New Sesquiterpene Esters from *Euonymus europaeus* and *E. latifolius*

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Ten new sesquiterpenoid esters based on the dihydroagarofuran moiety, *viz.* (16), (28), (29), (30a), (30b), (31), (32), (36), (37), and (40), have been isolated from *Euonymus europaeus* and *E. latifolius* in addition to three known compounds (10), (14), and (15). Structures of the isolated compounds were deduced from 1 D and 2D COSY and NOESY ¹H n.m.r. and mass spectral data.

Recently a series of sesquiterpenoid esters/alkaloids based on the dihydroagarofuran moiety has been isolated from *Euonymus verrucosus*[1] and *E. japonicus*.[2] Continuing our screening of native or locally cultivated *Euonymus* species for sesquiterpene derivatives, *E. europaeus* and *E. latifolius* were investigated. From the former species a number of sesquiterpene alkaloids[3]—evonoline (= 4-deoxyevonine) (1), evonine (= alkaloid C) (2), neoevonine (= evorine = alkaloid A) (3), evozine (= alkaloid B) (4), 2-deacetylevonine (5), 2,6-dideacetyl-evonine (6), isoevonine (= evonimine) (7), isoevorine (= alkaloid D), evoline, evopine, euroline (the latter alkaloids are not yet identified)—and sesquiterpene esters—esters of Alcohol A (8):[4] A-1 (9), A-2 (10), A-3 (11), A-4 (12), A-5 (13), A-6 (14) and of Alcohol B (18):[5] B-1 (19), B-2 (20), B-3 (21), B-4 (22), B-5 (23), B-6 (24),[6] B-7 (25), and euolaline[7] (27)—have been isolated; from the latter species only one sesquiterpene alcohol (33) has been reported up till now.[8]

Thirteen esters have been isolated by chromatography on a polyamide column, followed by silica gel and alumina preparative t.l.c. (p.l.c.) of the light petroleum–soluble fractions of methanolic extracts of the fruits of *E. europaeus* and *E. latifolius*. In this paper the structures of these components (10), (14)—(16), (28)—(32), (36), (37), and (40) are presented.

The extractives have four different sesquiterpene cores. Compounds (10) ($C_{37}H_{42}O_{13}$), (14) ($C_{32}H_{40}O_{13}$), and (15) and (16) (both $C_{35}H_{40}O_{12}$) form the first set. ¹H N.m.r. chemical shifts and the coupling constants ($J_{1,2}$ and $J_{7,8}$ ~ 4 Hz, $J_{8,9}$ ~ 6 Hz; Table) suggest them to be the esters of Alcohol A (8).

¹H N.m.r. data of compounds (10), (14), and (15) are identical with those of Ester A-2, Ester A-6, and a hydrolysed product of Ester A-2,[4] respectively, isolated earlier from *E. europaeus* by Römer *et al.* (Table; Experimental section).

Compound (16) contains three acetates (δ_H 2.09, 1.97, and 1.39) and a benzoate group [δ_H 7.6—7.4 (6 H), 7.95 and 8.02 (each 2 H)] (Table; Experimental section).

A positive shift of the 1-H resonance in compound (16) (δ_H 4.46) shows C(1)–OH to be unsubstituted. Similar ¹H n.m.r. resonances for 6-H, 8-H, and 9-H in compounds (16) and (17) (Ejap-12)[2] suggest the same substitution pattern on C(6), C(8), and C(9) in both compounds. On the basis of the negative shifts of 2-H (δ_H 5.62) and 15-H_a (δ_H 5.48) compared with those of compound (17) (2-H δ_H 5.23, 15-H_a δ_H 5.11) the second benzoyl substituent for compound (16) is proposed to be at C(2).

The second group of extractives consists of six compounds. Their ¹H n.m.r. data are summarized in the Table. Compounds (28) ($C_{34}H_{36}O_{15}$), (29) ($C_{35}H_{40}O_{12}$), (30a) and (30b) (both $C_{34}H_{42}O_{14}$), (31) ($C_{36}H_{50}O_{12}$), and (32) ($C_{34}H_{48}O_{13}$) seem to be esters of 3-deoxymaytol (26). The relative configuration of 9-H was confirmed by 2D n.O.e. spectroscopy, as is illustrated for structure (28) in Figure 1. In all cases there was significant

n.O.e. interaction between 15-H_b and 9-H besides many other interactions along the sesquiterpene core. An indirect, negative effect (see later) could be detected in each case in the homonuclear 2D NOESY spectrum between 15-H_b and the C-14 (CH_3) group.

