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# Lycopodium Triterpenoids. (10).[1] Triterpenoid Constituents of *Lycopodium wightianum* collected in Borneo[2]

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From *Lycopodium wightianum* collected in Borneo, two new triterpenoids named wightianol-A and wightianol-B were isolated together with α-onocerin, tohogenol, and lycoclavanin. The structures of the new compounds were established as 14β-serratane-3β,14β,20β,21β,24-pentol (**4a**) and serrat-14-ene-3β,20β,21β,24-tetrol (**5a**), respectively. For comparison, the $C_3$-epimer of lycoclavanin, 16-oxoserrat-14-ene-3β,20β,21β,24-tetrol (**14**), was prepared and characterized as its tetraacetate.

**Keywords**——Lycopodiaceae; *Lycopodium wightianum*; triterpenoids; 14β-serratanes; wightianol-A; wightianol-B; α-onocerin; tohogenol; lycoclavanin; 3-epi-lycoclavanin

Plants of the genus *Lycopodium* characteristically contain triterpenoids of the serratane group or its biogenetic precursor, α-onocerin (**1a**).[4] More than 30 triterpenoids of this group have so far been isolated (and their structures elucidated) from various plants of this genus including 19 Japanese,[4,5] a New Guinean,[6] a Sri Lankan,[7] and a Canadian species.[8]

In 1974 one of the authors (Y.I.) visited Mt. Kinabalu in Borneo and collected several kinds of Lycopodium plants: *L. clavatum*, *L. casuarinoides*, *L. complanatum*, and *L. wightianum*.[9] Preliminary examination of the triterpenoid constituents of these plants according to the procedure of Tsuda *et al.*[4] revealed that thin-layer chromatography (TLC) of *L. wightianum* gave spots different in mobility from any other serratane triterpenoid so far characterized. This finding prompted us to carry out further investigation of this plant.

*L. wightianum* was collected at panar Raban (3600 m) on Mt. Kinabalu in March, 1974. The dried plant was extracted with methanol and the non-basic fraction of the methanol extract was saponified. The resulting neutral fraction was successively extracted in a Soxhlet apparatus with *n*-hexane, ether, chloroform, and chloroform–methanol to provide 7 fractions

1) Triterpenoid Chemistry. Part XV. Part XIV: Y. Tsuda and T. Sano, *Chem. Pharm. Bull.*, **28**, 3134 (1980); Lycopodium Triterpenoids. (9): T. Sano, T. Fujimoto, and Y. Tsuda, *Chem. Pharm. Bull.*, **23**, 1784 (1975).
2) This work was presented at the 96th Annual Meeting of the Pharmaceutical Society of Japan, Abstract II, 6F1-1, Nagoya, April, 1976.
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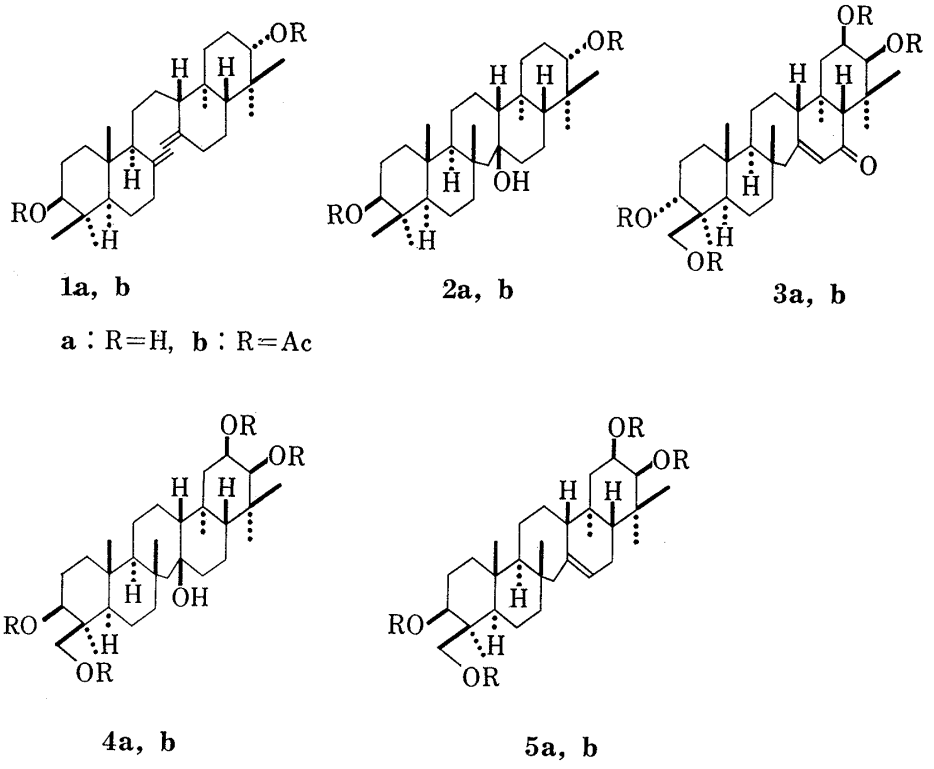
4) Y. Tsuda, T. Fujimoto, K. Isobe, T. Sano, and M. Kobayashi, *Yakugaku Zasshi*, **94**, 970 (1974). This paper recommends saponification prior to detailed fractionation for isolation of the triterpenoids, since they may exist in the plants as bound forms, such as esters, which could give poorly separated spots of low mobility on TLC.
5) Y. Inubushi, T. Harayama, T. Hibino, and M. Akatsu, *Yakugaku Zasshi*, **91**, 980 (1971).
6) Y. Inubushi, T. Sano, and J.R. Price, *Australian J. Chem.*, **20**, 387 (1967).
7) *a)* Y. Inubushi, T. Hibino, T. Harayama, T. Hasegawa, and R. Somanathan, *J. Chem. Soc.* (*C*), **1971**, 3101; *b)* Y. Inubushi, T. Hibino, T. Hasegawa, and R. Somanathan, *Chem. Pharm. Bull.*, **19**, 2640 (1971).
8) K. Orito, R.H. Manske, and R. Rodrigo, *Can. J. Chem.*, **50**, 3280 (1972).
9) Notes by P.F. Cockburn, drawings by Yap Pak Hau, "Plant Life on Mt. Kinabalu," 2nd ed., 1972.

