

New Sesquiterpene Esters and Alkaloids from *Euonymus japonicus*: The 'Ejap' Series. X-Ray Molecular Structures of Ejap-2, -3, -4, -5, -6, and -10

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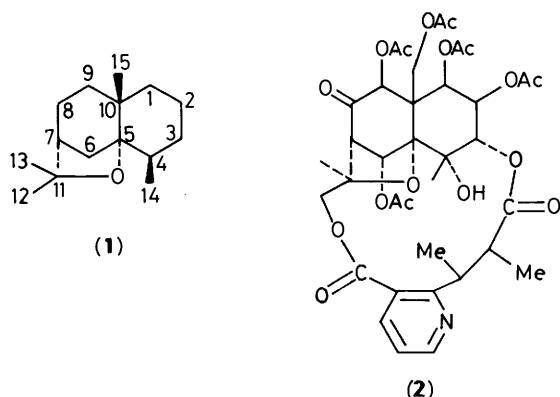
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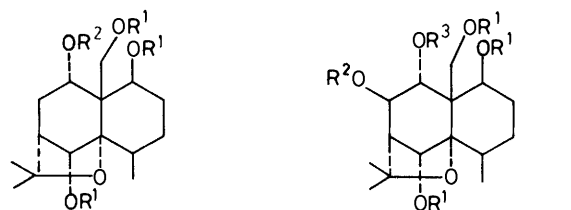
Nine new sesquiterpenoid esters (Ejap-2, -3, -4, -6, -7, -10, -12, -13, and -14) have been isolated from *Euonymus japonicus*, besides a known compound (Ejap-5). Structures of the isolated substances were deduced from 1D, as well as 2D COSY and NOESY, ¹H n.m.r. and mass spectra. The position of the benzoyl groups among the other esterifying moieties was located by X-ray diffraction for Ejap-2, -3, -4, -5, -6, and -10. Among the sesquiterpene cores, 8-deoxypolyalcohol C, 8-*epi*-polyalcohol C, 9-*epi*-alcohol A, and 4,12-dideoxyeuonyminol have been obtained in neither a synthetic nor a natural product until now.

The sesquiterpene esters based on the dihydroagarofuran moiety (1) occur mainly within the Celastraceae family. This type of compound has already been isolated from some *Euonymus* species; e.g. *E. europaeus*, *E. alatus*, *E. sieboldianus*, *E. latifolia*, *E. oxyphyllus*, and *E. verrucosus*.¹⁻³ The esters and alkaloids of a hydroxylated dihydroagarofuran of *E. japonicus* have not been investigated in detail so far; a sesquiterpene alkaloid, evonine (2), was the only product isolated from it,¹ thus we started a systematic investigation on the extract of *E. japonicus*, which is cultivated as a decorative shrub in Hungary.

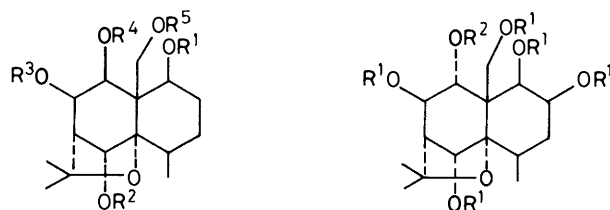


Ten pure esters have been isolated by chromatography, on polyamide and silica columns, of the light petroleum-soluble fraction of a methanolic extract of the fruits. In this paper the structures of these components (4), (5), (7)–(9), (11), (13), (15), (16), and (18) are presented.

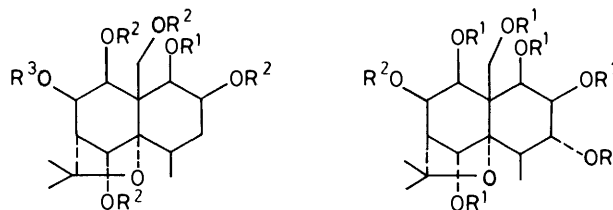
Ejap-2 and Ejap-7 form the first set of the extractives. ¹H N.m.r. spectral data (Table 1) suggest a 1,6,9,15-tetrahydroxy-dihydroagarofuran core (3) in both compounds. Ejap-2 (C₂₈H₃₆O₉) contains three acetate groups (δ_H 2.24, 2.09, 1.54) and a benzoate [δ_H 7.59–7.40 (3 H), 8.07–8.03 (2 H)], and Ejap-7 (C₂₇H₃₅NO₉) has three acetates (δ_H 2.25, 2.10, 1.60) and a nicotinate unit [characteristic four protons δ_H 9.3–7.4 (see Experimental section)]. On the basis of coupling constants of



- (3) R^{1,2} = H
 (4) R¹ = MeCO, R² = PhCO
 (5) R¹ = MeCO, R² = nicotinoyl
 (6) R^{1,2,3} = H
 (7) R^{1,2} = MeCO, R³ = PhCO
 (8) R^{1,2} = MeCO, R³ = nicotinoyl
 (9) R¹ = MeCO, R² = H, R³ = PhCO



- (10) R¹⁻⁵ = H
 (11) R¹⁻⁵ = 1 × PhCO,
 1 × nicotinoyl, 3 × MeCO
 (12) R^{1,2} = H
 (13) R¹ = MeCO, R² = PhCO



- (14) R¹⁻³ = H
 (15) R^{1,2} = MeCO, R³ = PhCO
 (16) R¹ = H, R² = MeCO, R³ = PhCO
 (17) R^{1,2} = H
 (18) R¹ = MeCO, R² = PhCO

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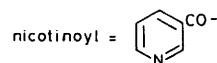


Table 1. ¹H N.m.r. data (CDCl₃; J/Hz)

Compd.	1-H	2-H	3-H	4-H	6-H	7-H	8-H	9-H	12- and 13-H	14-H	15-H _a	15-H _b
Ejap-2	5.57dd	1.92,* 1.51*	2.26,* 1.43*	2.30*	5.95s	2.19*	2.48ddd (16.6, 7.3, 4.2)	5.39d	1.44s, 1.41s	0.99d	4.68d	4.45d
(4)	(12.0, 4.5)						2.21*	(7.3)		(7.6)	(12.3)	(12.3)
Ejap-7	5.56dd	1.86,* 1.52	2.25,* 1.47*	2.29*	5.94s	2.22*	2.47ddd (16.8, 7.5, 4.5)	5.41d	1.42, 1.42s	0.99d	4.68d	4.45d
(5)	(12.4, 4.5)						2.20*	(7.1)		(7.6)	(12.5)	(12.5)
Ejap-3	5.57dd	2.00,* 1.61*	2.26,* 1.45*	2.29*	6.34s	2.37d	5.27d	5.51s	1.55s, 1.42s	0.98d	4.65d	4.60d
(7)	(12.0, 5.0)					(3.0)	(3.0)			(7.5)	(12.5)	(12.5)
Ejap-14	5.57dd	2.00,* 1.62*	2.26,* 1.45*	2.30*	6.33s	2.37d	5.28d	5.33s	1.53s, 1.42s	0.98d	4.67d	4.59d
(8)	(11.9, 4.6)					(2.9)	(2.9)			(7.5)	(12.7)	(12.7)
Ejap-10	5.60dd	1.98*, 1.62*	2.29*, 1.48*	2.31*	6.40s	2.33d	4.26dd †	5.30s	1.43s, 1.41s	1.00d	4.72d	4.55d
(9)	(11.9, 4.6)					(3.0)	(5.0, 3.0)			(7.7)	(12.5)	(12.5)
Ejap-13	5.74dd	2.30,* 1.90*	2.32,* 1.55*	2.30*	6.80s	2.56d	5.66dd	5.59d	1.59s, 1.46s	1.00d	4.82d	4.64d
(11)	(8.8, 7.9)					(3.5)	(5.7, 3.5)	(5.7)		(7.8)	(13.2)	(13.2)
Ejap-4	5.71d	5.60td (3.8, 3.8, 2.7)	2.49* 1.77ddd (15.1, 6.6, 3.8)	2.38*	6.38s	2.39d	5.27d	5.52s	1.56s, 1.43s	1.17d	5.10d	4.55d
(13)	(3.8)					(2.5)	(2.5)			(7.6)	(13.0)	(13.0)
Ejap-5	5.52d	5.42td	2.45ddd (15.9, 7.7, 3.9)	2.32br p	6.85s	2.56d	5.63dd	5.47d	1.54s, 1.44s	1.12d	5.23d	4.40d
(15)	(3.9)	(3.9, 3.9, 2.2)	1.76br d (15.9)	(7.7)		(3.9)	(6.1, 3.9)	(6.1)		(7.7)	(13.5)	(13.5)
Ejap-12	4.34dd	5.23td	2.31,* 1.92*	2.29*	6.30s	2.59d	5.72dd	5.63d	1.58s, 1.42s	1.15d	5.11d	4.77d
(16)	(8.5, 3.5)	(3.5, 3.5, 2.7)				(4.0)	(5.6, 4.0)	(5.6)		(7.7)	(12.5)	(12.5)
Ejap-6	5.81d	5.39ddd (4.0, 2.5, ~1.0)	4.80dd	2.50br q	6.72s	2.52d	5.63dd	5.50d	1.54s, 1.39s	1.16d	5.13d	4.40d
(18)	(4.0)		(2.5, 1.2)	(7.9)		(4.0)	(6.0, 4.0)	(6.0)		(7.9)	(13.0)	(13.0)

* From 2D H,H-COSY spectrum without identification of multiplicity. † 8-OH: 2.69d (5.0).