The core in compound (28) is esterified with three 3-furoic (characteristic 9 protons δ_H 8.25—6.33) and two acetic moieties (δ_H 2.31, 2.12); compound (29) with two benzoic [δ_H 7.8—7.1 (10 H)] and three acetic (δ_H 2.31, 2.13, 2.05); compound (31) with a benzoic [δ_H 8.03 (2 H), 7.60—7.40 (3 H)], two acetic (δ_H 2.27, 2.11), and two α-methylbutyric [δ_H 1.18, 0.91, 0.78, 0.52 (each 3 H)]; and compound (32) with a 3-furoic (characteristic three protons δ_H 8.01—6.73), two acetic (δ_H 2.26, 2.11), and two α-methylbutyric acids [δ_H 1.20, 0.92, 0.88, 0.68 (each 3 H)]. Isomers (30a) and (30b) have two acetates (Eur-6: δ_H 2.29, 2.12; Eur-15: δ_H 2.30, 2.11), two 3-furoates, and an α-methylbutyrate. Various chemical shifts for the latter substituents [(30a): δ_H 7.87—6.38 (6 H), 1.13, 0.81 (each 3 H); (30b): δ_H 8.27—6.78 (6 H), 0.82, 0.60 (each 3 H)] suggest that locations to be different but on the same skeleton. The position of the esterifying groups in compounds (28), (29), (30a) and (30b), (31), and (32) can be determined only by the help of more sophisticated spectroscopic investigation, the results of which will be published elsewhere.[9]

Two compounds belong to the third group. Compounds (36) and (37) seem to be the esters of 1,2,6,9,15-pentahydroxy-dihydroagarofuran (34) on the basis of ¹H n.m.r. data (Table). Compound (36) ($C_{30}H_{38}O_{11}$) has four acetates (δ_H 2.24, 2.10, 2.08, 1.54) and a benzoate [δ_H 7.6—7.4 (3 H), 8.04 (2 H) (Table; Experimental section)] unit, whereas compound (37) ($C_{35}H_{40}O_{11}$) contains three acetates (δ_H 2.27, 2.10, 1.52) and two benzoates [δ_H 7.6—7.4 (6 H), 8.11 (2 H), 8.07 (2 H) (Table; Experimental section)]. A coupling constant $J_{1,2}$ ~ 3.5 Hz shows a *cis*-1-H,2-H relationship (*cf.* 3.2—3.8[10]). One can detect a significant n.O.e. between 15-H_b and 9-H in compound (36), as shown in Figure 2, thus the latter proton is equatorial.[11] 6-H Should be axial, having n.O.e. cross-peaks on the 2D NOESY map[12] to 15-H_a, 8-H_a, and the C-14 (CH_3) protons.[13]

It is worth noting that an indirect, negative n.O.e. could, for the first time in the literature (to our best knowledge), be detected on the regular homonuclear 2D NOESY map between 15-H_b and the C-14 (CH_3) protons (see Figures 1 and 2). Details of the phenomenon will be presented elsewhere.[14]

¹H N.m.r. data of compounds (36) and (37) show close similarity to those of Ever-1 (35) obtained from *E. verrucosus*[1] and having the same sesquiterpene core (Table). It is known that the ring effects created by benzoate and nicotinoate groups are quite similar,[15] thus we suggest that C(9) is substituted with a benzoate in both compounds (36) and (37). The second benzoyl group in compound (37) can probably be located at C(2) on the basis of a downfield shift of 2-H for (37) (δ_H 5.88) compared with that of (36) (δ_H 5.58).

Compound (40) ($C_{37}H_{42}O_{13}$) has characteristic ¹H n.m.r.

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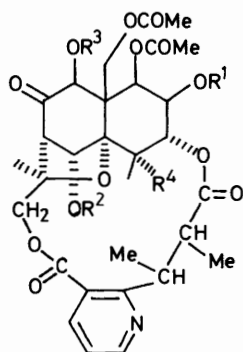
(1) R^{1-3} = MeCO, R^4 = H
(2) R^{1-3} = MeCO, R^4 = OH
(3) $R^{1,3}$ = MeCO, R^2 = H, R^4 = OH
(4) R^1 = MeCO, $R^{2,3}$ = H, R^4 = OH
(5) R^1 = H, $R^{2,3}$ = MeCO, R^4 = OH
(6) $R^{1,2}$ = H, R^3 = MeCO, R^4 = OH
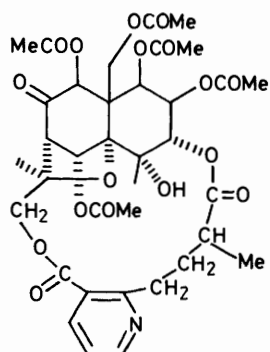
(7)
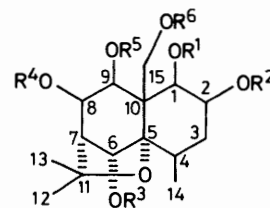
(8) R^{1-6} = H
(9) $R^{1,2,4}$ = PhCO, $R^{3,5,6}$ = MeCO
(10) $R^{1,4}$ = PhCO, $R^{2,3,5,6}$ = MeCO
(11) $R^{1,4}$ = PhCO, R^2 = H, $R^{3,5,6}$ = MeCO
(12) $R^{1,4}$ = PhCO, R^2 = n-C_7H_{15}CO, $R^{3,5,6}$ = MeCO
(13) $R^{1,4}$ = PhCO, R^2 = n-C_9H_{19}CO, $R^{3,5,6}$ = MeCO
(14) $R^{1-3,5,6}$ = MeCO, R^4 = PhCO
(15) $R^{1,4}$ = PhCO, $R^{2,5,6}$ = MeCO, R^3 = H
(16) R^1 = H, $R^{2,4}$ = PhCO, $R^{3,5,6}$ = MeCO
(17) R^1 = H, $R^{2,3,5,6}$ = MeCO, R^4 = PhCO
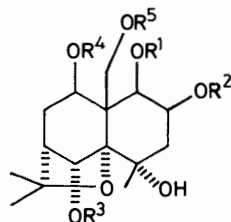
(18) R^{1-5} = H
(19) $R^{1,2}$ = (3-furoyl), R^3 = (MeCO), $R^{4,5}$ = (MeCO, α-methylbutyryl)
(20) $R^{1,2}$ = (aryl), R^3 = (MeCO), $R^{4,5}$ = (MeCO, α-methylbutyryl)
(21) $R^{1,2}$ = (aryl), R^3 = (MeCO), $R^{4,5}$ = (MeCO, aryl)
(22) $R^{1,2,4}$ = 3-furoyl, $R^{3,5}$ = MeCO
(23) $R^{1,2}$ = PhCO, $R^{3,5}$ = MeCO, R^4 = α-methylbutyryl
(24) R^{1-5} = 2 × 3-furoyl, 2 × MeCO, 1 × α-methylbutyryl
(25) R^1 = (PhCO), R^2 = (α-methylbutyryl), $R^{3,4}$ = MeCO, R^5 = (MeCO)
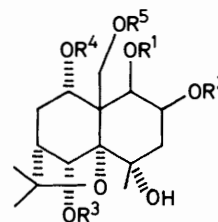
(26) R^{1-5} = H
(27) $R^{1,2}$ = PhCO, $R^{3,5}$ = MeCO, R^4 = α-methylbutyryl
(28) R^{1-5} = 3 × 3-furoyl, 2 × MeCO
(29) R^{1-5} = 2 × PhCO, 3 × MeCO
(30a), (30b) R^{1-5} = 2 × 3-furoyl, 2 × MeCO, 1 × α-methylbutyryl
(31) R^{1-5} = 1 × PhCO, 2 × MeCO, 2 × α-methylbutyryl
(32) R^{1-5} = 1 × 3-furoyl, 2 × MeCO, 2 × α-methylbutyryl