which, after acetylation (except in the case of fraction I), were subjected to further separation by chromatography as described in the experimental section.

Fraction I afforded mixtures of normal chain alcohols and of phytosterols, as has been found with other Lycopodium plants.[4] Fraction II gave α-onocerin diacetate (**1b**).[4] Fr. III gave leaflets of mp. >300°, which were not further investigated. Fr. IV gave tohogenol diacetate (**2b**)[10] and two new triterpenoids (as the acetates), which were named wightianol-B acetate (**5b**), mp. 159—160°, needles from methanol, $[\alpha]_D$ −5.95°, and wightianol-A acetate (**4b**), mp 199—200°, needles from *n*-hexane, $[\alpha]_D$ +4.56°. Fr. V was a mixture of **4b** and **5b**. Frs. VI and VII yielded **4b** and lycoclavanin tetraacetate (**3b**).[11]




**1a, b** **2a, b** **3a, b**

**a** : R=H, **b** : R=Ac

**4a, b** **5a, b**

Chart 1

## Wightianol-A and Wightianol-B

Alkaline hydrolysis of **4b** and **5b** gave the corresponding alcohols, wightianol-A (**5a**), mp 347—350°, and wightianol-B (**5a**), mp >360°, respectively.

The IR spectrum of **4b** showed the OH group absorption at 3510 $cm^{-1}$ together with acetoxy group absorptions (1745, 1725 and 1250 $cm^{-1}$). Its NMR spectrum (Table I) showed the presence of six *C*-methyls and four acetoxy groupings, three of the latter being secondary and one primary. No olefinic proton signal was observed, however.

Wightianol-B acetate (**5b**) crystallized as needles of mp 159—160° from methanol, but it formed needles of mp 198—200° from *n*-hexane–ether. The former was a hydrated and the latter an anhydrous form, as deduced from their IR and NMR spectra. The anhydrous form showed in its NMR spectrum the presence of six *C*-methyls and four acetyl methyls. Three of the four acetoxy groupings are secondary and one is primary, as in **4b**. However, it did not show OH absorption in the IR spectrum, and its NMR spectrum showed a new absorption of one olefinic proton at $\delta$ 5.37.

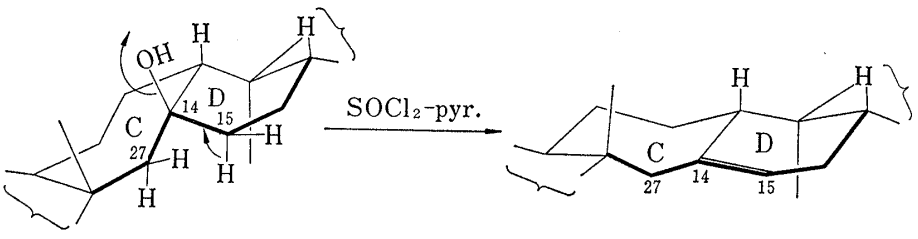
10) T. Sano, Y. Tsuda, and Y. Inubushi, *Tetrahedron*, **26**, 2981 (1970).
11) Y. Tsuda, T. Fujimoto, and A. Morimoto, *Chem. Pharm. Bull.*, **23**, 1336 (1975).