4.5 and 12.0 Hz, respectively, 1-H is *axial* in these compounds (*cf.* $J_{1ax,2ax}$ 10–12 Hz; $J_{1ax,2eq}$ 4–6 Hz). The signal for 9-H shows, on the 2D n.O.e. map,⁵ an intense cross-peak, among others, to 15-H_b; consequently 9-H is equatorial. According to the *X*-ray analysis the benzoate group is at C(9) in Ejap-2, thus it has structure (4). Chemical shifts for sesquiterpene core protons of Ejap-7 are practically identical with those of Ejap-2 (Table 1); this suggests that the nicotinoyl group is located at C(9), structure (5).

Four compounds belonging to the second set seem to be the esters of 1,6,8,9,15-pentahydroxydihydroagarofurans (6) and (10) on the basis of ¹H n.m.r. data (Table 1). Ejap-3 (C₃₀H₃₈O₁₁) has four acetates (δ_H 2.25, 2.18, 2.09, 1.47) and a benzoate residue [δ_H 7.60–7.40 (3 H), 8.03–8.00 (2 H)]; Ejap-14 (C₂₉H₃₇NO₁₁) four acetates (δ_H 2.25, 2.19, 2.09, 1.47) and a nicotinate unit (characteristic four protons δ_H 9.3–7.3); Ejap-10 (C₂₈H₃₆O₁₀) three acetals (δ_H 2.25, 2.11, 1.49) and a benzoyl [δ_H 7.62–7.41 (3 H), 8.05–8.01 (2 H)]; Ejap-13 (C₃₄H₃₉NO₁₁) three acetals (δ_H 2.14, 2.03, 1.46), a benzoyl [δ_H 7.61–7.43 (3 H), 8.15–8.10 (2 H)], and a nicotinoyl group [characteristic four protons δ_H 9.2–7.3 (see Experimental section)]. Each compound has characteristic coupling constants for 1-H_{ax} (Table 1). Significant n.O.e. interaction⁵ with 15-H_b and no observed coupling for 9-H in Ejap-3, Ejap-14, and Ejap-10, but $J_{9,8}$ 5.7 Hz in Ejap-13, is appropriate for 8-H_{eq}–9-H_{eq} and 8-H_{eq}–9-H_{ax}, respectively.⁴ *X*-Ray analysis of Ejap-3 shows a benzoyl group at C(9), with acetyl units at C(1), C(6), C(8), and C(15), *i.e.* structure (7). The nicotinoyl residue in Ejap-14 can also be located at C(9) by a similarity of ¹H n.m.r. data of both Ejap-3 and Ejap-7 (Table 1), as shown in structure (8). The upfield shift of 8-H of Ejap-10 (δ_H 4.26) compared with that of Ejap-3 (δ_H 5.27), as well as its *X*-ray analysis, show it to have structure (9). At present it is not possible to establish the position of the esterifying residues in Ejap-13 (11).

The third group contains three compounds. Ejap-4, Ejap-5,

and Ejap-12 are the esters of 1,2,6,8,9,15-hexahydroxydihydroagarofurans (12) and (14) (Table 1). Both Ejap-4 (C₃₂H₄₀O₁₃) and Ejap-5 (C₃₂H₄₀O₁₃) have five acetyl groups (Ejap-4; δ_H 2.26, 2.19, 2.10, 2.07, 1.46; Ejap-5; δ_H 2.14, 2.09, 1.97, 1.93, 1.88) and a benzoyl group [Ejap-4: δ_H 7.60–7.40 (3 H), 8.01–7.98 (2 H); Ejap-5: δ_H 7.61–7.44 (3 H), 8.17–8.14 (2 H)]. The hexaol core in Ejap-12 (C₃₀H₃₈O₁₂) is substituted with four acetyl groups (δ_H 2.11, 2.05, 1.98, 1.95) and a benzoyl residue [δ_H 7.63–7.44 (3 H), 8.17–8.15 (2 H) (see Experimental section)]. A coupling constant $J_{1,2}$ 3.5–3.9 Hz shows a *cis*-1-H,2-H relationship (*cf.* usual value between 3.2–3.8 Hz⁶) in each compound. Ejap-4 contains 7-H_{eq}–8-H_{eq}–9-H_{eq} ($J_{7,8}$ 2.5 Hz; $J_{8,9}$ 0 Hz⁷), while Ejap-5 and Ejap-12 have 7-H_{eq}–8-H_{eq}–9-H_{ax} ($J_{7,8}$ ~ 4 Hz; $J_{8,9}$ ~ 6 Hz⁸), as could be directly shown by 2D n.O.e. experiments.⁹ *X*-Ray investigation of Ejap-4 confirms the esterified hydroxy groups to be 1_{eq}, 2_{ax}, 6_{eq}, 8_{ax}, and 9_{ax} on the dihydroagarofuran core; 9_{ax}-OH is esterified with benzoic acid, the other hydroxy groups with acetic acid, to give structure (13). As shown by *X*-ray analysis, the structure of Ejap-5 is identical with that of the Ester A-6 (15) isolated from *Euonymus europaeus*.⁶

The chemical shift of 1-H in Ejap-12 (δ_H 4.34) compared with that of Ejap-5 (δ_H 5.52) shows C(1)-OH to be unsubstituted in this compound, while the equatorial C(1)-OH causes a slight paramagnetic shielding on 6-H.¹⁰ The other protons of Ejap-12, (2-H, 8-H, 9-H, 15-H_a, and 15-H_b) give similar δ -values as for Ejap-5 (15) (Table 1), thus Ejap-12 can be considered to be the 1-deacetyl derivative (16) of Ejap-5.

¹H n.m.r. spectral data suggest the tenth compound, Ejap-6 (C₃₄H₄₂O₁₅), is an ester of 4,12-dideoxyeuonyminol (17). This moiety is substituted with six acetyl groups [δ_H 2.13, 2.10 (6 H), 1.97, 1.91, 1.90] and a benzoyl group [δ_H 7.62–7.44 (3 H), 8.16–8.13 (2 H) (see Experimental section)]. Relative configuration of substituted carbons throughout the molecule can be determined by a single 2D n.O.e. experiment,⁵ as highlighted in

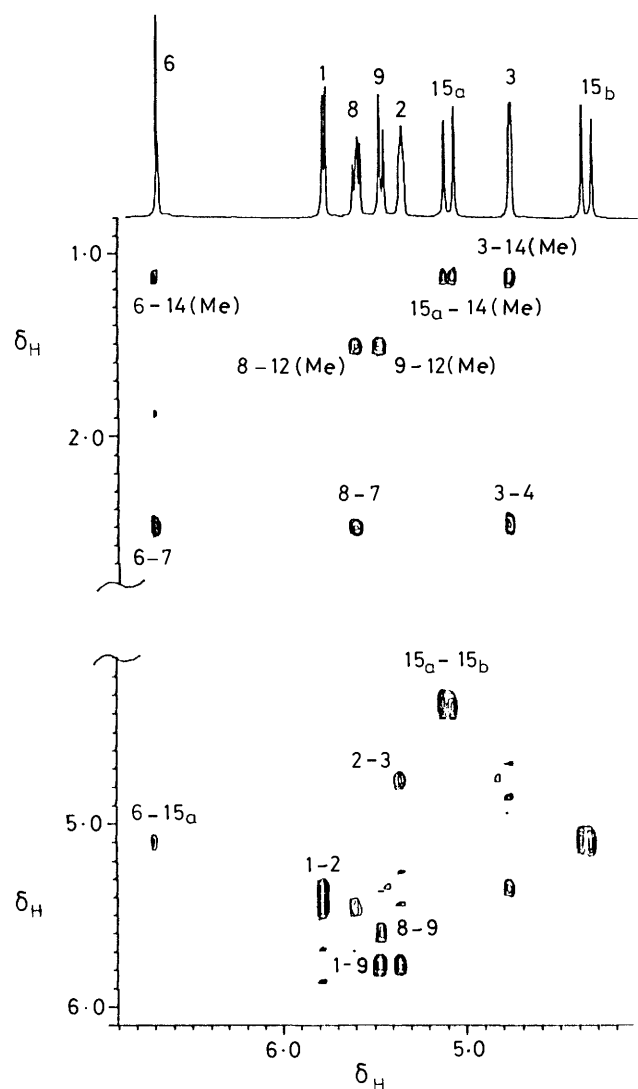


Figure 1. Parts of absorption-mode phase-sensitive 2D n.o.e. spectrum of Ejap-6 (**18**) with a mixing time of 800 ms.⁹ Only positive levels were plotted. For assignments see also Table 1

Figure 1. The assigned n.o.e. cross-peaks show that the stereostructure is (**18**), in agreement with coupling constants between 1-H and 2-H (4 Hz; *cis*¹¹), and 7-H, 8-H, and 9-H ($J_{7,8} \sim 4$ Hz, $J_{8,9} \sim 6$ Hz⁸). The relative configuration of 8-H and 9-H is identical with that of compounds (**11**), (**15**), and (**16**). X-Ray analysis shows the benzoyl residue to be attached to C(8) in Ejap-6 (**18**).

