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THE STRUCTURE OF ABIESLACTONE

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Abieslactone is an interesting triterpene for which structure I has been advanced (1,2). Recent investigations in our laboratory on some novel cyclopropane triterpene lactones (3) have drawn attention to the need for some revision in this assignment. We wish to report our findings which establish the structure and absolute stereochemistry of abieslactone as shown in VII (R=H; R_1=OCH_3).

The original degradation sequence of abieslactone along with the pertinent NMR data is outlined in Figure 1. Examination of the NMR data for compounds I-III reveals that the olefinic signals are at lower field than normally expected for C_9-C_{11} unsaturated triterpenes (for example, grandisolide for which structure I is established (3), τ4.80; dihydroparkeyl acetate, τ4.81 (4); arborene, τ4.73 (5)) and the methyl group signals (τ8.7-9.1) appear to lower field than those normally obtained in these compounds (for example, grandisolide (I), τ8.95-9.36 (4)). Considerable NMR data is now available in the triterpene series (6-9) and it was significant to us that the appropriate NMR signals in compounds IV-VI had shifted and indeed were now in the expected positions for C_9-C_{11} unsaturated triterpene systems (see Figure 1). The possibility that a rearrangement of the molecule during the conversion III → IV, (ethanedithiol, BF_3) became a serious consideration.

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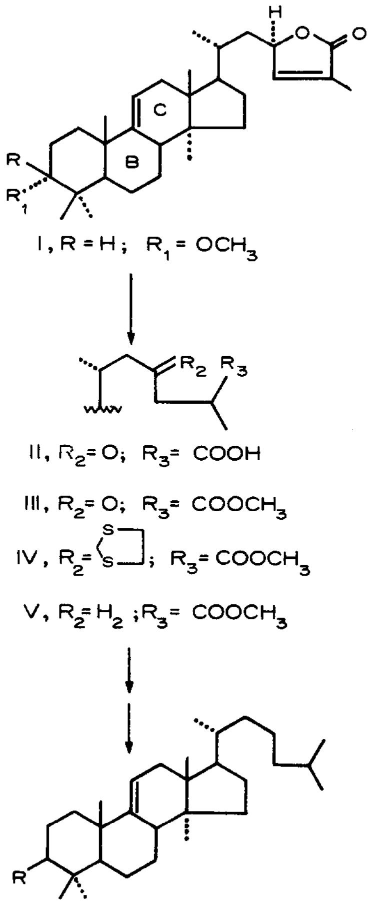


	NMR Data	
	olefinic region	C-methyl region
I, R = H; R_1 = OCH$_3$	4.48	8.90–9.08
II, R_2= O; R_3= COOH	4.48	8.73–9.09
III, R_2= O; R_3= COOCH$_3$	4.45	8.76–9.07
IV, R_2= S S; R_3= COOCH$_3$	4.78	8.73–9.31
V, R_2= H$_2$;R_3= COOCH$_3$	4.78	8.82–9.37
VI R = OAc	4.75	8.92–9.35

Figure1.

Brief outline of original degradation of abieslactone and pertinent nmr data (1,2).

Additional evidence in support of the above came forth from our investigations on Pacific silver fir [Abies amabilis (Dougl.) Forbes]. Apart from abieslactone we isolated two minor components which proved to be the 3α-hydroxy (VII, R_1=OH; R=H) and 3-keto (VII, R=R_1=O) relatives of abieslactone. The ORD comparison of the keto compound (VII, R=R_1=O) and its dihydro derivative (VII, saturated lactone) with authentic 5α-lanost-9(11)-en-3-one is shown in Figure 2. This data again revealed the inconsistency of a 9,11-double bond in abieslactone.

