Isolation and Structure Elucidation of Four New Dihydro-β-agarofuran Polyesters from *Euonymus sachalinensis*

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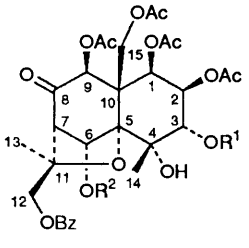
Four new dihydro-β-agarofuran polyesters **1–4** have been isolated from the fruit of *Euonymus sachalinensis* (*Celastraceae*) and their structures elucidated by means of ^{1}H and ^{13}C NMR spectroscopy, including ^{1}H–^{1}H COSY, DEPT, ^{1}H–^{13}C COSY and COLOC measurements, mass spectrometry and chemical reactions. The configurations have been determined on the basis of NOESY spectra and X-ray analysis. The isolated compounds are the first native representatives of 3,12-oxygenated dihydro-β-agarofuran in which the usual macrocycle is missing. The structural similarity of compounds **1–4** and the macrocyclic derivatives is noteworthy from a biogenetic point of view.

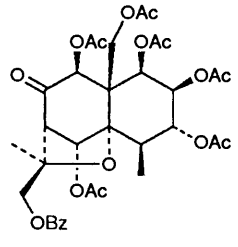
The *Celastraceae* family is a rich source of sesquiterpene esters based on the dihydro-β-agarofuran skeleton. In recent years these compounds have aroused interest as a result of their biological activity: cytotoxic,[1] anti-tumour promoting,[2] immunosuppressive,[3] insecticidal and insect antifeedant[4–5] activity. The number of known compounds is more than 300, many of them containing a 15- or 16-membered macrocycle due to esterification of dicarboxylic acids (*e.g.* evoninic acid, wilfordinic acid, edulinic acid, *etc.*) at positions 3 and 12.[6]

As part of an intensive investigation into biologically active metabolites from the *Celastraceae* family, *Euonymus sachalinensis* (F. Schmidt) Maxim. is being studied. This species is indigenous to South-East Asia, and especially to Sachalin Island; it occurs in Europe as a decorative shrub. Preliminary insecticidal screening showed that a cyclohexane extract of the fruit possessed moderate toxicity against the L_4 larvae of *Pieris brassicae*. Examination of the extract resulted in the isolation of four new sesquiterpene polyesters.

The present paper deals with structural and conformational studies of compounds **1–4**. The marked structural similarity of compounds **1** and **2** and the macrocyclic dihydro-β-agarofuran esters raises a biogenetic question, which is also discussed.



	R^1	R^2
1	$MeCH_2CH(Me)CO$	Ac
2	$MeCH_2CH(Me)CO$	H
3	3-Furoyl	Ac



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Results and Discussion

A cyclohexane-soluble portion of a methanolic extract of fruit (4800 g) of *Euonymus sachalinensis* was subjected to polyamide column chromatography (CC). The fractions obtained were further separated by silica gel CC, preparative TLC and HPLC to give new sesquiterpene polyesters **1** (36 mg), **2** (2.3 mg), **3** (18.5 mg) and **4** (230 mg).