(33)
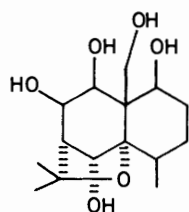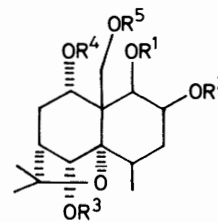
(34) R^{1-5} = H
(35) R^1 = α-methylbutyryl, $R^{2,3,5}$ = MeCO, R^4 = nicotinoyl
(36) $R^{1-3,5}$ = MeCO, R^4 = PhCO
(37) $R^{1,3,5}$ = MeCO, $R^{2,4}$ = PhCO

nicotinoyl =
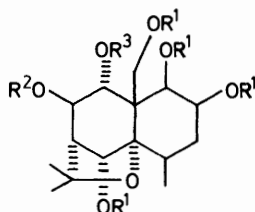
(38) R^{1-3} = H
(39) $R^{1,2}$ = MeCO, R^3 = PhCO
(40) R^1 = MeCO, $R^{2,3}$ = PhCO

Figure 1. Pure-phase 2D H,H-NOESY spectrum of compound (28). Only positive levels are shown. 1K × 128 Data points were collected with 800 ms mixing time, using the TPPI method. Gaussian and cosine weighting functions, and zero-filling to 2K and 1K, were applied in the second and first dimensions, respectively, before the 2D FT. Assigned n.O.e. cross-peaks are noted on the contour map. The slice in the inset clearly shows the indirect, negative effect between the 15-H_b and the C-14 (CH_3) group
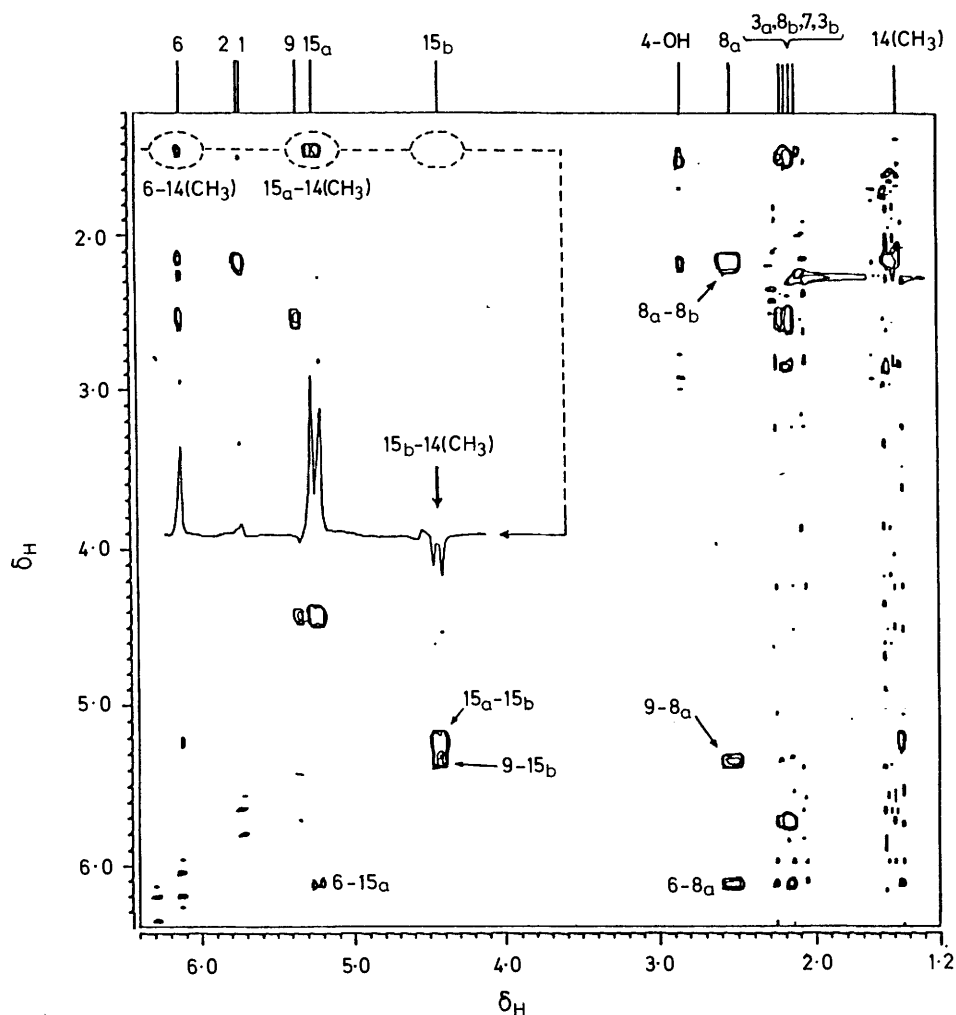
chemical shifts and coupling constants for the parent skeleton (38) ($J_{1,2}$ 4.0 Hz, 1-H_{ax}–2-H_{eq}; $J_{7,8}$ 2.5 Hz and $J_{8,9}$ ~ 0 Hz, 7-H_{eq}–8-H_{eq}–9-H_{eq}) esterified with 4 acetic (δ_H 2.12, 2.07. 2.05, 1.47) and two benzoic acid groups [δ_H 8.17 (2 H), 8.04 (2 H), 7.6—7.4 (6 H) (Table; Experimental section)]. Identical δ-values for 1-H, 2-H, 15-H_a, and 15-H_b in compounds (40) and (39) (Ejap-4),[2] as well as a shift of 8-H ($\Delta\delta$ +0.27), 9-H ($\Delta\delta$ +0.25), and 6-H ($\Delta\delta$ +0.17)[4] in compound (40) compared with the corresponding protons of compound (39), suggest the benzoyl groups to be at C(8) and C(9), while the acetyl substituents can be assigned to C(1), C(2), C(6), and C(15).

Among the above mentioned components, (10), (15), (16), (28), (29), (30a), (30b), (31), (32), and (36) were isolated from *E. europaeus*, while (10), (14), (36), (37), and (40) were obtained from *E. latifolius*.

