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A NEW RELATIVE OF GRANDISOLIDE FROM THE NEEDLES OF *ABIES ALBA*

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Key Word Index—*Abies alba*, Pinaceae, triterpenoid lactone, 3α-hydroxylanosta-9(11)-en-26,23 olide

Source. *Abies alba* Mill needles (fir, formerly *A. pectinata* D.C). Collected in Spring 1972 on Mont Pilat (France). *Previous related work.* Abieslactone **7** from *Abies mariesii* M. bark and leaves,[1,2] and from *Abies amabilis* D.[3] Cyclograndisolide **6** and epicyclograndisolide from *Abies grandis* (Dougl.) Lindl. bark.[4] *Extraction.* Acetone extract of dried needles. Column chromatography of the crude extract (20 g) over silica gel gave sitosterol, campesterol and the alcohol **1** (110 mg) as a white solid. *Characteristics. Alcohol* **1**; m.p. 239–280°; $[\alpha]_D^{18} = +47°$ ($c = 0{\cdot}085$, $CHCl_3$); IR: ν_{max}^{KBr}: 3480 and 1764 cm^{-1}; NMR. see Table 1; MS: $M^+ = 456{\cdot}3603$ (Calc. for $C_{30}H_{48}O_3$: $M^+ = 456{\cdot}3594$).

Acetate **2** (Ac_2O, Py): m.p. 249–250°; $[\alpha]_D^{18} = +36°$ ($c = 0{\cdot}112$, $CHCl_3$); IR: ν_{max}^{KBr}: 1762 and 1720 cm^{-1}; NMR: see table; MS: $M^+ = 498{\cdot}3703$ (Calc. for $C_{32}H_{50}O_4$: $M^+ = 498{\cdot}3709$).

Ketone **3** (CrO_3, Py): m.p. 199–201°; $[\alpha]_D^{18} = +78°$ ($c = 0{\cdot}128$, $CHCl_3$); IR ν_{max}^{KBr}: 1775 and 1723 cm^{-1}; MS: $M^+ = 454{\cdot}3447$ (Calc. for $C_{30}H_{46}O_3$: $M^+ = 454{\cdot}3443$).

Structural determination. The hypothetical structure **1** (or a Δ^7 isomer) was deduced from a cursory examination of the IR, NMR and MS spectra. It is confirmed by a precise comparison of observed NMR and MS spectral values with values obtained by assuming an additivity of the three structural units: (a) 3α-hydroxytriterpene, (b) $\Delta^{9(11)}$ (but not Δ^7) double bond in a lanostane system and (c) side chain corresponding to dihydrograndisolide **4**.[5] Thus the fragmentation patterns, in the mass spectra of **1** and **2**, are very similar to the ones observed for 24,25-dihydrograndisolide **4** and parkeyl acetate.

In the NMR spectra of compounds **1**, **2** and **3**, the olefinic signals are at the expected field for a 9(11) unsaturated triterpene. The chemical shifts of the C-Me groups for compounds **1** and **2** (1·08–0·69) are also in the range for a lanost-9(11)-en-3α-ol skeleton[6] (see Table 1), but not for a Δ^7 isomer.

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[1] TAKAHASHI, T (1938) *J Pharm Soc Japan* **58,** 888

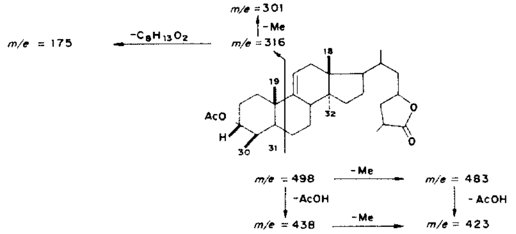
[2] (a) MATSUNUGA, S, OKADA, J and UYEO, S (1965) *Chem Commun* 525, (b) UYEO, S, OKADA, J, MATSUNUGA, S and ROWE, J W (1968) *Tetrahedron* **24,** 2859

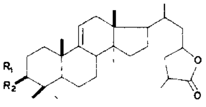
[3] HERGERT, H L (1969) *Abstracts, Northwest Regional Meetings Amer Chem Soc*, Seattle, June

[4] (a) ALLEN, F H, KUTNEY, J P, TROTTER, J and WESTCOTT, N D (1971) *Tetrahedron Letters* 283, (b) KUTNEY, J P, GRIERSON, D S, KNOWLES, G D, WESTCOTT, N D and ROGERS, I H (1973) *Tetrahedron* **29,** 13

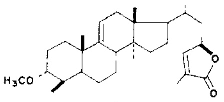
[5] We thank Pr J P KUTNEY (Vancouver) for a sample of 24,25-dihydrograndisolide

[6] For a well documented discussion of NMR spectra of this skeleton see Ref 4b

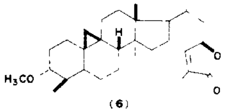




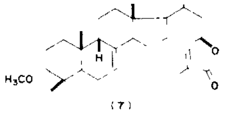
(1) R_1 = OH, R_2 = H
(2) R_1 = OAc, R_2 = H
(3) R_1, R_2 = O
(4) R_1 = OMe, R_2 = H



(5)



(6)



(7)

For **1** and **2**, the signal of 3-H is the triplet (*J* 3 Hz) expected for an equatorial proton, the hydroxyl is therefore 3α, like the methoxy group of the other *Abies* triterpenes.

The structures used for this comparison are unambiguous: grandisolide **5** has been obtained by unambiguous chemical transformations from cyclo-grandisolide **6**[4a] and abieslactone **7**,[7] the structures of which have been proved by radiocrystallography [2b,7a] A $\Delta^{9(11)}$ structure is further indicated by the stability of the acetate **2** in $CF_3CO_2H/CHCl_3$. abieslactone **7**, in these conditions, is easily isomerized to grandisolide **5**

TABLE 1 NMR DATA ON TRITERPENOIDS (δ VALUES)

	C-Methyl peaks					
	18	32	30	31	19	Olefinic peaks
$\Delta^{9(11)}$ Lanost-9(11)-en-3α-ol calc[4b]	0.66	0.76	0.89	0.98	1.11	
Grandisolide **5**	0.64	0.74	0.88	0.98	1.05	5.20
Alcohol **1**	0.67	0.76	0.90	0.97	1.07	5.26
Acetate **2**	0.69	0.79	0.87	0.98	1.08	5.20
Δ^7 Abieslactone **7**	(0.92–1.10) six C-Me's					5.52

Because of the limited amount of alcohol **1** isolated further chemical work was not possible. We assign to lactone **1** the structure of 3α-hydroxylanost-9(11)-en-26,23 olide.

Acknowledgement—We thank Mme M Faure-Raynaud for the extract of needles used in this work

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[7] (a) KUTNEY, J P and WESTCOTT, N D (1971) *Tetrahedron Letters* 3463, (b) IRIE, H and UYEO S (1971) *Tetrahedron Letters* 3467