During our work no derivatives of 3-deoxymaytol,¹ 4-deoxyevoninol,¹ cassinol,¹² evoninol,¹ or euonyminol¹ could be detected or isolated from the fruits of *E. japonicus*. The extractives contain none of the dicarboxylic acids considered earlier to be characteristic for *Euonymus* sesquiterpene alkaloids.¹ It is interesting that the species synthesize two pairs of alcohols having an axial and an equatorial 9-H: (**6**) and (**12**), (**10**) and (**14**), respectively.

X-Ray Analysis.—The solid-state conformations of the Ejap-2, -3, -10, -4, -5, and -6 molecules computed from the final fractional atomic co-ordinates (Tables 5–10) are depicted in Figure 2.

The lowest *R* values and other parameters of internal

Table 2. Puckering parameters Q and ψ for the tetrahydrofuran ring as found in the Ejap series

	Q	ψ^*
Ejap-2 a	0.449(8)	275°
b	0.433(4)	278°
Ejap-3	0.425(4)	274°
Ejap-10	0.429(2)	276°
Ejap-4	0.419(3)	277°
Ejap-5	0.421(6)	276°
Ejap-6	0.417(7)	274°

* In the ideal case; *T*, ψ 270°; *E*, ψ 288°.

Table 3. The orientation of the acetyl moieties [on C(1), C(6), and C(15)] relative to the dihydroagarofuran skeleton expressed by the amount of rotation (τ°) about the O(3)–C(1), O(5)–C(6), and O(2)–C(15) bonds. The last column presents the orientation of the C(9)-benzoyl group about the O(7)–C(9) bond

Compd.	τ_1	τ_2	τ_3	τ_4
Ejap-2 a	84.9(11)	166.6(11)	166.3(11)	–142.0(10)
Ejap-2 b	86.2(6)	164.4(6)	178.1(7)	–153.1(6)
Ejap-3	80.5(5)	140.0(6)	170.2(6)	–140.3(5)
Ejap-10	89.1(3)	124.0(3)	–115.5(3)	–140.2(3)
Ejap-4	78.5(3)	143.6(4)	–172.8(3)	–138.1(3)
Ejap-5	95.4(7)	133.4(7)	159.4(6)	
Ejap-6	94.0(10)	139.3(10)	155.7(10)	
Ever-1	157.7(5)	159.2(10)		–144.3(9)

τ_1 : C(2)–C(1)–O(3)–C(31), τ_2 : C(5)–C(6)–O(5)–C(51), τ_3 : C(10)–C(15)–O(2)–C(21), τ_4 : C(10)–C(9)–O(7)–C(71).

consistency listed in Table 4 suggest that Ejap-10 is the most suitable structure to characterize the common dihydroagarofuran skeleton. The other five structure analyses have helped only to clarify the steric arrangement of the acetyl and benzoyl substituents.

Similarly to the central ring system of Ever-1,³ in Ejap-10 (**9**) one of the *trans*-fused six-membered carbocyclic rings deviates characteristically from the expected conformation. It is also sharpened at C(6) and flattened at C(9) to accommodate the C(11)–O(1) ether bridge formed between C(5) and C(7). The C–C bonds pertaining to C(10) [e.g. C(5)–C(10) 1.577(2) Å in the ring junction] are somewhat longer than the others. The 5-membered tetrahydrofuran ring closed by this ether bridge adopts a transitional conformation: *i.e.* a half-chair (*H*) distorted towards envelope (*E*) as shown by the Cremer and Pople puckering parameters¹³ listed for all structures in Table 2. Since in each structure the substituents on C(1), C(6), and C(15) are invariably acetyl moieties it seemed worthwhile to compare their orientation with that of the dihydroagarofuran skeleton. Each substituent orientation is characterized by the same type of torsion angle (Table 3). Except for Ejap-5 (**15**) and Ejap-6 (**18**) all structures (including Ever-1) possess a benzoyl group on C(9). Its orientation is also given in Table 3.

The amount of rotation about the C(1)–O(3) ester bond varies within a narrow range of 16°. Such a narrow range of rotation (–138° and –153°) is also exhibited by the C(9)-benzoyl substituent.

Significantly greater differences can be seen in the orientation of C(15)-acetyl ($\Delta = 88^\circ$) and C(6)-acetyl ($\Delta = 43^\circ$) moieties about the C(15)–O(2) and C(6)–O(5) ester bonds, respectively. The wide range occupied by the C(2)-substituent can be attributed to the CH₂ group between the C(2)-acetyl and the ring system.

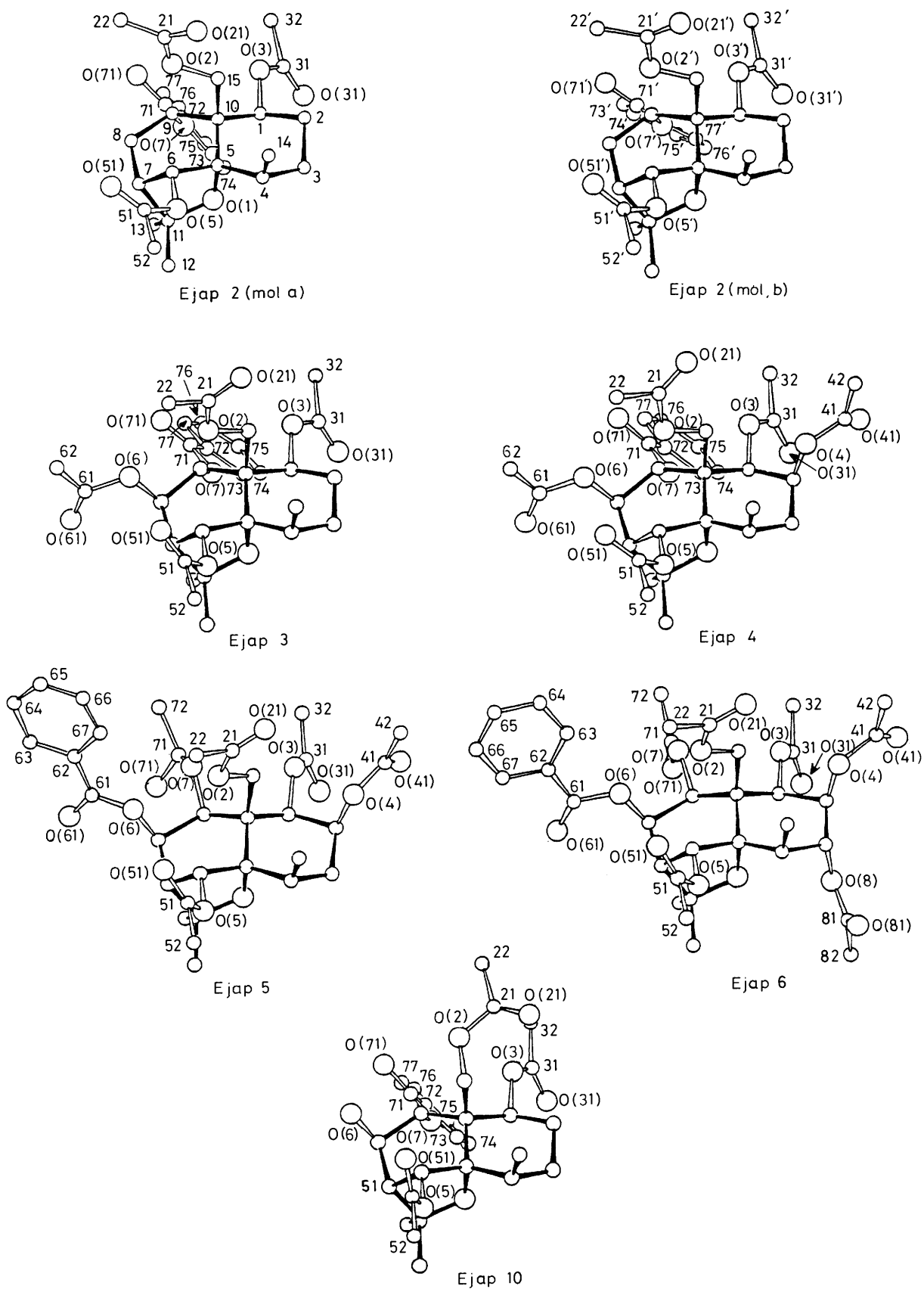


Figure 2. Perspective view of the molecules Ejap-2a, -2b, -3, -10, -4, -5, and -6 showing the crystallographic numbering schemes. The atomic numbering for the common dihydroagarofuran skeleton represented by full lines is given only for molecule Ejap-2a. The unlettered numbers are for carbon atoms unless indicated otherwise. For clarity the H atoms are deliberately omitted

