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ISOLATION AND THE STRUCTURE OF EUOLALIN, A NEW SESQUITERPENE POLYESTER, FROM EUONYMUS ALATUS FORMA STRIATUS (THUNB.) MAKINO

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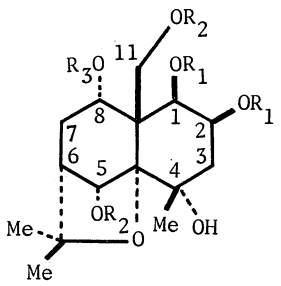
A new sesquiterpene polyester of eudesmane type was isolated from Euonymus alatus forma striatus (Thunb.) Makino, and the structure was established to be (1), based on chemical and spectral evidences.

In recent years, the structures of a number of complex alkaloids from Celastraceae family have been elucidated:[1 - 5] their structural feature is that the sesquiterpene polyalcohols of eudesmane type are esterified with acids including various pyridine carboxylic acids. We herein describe the isolation and the structural determination of euolalin, a new sesquiterpene polyester of this type lacking the nitrogen function from Euonymus alatus forma striatus (Thunb.) Makino. A non-basic fraction obtained from the hexane extract of dried fruits of the plant was chromatographed on silicic acid with chloroform provided euolalin (1),[6] mp 219 - 221°, $C_{38}H_{46}O_{12}$, $[\alpha]_D^{27}$ + 88.5° (c 2.3, $CHCl_3$), ir ($CHCl_3$) 3560, 3000, 1740, 1605, 1590 cm^{-1}; mass 694 (M+); nmr (Table). Euolalin, on alkaline hydrolysis (10% KOH - MeOH, room temp.) afforded a hexaol (2),[6] (mp 184 - 186°, $C_{15}H_{26}O_7$), which formed the pentaacetate (3),[6] (mp 209.5 - 211°, $C_{25}H_{36}O_{12}$) by acetylation (Ac_2O - Py, 80°). Based on the nmr spectral analysis and the NOE experiments as to (2) and (3), the hexaol was deduced to be deoxymaytol,[7] and the identification was made by nmr spectral comparison.[8] The nmr spectrum of euolalin (1), coupled with the detection of methyl benzoate by tlc on methanolysis of (1), suggested the presence of two acetate groups (δ 1.71, 1.98, 3H each) and of two benzoate groups (δ 7.1 - 8.4, 10H). Considering the molecular formula and the nmr spectrum of euolalin, the remaining acid which forms the ester linkage with a hydroxyl of deoxymaytol was deduced to be α-methylbutyric acid. Partial hydrolysis of euolalin (1) (18% HCl - dioxane (1 : 1), 70°, 3 hr) gave bisdeacetyl euolalin (4),[6] (mp 203 - 204°, $C_{34}H_{42}O_{10}$), acetylation of which (Ac_2O - Py, room temp.) regenerated euolalin (1). Comparison of the nmr spectra of (1) and (4) clearly indicated the location of the two acetate groups to be at C-5 and C-11 in euolalin (see Table).



	R_1	R_2	R_3	
1	PhCO	Ac	Et(Me)CHCO	(euolalin)
2	H	H	H	
3	Ac	Ac	Ac	
4	PhCO	H	Et(Me)CHCO	
5	PhCO	Me	Et(Me)CHCO	
6	H	Me	H	
7	PhCO	Me	H	

Table. NMR Spectral Data (δ in ppm, 100 MHz)

	solvent	H-1	H-2	H-5	H-8	H-11
1[a]	benzene-d_6	6.11 d 3.1	6.23 ddd 1.0, 3.1, 4.2	6.33 br.s	5.81 d 6.4	4.83, 5.67 AB q 13.0
2	pyridine-d_5	4.99 d 3.0	4.63 ddd 1.0, 3.1, 5.0	5.16 br.s	4.87 dd 4.0, 4.0	4.41, 5.14 AB q 11.0
3	$CDCl_3$	5.50 d 3.0	5.46 m	6.05 br.s	5.13 dd 4.5, 1.5	4.35, 4.96 AB q 13.0
4[b]	benzene-d_6	6.01 d 4.0	6.05 ddd 3.8, 4.0, 5.5	5.08 br.s	5.82 d 4.7	4.32 s
5[c]	$CDCl_3$	5.70 d 3.2	5.72 m	4.82 br.s	5.23 d 4.5	3.72, 4.43 AB q 10.5
6[d]	$CDCl_3$	4.10 d 3.1	4.23 m	3.85 br.s	3.93 d 6.1	3.22, 3.56 AB q 10.5
7[d]	$CDCl_3$	5.79 d 3.8	5.88 ddd 3.8, 3.0, 5.1	4.76 br.s	3.86 m	3.97, 4.45 AB q 11.0

a) Ac × 2 (1.71, 1.98); benzoate × 2 (7.1 - 8.4, 10H); Et(Me)CHCO- [1.43 (3H, t, 7.2), 1.78 (3H, d, 7.0)].
b) benzoate × 2 (7.2 - 8.3, 10H); Et(Me)CHCO- [0.42 (3H, t, 7.0), 1.78 (3H, d, 7.0)].
c) benzoate × 2 (7.2 - 8.3, 10H); Et(Me)CHCO- [0.45 (3H, t, 6.7), 0.68 (3H, d, 6.8)].
d) benzoate × 2 (7.2 - 8.2, 10H).

Methylation of (4) (MeI - Ag_2O, DMF, 50°, 10 hr) afforded the dimethyl ether (5),[6] (mp 211 - 213°, $C_{36}H_{46}O_{10}$), which on alkaline hydrolysis (10% KOH - MeOH, room temp., 4 hr) yielded a tetraol dimethyl ether (6),[6] (mp 216 - 220°, $C_{17}H_{30}O_7$). This derivative (6), on benzoylation (PhCOCl - Py, 50°, 6 hr) formed the dibenzoate (7),[6] whose nmr spectrum showed that the hydroxyls benzoylated were at C-1 and C-2. Treatment of the dibenzoate (7) with (±)-α-methylbutyryl chloride in the presence of triethylamine and 4-dimethylaminopyridine (DME, reflux, 8 hr) afforded a mixture of two diastereomers, one of which was shown to be identical with the dimethyl ether (5). These results clearly established the location of the five acyl groups in euolalin. Thus the structure of euolalin was proved to be (1).

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