Table I. NMR Spectra of Wightianol-A, -B, and Related Triterpenoids (Acetates) at 60 MHz (Solvent: $CDCl_3$)

| Compound | $-\overset{|}{C}-CH_3$[b] | $-OCOCH_3$[b] | $-\overset{|}{C}-CH_2-OAc$[c] | >CH–OAc | >C=CH– |
|---|---|---|---|---|---|
| Wightianol-A tetraacetate (**4b**) | 0.87(2)<br>0.92(1)<br>0.97(1)<br>1.00(1)<br>1.08(1) | 1.97(1)<br>2.02(1)<br>2.05(1)<br>2.10(1) | 4.20 | 4.63 (1H, m)[d]<br>4.80 (1H, d, $J$=4 Hz)[e]<br>5.0—5.4 (1H)[f] | — |
| Wightianol-B tetraacetate (**5b**) | 0.80(1)<br>0.83(3)<br>1.00(1)<br>1.03(1) | 1.97(1)<br>2.02(1)<br>2.05(1)<br>2.10(1) | 4.20 | 4.60 (1H, m)[d]<br>5.00 (1H, d, $J$=4 Hz)[e]<br>5.0—5.4 (1H)[f] | 5.37 (1H, m) |
| Lyclaninol tetraacetate (**8b**)[a] | 0.81(1)<br>0.87(3)<br>0.95(1)<br>1.05(1) | 1.98(1)<br>2.05(1)<br>2.08(1)<br>2.11(1) | 4.10 | 4.99 (2H)[g]<br>5.0—5.5 (1H)[f] | 5.37 (1H, m) |
| 3-Epilycoclavanin tetraacetate (**14b**) | 0.90(3)<br>1.03(1)<br>1.18(1)<br>1.32(1) | 2.02(1)<br>2.07(1)<br>2.08(1)<br>2.17(1) | 4.28 | 4.61 (1H, m)[d]<br>4.95 (1H, d, $J$=4 Hz)[e]<br>5.1—5.5 (1H)[f] | 5.82 (1H, bs) |
| Lycoclavanin tetraacetate (**3b**)[a] | 0.86(1)<br>0.91(2)<br>0.95(1)<br>1.18(1)<br>1.31(1) | 1.99(1)<br>2.05(1)<br>2.09(1)<br>2.15(1) | 4.09 | 4.94 (2H)[g]<br>5.0—5.5 (1H)[f] | 5.75 (1H, bs) |

a) Y. Tsuda, T. Fujimoto, and A. Morimoto, *Chem. Pharm. Bull.*, **23**, 1336 (1975).
b) Numbers in parentheses indicate numbers of methyl groups.
c) Signals appeared as ABq of 2H, with $\Delta\delta$=18 Hz, $J$=12 Hz.
d) $C^3$–H signal.
e) $C^{21}$–H signal.
f) $C^{20}$–H signal. This appeared as a multiplet and, in most cases, overlapped with other signals.
g) $C^3$–H(bs) and $C^{21}$–H(d, $J$=4—6 Hz) signals are overlapped.

The above evidence suggests that wightianol-A has a hydroxyl group at $C_{14}$ of the serratane skeleton, while wightianol-B has a double bond at $C_{14-15}$, analogous with the reported[10] relationship between tohogenol and serratenediol and between tohogeninol and serratriol. This assumption was confirmed by transforming wightianol-A acetate (**4b**) into wightianol-B acetate (**5b**) by dehydration with $SOCl_2$–pyridine.




tohogenol diacetate
tohogeninol triacetate
wightianol-A tetraacetate

serratenediol diacetate
serratriol triacetate
wightianol-B tetraacetate

Fig. 1. Dehydration of 14$\beta$-Hydroxyserratanes to Serrat-14-enes

Upon forced acetalization[12] wightianol-B formed the diacetonide (**6**), in which one of the *O*,*O*-isopropylidene functions was formed between two secondary hydroxyl groups and the other between a primary hydroxyl group and a secondary hydroxyl group, as shown by the NMR spectrum. Moreover, the type classification signals[13] of the latter acetonide function

12) Y. Tsuda, T. Sano, K. Morimoto, M. Hatanaka, and Y. Inubushi, *Chem. Pharm. Bull.*, **22**, 2383 (1974).
13) Y. Tsuda, T. Sano, K. Isobe, and M. Miyauchi, *Chem. Pharm. Bull.*, **22**, 2396 (1974).