Compound **1**, $C_{37}H_{46}O_{17}$, was analysed by HRMS and NMR spectroscopy. It exhibited IR absorption bands at 3520, 1740, 1700, 1600, 1430 and 700 cm^{-1} and UV maxima at 232, 267sh, 273 and 282 nm, characteristic of hydroxy, ester and phenyl groups. The ^{1}H and ^{13}C NMR spectra of compound **1** revealed the presence of five acetate, one 2-methylbutanoate and one benzoate groups (Tables 1 and 2). The ^{13}C NMR and JMOD (*J*-Modulated Spin Echo Experiment; *J* = scalar coupling) spectra suggested that the remaining skeleton consisted of 15 carbons: two methyls, two methylenes, six methines and five quaternary carbons. The ^{13}C NMR chemical shift values indicated a nonasubstituted dihydro-β-agarofuran skeleton bearing an oxo group according to the signal at δ_C 196.6. The ^{1}H NMR spectrum contained thirteen signals due to the parent skeleton, which were unequivocally assigned from the ^{1}H–^{1}H COSY spectrum. An isolated spin–spin system of three methine protons was seen at δ_H 5.68 d, 5.28 t and 4.79 d, with coupling constants 3.2 and 3.0 Hz. These data are compatible with substitution at C-1, C-2 and C-3 with stereochemistry 1-H_{ax}, 2-H_{eq} and 3-H_{eq}.[7] One downfield methine proton was observed as a slightly broadened singlet (δ_H 6.66, J < 1.0 Hz) which correlated with the proton signal at δ_H 3.16; these are assignable to axial 6-H and equatorial 7-H.[8] Additionally, the ^{1}H NMR spectrum contained two sets of methylene protons. One of them corresponded to 12-H, on the basis of its correlation peak with the 13-methyl group, and the other to 15-H. The signal at δ_H 5.60, which did not exhibit any correlations, corresponded to 9-H. According to the singlet signal of 9-H, and the paramagnetically shifted 7-H (δ_H 3.16 s), the oxo group mentioned above must be sited at C-8. The remaining two methyl signals are attributed to 13-H (δ_H 1.63 s) and 14-H (δ_H 1.57 s), the latter indicating a substituent at C-4.

The relative configuration of compound **1** was studied by means of NOESY measurements. Cross-peaks between 15-H, 14-H and 6-H proved a *trans*-fused chair–chair decalin core and the axial orientation of 6-H and the 14-methyl group. The

Table 1 ^{1}H NMR spectral data of compounds **1**–**4** [400 MHz, $CDCl_3$, δ/ppm (J/Hz)]

Proton	1	2	3	4
1	5.68 d (3.2)	5.65 d (3.3)	5.84 d (3.1)	5.92 d (3.4)
2	5.28 t (3.0)	5.28 t (3.0)	5.32 t (3.0)	5.36 ddd (3.3, 2.2, 1.1)
3	4.79 d (3.0)	4.77 d (3.0)	5.10 d (3.0)	4.89 dd (2.2, 1.1)
4	—	—	—	2.65 m
4-OH	4.08 d (0.9)	5.79 s	4.65 s	—
6	6.66 brs	5.34 brd (3.2)[a]	6.71 s	6.40 d (0.9)
7	3.16 s	3.20 d (0.9)	3.13 s	3.34 d (0.9)
9	5.60 s	5.58 s	5.64 s	5.65 s
12a	5.14 d (11.5)	5.77 d (11.8)	5.37 d (11.8)	4.66 d (10.8)
12b	4.36 d (11.5)	3.85 d (11.8)	4.15 d (11.8)	4.25 d (10.8)
13	1.63 s	1.67 s	1.66 s	1.60 s
14	1.57 s	1.90 s	1.62 s	1.28 d (7.9)
15a	4.86 d (13.0)	4.90 d (13.0)	4.90 d (13.0)	4.87 d (13.0)
15b	4.47 d (13.0)	4.39 d (13.0)	4.50 d (13.0)	4.46 d (13.0)
Benzoyl				
2',6'	8.02 'd' (7.2)	8.07 'd' (7.2)	7.79 'd' (7.2)	7.99 'd' (8.5)
3',5'	7.48 't' (7.9)	7.49 't' (7.5)	7.37 't' (7.8)	7.46 't' (8.0)
4'	7.62 't' (7.9)	7.63 't' (7.8)	7.57 't' (7.5)	7.60 't' (8.0)
Acetyls				
1-OAc	1.92 s	1.90 s[b]	1.93 s[c]	1.98 s
2-OAc	2.15 s	2.16 s[b]	2.18 s[c]	2.14 s
3-OAc	—	—	—	2.01 s
6-OAc	2.17 s	—	2.18 s[c]	2.13 s
9-OAc	2.12 s	2.09 s[b]	2.13 s[c]	2.13 s
15-OAc	2.04 s	1.98 s[b]	2.05 s[c]	2.02 s
2-Methylbutanoyl				
=CH–	2.40 m	2.24 m	—	—
CH_2	1.72 m, 1.41 m	1.65 m, 1.25 m	—	—
CH(*Me*)	1.11 d (7.1)	0.89 d (7.3)	—	—
CH_2*Me*	0.86 t (7.4)	0.78 t (7.5)	—	—
3-Furoyl				
2''	—	—	7.96 s	—
4''	—	—	7.09 t (1.6)	—
5''	—	—	6.66 d (1.6)	—

[a] 6-OH: δ_H 5.89 d (4.0). [b,c] Assignments may be interchanged.