The acid instability of abieslactone was shown when treatment of this compound with hydrogen chloride in chloroform provided a product identical in every respect (mixed m.p., TLC, IR) with

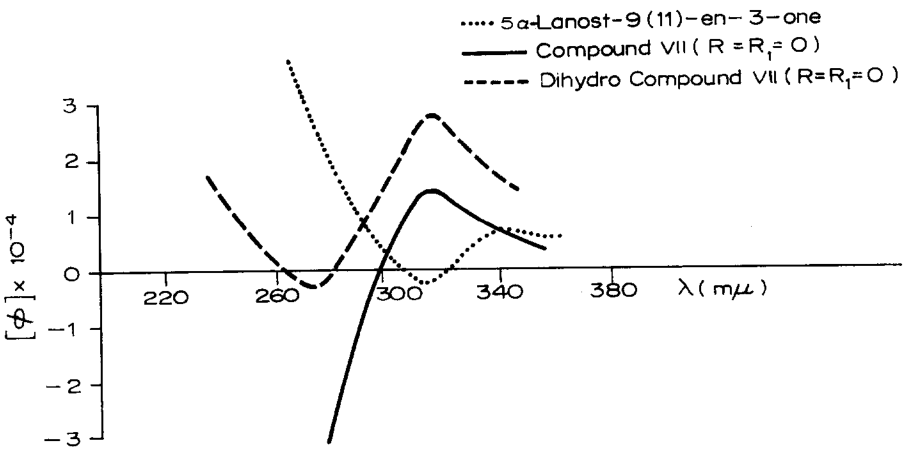
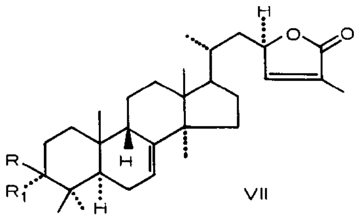


Figure 2.

ORD curves of 5α-lanost-9(11)-en-3-one, compound VII and dihydro compound VII.

grandisolide (I). Since it is known that compounds such as 5α-lanost-7-en-3β-yl acetate (10), 5α-euph-7-en-3β-yl acetate (11) and 5α-tirucall-7-en-3β-yl acetate (12) are readily converted to the C_8-C_9 unsaturated derivatives, it was clear that the usual C_9-αH configuration could not prevail in abieslactone (13). On the basis of all the above results the most plausible alternative for abieslactone appeared to be VII (R=H, R_1=OCH_3). The problem was finally settled by X-ray analysis.



VII

Crystals of abieslactone are colourless needles elongated along a. The cell parameters were obtained by a least-squares treatment of 2θ-values measured on a diffractometer.

Crystal Data. Abieslactone, $C_{31}H_{48}O_3$, $\underline{M}$ = 478.8, Orthorhombic. $\underline{a}$ = 6.633(3), $\underline{b}$ = 11.761(6), $\underline{c}$ = 35.009(19) Å, $\underline{U}$ = 2731(1) Å, $\underline{D}_m$ = 1.13±0.03 g.cm.$^{-3}$, $\underline{Z}$ = 4, $\underline{D}_c$ = 1.140 g.cm.$^{-3}$. The systematic absences uniquely defined the space group as $\underline{P}2_12_12_1$ (D_2^4, No. 19).

Intensity data were collected with CuKα radiation on a Picker four-circle automatic diffractometer, equipped with a graphite monochromator. The θ-2θ scan technique was used at a speed of 2° per minute in 2θ. Of 2011 independent reflexions with 2θ > 100°, 1860 were classified as observed.

The structure was solved by direct methods (14) using iterative application of the tangent formula (15); 187 reflexions with $|E| > 1.60$ were employed. The phase set with the lowest R_{Karle} (15) (22.4%) yielded a Karle-map in which 31 of the 34 non-hydrogen atoms were immediately located. The remaining three atoms were located by Fourier methods. Full-matrix least-squares refinement has given a current *R* value of 0.098. This analysis establishes abieslactone as (23*R*)-3α-methoxy-5α, 9β-lanosta-7,24-dien-26,23-olide (VII, R=H, R_1=OCH_3).

Very recent investigations in Professor Uyeo's laboratory on the interesting acid-catalyzed rearrangements and related reactions of abieslactone are outlined in the accompanying communication (16).

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