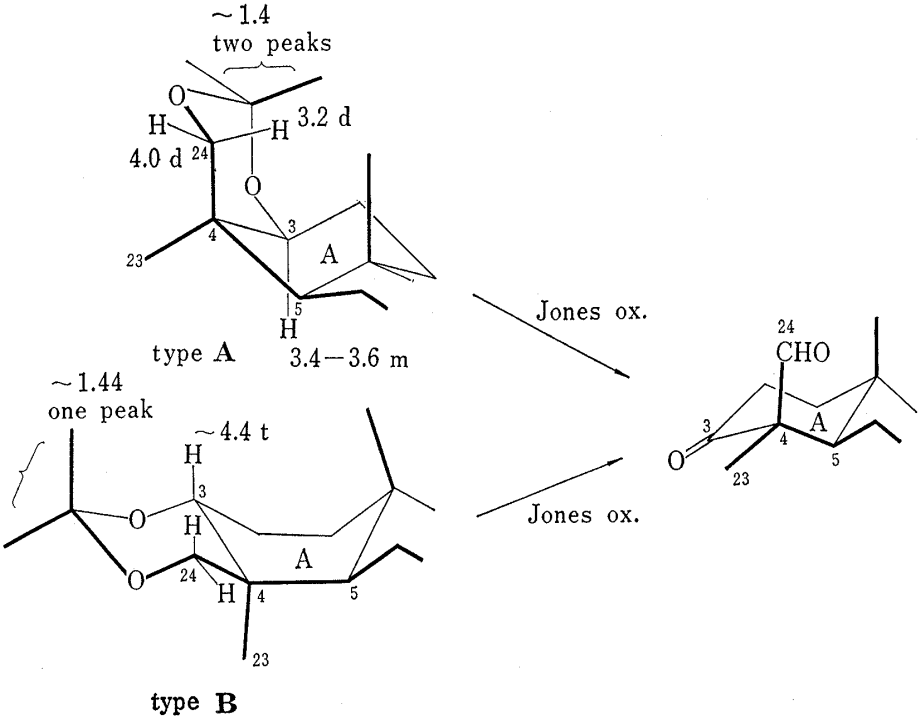



Fig. 2. Characterization of Acetonide Types

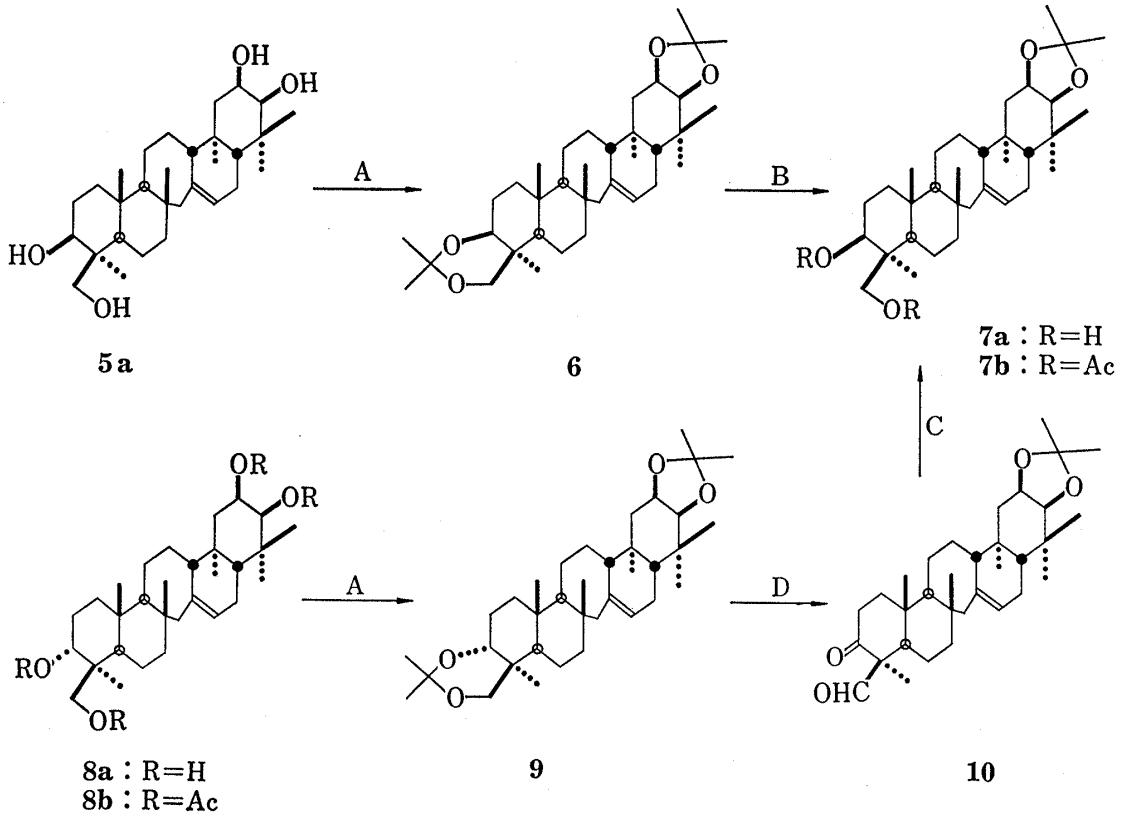
disclosed that it is of type **A**, formed between the 3$\beta$- and 24-hydroxyl groups, since it showed two separated *C*-methyl peaks at $\delta$ 1.37 and 1.41, two well-separated doublets at $\delta$ 3.17 and 4.01 with $J$=11 Hz (the methylene protons on the *m*-dioxane ring), and >CH–O– as a multiplet at 3.37—3.60. In agreement with this evidence, mild hydrolysis of **6** with AcOH–$CHCl_3$–MeOH–$H_2O$ resulted in selective cleavage of one acetonide function to provide the monoacetonide (**7a**), which was characterized as the diacetate (**7b**).