Table 4. Crystal and relevant X-ray data

	Ejap-2	Ejap-3	Ejap-10	Ejap-4	Ejap-5	Ejap-6
Formula	C ₂₈ H ₃₆ O ₉	C ₃₀ H ₃₈ O ₁₁	C ₂₈ H ₃₆ O ₁₀	C ₃₂ H ₄₀ O ₁₃	C ₃₂ H ₄₀ O ₁₃	C ₃₄ H ₄₂ O _{15.5} · $\frac{1}{2}$ CH ₃ OH
Cryst. size (10 ⁻² mm)	30 × 40 × 50	26 × 28 × 33	20 × 30 × 30	40 × 45 × 50	20 × 30 × 40	17 × 20 × 30
M.w.	516.59	574.63	532.59	632.67	632.67	706.72
Cryst. symm.	monoclinic	hexagonal	hexagonal	hexagonal	monoclinic	monoclinic
Space group	P2 ₁	P3 ₁	P3 ₁	P3 ₁	P2 ₁	P2 ₁
a/Å	9.355(1)	14.761(5)	16.027(2)	15.035(2)	12.079(1)	9.829(2)
b/Å	16.847(2)				9.934(2)	19.807(4)
c/Å	17.478(3)	12.448(1)	9.432(1)	12.524(1)	14.467(2)	10.171(1)
β/°	91.54(1)				104.91(1)	107.54(1)
V/Å ³	2 753.5(11)	2 348.8(18)	2 098.1(7)	2 451.7(9)	1 677.5(8)	1 888.1(11)
D _c /g cm ⁻³	1.25	1.22	1.26	1.29	1.25	1.24
Z	4	3	3	3	2	2
μ/cm ⁻¹	7.3	7.4	7.6	8.0	7.8	7.9
F(000)	1 104	918	852	1 008	672	750
N(F _{tot})	5 532	3 654	5 695	5 132	3 658	3 458
N(F _{obs})	4 635	2 554	4 597	4 356	2 883	2 578
k	5	2	5	5	3	3
R _{obs}	0.049	0.047	0.039	0.040	0.046	0.057
R _w	0.065	0.056	0.056	0.050	0.042	0.057
Abs. corr. min.	0.799	0.373	0.892	0.828	0.811	0.604
Abs. corr. max.	1.149	6.793	1.076	1.244	1.451	1.758
l-sq parameter	0.01	0.04	0.04	0.01	*	*
parameter shift	0.89	0.83	0.38	1.12	1.2	0.88
max. peak	0.21	0.37	0.64	0.25	0.16	0.29

* With unit weight.

Table 5. Atomic fractional co-ordinates of the non-hydrogen atoms of Ejap-2 (4) with e.s.d.s in parentheses

	x	y	z		x	y	z
O(1)	0.240 8(4)	-0.073 2(0)	-0.041 7(2)	O(1')	0.031 5(2)	-0.058 3(1)	-0.456 4(1)
O(2)	0.312 4(5)	0.129 9(2)	0.125 4(2)	O(2')	0.063 6(3)	-0.260 4(1)	-0.621 1(1)
O(3)	0.595 8(4)	0.075 1(2)	-0.020 4(2)	O(3')	0.377 4(2)	-0.209 2(1)	-0.481 6(1)
O(5)	0.066 5(5)	-0.088 5(2)	0.102 4(2)	O(5')	-0.169 8(2)	-0.046 0(1)	-0.598 9(1)
O(7)	0.332 7(4)	0.083 1(2)	-0.101 7(2)	O(7')	0.128 9(2)	-0.217 0(1)	-0.394 7(1)
O(21)	0.394 8(8)	0.125 5(4)	0.245 5(3)	O(21')	0.167 3(5)	-0.284 4(3)	-0.728 4(2)
O(31)	0.703 4(5)	0.018 4(3)	-0.118 9(3)	O(31')	0.507 3(3)	-0.155 7(1)	-0.385 5(1)
O(51)	-0.089 6(5)	-0.009 5(3)	0.161 0(2)	O(51')	-0.325 4(3)	-0.129 7(2)	-0.654 1(1)
O(71)	0.321 5(7)	0.214 2(3)	-0.119 0(2)	O(71')	0.073 5(4)	-0.344 4(1)	-0.373 8(1)
C(1)	0.508 8(7)	0.003 5(4)	-0.009 2(3)	C(1')	0.291 0(3)	-0.137 4(2)	-0.488 9(2)
C(2)	0.589 1(6)	-0.058 5(4)	0.036 0(4)	C(2')	0.365 0(4)	-0.075 3(2)	-0.537 2(2)
C(3)	0.496 2(7)	-0.131 8(4)	0.038 8(4)	C(3')	0.271 2(4)	-0.001 0(2)	-0.541 1(2)
C(4)	0.352 7(7)	-0.116 8(4)	0.075 5(3)	C(4')	0.123 0(4)	-0.017 4(2)	-0.576 4(2)
C(5)	0.277 3(6)	-0.045 6(3)	0.035 0(3)	C(5')	0.052 4(3)	-0.086 4(2)	-0.534 3(1)
C(6)	0.133 1(6)	-0.021 6(4)	0.068 9(3)	C(6')	-0.095 8(3)	-0.112 3(2)	-0.564 0(1)
C(7)	0.058 2(6)	0.009 8(4)	-0.001 4(3)	C(7')	-0.160 2(3)	-0.139 6(2)	-0.489 3(2)
C(8)	0.125 0(6)	0.090 6(4)	-0.018 8(3)	C(8')	-0.093 0(3)	-0.220 9(2)	-0.473 2(2)
C(9)	0.289 0(6)	0.092 9(3)	-0.021 7(3)	C(9')	0.071 5(3)	-0.225 8(2)	-0.471 7(2)
C(10)	0.371 4(6)	0.029 4(3)	0.027 2(3)	C(10')	0.145 4(3)	-0.164 0(2)	-0.525 2(1)
C(11)	0.091 5(6)	-0.054 4(4)	-0.062 2(3)	C(11')	-0.114 1(3)	-0.074 7(2)	-0.433 4(2)
C(12)	0.003 5(8)	-0.130 0(5)	-0.056 8(4)	C(12')	-0.204 0(4)	0.002 1(3)	-0.441 4(2)
C(13)	0.082 8(7)	-0.026 8(5)	-0.146 1(4)	C(13')	-0.112 8(5)	-0.098 3(3)	-0.349 2(2)
C(14)	0.371 0(9)	-0.133 1(5)	0.164 4(4)	C(14')	0.126 8(4)	-0.022 7(3)	-0.663 9(2)
C(15)	0.411 6(6)	0.069 0(4)	0.105 2(3)	C(15')	0.176 4(3)	-0.205 7(2)	-0.601 2(2)
C(21)	0.319 2(8)	0.156 2(5)	0.198 3(4)	C(21')	0.074 1(5)	-0.299 1(3)	-0.686 8(2)
C(22)	0.226(1)	0.221 7(7)	0.210 7(6)	C(22')	-0.040 4(7)	-0.357 6(4)	-0.697 6(3)
C(31)	0.684 3(6)	0.075 8(5)	-0.079 3(3)	C(31')	0.477 0(3)	-0.211 5(2)	-0.425 1(2)
C(32)	0.749 7(9)	0.154 1(6)	-0.091 9(5)	C(32')	0.542 8(4)	-0.291 7(3)	-0.418 3(2)
C(51)	-0.045 8(7)	-0.074 3(4)	0.148 4(3)	C(51')	-0.285 6(3)	-0.063 2(2)	-0.643 7(2)
C(52)	-0.105(1)	-0.151 6(6)	0.175 1(5)	C(52')	-0.352 3(5)	0.008 4(3)	-0.676 3(2)
C(71)	0.348 9(7)	0.147 3(3)	-0.142 9(3)	C(71')	0.124 3(4)	-0.283 4(2)	-0.351 3(2)
C(72)	0.395 9(6)	0.132 0(4)	-0.221 6(3)	C(72')	0.189 3(4)	-0.272 7(2)	-0.273 4(2)
C(73)	0.418 4(7)	0.055 1(4)	-0.247 2(3)	C(73')	0.268 9(4)	-0.206 0(2)	-0.252 4(2)
C(74)	0.460(1)	0.045 0(5)	-0.322 4(4)	C(74')	0.328 7(5)	-0.200 9(2)	-0.180 9(2)
C(75)	0.474 3(9)	0.107 6(6)	-0.370 1(4)	C(75')	0.308 8(5)	-0.260 6(3)	-0.128 6(2)
C(76)	0.456 3(8)	0.181 4(5)	-0.345 7(4)	C(76')	0.231 2(5)	-0.326 9(2)	-0.148 5(2)
C(77)	0.413 5(7)	0.196 7(4)	-0.269 5(4)	C(77')	0.171 1(4)	-0.332 9(2)	-0.221 0(2)