E. latifolius and *E. japonicus*[2] both synthesize esters of the 9-epimeric alcohols (8) and (38). During our investigations no sesquiterpene alkaloids have been detected in the extracts of the two species until now.

Experimental

hR_F Values were determined on Kieselgel 60F_{254} with toluene–ethyl acetate (3:2) (A-system), cyclohexane–ethyl acetate–

ethanol (120:30:1) (B-system) or (60:30:1) (C-system) and on alumina 60F_{254} with cyclohexane–ethyl acetate–ethanol (60:30:0.1) (D-system).

[1]H Chemical shifts and coupling constants were measured at 250.13 MHz (Bruker WM-250) in deuteriochloroform solutions at 303 K (controlled temperature), with $SiMe_4$ as internal standard. Routine 1D, and double-resonance difference spectra,[16] as well as 2D, H,H-COSY[17,18] and pure phase[19] NOESY spectra[12] were also analysed for the determination of the structure of the isolated sesquiterpene derivatives. Typical parameters for 2D experiments: 1K × 128 or 256 (zero-filled to 512 or 1K prior to 2D FT) data points, respectively, for *ca.* 2 kHz spectral width, 2—5 s relaxation delay, 16—64 scans for each t_1 value. For a more detailed evaluation of the [1]H n.m.r. spectroscopic results see ref. 9.

I.r. spectra were run on a Bruker IFS 85 FT spectrometer for chloroform solutions, in a 0.027 mm KBr cell, with 4 cm^{-1} resolution. Mass spectra were run on a Finnigan MAT 8430 mass spectrometer, with chemical ionization (CH_4), $T_{ion\ source}$ 250 °C, resolution: 1 000 (10% valley). In the case of new compounds some of the characteristic fragments are presented, too. [Abbreviation used: Fu = 3-furyl (C_4H_3O)]. Light petroleum refers to the fraction boiling in the range 40—60 °C.