Table 2 ^{13}C NMR spectral data of compounds **1**, **3** and **4** (100 MHz, $CDCl_3$, δ/ppm)

C	1[a]	3[b]	4[c]	C	1[a]	3[b]	4[c]
1	71.7	71.4	72.2	Bz*C*O	166.4	166.3	165.7
2	68.6	69.1	69.7	1'	129.5	129.0	129.3
3	75.3	74.8	73.1	2',6'	129.8	129.6	129.6
4	69.6	79.0	37.4	3',5'	128.8	128.4	128.6
5	94.5	94.7	91.8	4'	133.8	133.5	133.6
6	74.0	73.9	74.6	1-CO	169.2	169.2	169.2
7	62.0	62.3	60.5	1-CO*Me*	20.6	20.5	20.6
8	196.6	196.3	197.0	2-CO	168.5	168.5	168.8
9	78.6	78.6	78.6	2-CO*Me*	21.1	21.0	21.0
10	52.3	52.3	51.1	3-CO	174.9	161.1	169.9
11	86.1	86.3	83.9	6-CO	169.6	169.4	169.1
12	69.8	69.8	69.8	6-CO*Me*	21.4	21.3	21.1
13	19.4	19.0	20.9	9-CO	169.4	169.3	169.2
14	24.0	23.8	15.5	9-CO*Me*	20.3	20.2	20.2
15	60.5	60.4	59.9	15-CO	169.8	169.7	169.7
				15-CO*Me*	20.6	20.5	20.5

[a] 2-Methylbutanoyl: δ_C 41.0 (=CH–), 25.9 (–CH_2–), 16.6 (=CH*Me*–) and 11.6 (–CH_2*Me*). [b] Assignments of chemical shifts were made on the basis of DEPT spectrum and analogy with **1**; 3-furoyl: δ_C 148.3 (C-2''), 118.6 (C-3''), 143.8 (C-4'') and 109.7 (C-5''). [c] 3-CO*Me*: δ_C 21.1.

proton signal at δ_H 5.60 (9-H) was correlated with the proton signals at δ_H 5.68 (1-H) and 1.63 (13-H); therefore, 1-H and 9-H have axial stereochemistry. Correlative signals between 3-H (δ_H 4.79) and 14-H (δ_H 1.57) suggested an equatorial 3-H. Observation of a cross-peak between 14-H and the hydroxy group (δ_H 4.08) revealed the presence of a free hydroxy at C-4, characteristic for this group of compounds.[6] The ester group distribution of compound **1** was established by using ^{1}H–^{13}C long-range correlation spectroscopy (COLOC). The correlations of the carbonyl signal at δ_C 166.4 (benzoyl-*C*O) with the proton signals at δ_H 5.14 and 4.36 (12a,b-H) indicated the presence of a benzoyl group at C-12. The carbonyl signal at δ_C 174.9 correlated with 3-H (δ_H 4.79) and the methyl signals of the 2-methylbutanoyl group (δ_H 1.11 d), and it could therefore be placed at C-3. Similarly, the long-range couplings of the carbonyl carbon signals at δ_C 169.8, 169.6, 169.4, 169.2 and 168.5 with the proton signals at δ_H 4.86 (15a-H), 6.66 (6-H), 5.60 (9-H), 5.68 (1-H) and 5.28 (2-H) and the acetyl methyl signals at δ_H 2.04, 2.17, 2.12, 1.92 and 2.15 showed the presence of acetyl groups on C-15, C-6, C-9, C-1 and C-2, respectively. With regard to the above data, the structure of this compound is formulated as **1**. The complete assignments of all ^{1}H and ^{13}C NMR signals were also performed on the basis of the ^{1}H–^{1}H COSY and ^{1}H–^{13}C COSY spectra. As quaternary carbons could not be assigned by this method, COLOC measurements were applied (Fig. 1).