Table 6. Atomic fractional co-ordinates of the non-hydrogen atoms of Ejap-3 (7) with e.s.d.s in parentheses

	x	y	z		x	y	z
O(1)	0.178 9(1)	0.477 3(1)	0.691 2(0)	C(11)	0.168 1(2)	0.557 4(2)	0.634 4(3)
O(2)	-0.109 8(2)	0.194 3(2)	0.590 8(2)	C(12)	0.265 0(3)	0.620 9(3)	0.565 2(3)
O(3)	-0.015 9(1)	0.252 2(2)	0.903 6(2)	C(13)	0.164 0(3)	0.630 7(3)	0.716 8(3)
O(5)	0.150 2(1)	0.420 1(1)	0.451 9(1)	C(14)	0.143 7(3)	0.228 2(3)	0.564 1(3)
O(6)	-0.118 7(1)	0.395 4(2)	0.566 2(2)	C(15)	-0.058 2(3)	0.200 8(3)	0.689 9(3)
O(7)	-0.019 1(1)	0.428 1(1)	0.829 4(2)	C(21)	-0.167 5(4)	0.102 2(4)	0.546 5(4)
O(21)	-0.176 5(4)	0.026 9(3)	0.593 2(4)	C(22)	-0.215 1(4)	0.102 9(5)	0.445 5(5)
O(31)	0.096 1(2)	0.331 3(2)	1.038 0(2)	C(31)	0.009 3(3)	0.272 5(3)	1.008 5(3)
O(51)	0.022 6(3)	0.335 9(4)	0.338 0(2)	C(32)	-0.081 7(5)	0.210 8(4)	1.079 4(4)
O(61)	-0.104 7(2)	0.549 6(2)	0.522 1(3)	C(51)	0.114 4(3)	0.382 7(4)	0.355 0(3)
O(71)	-0.185 3(2)	0.387 7(2)	0.842 3(2)	C(52)	0.196 4(4)	0.404 6(4)	0.277 7(3)
C(1)	0.069 2(3)	0.310 4(2)	0.827 9(3)	C(61)	-0.145 5(3)	0.456 0(4)	0.508 6(4)
C(2)	0.136 1(3)	0.260 6(3)	0.819 0(3)	C(62)	-0.226 3(4)	0.394 0(5)	0.430 0(5)
C(3)	0.225 9(3)	0.319 6(3)	0.740 1(3)	C(71)	-0.099 2(3)	0.427 0(3)	0.880 1(3)
C(4)	0.188 9(3)	0.330 1(3)	0.630 3(3)	C(72)	-0.071 0(3)	0.477 7(2)	0.986 8(3)
C(5)	0.113 9(2)	0.375 5(2)	0.641 5(2)	C(73)	0.024 8(3)	0.510 2(3)	1.032 7(3)
C(6)	0.077 2(2)	0.398 5(2)	0.537 8(3)	C(74)	0.043 4(3)	0.548 7(4)	1.136 3(4)
C(7)	0.068 2(2)	0.491 2(2)	0.569 7(3)	C(75)	-0.035 0(4)	0.553 6(3)	1.192 2(3)
C(8)	-0.029 9(2)	0.450 5(3)	0.638 0(3)	C(76)	-0.127 3(3)	0.523 4(3)	1.145 7(4)
C(9)	-0.042 9(2)	0.373 5(2)	0.727 9(2)	C(77)	-0.148 3(3)	0.485 6(3)	1.043 3(3)
C(10)	0.019 6(2)	0.314 5(2)	0.718 9(3)				

Table 7. Atomic fractional co-ordinates of the non-hydrogen atoms of Ejap-10 (9) with e.s.d.s in parentheses

	x	y	z		x	y	z
O(1)	0.547 73(9)	0.764 66(9)	0.101 2(0)	C(10)	0.673 3(1)	0.838 7(1)	0.277 8(2)
O(2)	0.811 45(8)	0.929 20(9)	0.441 5(1)	C(11)	0.576 7(1)	0.796 7(1)	-0.043 3(2)
O(3)	0.698 02(9)	0.732 69(9)	0.433 3(1)	C(12)	0.494 4(1)	0.798 9(1)	-0.121 0(2)
O(5)	0.567 54(9)	0.966 72(9)	0.070 3(1)	C(13)	0.596 5(1)	0.725 1(1)	-0.118 5(2)
O(6)	0.833 02(9)	0.994 0(1)	0.046 1(1)	C(14)	0.521 5(1)	0.911 5(1)	0.397 7(2)
O(7)	0.730 16(8)	0.747 86(8)	0.135 1(1)	C(15)	0.727 6(1)	0.925 3(1)	0.380 1(2)
O(21)	0.747 8(1)	0.906 2(1)	0.660 2(1)	C(21)	0.812 6(1)	0.917 4(1)	0.583 2(2)
O(31)	0.614 8(1)	0.572 6(1)	0.400 4(2)	C(22)	0.904 3(1)	0.923 8(1)	0.628 5(2)
O(51)	0.659 4(1)	1.108 9(1)	0.174 5(3)	C(31)	0.684 8(1)	0.643 2(1)	0.445 4(3)
O(71)	0.889 51(9)	0.804 1(1)	0.134 1(2)	C(32)	0.764 4(2)	0.645 2(2)	0.525 6(5)
C(1)	0.624 5(1)	0.741 5(1)	0.356 6(2)	C(51)	0.590 5(1)	1.056 4(1)	0.103 4(3)
C(2)	0.546 1(1)	0.729 9(1)	0.459 0(2)	C(52)	0.519 2(1)	1.081 4(1)	0.051 2(3)
C(3)	0.466 4(1)	0.735 3(1)	0.378 2(2)	C(71)	0.807 5(1)	0.737 4(1)	0.120 4(2)
C(4)	0.504 8(1)	0.830 0(1)	0.297 5(2)	C(72)	0.783 6(1)	0.637 3(1)	0.088 2(2)
C(5)	0.589 2(1)	0.845 0(1)	0.201 0(2)	C(73)	0.689 5(1)	0.561 0(1)	0.087 2(3)
C(6)	0.635 1(1)	0.936 0(1)	0.108 3(2)	C(74)	0.672 4(2)	0.468 8(2)	0.061 6(4)
C(7)	0.664 6(1)	0.897 5(1)	-0.019 3(2)	C(75)	0.746 5(2)	0.452 7(1)	0.034 3(4)
C(8)	0.756 2(1)	0.897 5(1)	0.025 4(2)	C(76)	0.841 0(2)	0.529 8(2)	0.032 4(5)
C(9)	0.748 9(1)	0.844 7(1)	0.166 5(2)	C(77)	0.859 0(1)	0.621 8(1)	0.058 2(3)

Experimental

$h\nu_F$ Values were determined on Kieselgel 60F₂₅₄ with toluene-ethyl acetate (3:2) (A-system) and cyclohexane-ethyl acetate-ethanol (60:30:1) (B-system).

¹H N.m.r. spectra were recorded at 250.13 MHz (Bruker WM-250) in deuteriochloroform, using SiMe₄ as internal standard at 303 ± 0.5 K. Besides the usual 1D experiments, 2D H,H-COSY¹⁴ spectra were also analysed for unambiguous assignment of resonances. Typical parameters are: 1 K × 128 (zero-filled to 512 prior the 2D FT) data points for ~2 kHz spectral with, non-shifted sine-bell and squared sine-bell weighting in the t_2 and t_1 , dimensions, respectively, and absolute value calculation. Dipolar connectivities were mapped out using, beside selective n.O.e.d.s.¹⁵ experiments in some cases, pure phase-phase sensitive (using the TPPI method¹⁶) 2D n.O.e. spectroscopy.⁵ Typical parameters are as follows: 1 K × 256 (zero-filled to 1 K prior to 2D FT) data points for ~2 kHz spectral with, mixing time 800 ms, appropriate Gaussian and cosine weighting in the t_2 and t_1 dimensions,

respectively. For a more detailed description of the 2D n.m.r. technique see ref. 9.

I.r. and mass spectral measurements were carried out on a Bruker IFS 85 FT spectrometer for chloroform solutions in a 0.027 mm KBr cell and on a Finnigan MAT 8430 mass spectrometer (chemical ionization with CH₄; $T_{ion\ source}$ 250 °C; resolution 1000/10% valley), respectively. Abbreviations used in the lists of characteristic fragments of the new compounds: Nic = nicotinoyl (C₆H₄NO), Fu = 3-furyl (C₄H₃O). Light petroleum refers to the fraction boiling in the range 40–60 °C.