Figure 2. Selected columns, with some assignments above the normal 1D spectrum of compound (36), from the phase-sensitive 2D NOESY map at the chemical shifts of a: 6-H, b: 1-H, c: 2-H, d: 9-H, e: 15-H$_a$, f: 15-H$_b$, respectively. Cross-peaks between 9-H$_{eq}$ and 15-H$_b$, and highlighted indirect, negative n.O.e. cross-peak from 15-H$_b$ to the C-14 (CH$_3$) group, are indicated by arrows and star, respectively

Extraction of Euonymus europaeus.—Fresh fruits (600 g) of *E. europaeus* were collected from shrubs (~60 cm height) cultivated near Debrecen, Hungary. The starting material was extracted at ambient temperature with methanol (3 dm³). The extract was evaporated to 500 cm³ and extracted with light petroleum (5 × 250 cm³). Evaporation of the organic phase gave a residue (26.5 g), which was chromatographed on polyamide (185 g) and eluted with methanol–water (2:3) (17 fractions), (1:1) (14 fractions), (3:2) (10 fractions), (1:4) (15 fractions), then with acetone (6 fractions). 300-cm³ Fractions were collected. Fractions eluted with methanol–water (2:3)

(fractions 3—11; 2.42 g) were rechromatographed on silica column (55 g) with cyclohexane (9 fractions), cyclohexane–ethyl acetate (95:5) (20 fractions), (9:1) (18 fractions), (4:1) (18 fractions), (7:3) (32 fractions), and (1:1) (25 fractions). 20-cm³ Fractions were collected.

The fractions eluted with cyclohexane–ethyl acetate (4:1) (fractions 52—56, 56—61, 62—68), and (7:3) (fractions 69—77, 78—84) were further purified on p.l.c. (silica) with cyclohexane–acetone–ethanol (120:30:1), and then on alumina [cyclohexane–acetone–ethanol (90:30:0.1)]. Fractions 52—56 yielded compounds (31) (3.9 mg), (36) (5.9 mg), and (32) (2.7 mg); fractions

Table. ^{1}H N.m.r. data (CDCl$_3$; δ, J/Hz)

Compound	1-H	2-H	3-H	4-H	6-H	7-H	8-H	9-H	12-,13-H	14-H	15$_a$-H	15$_b$-H
(10)	5.83d	5.51dt	2.52ddd (15.2, 6.3, 4.0), 1.84br d (15.2)	2.37br p	6.90s	2.59d	5.65dd	5.54d	1.60s, 1.47s	1.15d	5.47d	4.60d
	(4.0)	(4.0, 4.0, 2.5)		(7.7)		(4.0)	(5.7, 4.0)	(5.7)		(7.7)	(13.5)	(13.5)
(14)	5.52d	5.42td	2.45ddd (15.9, 7.7, 3.9), 1.76br d (15.9)	2.32br p	6.85s	2.56d	5.63dd	5.47d	1.54s, 1.44s	1.12d	5.23d	4.40d
	(3.9)	(3.9, 3.9, 2.2)		(7.7)		(3.9)	(6.1, 3.9)	(6.1)		(7.7)	(13.5)	(13.5)
(15)	5.88d	5.51^a	2.50,^{a} 1.80ddd (14.2, 2.6)	2.43^a	5.40^a	2.59d	5.64dd	5.51^a	1.58s, 1.56s	1.38d	5.37d	4.81d
	(3.7)					(3.6)	(5.8, 4.1)			(7.8)	(13.1)	(13.1)
(16)	4.46dd ^{b}	5.62q	2.43,^{a} 2.00^a	2.35^a	6.33s	2.62d	5.74dd	5.67d	1.56s, 1.45s	1.19d	5.48d	4.72d
	(8.5, 3.5)	(3.5)				(4.0)	(5.6, 4.0)	(5.6)		(7.3)	(12.5)	(12.5)
(28)^d	5.81^a	5.78^a	2.27,^{a} 2.09^a	2.88^{c}q	6.16s	2.22^a	2.59ddd (16.6, 7.4, 4.5), 2.21^a	5.39d	1.58s, 1.54s	1.49br s	5.27d	4.47d
				(~1.0)				(7.1)			(12.9)	(12.9)
(29)	5.81d	5.66q	2.26,^{a} 2.08^a	2.90^{c}q	6.19s	2.21^a	2.59ddd (16.8, 7.4, 4.3), 2.22^a	5.47d	1.59s, 1.56s	1.51br s	5.11d	4.62d
	(3.4)	(3.4)		(~1.0)				(7.1)			(13.0)	(13.0)
(30a)	5.70d	5.64q	2.22,^{a} 2.02dd (15.2, 2.9)	2.87^{c}q	6.18s	2.20^a	2.57ddd (12.1, 7.3, 4.3), 2.21^a	5.33d	1.57s, 1.53s	1.50br s	5.05d	4.53d
	(3.5)	(3.5)		(~1.0)				(7.1)			(13.0)	(13.0)
(30b)	5.66^a	5.66^a	2.21,^{a} 2.06^a	2.89^{c}q	6.14s	2.20^a	2.59ddd (15.9, 7.1, 3.7), 2.29^a	5.29d	1.56s, 1.47s	1.49br s	5.21d	4.42d
				(~1.0)				(6.8)			(12.7)	(12.7)
(31)	5.69d	5.55q	2.22,^{a} 2.00^a	2.90^{c}q	6.18s	2.22^a	2.58ddd (15.9, 7.0, 3.5), 2.30^a	5.33d	1.55s, 1.47s	1.50br s	5.04d	4.42d
	(3.5)	(3.5)		(~1.0)				(6.8)			(13.0)	(13.0)
(32)	5.68d	5.54q	2.20,^{a} 2.00^a	2.88^{c}q	6.13s	2.20^a	2.54,^{a} 2.30^a	5.22d	1.54s, 1.47s	1.48br s	5.04d	4.39d
	(3.7)	(3.7)		(~1.0)				(6.8)			(12.7)	(12.7)
(35)	5.78d	5.52m	2.5—1.8m		5.97s	2.5—1.8m		5.32br d	1.42s, 1.36s	1.18d	5.07d	4.41d
	(3.5)							(6.8)		(7.8)	(13.0)	(13.0)
(36)	5.70d	5.58m	2.49,^{a} 1.82^a	2.41^a	5.97s	2.27^a	2.55,^{a} 2.24^a	5.41d	1.45s, 1.42s	1.19d	5.05d	4.35d
	(3.5)							(7.1)		(7.6)	(13.0)	(13.0)
(37)	5.83d	5.88q	2.53,^{a} 1.97br d (15.1)	2.41^a	6.02s	2.25^a	2.56,^{a} 2.24^a	5.47d	1.48s, 1.45s	1.23d	5.36d	4.43d
	(3.5)	(3.5)						(7.1)		(7.6)	(12.5)	(12.5)
(39)	5.71d	5.60td (3.8, 3.8, 2.7)	2.49,^{a} 1.77ddd (15.1, 6.6, 3.8)	2.38^a	6.38s	2.39d	5.27d	5.52s	1.56s, 1.43s	1.17d	5.10d	4.55d
	(3.8)					(2.5)	(2.5)			(7.6)	(13.0)	(13.0)
(40)	5.72d	5.61br q	2.47,^{a} 1.78^a	2.39^a	6.56s	2.54d	5.54d	5.77s	1.67s, 1.49s	1.17d	5.14d	4.63d
	(4.0)	(4.0)				(2.5)	(2.5)			(7.5)	(12.8)	(12.8)