Compound **2** was isolated as an amorphous solid with molecular formula $C_{35}H_{44}O_{16}$. It contained one benzoate, one 2-methylbutanoate and four acetate groups and the same dihydro-β-agarofuran polyol as in compound **1** (Table 1). Determination of the ester group positions was accomplished by means of NOESY measurements. The cross-peaks of all four

acetyl methyl groups proved their steric proximity, which suggested 1,2,9,15-tetraacetyl substitution; the cross-peak between 4-OH and one methylene proton signal of the 2-methylbutanoyl unit (δ_H 1.65 m) indicated the 2-methylbutanoyl group at position 3. The downfield 6-H signal (δ_H 5.34 d) indicated a free hydroxy group at position 6. From these results compound **2** was concluded to be the 6-desacetyl derivative of **1**. Chemical transformations confirmed this fact: compound **2** was converted into **1** by acetylation with acetic anhydride in pyridine, and conversely, partial hydrolysis of **1** with diethylamine at 5 °C afforded **2**.

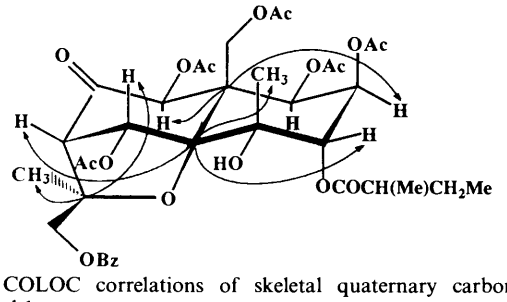


Fig. 1 COLOC correlations of skeletal quaternary carbons of compound **1**

Compound **3** was obtained as prisms with the molecular formula $C_{37}H_{40}O_{18}$. The ^1H and ^{13}C NMR spectra of **3** (Tables 1 and 2) showed it to be an 8-oxodihydro-β-agarofuran derivative with one hydroxy, five acetate, one benzoate and one 3-furoate groups in positions 1β, 2β, 3α, 4α, 6α, 9β, 12 and 15.[7,9] The ester group distribution, absolute configuration and molecular conformation were established by X-ray analysis (Fig. 2). The tetrahydrofuran ring is closed by a $-CH_2O-$ bridge between C-5 and C-7 atoms, which gives rise to increased angle and torsional strains, in particular at C-5, C-6 and C-10. In the cyclohexanone **B** ring the C(5)–C(6)–C(7) angle is diminished from 111° [claimed for cyclohexane[10] if an equilibrium between the Baeyer and Pitzer strains is established with respective torsion angle (s) of $\varphi = 56°$] to 100.1(3)° and accompanied by two extra high endocyclic torsion angles [79.1(3)° and −73.8(3)°] about the C(5)–C(6) and C(6)–C(7) bonds, respectively. The high ring pucker at C-6 is somewhat eased, however, by the stretch of the C(5)–C(10) bond [1.601(3) Å] along the ring junction and partly counterbalanced by the low torsional parameters around the opposite C-9 atom [C(5)–C(10)–C(9)–C(8) = 42.3(3)° and C(10)–C(9)–C(8)–C(7) = −43.5(3)°]. Simultaneously, the endocyclic bond angle [114.4(3)°] at C-9 is increased at the expense of the sp^2-bond