These results suggest that wightianol-B is the $C_3$-epimer of lyclaninol (**8a**).[11] Detailed comparison of the NMR spectra of both tetraacetates, **4b** and **8b**, confirmed this assignment. Appreciable differences between them were seen in the signals of $-C^{24}H_2-$OAc and $C^3$–H; the former AB quartet ($\Delta\delta$=18 Hz, $J$=12 Hz) appeared at $\delta$ 4.20 in **5b** and at 4.10 in **8b**, and the $C^3$–H signal in **8b** was a broad singlet at $\delta$ 4.99 while in **5b** it was a multiplet at 4.60 with $W$h/2=15 Hz, indicating that the configuration of $C^3$–OAc in **5b** is equatorial, whereas it is axial in **8b**.[11]

Partial synthesis of wightianol-B (**5a**) from lyclaninol (**8a**) was therefore attempted. For this purpose, the configuration of $C^3$–OH in **8a** should be inverted while leaving the other hydroxyl groups intact.

Tsuda *et al.*[13] found that direct oxidation of acetonides of type **A** and **B** (the acetonides formed between 3- and 24 hydroxyl groups) (see Fig. 2) with the Jones reagent gave, in excellent yield, the keto-aldehyde, which was otherwise hardly obtainable by oxidation of the corresponding diol. Under these conditions the 5-membered ring acetonide at ring E was stable. Application of this method of lyclaninol diacetonide (**9**) smoothly gave the expected keto-aldehyde (**10**), which, on $NaBH_4$ reduction in methanol under cooling, yielded the diol. This was different from lyclaninol monoacetonide and proved to be identical with wightianol-B monoacetonide (**7a**) (see above), the identity being confirmed by converting it into the diacetate (**7b**).

Therefore, the structure of wightianol-B was determined as serrat-14-ene-3$\beta$,20$\beta$,21$\beta$,24-tetrol (**5a**), and hence that of wightianol-A was 14$\beta$-serratane-3$\beta$,14$\beta$,20$\beta$,21$\beta$,24-pentol (**4a**). Elucidation of the stereochemistry at $C_{14}$ in **4a** is based on the fact that the dehydration of **4b** gave only one $\Delta^{14}$-isomer (**5b**). As discussed already in connection with the transformation




A: $Me_2C(OMe)_2$, DMF, TsOH, B: AcOH, C: $NaBH_4$, D: Jones oxidation

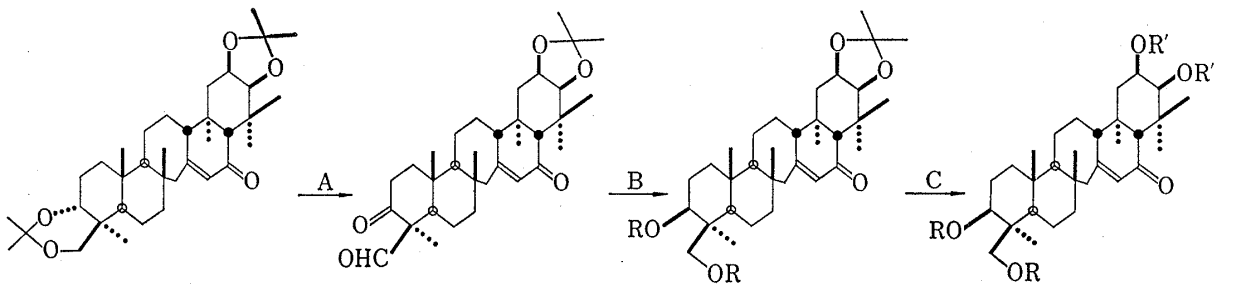
Chart 2

of tohogenol to serratendiol,[10] this is due to the boat conformation of ring D in 14$\beta$-serratane, where 14$\beta$-OH and 15$\alpha$-H are in antiperiplanar orientations.

**Transformation of Lycoclavanin to 3-Epilycoclavanin**

Among the isolated five triterpenoids of *L. wightianum*, only lycoclavanin (**3a**) has a 3$\alpha$ (axial) configuration, while the others are of 3$\beta$ configuration. This finding prompted us to check for the presence of the 3$\beta$-isomer of lycoclavanin in this plant. For this purpose, we prepared 3-epilycoclavanin (**14a**) from lycoclavanin (**3a**). The transformation was accomplished as shown in Chart 3.