^{a} From 2D H,H-COSY spectrum, without identification of the multiplicity. ^{b} 1-OH: 2.99d (8.5). ^{c} 4-OH. ^{d} Spectral data are identical with those of Ester B-4 (ref. 3).

57—61 gave compounds (32) (1 mg), (16) (3.2 mg), and (30b) (2.2 mg); from fractions 62—68, compound (30a) (10 mg); fractions 69—77 gave compounds (30a) (2.4 mg), and (28) (27.9 mg); and fractions 78—84 gave compound (29) (10.1 mg).

The fractions eluted from the polyamide column with methanol–water (2:3) (fractions 12—21; 1.21 g) were also chromatographed on a silica column (28 g), fractions 3—11 were subjected to chromatography with cyclohexane (14 fractions), cyclohexane–ethyl acetate (95:5) (18 fractions), (9:1) (20 fractions), (4:1) (97 fractions), (1:1) (25 fractions), and then with acetone (5 fractions). 10-cm^3 Fractions were collected.

The fractions eluted with cyclohexane–ethyl acetate (4:1) (fractions 66—75, 85—109) were further purified by p.l.c. (silica) with cyclohexane–acetone–ethanol (120:30:1), and toluene–ethyl acetate (2:3). Fractions 66—75 gave compounds (10) (11.7 mg) and (15) (14.6 mg).

Extraction of Euonymus latifolius.—Fresh fruits (200 g) of *E. latifolius* were extracted at ambient temperature with methanol (0.8 dm³). The extract was evaporated to 100 cm³ and extracted with light petroleum (5 × 100 cm³). Evaporation of the organic phase gave a residue (2.1 g), which was chromatographed on polyamide (13.65 g) and eluted with methanol–water (2:3) (22 fractions), (1:1) (28 fractions), (3:2) (22 fractions), (1:4) (22 fractions), and then with acetone (10 fractions). 20-cm³ Fractions were collected. Fractions eluted with methanol–water (2:3) (fractions 1—22) were rechromatographed by p.l.c. (silica) with cyclohexane–ethyl acetate–ethanol (60:30:1). From band 6 compound (**36**) (17.8 mg) was obtained. Band 4 yielded compound (**14**) (8.8 mg) after purification by p.l.c. (alumina) with cyclohexane–ethyl acetate–ethanol (60:30:0.1). Fractions eluted with methanol–water (1:1) (fractions 23—50) were rechromatographed at first by p.l.c. (silica) as above. Band 6 gave compound (**37**) (9.2 mg), while compounds (**10**) (0.9 mg) and (**40**) (0.8 mg) were obtained from band 4 by p.l.c. (alumina) with cyclohexane–ethyl acetate–ethanol (60:30:0.1), then (silica) with cyclohexane–ethyl acetate–ethanol (60:30:0.3).

Compound (**10**) (Eur-2 = Elat-6) hR_F (A) 65; (C) 76; M^+, 694 ($C_{37}H_{42}O_{13}$); δ_H 8.1 and 7.9 (both 2 H, m, 2 × 2″- and 6″-H), 7.6—7.3 (6 H, m, 2 × 3″-, 4″-, and 5″-H), and 2.14, 2.09, 1.98, and 1.42 (each 3 H, s, COMe).

Compound (**14**) (Elat-4) hR_F (C) 69; (D) 34; M^+, 632 ($C_{32}H_{40}O_{13}$); δ_H 8.15 (2 H, m, 2″- and 6″-H), 7.6—7.4 (3 H, m, 3″-, 4″-, and 5″-H), and 2.14, 2.09, 1.97, 1.93, and 1.88 (3 H each, s, COMe).