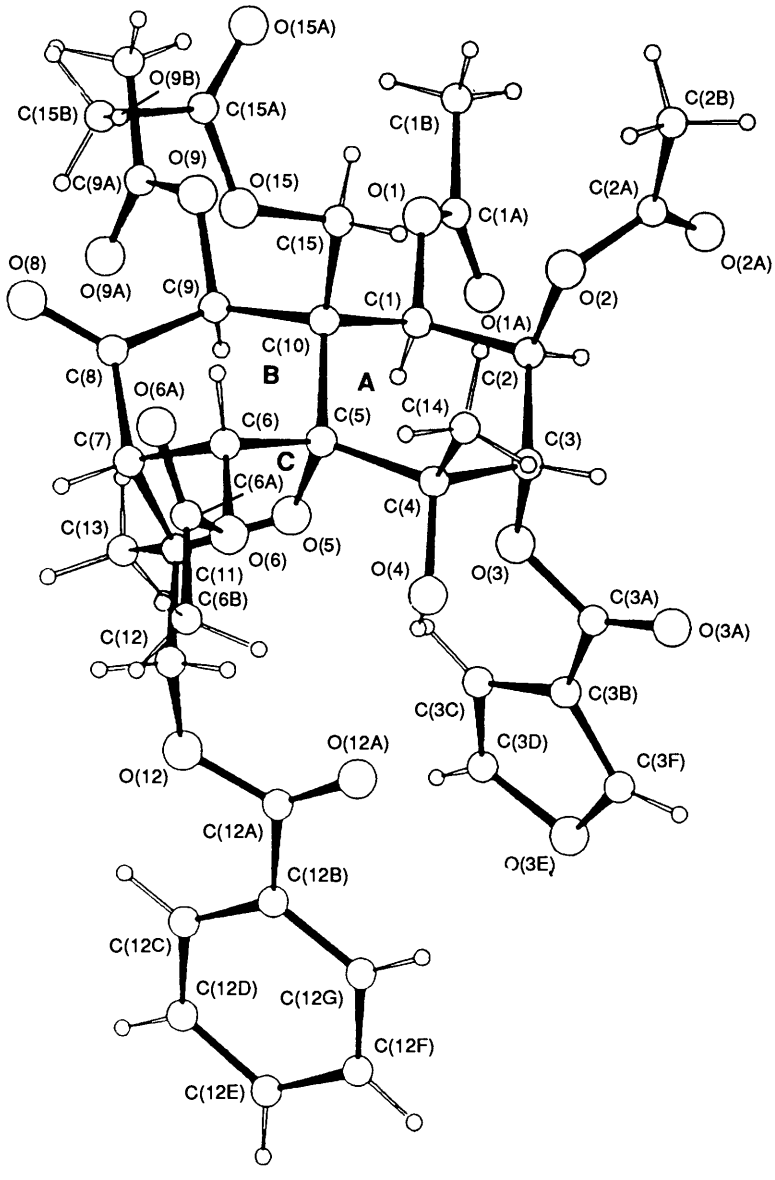


Fig. 2 X-Ray molecular structure of compound **3**

angle at the carbonyl C-8, which is narrowed from the theoretical 120° to 115.1(3)°. Notwithstanding, as shown by the puckering parameters[11] [Q = 0.700(3) Å, θ = 22.9(2)°], the cyclohexanone ring remains in the chair conformation with strong distortion. According to the Bucourt's formulae the Pitzer strain amounts to 11.3 kcal mol^{-1}.* Of the D_{3d} symmetry only a mirror plane bisecting C-6 and C-9 atoms is retained with the asymmetry factor[12] C_s = 3.5 pm.

In contrast, the cyclohexane ring **A** with its own five substituents and with two others, [O-5: α(ax) and C-15: β(ax)] shared with ring **B**, is a rather flattened chair. The Pitzer strain is only about 2.3 kcal mol^{-1}. The puckering amplitude is low Q = 0.530(3) Å with θ = 9.8(3)°, while the endocyclic bond angles are increased somewhat at C-1, C-3 and C-5, and closed to 106.4(3)° at C-10. The congestion of the substituents results in a distorted tetrahedron around C-5, the mean bond angle (109.3°) has a r.m.s. deviation of 4.2°. In particular, the 1,3-diequatorial substituents at C-4 and C-6 give rise to a high C(4)–C(5)–C(6) angle of 116.0(3)°. Similarly, the r.m.s. deviation of the mean tetrahedral angle (109.4°) about C-10 is 3.8°. The largest angle [117.2(3)°] around C-10 is maintained by the C-5 and the axial C-15 atoms.