Extraction of Euonymus japonicus.—Fresh fruits (3 kg) of *E. japonicus* were extracted at ambient temperature with methanol (21 dm³). The extract was evaporated to 3 dm³ and extracted with light petroleum (5 × 8 dm³). Evaporation of the organic phase gave a residue (308 g), which was absorbed on polyamide (440 g) and eluted with methanol-water (2:3) (55 fractions), (3:2) (16 fractions), (1:4) (21 fractions), then acetone (5 fractions). 300-cm³ Fractions were collected. Fractions eluted

Table 8. Atomic fractional co-ordinates of the non-hydrogen atoms of Ejap-4 (13) with e.s.d.s in parentheses. Disordered atomic positions are marked

	x	y	z		x	y	z
O(1)	0.487 7(1)	0.848 8(1)	0.050 9(0)	C(12)	0.403 2(1)	0.710 6(1)	-0.076 8(2)
O(2)	0.770 4(1)	1.129 7(1)	-0.047 7(1)	C(13)	0.503 7(1)	0.698 4(1)	0.072 3(2)
O(3)	0.679 2(1)	1.069 4(1)	0.262 8(1)	C(14)	0.515 3(2)	1.093 3(1)	-0.071 4(2)
O(4)	0.573 5(1)	1.161 6(1)	0.172 1(1)	C(15)	0.718 4(1)	1.124 1(1)	0.050 4(1)
O(5)	0.515 2(1)	0.910 7(1)	-0.187 5(1)	C(21)	0.846 8(1)	1.224 3(1)	-0.075 4(2)
O(6)	0.780 8(1)	0.933 8(1)	-0.077 7(1)	C(22)	0.891 1(2)	1.222 1(2)	-0.179 1(3)
O(7)	0.686 3(1)	0.899 1(1)	0.184 2(1)	C(31)	0.658 3(2)	1.044 8(2)	0.367 3(2)
O(21)	0.870 4(1)	1.297 1(1)	-0.019 8(2)	C(32)	0.750 8(2)	1.104 2(2)	0.434 5(2)
O(31)	0.575 6(1)	0.979 1(1)	0.397 4(1)	C(41)	0.573 5(2)	1.221 6(2)	0.249 8(3)
O(41) ^a	0.555 4(3)	1.185 2(2)	0.343 6(3)	C(42)	0.625 7(2)	1.330 6(2)	0.222 4(3)
O(51) ^a	0.642 0(2)	0.965 8(3)	-0.303 8(3)	C(51)	0.551 4(2)	0.945 5(2)	-0.284 3(2)
O(61)	0.765 5(1)	0.784 1(1)	-0.128 9(2)	C(52)	0.472 4(2)	0.926 0(2)	-0.362 5(2)
O(71)	0.852 1(1)	0.945 1(1)	0.196 9(2)	C(61)	0.806 9(2)	0.875 9(2)	-0.137 6(2)
C(1)	0.595 7(1)	1.011 4(1)	0.188 6(1)	C(62)	0.888 1(2)	0.940 1(3)	-0.215 2(3)
C(2)	0.520 2(1)	1.051 1(1)	0.188 8(2)	C(71)	0.766 9(1)	0.903 2(1)	0.235 5(2)
C(3)	0.438 0(1)	0.999 4(1)	0.105 6(2)	C(72)	0.741 9(1)	0.853 6(1)	0.339 8(2)
C(4)	0.475 9(1)	0.994 1(1)	-0.005 4(2)	C(73)	0.643 9(2)	0.811 6(2)	0.385 2(2)
C(5)	0.549 3(1)	0.950 8(1)	0.001 9(1)	C(74)	0.627 3(2)	0.773 1(2)	0.486 9(2)
C(6)	0.587 1(1)	0.930 7(1)	-0.102 6(1)	C(75)	0.705 0(2)	0.774 9(2)	0.545 7(2)
C(7)	0.595 6(1)	0.837 3(1)	-0.072 9(1)	C(76)	0.800 8(2)	0.812 0(2)	0.500 3(2)
C(8)	0.693 6(1)	0.878 2(1)	-0.006 6(2)	C(77)	0.819 2(2)	0.051 8(2)	0.399 5(2)
C(9)	0.707 1(1)	0.953 9(1)	0.084 5(1)	O(41') ^b	0.495 1(4)	1.188 0(4)	0.302 6(5)
C(10)	0.643 3(1)	1.010 5(1)	0.079 0(1)	O(51') ^b	0.639 9(3)	1.024 4(3)	-0.297 1(4)
C(11)	0.497 6(1)	0.771 7(1)	-0.007 9(2)				

^a Site occupancy 0.58. ^b Site occupancy 0.42.**Table 9.** Atomic fractional co-ordinates of the non-hydrogen atoms of Ejap-5 (15) with e.s.d.s in parentheses. Disordered atomic positions are marked

	x	y	z		x	y	z
O(1)	0.054 0(2)	0.782 9(0)	0.236 0(1)	C(14)	-0.047 4(3)	1.041 3(5)	0.388 5(3)
O(2)	0.186 7(2)	1.188 2(3)	0.335 0(2)	C(15)	0.221 7(3)	1.067 9(4)	0.390 6(2)
O(3)	0.334 5(2)	0.843 0(3)	0.466 4(2)	C(21)	0.179 6(3)	1.300 0(4)	0.387 6(3)
O(4)	0.155 7(2)	0.910 4(3)	0.545 5(1)	C(22)	0.135 7(5)	1.416 6(6)	0.323 4(5)
O(5)	-0.092 6(2)	1.034 9(3)	0.162 4(2)	C(31)	0.405 3(4)	0.739 8(5)	0.487 2(4)
O(6)	0.237 4(2)	1.093 4(3)	0.145 6(1)	C(32) ^a	0.517 0(7)	0.789(1)	0.566 1(8)
O(7)	0.373 2(2)	0.968 1(3)	0.292 5(2)	C(41)	0.225 5(4)	0.887 5(6)	0.633 7(3)
O(21)	0.205 7(2)	1.300 8(3)	0.472 7(2)	C(42)	0.233 4(6)	1.008 9(8)	0.695 6(4)
O(31) ^a	0.382 0(7)	0.633 2(9)	0.436 5(7)	C(51)	-0.130 4(4)	1.163 7(6)	0.146 6(3)
O(41)	0.274 2(3)	0.783 9(4)	0.657 1(2)	C(52)	-0.256 9(4)	1.168 2(8)	0.115 1(4)
O(51) ^b	-0.064 4(4)	1.255 4(6)	0.146 1(4)	C(61)	0.306 8(3)	1.119 9(5)	0.089 3(3)
O(61) ^b	0.313 6(4)	1.044 0(6)	0.024 8(3)	C(62)	0.356 1(3)	1.258 7(5)	0.103 7(3)
O(71) ^c	0.449 3(6)	0.788(1)	0.233 0(6)	C(63)	0.417 5(4)	1.303 2(7)	0.042 2(4)
C(1)	0.219 4(3)	0.822 1(4)	0.408 7(2)	C(64)	0.469 1(4)	1.430 7(7)	0.057 4(4)
C(2)	0.140 7(3)	0.803 6(4)	0.474 8(2)	C(65)	0.453 6(5)	1.507 9(6)	0.128 5(5)
C(3)	0.016 7(3)	0.797 1(4)	0.418 8(2)	C(66)	0.393 3(6)	1.465 0(7)	0.188 4(5)
C(4)	-0.022 0(3)	0.908 1(4)	0.344 5(2)	C(67)	0.344 8(4)	1.339 6(6)	0.177 4(3)
C(5)	0.060 4(3)	0.915 6(4)	0.279 7(2)	C(71)	0.462 0(3)	0.899 3(6)	0.278 7(4)
C(6)	0.031 0(3)	1.013 8(4)	0.195 7(2)	C(72) ^b	0.568 1(6)	0.980(1)	0.301 1(6)
C(7)	0.078 7(3)	0.938 9(5)	0.123 5(2)	O(31a) ^a	0.373 8(6)	0.628 3(7)	0.475 9(5)
C(8)	0.208 3(3)	0.955 1(4)	0.155 2(2)	C(32a) ^a	0.518(1)	0.771(1)	0.533 6(9)
C(9)	0.260 5(3)	0.910 3(4)	0.259 3(2)	O(51a) ^c	-0.072 4(8)	1.257(1)	0.171 8(7)
C(10)	0.189 7(2)	0.935 8(4)	0.334 4(2)	O(61a) ^c	0.359 4(8)	1.026(1)	0.064 5(7)
C(11)	0.041 4(3)	0.792 1(5)	0.133 3(2)	O(71a) ^c	0.460 5(8)	0.777(1)	0.280 8(8)
C(12)	-0.082 3(4)	0.765 7(6)	0.079 6(3)	O(71b) ^c	0.441 0(7)	0.824(1)	0.211 0(8)
C(13)	0.117 2(4)	0.683 6(6)	0.107 1(3)	C(72a) ^c	0.581(1)	0.950(2)	0.331(1)

^a Site occupancy 0.58. ^b Site occupancy 0.42.

with methanol-water (2:3) (fractions 1—55; 23.8 g) containing the sesquiterpene esters were rechromatographed on a silica column (552 g) with cyclohexane (12 fractions), cyclohexane-ethyl acetate (95:5) (19 fractions), (9:1) (31 fractions), (4:1) (20 fractions), (7:3) (18 fractions), and (1:1) (10 fractions). 300-cm³ fractions were collected. Ejap-2 (2.4 g) was crystallized from fractions (37—39, Ejap-3 (1.03 g) from fractions 42—50, Ejap-4 (0.79 g) from fractions 52—65, Ejap-5 (1.03 g) from

fractions 66—78, and Ejap-6 (0.40 g) from fraction 92. The fractions 85—91 after preparative t.l.c. (silica) with toluene-ethyl acetate (3:2) yielded Ejap-7 (60 mg), Ejap-10 (90 mg), and Ejap-12 (60 mg), while fractions 93—105 gave Ejap-6 (60 mg), Ejap-12 (12 mg), Ejap-13 (25 mg), and Ejap-14 (5 mg) by the same method.