Compound (**15**) (Eur-21) hR_F (B) 14; M^+, 652 ($C_{35}H_{40}O_{12}$); δ_H 8.02 and 7.95 (both 2 H, m, 2 × 2″- and 6″-H), 7.6—7.4 (6 H, m, 2 × 3″-, 4″-, and 5″-H), and 2.09, 1.97, and 1.39 (each 3 H, s, COMe).

Compound (**16**) (Eur-14) hR_F (B) 17; $v_{C=O}$ 1 711 cm⁻¹; m/z (%) 592 (2.2, $M - CH_3CO_2H$), 530 (24.4, $M - PhCO_2H$), 470 (37.5, $M - PhCO_2H - CH_3CO_2H$), 366 (45.2, $M - 2 × PhCO_2H - CH_2CO$), 123 [100, PhC(OH)₂⁺], and 105 (45, PhCO⁺); δ_H 8.19 and 8.01 (both 2 H, m, 2 × 2″- and 6″H), 7.6—7.4 (6 H, m, 2 × 3″-, 4″-, and 5″-H), and 2.11, 1.90, and 1.75 (each 3 H, s, COMe).

Compound (**28**) (Eur-1) hR_F (A) 46; $v_{C=O}$ 1 732 cm⁻¹; m/z (%) 666 (55.3, $M - H_2O$), 512 (27.7, $M - FuCO_2H - CH_3COOH$), 460 (52, $M - 2 × FuCO_2H$), 400 (34, 460 − CH_3CO_2H), 289 (36.6, 400 − $FuCO_2$), and 95 (100, $FuCO^+$); δ_H 8.25 (1 H, dd, J 0.7 and 1.7 Hz, 2′-H), 7.88 (1 H, dd, J 0.7 and 1.7 Hz, 2′-H), 7.44 (1 H, t, J 1.7 Hz, 4′-H), 7.34 (1 H, t, J 1.7 Hz, 4′-H), 6.83 (1 H, dd, J 0.7 and 1.7 Hz, 5′-H), 6.55 (1 H, dd, J 0.7 and 1.7 Hz, 5′-H), 7.65 (1 H, dd, J 0.7 and 1.7 Hz, 2′-H), 7.24 (1 H, t, J 1.7 Hz, 4′-H), 6.33 (1 H, dd, J 0.7 and 1.7 Hz, 5′-H), and 2.31 and 2.12 (each 3 H, s, COMe).

Compound (**29**) (Eur-3) hR_F (A) 35; $v_{C=O}$ 1 740 cm⁻¹; m/z (%) 634 (16.6, $M - H_2O$), 592 (8.4, $M - CH_3CO_2H$), 530 (18.5, $M - PhCO_2H$), 470 (32, $M - PhCO_2H - CH_3CO_2H$), 367 (22, $M - PhCO_2H - 2 × CH_3CO_2H - CH_3CO$), 289 (22.6, $M - PhCO_2H - 2 × CH_3CO_2H - PhCO_2$), and 105 (100, PhCO⁺); δ_H 7.8—7.1 (10 H, m, 2 × 2″-, 3″-, 4″-, 5″-, and 6″-H) and 2.31, 2.13, and 2.05 (each 3 H, s, COMe).

Compound (**30a**) (Eur-6) hR_F (A) 45; $v_{C=O}$ 1 738 cm⁻¹; m/z (%) 656 (64, $M - H_2O$), 562 (20, $M - FuCO_2H$), 554 (17.2, $M - 2 × CH_3CO_2H$), 512 (25, $M - Bu^sCO_2H - CH_3CO_2H$), 460, (67, $M - Bu^sCO_2H - FuCO_2H$), 367 [63.3, $M - Bu^sCO_2H - CH_3CO_2H - C_5H_{10}O_2$ (from fission of the ring system) − CH₃CO], 95 (100, FuCO⁺), and 85 (75.4, Bu^{s}CO⁺); δ_H 7.87 (1 H, dd, J 0.7 and 1.8 Hz, 2′-H), 7.69 (1 H, dd, J 0.7 and 1.8 Hz, 2′-H), 7.34 (1 H, t, J 1.8 Hz, 4′-H), 7.26 (1 H, t, J 1.8 Hz, 4′-H), 6.54 (1 H, dd, J 0.7 and 1.8 Hz, 5′-H), 6.38 (1 H, dd, J 0.7 and 1.8 Hz, 5-H), 2.29 and 2.12 (each 3 H, s, COMe), 1.13 (3 H, d, J 7.0 Hz, *Me*CH), and 0.81 (3 H, t, J 7.4 Hz, *Me*CH₂).

Compound (**30b**) (Eur-15) hR_F (B) 10; $v_{C=O}$ 1 711 cm⁻¹; m/z

(%) 656 (33.5, $M - H_2O$), 562 (14, $M - FuCO_2H$), 460 (31, $M - FuCO_2H - Bu^sCO_2H$), 366 (53.2, $M - Bu^sCO_2H - PhCO_2H - 2 × CH_2CO$), 105 (37.6, PhCO⁺), 95 (65.7, FuCO⁺), and 85 (100, BuCO⁺); δ_H 8.27 (1 H, dd, J 0.7 and 1.7 Hz, 2′-H), 8.02 (1 H, dd, J 0.7 and 1.7 Hz, 2′-H), 7.46 (1 H, t, J 1.7 Hz, 4′-H), 7.42 (1 H, t, J 1.7 Hz, 4′-H), 6.87 (1 H, dd, J 0.7 and 1.7 Hz, 5′-H), 6.73 (1 H, dd, J 0.7 and 1.7 Hz, 5′-H), 2.30 and 2.11 (each 3 H, s, COMe), 0.82 (3 H, d, J 7.0 Hz, *Me*CH), and 0.60 (3 H, t, J 7.4 Hz, *Me*CH₂).