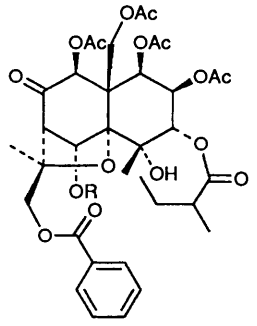
The conformation of the five-membered hetero ring **C** is close to half-chair with a C_2 symmetry axis bisecting O-5. In accordance with the large pucker of ring **B** at C-6, the biggest out-of-plane amplitudes are shown by the C-6 and C-7 atoms [the puckering amplitude Q = 0.437(3) Å]. The corresponding lowest asymmetry factor[12] fC_2 = 3.2 pm.† Both O-6 and C-12 are axial to the hetero ring, whereas C-13 assumes a pseudo-equatorial position.

Compound **4** was obtained as an amorphous solid with the molecular formula $C_{34}H_{40}O_{16}$. The ^{1}H and ^{13}C NMR spectra (Tables 1 and 2) proved it to be a sesquiterpene polyester with one benzoyl and six acetyl ester groups. The multiplicity and coupling constants of the ^{1}H NMR signals in the region δ_H 4.2–6.4 suggested that compound **4** is a 1β,2β,3α,6α,9β,12,15-heptasubstituted-8-oxodihydro-β-agarofuran derivative.[14] In contrast with the above compounds, in **4** the 4-hydroxy group is missing as indicated by a doublet for the 14-methyl, a double doublet for 3-H and long-range coupling (J 1.1 Hz) between 2-H and 4-H.

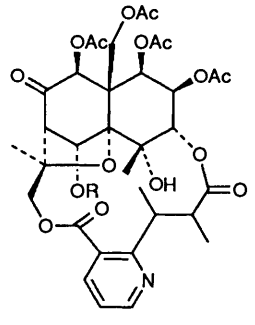
The relative configuration of **4** was elucidated by means of NOESY measurements. The proton signal at δ_H 5.65 (9-H) correlated with the proton signals at δ_H 5.92 (1-H) and 1.60 (13-H), and therefore 9-H has axial stereochemistry. The cross-peaks between 3-H (δ_H 4.89 dd) and 14-H (δ_H 1.28 d), between 1-H (δ_H 5.92 d) and 2-H (δ_H 5.36 ddd) and between 7-H (δ_H 3.34 d) and 12-H (δ_H 4.66 d, 4.25 d) indicated the axial orientation of 6-H and the 14-methyl group, and the equatorial orientation of 2-H and 3-H, and confirmed the assignments of the ^{1}H NMR chemical shifts to the 12- and 15-methylene protons.

The ester groups were located on the basis of a COLOC spectrum. The correlations of the carbonyl carbon signal at δ_C 165.7 with the proton signals at δ_H 7.99 'd' (*ortho*-benzoyl) and δ_H 4.66 d, 4.25 d (12-H) confirmed the siting of the benzoyl group at C-12. On the other hand, acetate groups could be placed at C-1, C-2, C-3, C-6, C-9 and C-15 from the correlation peaks of the carbonyl carbons at δ_C 169.2 168.8, 169.9, 169.1, 169.2 and 169.7 with 1-H, 2-H, 3-H, 6-H, 9-H and 15-H and the acetyl methyl protons at δ_H 1.98, 2.16, 2.01, 2.13, 2.13 and 2.02, respectively. Thus, the structure of this compound was elucidated as shown in formula **4**. The full ^{13}C NMR chemical shift assignments were made with ^{1}H–^{13}C COSY spectral analysis. The data are listed in Table 2.

The isolated compounds are the first native representatives of 3,12-oxygenated dihydro-β-agarofurans which are esterified with monocarboxylic acids, and in which the characteristic macrocycle is missing. In compounds **1–3** an aromatic ester group is present in position 12 and a C_5-unit (a 2-methylbutanoyl or 3-furoyl group) is found at C-3. There are marked structural similarities between compound **1** and the macrocyclic evonine **5**, and between **2** and neoevonine **6**. This fact raises the biogenetic question: could the dilactone structure not be formed in **1** and **2** because a benzoyl group is found at C-12 instead of a nicotinoyl group? Is it possible that the dicarboxylic bridges are formed from the corresponding monocarboxylic acids only after their binding to the sesquiterpene polyol nucleus? This is suggested by the sesquiterpene alkaloids of *Catha edulis*, *e.g.* katedulin K-19 and katedulin K-17.[15] To our knowledge, the dicarboxylic acids mentioned above have not been found in free form or as substituents in other types of compounds.