Ejap-2 (4), *h*R_F (A) 84, (B) 86; m.p. 149—150 °C (from cyclohexane-ethyl acetate); ν_{C-O} 1732 cm⁻¹; *m/z* (%) 516 (12.6,

Table 10. Atomic fractional co-ordinates of the non-hydrogen atoms of Ejap-6 (**18**) with e.s.d.s in parentheses. Disordered atomic positions are marked

	x	y	z		x	y	z
O(1)	0.635 7(4)	0.469 0(0)	0.888 7(4)	C(12)	0.890 6(6)	0.452 5(4)	0.954 0(7)
O(2)	0.415 7(4)	0.450 4(2)	1.208 4(4)	C(13)	0.726 7(7)	0.365 2(4)	0.826 3(7)
O(3)	0.201 8(4)	0.445 6(2)	0.787 1(4)	C(14)	0.535 9(8)	0.603 4(3)	1.110 5(7)
O(4)	0.239 3(4)	0.581 8(2)	0.886 5(4)	C(15)	0.341 2(6)	0.466 9(3)	1.069 0(6)
O(5)	0.798 8(4)	0.506 9(2)	1.184 0(4)	C(21)	0.372 7(7)	0.483 5(4)	1.305 0(7)
O(6)	0.586 5(4)	0.328 1(2)	1.184 5(4)	C(22)	0.458 0(9)	0.464 6(5)	1.445 5(7)
O(7)	0.343 1(4)	0.337 0(2)	0.977 0(4)	C(31)	0.148 4(7)	0.423 0(4)	0.659 6(6)
O(8)	0.523 0(4)	0.581 6(2)	0.735 9(4)	C(32)	0.006 8(8)	0.391 8(5)	0.632 1(8)
O(21)	0.277 1(7)	0.523 6(3)	1.274 9(6)	C(41)	0.106 6(7)	0.604 6(4)	0.821 2(7)
O(31)	0.207 1(6)	0.429 6(4)	0.575 8(5)	C(42)	0.043 2(8)	0.636 6(4)	0.920 8(9)
O(41)	0.051 3(5)	0.601 4(4)	0.701 1(6)	C(51)	0.845 5(7)	0.515 6(4)	1.320 2(7)
O(51)	0.793 4(6)	0.489 3(4)	1.397 7(5)	C(52)	0.970 5(9)	0.562 7(5)	1.358 8(8)
O(61)	0.742 2(5)	0.245 5(2)	1.196 5(5)	C(61)	0.663 2(7)	0.275 5(3)	1.247 9(7)
O(71)	0.332 0(7)	0.275 7(3)	0.793 0(6)	C(62)	0.638 2(7)	0.257 7(3)	1.377 1(7)
O(81)	0.664 9(5)	0.669 9(2)	0.808 3(5)	C(63)	0.531 6(8)	0.284 7(4)	1.416 5(8)
C(1)	0.341 9(6)	0.477 6(3)	0.823 9(6)	C(64)	0.508(1)	0.264 0(5)	1.540 8(8)
C(2)	0.322 4(6)	0.553 9(3)	0.804 1(6)	C(65)	0.597(1)	0.217 6(5)	1.621 5(8)
C(3)	0.465 2(7)	0.590 7(3)	0.850 2(6)	C(66)	0.703(1)	0.190 7(4)	1.583 5(9)
C(4)	0.567 9(6)	0.567 4(3)	0.987 9(6)	C(67)	0.725 4(9)	0.210 4(4)	1.461 6(8)
C(5)	0.576 5(6)	0.490 9(3)	0.998 4(5)	C(71)	0.288 3(3)	0.288 3(3)	0.884 7(8)
C(6)	0.678 7(6)	0.461 3(3)	1.129 6(6)	C(72)	0.165 0(9)	0.256 2(4)	0.913(1)
C(7)	0.725 9(6)	0.396 4(3)	1.073 3(6)	C(81)	0.626 4(7)	0.624 9(4)	0.729 8(7)
C(8)	0.602 1(6)	0.347 0(3)	1.051 2(6)	C(82)	0.682 1(8)	0.608 2(5)	0.612 4(8)
C(9)	0.460 0(6)	0.376 9(3)	0.959 2(6)	O(91) ^a	0.111(1)	0.305(1)	0.298(1)
C(10)	0.427 9(5)	0.453 2(3)	0.968 7(5)	C(91) ^a	0.082(2)	0.369(1)	0.296(1)
C(11)	0.749 4(6)	0.419 4(3)	0.938 1(6)				

^a Site occupancy 0.50.

M^{+}), 501 (8.4, $M - CH_3$), 474 (100, $M - CH_2CO$), 457 (52, $M - CH_3CO_2$), 352 (12.5, $M - CH_2CO - PhCO_2H$), 204 (31.4, ring-A fission), and 105 (58, $PhCO^+$); δ_H 8.07—8.03 (2 H, m, 2'- and 6''-H), 7.59—7.40 (3 H, m, 3''-, 4''-, and 5''-H), and 2.24, 2.09, 1.54 (each 3 H, s, COMe).

Ejap-7 (**5**) hR_F (A) 26, (B) 60; amorphous; $\nu_{C=O}$ 1 732 cm^{-1} ; m/z (%) 517 (100, M^{+}), 474 (12, $M - CH_3CO$), 457 (33, $M - CH_3CO_2H$), 275 (12, $M - CH_3CO_2H - NicCO_2H - CH_3CO_2$), 215 (13, 275 - CH_3CO_2H), and 124 (14.5, $NicC(OH)_2^+$); δ_H 9.25 (1 H, d, J 2 Hz, 2'-H), 8.78 (1 H, dd, J 2 and 5 Hz, 6'-H), 8.30 (1 H, ddd, J 2, 2, and 8 Hz, 4'-H), 7.40 (1 H, dd, J 5 and 8 Hz, 5'-H), and 2.25, 2.10, and 1.60 (each 3 H, s, COMe).

Ejap-3 (**7**) hR_F (A) 70, (B), 78; m.p. 118—122 °C (from cyclohexane-ethyl acetate); $\nu_{C=O}$ 1 738 cm^{-1} ; m/z (%) 574 (5.4, M^{+}), 559 (4.5, $M - CH_3$), 532 (100, $M - C_2H_5O$), and 105 (95, $PhCO^+$); δ_H 8.03—8.00 (2 H, m, 2'- and 6''-H), 7.60—7.41 (3 H, m, 3''-, 4''-, and 5''-H), and 2.25, 2.18, 2.09, and 1.47 (each 3 H, s, COMe).

Ejap-14 (**8**) hR_F (A) 20, (B) 40; amorphous; $\nu_{C=O}$ 1 738 cm^{-1} ; m/z (%) 575 (100, M^{+}), 532 (19, $M - CH_3CO$), 515 (26, $M - CH_3CO_2H$), 473 (22, 515 - CH_2CO), 395 (9, $M - 3 \times CH_3CO_2H$), and 350 (9, 473 - $NicCO_2H$); δ_H 9.23 (1 H, s, 2'-H), 8.79 (1 H, br s, 6'-H), 8.26 (1 H, d, J 8 Hz, 4'-H), 7.6—7.3 (1 H, m, 5'-H), and 2.25, 2.19, 2.09, and 1.46 (each 3 H, s, COMe).

Ejap-10 (**9**) hR_F (A) 45, (B) 26; m.p. 203—205 °C (from methanol); $\nu_{C=O}$ 1 740 cm^{-1} ; m/z (%) 514 (3, $M - H_2O$), 489 (5, $M - CH_3CO$), 472 (100, $M - CH_3CO_2H$), 412 (18, $M - 2 \times CH_3CO_2H$), 350 (25.5, 472 - $PhCO_2H$), 291 (57, 350 - CH_3CO_2), 231 (68, 291 - CH_3CO_2H), and 105 (51, $PhCO^+$); δ_H 8.05—8.01 (2 H, m, 2'- and 6''-H), 7.62—7.41 (3 H, m, 3''-, 4''-, and 5''-H), and 2.25, 2.11, and 1.49 (each 3 H, s, COMe).

Ejap-13 (**11**) hR_F (A) 30, (B) 48; amorphous; $\nu_{C=O}$ 1 738 cm^{-1} ; m/z (%) 637 (100, M^{+}), 594 (10, $M - CH_3CO$), 577 (8, $M - CH_3CO_2H$), and 514 (11, $M - NicCO_2H$); δ_H 9.13 (1 H, s, 2'-H), 8.76 (1 H, d, J 5 Hz, 6'-H), 8.21 (1 H, ddd, J 2, 2, and 8 Hz, 4'-H), 8.15—8.10 (2 H, m, 2'- and 6''-H), 7.61—

7.43 (3 H, m, 3''-, 4''-, and 5''-H), 7.36 (1 H, dd, J 5 and 8 Hz, 5'-H), and 2.14, 2.03, and 1.46 (each 3 H, s, COMe).

Ejap-4 (**13**) hR_F (A) 55, (B) 62; m.p. 245—247 °C (from cyclohexane-ethyl acetate); $\nu_{C=O}$ 1 740 cm^{-1} ; m/z (%) 632 (11, M^{+}), 589 (14, $M - CH_3CO$), 572 (86.4, $M - CH_3CO_2H$), 530 (65, $M - CH_3CO_2H - CH_2CO$), 512 (43, $M - 2 \times CH_3CO_2H$), 408 (100, 530 - $PhCO_2H$), and 105 (68, $PhCO^+$); δ_H 8.01—7.98 (2 H, m, 2'- and 6''-H), 7.60—7.40 (3 H, m, 3''-, 4''-, and 5''-H), and 2.26, 2.19, 2.10, 2.07, and 1.46 (each 3 H, s, COMe).