Compound (**31**) (Eur-7) hR_F (B) 14; $v_{C=O}$ 1 738 cm⁻¹; m/z (%) 656 (34, $M - H_2O$), 512 (20.5, $M - Bu^sCO_2H - CH_3CO_2H$), 450 (38, $M - PhCO_2H - Bu^sCO_2H$), 367 [52, $M - Bu^sCO_2H - C_5H_{10}O_2$ (from fission of the ring system) − CH₃CO₂H − CH₃CO], 105 (100, PhCO⁺), and 85 (84, BuCO⁺); δ_H 8.03 (2 H, m, 2″- and 6″-H), 7.6—7.4 (3 H, m, 3″-, 4″-, and 5″-H), 2.27 and 2.11 (each 3 H, s, COMe), 1.18 (3 H, d, J 7.0 Hz, *Me*CH), 0.91 (3 H, t, J 7.4 Hz, *Me*CH₂), 0.78 (3 H, d, J 7.0 Hz, *Me*CH), and 0.53 (3 H, t, J 7.4 Hz, *Me*CH₂).

Compound (**32**) (Eur-9) hR_F (B) 12; $v_{C=O}$ 1 738 cm⁻¹; m/z (%) 646 (24, $M - H_2O$), 502 (10.7, $M - Bu^sCO_2H - CH_3CO_2H$), 450 (38.6, $M - FuCO_2H - Bu^sCO_2H$), 367 [49.5, $M - H_2O - Bu^sCO_2H - CH_3CO_2H - C_3H_6O_2$ (from fission of the ring system) − CH₃CO], 105 (57, PhCO⁺), 95 (17.6, FuCO⁺), 85 (100, Bu^{s}CO⁺); δ_H 8.01 (1 H, dd, J 0.7 and 1.7 Hz, 2′-H), 7.41 (1 H, t, J 1.7 Hz, 4′-H), 6.73 (1 H, dd, J 0.7 and 1.7 Hz, 5′-H), 2.26 and 2.11 (each 3 H, s, COMe), 1.20 (3 H, d, J 7.0 Hz, *Me*CH), 0.92 (3 H, t, J 7.4 Hz, *Me*CH₂), 0.88 (3 H, d, J 7.0 Hz, *Me*CH), and 0.68 (3 H, t, J 7.4 Hz, *Me*CH₂).

Compound (**36**) (Eur-8 = Elat-2) hR_F (B) 25; $v_{C=O}$ 1 744 cm⁻¹; m/z (%) 574 (2, M^+), 531 (31, $M - CH_3CO$), 514 (87, $M - CH_3CO_2H$), 392 (55.3, $M - CH_3CO_2H - PhCO_2H$), 351 (100, $M - CH_3CO_2H - CH_2CO - PhCO_2$), 291 (47.4, 351 − CH_3CO_2H), and 105 (36, PhCO⁺); δ_H 8.04 (2 H, m, 2″- and 6″-H), 7.6—7.4 (3 H, m, 3″-, 4″-, and 5″-H), and 2.24, 2.10, 2.08, and 1.54 (each 3 H, s, COMe).

Compound (**37**) (Elat-1) hR_F (C) 94; (D) 56; $v_{C=O}$ 1 732 cm⁻¹; m/z (%) 593 (16.4, $M - CH_3CO$), 576 (44.5, $M - CH_3CO_2H$), 514 (43.3, $M - PhCO_2H$), 454 (63.4, $M - PhCO_2H - CH_3CO_2H$), 351 (100, $M - PhCO_2H - CH_2CO - PhCO_2$), 291 (51, 351 − CH_3CO_2H), and 105 (99, PhCO⁺); δ_H 8.11 and 8.07 (2 × 2 H, m, 2 × 2″- and 6″-H), 7.6—7.4 (6 H, m, 2 × 3″-, 4″-, and 5″-H), and 2.27, 2.10, and 1.52 (3 H each, s, COMe).

Compound (**40**) (Elat-5) hR_F (C) 80; (D) 42; $v_{C=O}$ 1 740 cm⁻¹; m/z (%) 694 (4.7, M^+), 634 (13, $M - CH_3CO_2H$), 514 (62, $M - 3 × CH_3CO_2H$), 392 (57.4, 514 − $PhCO_2H$), 351 (100, $M - 2 × CH_3CO_2H - PhCO_2H - PhCO_2$), and 105 (88, PhCO⁺); δ_H 8.17 and 8.04 (2 × 2 H, m, 2 × 2″- and 6″-H), 7.6—7.4 (6 H, m, 2 × 3″-, 4″-, and 5″-H), and 2.12, 2.07, 2.05, and 1.47 (3 H each, s, COMe).

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