1 R = Ac
2 R = H



5 R = Ac
6 R = H

Experimental

General.—Melting points were determined on a Boetius apparatus and are uncorrected. IR spectra were run as KBr discs on a Specord 75 instrument. UV spectra in MeOH were obtained on a Specord UV–VIS spectrophotometer. Mass spectral measurements were carried out on a VG ZAB2-SEQ tandem mass spectrometer operating under FAB conditions using Cs ion gun at 30 keV and NOBA matrix. ^{1}H and ^{13}C NMR spectra (spectral data see Tables 1 and 2) were recorded on a Bruker AM-400 spectrometer at 400.13 (^{1}H NMR) and 100.62 MHz (^{13}C NMR), using $CDCl_3$ as solvent and TMS as internal standard. Literature pulse sequences were used for the 1D and 2D NMR experiments; ^{1}H–^{1}H COSY: 512 × 512 data matrix size, time domain 512 in F1 and 1024 in F2, relaxation delay (rd) = 2 s, number of scans (ns) = 8, dummy scans (ds) = 4; NOESY: data matrix size 512 × 512, time domain 512 in F1 and 1024 in F2, rd = 2 s, ns = 32, ds = 4, mixing time 800 ms; HETCOR: data matrix size 2048 × 512, time domain 256, ns = 96, ds = 4, rd = 2 s; COLOC: data matrix 64 × 512, time domain 256, ns = 96, rd = 2 s, delay 0.0625 s.

Plant Material.—The fruit of *Euonymus sachalinensis* was collected in September 1989 in the Nursery Garden of the Parks and Gardens Department, Budapest-Tahi, Hungary. A voucher specimen has been deposited in the Herbarium of the Museum of Natural Sciences, Budapest.

Isolation. Fresh fruit (4800 g) was extracted with MeOH. The cyclohexane phase was chromatographed on a polyamide

* 1 cal = 4.184 J.

† To distinguish from Duax and co-workers' asymmetry parameters ΔC_2, ΔC_5,[13] Kálmán introduced the asymmetry factors denoted as fC_2 and fC_5.

(Woelm) column. Fractions eluted with MeOH–H_2O (3:2) were transferred to a silica gel (Kieselgel 60, 0.063–0.2 mm, REANAL) column and successively eluted with cyclohexane–EtOAc solvent mixtures of increasing polarity (9:1, 8:2 and 7:3). The fractions obtained with cyclohexane–EtOAc 7:3 were repeatedly separated by preparative TLC with the use of benzene–EtOAc (4:1), $CHCl_3$–Me_2CO (19:1) and hexane–THF–MeCN (60:30:7) as solvent systems. Further purification by HPLC [BST SI-100-S 250 × 4 mm column, with cyclohexane–EtOAc–EtOH (25:20:1) as eluent] yielded compounds **1**–**4**.

Compound **1**.—M.p. 185–190 °C (from MeOH). λ_{max}/nm 232 (log ε/dm^3 mol^{-1} cm^{-1} 3.989), 267sh (2.982), 273 (3.028) and 282 (2.961); ν_{max}/cm^{-1} 3520, 2950, 1740, 1700, 1600, 1430, 1350, 1260, 1230, 1210, 1070 and 700; *m/z* (FABMS) 785 (M + Na)$^+$, 763 (M + H)$^+$, 745 [(M + H) − H_2O]$^+$, 703 [(M + H) − CH_3COOH]$^+$ and 581 [(M + H) − CH_3CO_2H − $PhCO_2H$]$^+$; {Found: [(M + H) − H_2O]$^+$, 745.2627. $C_{37}H_{45}O_{16}$ requires 745.2707}.