Ejap-5 (**15**) hR_F (A) 60, (B) 56; m.p. 210—211 °C (from cyclohexane-ethyl acetate); m/z (%) 632 (0.4, M^{+}), 590 (62, $M - CH_2CO$), 530 (4, $M - CH_3CO_2H - CH_2CO$), 228 (9, $M - CH_2CO - 4 \times CH_3CO_2H - PhCO_2H$), 105 (100, $PhCO^+$), and 43 (30, CH_3CO^+); δ_H 8.17—8.14 (2 H, m, 2'- and 6''-H), 7.61—7.44 (3 H, m, 3''-, 4''-, and 5''-H), and 2.14 s, 2.09, 1.97, 1.93, and 1.88 (each 3 H, s, COMe).

Ejap-12 (**16**) hR_F (A) 40, (B) 20; m.p. 134—135 °C (from methanol); $\nu_{C=O}$ 1 738 cm^{-1} ; m/z (%) 590 (2, M^{+}), 572 (6.2, $M - H_2O$), 530 (60.6, $M - CH_3CO_2H$), 470 (69, $M - 2 \times CH_3CO_2H$), 408 (29.7, $M - CH_3CO_2H - PhCO_2H$), 367 [100, $M - H_2O - CH_3CO_2H - C_5H_{10}O_2$ (from fission of the ring system) - CH_3CO], and 105 (57.6, $PhCO^+$); δ_H 8.17—8.15 (2 H, m, 2'- and 6''-H), 7.63—7.44 (3 H, m, 3''-, 4''-, and 5''-H), and 2.11 2.05, 1.98, and 1.95 (each 3 H, s, COMe).

Ejap-6 (**18**) hR_F (A) 50, (B) 48; m.p. 140—142 °C (from methanol); $\nu_{C=O}$ 1 738 cm^{-1} ; m/z (%) 690 (8, M^{+}), 647 (15, $M - CH_3CO$), 630 (100, $M - CH_3CO_2H$), 570 (41, $M - 2 \times CH_3CO_2H$), 528 (50.5, 570 - CH_2CO), 406 (30, 528 - $PhCO_2H$), and 105 (35, $PhCO^+$); δ_H 8.16—8.13 (2 H, m, 2'- and 6''-H), 7.62—7.44 (3 H, m, 3''-, 4''-, and 5''-H), and 2.13 (3 H, s, COMe), 2.10 (6 H, s, 2 \times COMe), and 1.97, 1.91, and 1.90 (each 3 H, s, COMe).

Crystal Structure Determination of Ejap-2, -3, -10, -4, -5, and -6.—X-Ray intensities of compounds investigated were collected on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated $Cu-K\alpha$ (λ 1.541 84 Å) radiation using

an ω -2 θ scan in the range $1.5 \leq \theta \leq 75.0^\circ$. For each crystal, three standard reflections were monitored every hour, and these showed only a low decrease of intensities. No decay corrections were made. Cell constants (Table 4) for each crystal were determined by least-squares refinement on diffractometer angles for 25 automatically centred reflections with *ca.* 30° . After data corrections for Lorenz and polarization effects, the reflections with the criteria $|F|^2 > k \times \delta(F^2)$ (where *k* is given in Table 4) were taken as observed. Data reduction and subsequent crystallographic calculations were performed using an Enraf-Nonius SDP system.¹⁷

The phase problems for each structure were solved by the MULTAN program¹⁸ and subsequent structure factor and Fourier calculations. In the course of the isotropic least-squares refinement of the positional parameters for non-hydrogen atoms, empirical absorption corrections were calculated for the data sets using program DIFABS.¹⁹ The minimum and maximum absorption corrections are given in Table 4. Full-matrix least-squares refinement minimized $\sum w(\Delta F)^2$ with $w = [\delta^2(F_o) + 0.25(pF)^2]^{-1}$ (where *p* is also given in Table 4). In the case of Ejap-5 and Ejap-6 a unit weight only was used.

The fractional co-ordinates of hydrogen atoms were generated from assumed geometries. The hydrogen positions were added to the structure factor calculations with individual temperature factors ($B_{iH} = B_{iC} + 1$ in \AA^2), but their positions were not refined.

In the course of the anisotropic refinement of the non-hydrogen positions conformational disorder of a few acetyl groups in Ejap-4 and Ejap-5 was observed. The occupancies of the affected C and O atoms were also refined and are listed with the corresponding atomic co-ordinates (see Tables 8 and 9). Furthermore, in the lattice of Ejap-6 two strong peaks could be found which—in accordance with the solvent applied—were assigned as methanol. Since its occupancy factor invariably converged to 0.5 a half molecule of CH₃OH on the asymmetric unit was taken into account. It is worth mentioning that large thermal parameters were also found for a few acetyl groups in Ejap-2 and Ejap-3; no disordered atomic positions could be assigned to the affected atoms, however.*

All calculations were performed by the program system run on a PDP-11/34 minicomputer.¹⁷

* Full atomic co-ordinates and temperature factors, bond lengths and angles, and torsion angles for compounds Ejap-2, -3, -10, -4, -5, and -6 are available as Supplementary Publication SUP 56736 (43 pp.). See Instructions for Authors, section 4.4, in the January issue.

Lists of fractional atomic co-ordinates for non-H atoms, and bond lengths and angles, have been deposited at the Cambridge Crystallographic Data Centre (see Instructions for Authors, section 5.6.3, in the January issue).

Acknowledgements

We are very indebted to V. V. Kazinczy for the i.r. spectra and to Gy. Jerkovich (Institute for Drug Research, Budapest, Hungary) for mass spectral investigations, respectively. We thank Dr Z. Dinya (Department of Chemistry, Kossuth Lajos University, Debrecen, Hungary) for valuable assistance in measuring some of preliminary mass spectra.

The X-ray investigation of Ejap-2, Ejap-3, Ejap-4, Ejap-5, Ejap-6, and Ejap-10 was sponsored by the Ministry of Health, Budapest, Hungary.

References

- 1 R. Brüning and H. Wagner, *Phytochemistry*, 1978, **17**, 1821.
- 2 W. Olechnowicz-Stepien, H. Rzakowska-Bodalska, L. Novotny, and M. Masojdkova, *Pol. J. Chem.*, 1978, **52**, 1161.
- 3 M. J. Begley, L. Crombie, R. A. Fleming, D. A. Whiting, Zs. Rózsa, M. Kelényi, J. Hohmann, and K. Szendrei, *J. Chem. Soc., Perkin Trans. 1*, 1986, 535.
- 4 C. R. Smith, R. W. Miller, D. Weisleder, and W. K. Rohwedder, *J. Org. Chem.*, 1976, **41**, 3264.
- 5 J. Jeener, B. H. Meier, P. Bachmann, and R. R. Ernst, *J. Chem. Phys.*, 1979, **71**, 4546.
- 6 A. Römer, H. Thomas, and H. Budzikiewicz, *Z. Naturforsch., Teil B*, 1976, **31**, 607.
- 7 H. J. den Hertog, C. Kruk, D. D. Nanavati, and S. Dev, *Tetrahedron Lett.*, 1974, 2219.
- 8 Y. Shizuri, H. Wada, K. Sugiura, K. Yamada, and Y. Hirata, *Tetrahedron*, 1973, **29**, 1773.
- 9 I. Pelczer and Zs. Rózsa, submitted for publication in *Magn. Reson. Chem.*
- 10 E. Pretsch, T. Clerc, J. Seibl, and W. Simon, 'Tabellen zur Strukturklärung organischer Verbindungen mit spektroskopischen Methoden,' Springer Verlag, Berlin, 1976, pp. H195, H200.
- 11 R. L. Baxter, L. Crombie, D. J. Simmonds, and D. A. Whiting, *J. Chem. Soc., Perkin Trans. 1*, 1979, 2972.
- 12 H. Ishiwata, Y. Shizuri, and K. Yamada, *Phytochemistry*, 1983, **22**, 2839.
- 13 D. Cremer, and J. A. Pople, *J. Am. Chem. Soc.*, 1975, **97**, 1354.
- 14 A. Bax, 'Two-Dimensional Nuclear Magnetic Resonance in Liquids,' Reidel, Boston, 1982.
- 15 J. K. M. Sanders and J. D. Mersh, *Prog. NMR Spectrosc.*, 1982, **15**, 353.
- 16 D. Marion and K. Wüthrich, *Biochem. Biophys. Res. Commun.*, 1983, **113**, 967.
- 17 Enraf-Nonius, 'Structure Determination Package,' Delft, 1982.
- 18 P. Main, S. L. Fiske, S. E. Hull, L. Lessinger, G. Germain, J. P. DeClercq, and M. M. Woolfson, 'MULTAN, a System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data,' Universities of York, England and Louvain, Belgium, 1980.
- 19 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.

Received 28th August 1987; Paper 7/00007C