for 8 hr, concentrated to a half volume under reduced pressure and poured into water. The collected precipitate (1.9 g) was extracted twice with hot $CHCl_3$ (75 ml each). The insoluble part was recovered barringtogenol C (500 mg) (checked by TLC). The $CHCl_3$ extract was then chromatographed on alumina (Merck, standard, 120 g) eluting with $CHCl_3$–MeOH (99:1), $CHCl_3$–MeOH (99:1—98:2) successively. From the earlier eluate was obtained colorless needles (121 mg, XXX) of melting at 267.5—269° (recryst. from aq. MeOH), $[\alpha]_D$ +24° (c=0.54, MeOH). *Anal.* Calcd. for $C_{31}H_{50}O_5$: C, 74.06; H, 10.03. Found: C, 73.82; H, 9.81. IR ν_{max}^{Nujol} cm^{-1}: 3460, 3410 (OH). On recrystallization with MeOH–AcOEt, the later eluate gave colorless leaflets (XII) (264 mg). Analytical sample melted at 303—309°. *Anal.* Calcd. for $C_{30}H_{48}O_4$: C, 76.22; H, 10.24. Found: C, 76.42; H, 10.18.

Acid Treatment of XXX regenerating Barringtogenol C (I)——A solution of XXX (18 mg) in 5% HCl–MeOH was refluxed 30 min, evaporated under reduced pressure, and diluted with water to give precipitate, which was extracted with ether. The extract was then purified by TLC (Camag D-5, $CHCl_3$–MeOH (10:1)), and recrystallized with aq. MeOH giving colorless crystals (7 mg) of melting at 278—284°, which was identical with barringtogenol C (I) by mixed mp, IR (KBr), and TLC.

Acetylation of XXX affording XXXI and XXXII——a) Acetylation (at 26°, 40 hr) of XXX (80 mg) with pyridine (2.5 ml) and Ac_2O (1.5 ml) followed by crystallization from MeOH furnished colorless plates (65 mg) which was then recrystallized with CH_2Cl_2–MeOH to give XXXI, mp 307—313°. *Anal.* Calcd. for $C_{35}H_{54}O_7$: C, 71.64; H, 9.28. Found: C, 71.49; H, 9.24. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3630, 3450 (OH), 1738, 1240 ($OCOCH_3$).

b) A mixture of XXX (78 mg), Ac_2O (5 ml) and AcONa (100 mg) was refluxed for 3 hr. The major product (56 mg) having higher *Rf* value on TLC was collected by TLC (Camag D-5, $CHCl_3$–AcOEt (10:1)), recrystallized with aq. MeOH to afford XXXII, mp 281—283° (in a sealed capillary), $[\alpha]_D$ −11° (c=1.05, $CHCl_3$). *Anal.* Calcd. for $C_{37}H_{56}O_8$: C, 70.67; H, 8.98. Found: C, 70.92; H, 8.96. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1745, 1238 ($OCOCH_3$), no hydroxyl.

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