Compound **2**.—Amorphous solid. λ_{max}/nm 230 (log ε/dm^3 mol^{-1} cm^{-1} 3.622), 267sh (2.978), 273 (2.973) and 281 (2.920); ν_{max}/cm^{-1} 3520, 2920, 1760, 1740, 1700, 1450, 1370, 1270, 1250, 1220, 1100 and 700; *m/z* (FABMS) 743 (M + Na)$^+$, 721 (M + H)$^+$ and 703 [(M + H) − H_2O]$^+$.

Acetylation of **2**.—Compound **2** (2 mg) was treated with Ac_2O (200 mm^3) in pyridine (200 mm^3) during 23 h at room temperature. After the usual work-up, one product was obtained, which, on the evidence of TLC and the ^{1}H NMR spectra, was identical with **1**.

Partial Hydrolysis of **1**.—Diethylamine (5 mm^3) was added to a solution (at 5 °C) of compound **1** (5.8 mg) in MeOH (260 mm^3). After 16 h at 5 °C, the solution was evaporated to dryness under reduced pressure. TLC of the residue with toluene–EtOAc (13:7) as eluent separated two major components, unchanged **1** (1.7 mg) and **2** (2.3 mg).

Compound **3**.—M.p. 239–240 °C (from MeOH). λ_{max}/nm 234 (log ε/dm^3 mol^{-1} cm^{-1} 3.905), 275 (3.133) and 282sh (3.070); ν_{max}/cm^{-1} 3540, 2920, 1770, 1760, 1750, 1740, 1610, 1480, 1260, 1240, 1170, 1100, 1080 and 730; *m/z* (FABMS) 773 (M + H)$^+$ and 755 [(M + H) − H_2O]$^+$; {Found: [(M + H) − H_2O]$^+$, 755.2167. $C_{37}H_{41}O_{17}$ requires 755.2187}.

Compound **4**.—Amorphous solid. M.p. 95–100 °C (from MeOH). λ_{max}/nm 232 (log ε/dm^3 mol^{-1} cm^{-1} 3.884), 268sh (3.029), 274 (3.063) and 282 (3.012); ν_{max}/cm^{-1} 2900, 1740, 1730, 1710, 1440, 1360, 1260, 1210, 1100, 1070 and 700; *m/z* (FABMS) 727 (M + Na)$^+$, 705 (M + H)$^+$, 645 [(M + H) − CH_3CO_2H]$^+$ and 603 [(M + H) − CH_3CO_2H − CH_2CO]$^+$; [Found: (M + H)$^+$, 705.2524. $C_{34}H_{41}O_{16}$ requires 705.2394].

Crystal Structure Analysis of Compound **3**.—$C_{37}H_{40}O_{18}$, M = 772.69, orthorhombic, a = 9.985(1), b = 13.814(1), c = 28.824(2) Å, U = 3975.8(6) Å^3, Z = 4, D_c = 1.291 Mgm^{-3}, $F(000)$ = 1624, μ = 0.888 mm^{-1} for Cu-Kα radiation (λ = 1.5418 Å). Space group $P2_12_12_1$.

The intensities of 8208 unique reflections were collected from a colourless crystal having dimensions of 0.50 × 0.50 × 0.20 mm, on an Enraf–Nonius CAD-4 diffractometer, in the range $3.07 < \theta < 75.82$, by an ω–2θ scan, using a graphite monochromator. Cell constants were determined by least-squares refinement of 25 reflections ($32.1 < \theta < 36.8$). Three standard reflections were monitored every hour, and a decay correction (corr. factor from 1 to 1.12, av. = 1.05) was applied. The phase problems were solved by direct methods, using SHELXS-86.[16] The full matrix least-squares refinement on F^2 was carried out with the program SHELXL-93[17] for 8198 reflections [$I > 2\sigma(I)$] and 504 parameters. The final R values: $R1$ = 0.044, $wR2$ = 0.12 and S = 0.975. H-Atom coordinates were generated and constrained to the adjacent C or O atoms. Largest peak and hole in the final difference electron-density calculation: 0.093 and −0.081 eÅ^{-3}. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.*

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* For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 1*, 1994, Issue 1.

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