Jones oxidation of lycoclavanin diacetonide (**11**) yielded the keto-aldehyde (**12**), which, on reduction with $NaBH_4$ in the cold, gave the diol (**13a**). Acetylation, followed by acid hydro-




A: Jones oxidation, B: $NaBH_4$, C: AcOH

Chart 3

lysis of the acetonide function and reacetylation, furnished the desired 3-epilycoclavanin (3$\beta$,20$\beta$,21$\beta$,24-tetrahydroxy-16-oxoserrat-14-ene) as the tetraacetate (**14b**), mp 228—231°. It had the same mobility as **3b** on TLC, but the IR and NMR spectra of two compounds were distinctly distinguishable. We inspected the NMR spectrum of the lycoclavanin fraction of *L. wightianum*, monitoring the C–$CH_3$ signals, and the results indicated that the plant does not contain 3-epilycoclavanin.

## Experimental

Unless otherwise stated, the IR spectra were taken in a Nujol mull, and the NMR spectra were measured in $CDCl_3$ solution with a 60 MHz machine; the chemical shifts are given in $\delta$ ppm referred to internal TMS. Mp's below 300° were determined on a Yanagimoto mp apparatus and those above 300° were taken in an open capillary using an Ishii block-heater apparatus; all are uncorrected. Acid-washed alumina was used for column chromatography, and for TLC silica gel G was used as an adsorbent with $CHCl_3$–MeOH as a developing solvent.

**Extraction of L. Wightianum and Isolation of Triterpenoids**——The dried, cut plant (110 g) (collected at Panar Raban, Mt. Kinabaru, in March, 1974) was extracted six times with hot MeOH for 6 hr each. The combined extract was concentrated to give a paste, to which 5% AcOH was added with stirring. The ppt formed on standing overnight was collected by filtration and washed with $H_2O$ to yield 9.44 g (8.5%) of the neutral-acidic fraction. A portion (5 g) of this was saponified by heating with 5% KOH–MeOH (300 ml) under reflux for 3.5 hr, then concentrated to half the initial volume. Water (150 ml) was added and the ppt was collected by filtration, washed with water, and dried to give 2.88 g of neutral fraction. The filtrate was extracted with $CHCl_3$ to give a further crop of the neutral fraction (0.16 g). The combined neutral fraction was successively extracted in a Soxhlet apparatus with *n*-hexane, ether, $CHCl_3$, and $CHCl_3$–MeOH for 30 hr each. Each extract (except for Fr. VII) left a ppt which was collected by filtration to provide the following fractions.

| | | | |
|---|---|---|---|
| Fr. I | *n*-hexane | sol. | 0.32 g |
| Fr. II | *n*-hexane | ppt. | 0.4 g |
| Fr. III | ether | sol. | 0.65 g |
| Fr. IV | ether | ppt. | 0.95 g |
| Fr. V | $CHCl_3$ | sol. | 0.35 g |
| Fr. VI | $CHCl_3$ | ppt. | 0.2 g |
| Fr. VII | $CHCl_3$–MeOH | sol. | 0.15 g |

Fr. I was subjected to dry-column chromatography as described previously,[4] to yield a mixture of *n*-chain alcohols (71 mg), mp 77.5—78.5°, and a mixture of phytosterols (32 mg), mp 142—145°.

Frs. II—VII were acetylated by heating with pyridine (5—20 ml) and $Ac_2O$ (2.5—10 ml), and the products, obtained after work-up in the usual way, were chromatographed.

Fr. II crystallized out $\alpha$-onocerin diacetate (**1b**) (227 mg), on acetylation. The filtrate gave, on chromatography after the usual work-up, a further crop of **1b** (35 mg).

Fr. III gave a small amount of white scales, mp >300°, from the *n*-hexane–benzene (1: 2) eluate. Though the mp and TLC behavior of this compound were similar to those of serratenediol diacetate, the IR spectra of the two were not identical. This compound was not further investigated because of the limited amount available.

Fr. IV gave tohogenol diacetate (**2b**) (4 mg) from the *n*-hexane–benzene (2: 1) eluate. Further elution with the same solvent gave wightianol-B tetraacetate (**5b**) (10 mg). Elution with benzene gave wightianol-A tetraacetate (**4b**) (415 mg).

Fr. V gave **5b** (5 mg) from the *n*-hexane–benzene (2: 1) eluate. Elution with benzene gave **4b** (137 mg).

Fr. VI gave **5b** (150 mg) from the benzene eluate. Further elution with the same solvent gave lycoclavanin tetraacetate **3b** (26 mg).

