Tetrahedron Letters No. 41, pp 3807 - 3808, 1971. Pergamon Press. Printed in Great Britain.

ISOLATION AND STRUCTURE DETERMINATION OF A NEW TRITERPENE-TRIOL FROM PACHYSANDRA TERMINALIS SIEB. ET ZUCC.

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(Received in Japan 1 September 1971; received in UK for publication 9 September 1971)

In preceding papers[1, 2] we reported the structure elucidation of three friedelin-type triterpenes: pachysandiol-A (I), -B (IIa), and pachysonol (IIb)[3], isolated from *Pachysandra terminalis* SIEB. et ZUCC.. In succession, we recently isolated a new triol, which was now proved to have the structure IIIa.

The triol (IIIa) is an amorphous powder and was characterized as its triacetate (IIIb), $C_{36}H_{58}O_6$, mp 139-143°, $[\alpha]_D$+7°($CHCl_3$). Its IR spectrum[4] showed an intense absorption at 1725 cm^{-1} (OAc) and the NMR spectrum[4] revealed signals at τ 4.80 (1H, t., J=9 Hz, C$\underline{H}$-OAc), 5.17 (2H, br., 2×C$\underline{H}$-OAc), 7.93, 7.95, 8.01 (each 3H, 3×Ac), 9.20 (3H, d., J=6 Hz, *sec*-CH_3), and 8.75-9.08 (7×*tert*-CH_3). The NMR pattern is closely similar to those of I- and IIa-diacetate, suggesting that the triol (IIIa) is also a member of friedelin-type triterpene.

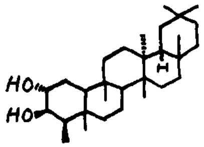
When IIIb was adsorbed on alumina for two days, partial hydrolysis took place to give a diacetate (IIIc), $C_{34}H_{56}O_5$, mp 254-255°, τ: 4.80 (1H, t., J=9 Hz, C$\underline{H}$-OAc), 5.30 (1H, t., J=3 Hz, C$\underline{H}$-OAc), 6.13 (1H, m., $W^{1/2}$=6.5 Hz, C$\underline{H}$-OH), 7.95 and 8.01 (each 3H, 2×Ac). Chromic acid oxidation of the latter (IIIc) gave a ketone (IV), $C_{34}H_{54}O_5$, mp 205-208°, ν: 1735 (OAc) and 1720 cm^{-1}(ketone), τ: 4.82 (1H, t., J=9 Hz, C$\underline{H}$-OAc) and 5.00 (1H, d., J=4 Hz, C$\underline{H}$-OAc), which on treatment with KOH in boiling methanol gave rise to a diosphenol (V)[1], $C_{30}H_{48}O_3$, mp 275-280°, ν(in KBr): 1662 and 1640 cm^{-1}, λ(in dioxane): 275 mμ(ε: 9475), τ(in pyridine-d_5): 8.04 (3H, s., C=C-CH_3). These observations indicated that the ketone (IV) has a partial structure -CO-CH(OAc)-CH(CH_3)-.

The above ketone (IV) was found to epimerize readily on alumina chromatography, yielding the corresponding epimer (VI), mp 208-210°, ν: 1730(sh) and

1720 cm^{-1}, τ: 4.82 (1H, t., J=9 Hz, C$\underline{H}$-OAc) and 5.03 (1H, d., J=12.5 Hz, C$\underline{H}$-OAc).

Wolff-Kishner reduction (Nagata's modification[5]) of both IV and VI resulted in the deacetoxylation and reduction of the carbonyl group to afford a saturated alcohol[6], which on acetylation furnished a crystalline acetate (VII), $C_{32}H_{54}O_2$, mp 214.5-215.5°, τ: 4.80 (1H, t., J=9 Hz, C$\underline{H}$-OAc) and 8.00 (3H, Ac). This compound was identified with a sample of VII, obtained by Wolff-Kishner reduction of pachysonol (IIb)[2] followed by acetylation.

Based on the foregoing spectroscopic and chemical evidence, the structure of the triol is assigned to the formula IIIa.



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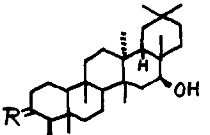
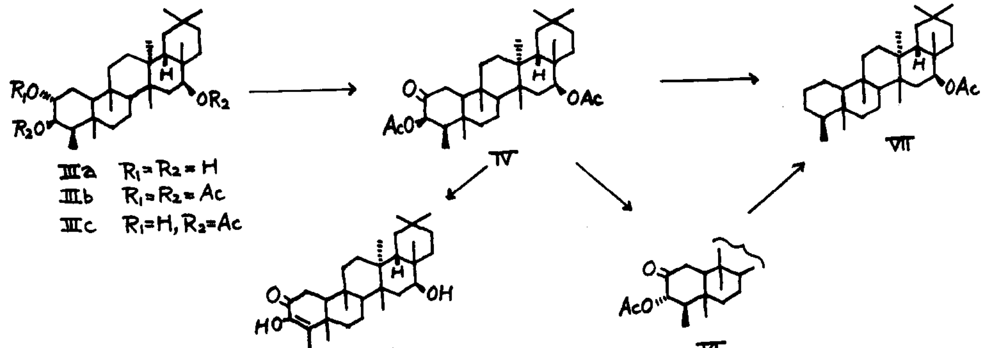


IIa R= $<^{OH}_{H}$
IIb R=O



IIIa R₁=R₂=H
IIIb R₁=R₂=Ac
IIIc R₁=H, R₂=Ac

IV

V

VI

VII

REFERENCES and FOOTNOTES

1) T. Kikuchi and T. Toyoda, Chem. Pharm. Bull. (Tokyo), **19**, 753 (1971).

2) T. Kikuchi, M. Takayama, T. Toyoda, M. Arimoto, and M. Niwa, Tetrahedron Letters, **1971**, 1535.

3) The 16-hydroxyl group in IIa and IIb was recently determined to have the β-configuration by X-ray analysis. The detail will be reported in near future.

4) IR and NMR spectra were taken in $CHCl_3$ and $CDCl_3$, respectively, unless otherwise stated.

5) W. Nagata and H. Itazaki, Chem. & Ind., **1964**, 1194.

6) Huang-Minlon, J. Am. Chem. Soc., **71**, 3301 (1949).