**$\alpha$-Onocerin Diacetate** (**1b**)——Needles from $CH_2Cl_2$–MeOH, mp 228—230°.

**Tohogenol Diacetate** (**2b**)——Needles from $CH_2Cl_2$–MeOH, mp>300°.

**Lycoclavanin Tetraacetate** (**3b**)——Needles from *n*-hexane–ether, mp 242—244°.

The identities of these compounds were confirmed by comparison (mp, TLC, IR and NMR spectra) with authentic specimens.

**Wightianol-A Tetraacetate** (**4b**)——Needles from *n*-hexane, mp 199—201.5°. $[\alpha]_D^{20} = +4.56°$ ($c = 1.03$ in $CHCl_3$). IR $cm^{-1}$: 3510 (OH), 1745, 1725, 1250 (OAc). NMR: see Table I. *Anal.* Calcd for $C_{38}H_{60}O_9$: C, 69.06; H, 9.15. Found: C, 68.88; H, 9.05.

Saponification of **4b** with 5% KOH–MeOH under reflux for 1.5 hr afforded wightianol-A (**4a**), mp 347—350°, needles from $CH_2Cl_2$–MeOH. IR $cm^{-1}$: 3350 (OH).

**Wightianol-B Tetraacetate (5b)**——The hydrated form: mp 159—161°, needles from MeOH. This contained OH (IR) but not $OCH_3$ (NMR). The anhydrous form: mp 198—200°, needles from *n*-hexane–ether. $[\alpha]_D^{20} = -5.95°$ ($c=0.92$ in $CHCl_3$). IR $cm^{-1}$: 1745, 1245 (OAc). NMR: see Table I. *Anal.* Calcd for $C_{38}H_{58}O_8$: C, 70.99; H, 9.09. Found: C, 71.12; H, 9.30.

Saponification of **5b** with 5% KOH–MeOH under reflux for 1.5 hr afforded wightianol-B (**5a**), mp>360°, needles from $CH_2Cl_2$–MeOH. IR $cm^{-1}$: 3350 (OH).

**Dehydration of Wightianol-A Tetraacetate (4b) to Wightianol-B Tetraacetate (5b)**——$SOCl_2$ (3 drops) was added to an ice-cooled solution of **4b** (55 mg) in pyridine, and the mixture was stirred for 2 hr at room temp., then poured into ice-water, and extracted with $CH_2Cl_2$. The organic extract was washed with 5% HCl and water, dried over $Na_2SO_4$, and concentrated to give a residue (43 mg) which was purified in benzene by passage through a short column of acid-washed alumina to afford **5b** as needles, mp and mixed mp 193—195° (from *n*-hexane–ether).

**Wightianol-B Diacetonide (6)**——Wightianol-B **5a** (70 mg) and *p*-TsOH·$H_2O$ (7 mg) in 2,2-dimethoxypropane (7 ml) and DMF (14 ml) were heated under gentle reflux (110°) for 3 hr. The cooled mixture was poured into 5% $K_2CO_3$ (50 ml) and extracted with $CH_2Cl_2$. The extract was washed with water, dried, and concentrated to give a residue, which was purified in benzene by passage through a column of Florisil. The benzene eluate was again chromatographed on Florisil, eluting with *n*-hexane, then with benzene. The benzene eluate, on concentration, gave **6** (15 mg), mp 200—203°, prisms from *n*-pentane. NMR: –Ç–$CH_3$ 0.66 (3H), 0.85 (3H), 0.95 (3H), 1.05 (3H), 1.08 (3H), 1.15 (3H); $^{-O}_{-O}$>$CMe_2$ 1.37 (3H), 1.41 (3H), 1.50 (3H); –Ç–$CH_2$–O– 3.17 (1H, d, $J=11$ Hz), 4.01 (1H, d, $J=11$ Hz); >CH–O– 3.37—3.67 (1H, m), 3.45 (1H, d, $J=4$ Hz), 4.17—4.37 (1H, m); >C=CH– 5.41 (1H, m). *Anal.* Calcd for $C_{30}H_{58}O_4$: C, 77.93; H, 10.54. Found: C, 77.52; H, 10.25.

**Wightianol-B Monoacetonide (7a) and Its Diacetate (7b)**——The diacetonide **6** (15 mg) in $CHCl_3$ (5 ml)–MeOH (4 ml)–$H_2O$ (1 ml)–AcOH (5 drops) was heated under reflux for 30 min. Removal of the solvent by evaporation, followed by crystallization of the residue from ether gave wightianol-B monoacetonide (**7a**), mp 262—264°, as prisms (7 mg). IR $cm^{-1}$: 3300 (OH).

The monoacetonide **7a** (7 mg) was acetylated with $Ac_2O$ (0.5 ml) and pyridine (1 ml). Work-up as usual and purification of the product by preparative TLC gave the diacetate **7b** (3 mg), mp 205—208°, as needles. IR (KBr) $cm^{-1}$: 1740 (OAc).

**The Keto-aldehyde (10)**——Lyclaninol diacetonide **9**[11] (60 mg) in acetone (10 ml) was oxidized with the Jones reagent (5 drops) for 7 min at 0°. The mixture was poured into water and extracted with $CH_2Cl_2$. The extract was washed with $H_2O$, dried, and concentrated. Crystallization of the residue from ether gave **10** (28 mg), mp 213—215°, as prisms. IR $cm^{-1}$: 2700, 1725 (CHO), 1710 (CO). NMR: –Ç–$CH_3$ 0.67 (3H), 0.90 (3H), 0.95 (3H), 1.05 (3H), 1.25 (3H); $^{-O}_{-O}$>$CMe_2$ 1.35 (3H), 1.52 (3H); >C=CH– 5.40 (1H, m); –CHO 9.70 (1H, s).

**The Diol (7a) and Its Diacetate (7b)**——The keto-aldehyde **10** (28 mg) and $NaBH_4$ (38 mg) in MeOH (15 ml) were stirred under ice-cooling for 30 min. The mixture was poured into ice-water and extracted with $CHCl_3$. Removal of the solvent from the dried extract gave a residue which was purified by preparative TLC to yield the diol **7a** (10 mg), mp 262—264°. The IR spectrum of this product was identical with that of wightianol-B monoacetonide (**7a**). Acetylation with $Ac_2O$–pyridine by the usual method gave the diacetate **7b** (5 mg), mp 206—208°, which was identical (IR and TLC) with wightianol-B monoacetonide diacetate (**7b**) obtained above. *Anal.* Calcd for $C_{37}H_{60}O_6$: C, 73.96; H, 10.07. Found: C, 73.61; H, 10.31.

**3-Epilycoclavanin Tetraacetate (3β,20β,21β,24-tetraacetoxy-16-oxoserrat-14-ene) (14b)**——i) The Keto-aldehyde (**12**): Lycoclavanin diacetonide **11**[11] (118 mg) in acetone (20 ml) was oxidized with the Jones reagent (10 drops) under ice-cooling for 10 min. The mixture was poured into ice-water and extracted with $CH_2Cl_2$ to give **12** (81 mg), mp 252—255°, as prisms. IR $cm^{-1}$: 2725, 1725 (CHO), 1705 (CO), 1670, 1620 (conj. CO). NMR: –Ç–$CH_3$ 0.80 (3H), 0.93 (3H), 0.97 (3H), 1.16 (3H), 1.29 (3H), 1.37 (3H); $^{-O}_{-O}$>$CMe_2$ 1.40 (3H), 1.52 (3H); >C=CH– 5.82 (1H, bs); –CHO 9.73 (1H, s).

ii) The Monoacetonide-diacetate (**13b**): **12** (81 mg) and $NaBH_4$ (68 mg) in MeOH (50 ml) were stirred at 0° for 30 min. Addition of water to the mixture and extraction with $CH_2Cl_2$ gave the diol (**13a**) (69 mg), mp 300—303°, prisms from $CH_2Cl_2$–MeOH. Acetylation of this product with pyridine (1 ml) and $Ac_2O$ (1 ml) and purification of the product by chromatography gave the diacetate **13b** (29 mg), mp 232—235°. IR $cm^{-1}$: 1750 (OAc), 1675, 1635 (conj. CO). NMR: –Ç–$CH_3$ 0.78 (3H), 0.88 (6H), 1.03 (3H), 1.17 (3H), 1.37 (3H); $^{-O}_{-O}$>$CMe_2$ 1.42 (3H), 1.52 (3H); $OCOCH_3$ 2.03 (3H), 2.07 (3H); >CH–OAc 4.40—4.73 (1H, m); –Ç–$CH_2OAc$ 4.23 (2H, ABq, $\Delta\delta=18$ Hz, $J=11$ Hz); >C=CH– 5.78 (1H, bs).

iii) 3-Epilycoclavanin Tetraacetate (**14b**): The diacetate **13b** (26 mg) was heated in $CHCl_3$ (5 ml)–

MeOH (6 ml)–AcOH (1.5 ml)–$H_2O$ (1.5 ml) under reflux for 7 hr. Removal of the solvent by evaporation and crystallization of the residue from ether gave the diol-diacetate **14c** (13 mg), mp 268—271°, as prisms. IR $cm^{-1}$: 3475 (OH), 1745 (OAc), 1660, 1620 (conj. CO).

Acetylation of this product with $Ac_2O$–pyridine by the usual method gave **14b** (6 mg), mp 228—231°, prisms from *n*-hexane–ether. IR $cm^{-1}$: 1740 (OAc), 1670, 1625 (conj. CO). NMR: see Table I. *Anal.* Calcd for $C_{38}H_{56}O_9$: C, 69.48; H, 8.59. Found: C, 69.29; H, 8.31.