Phytochemistry, Vol. 31, No. 3, pp. 929–933, 1992
Printed in Great Britain.

0031-9422/92 $5.00+0.00

AN OLEANANE TRITERPENE FROM *ANAGALLIS ARVENSIS*

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(*Received* 22 *May* 1991)

Key Word Index—*Anagallis arvensis*; Primulaceae; scarlet pimpernel; oleanane triterpene; X-ray diffraction analysis.

Abstract—A new triterpene metabolite with an oleanane skeleton, has been isolated from *Anagallis arvensis* and its structure established on the basis of spectral analyses (including ^1H–^1H and ^1H–^{13}C COSY), performed both on the original compound and its acid-catalysed hydrolysis product. A single crystal X-ray diffraction analysis performed on the *p*-iodobenzoate derivative enabled the assignment of the absolute configuration.

INTRODUCTION

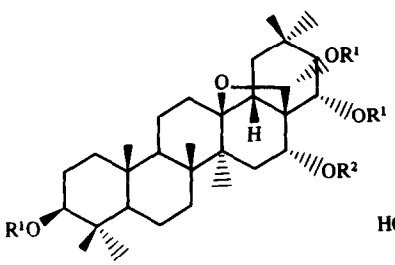
Anagallis arvensis (scarlet pimpernel) is a small but highly variable and adaptable winter or summer annual weed spread throughout the world, known to be poisonous if taken internally and to cause dermatitis in some individuals if the leaves or stems are handled [1]. An ethanol extract of this plant has been reported to possess *in vitro* antiviral activity against herpes simplex virus type 1 and polio virus [2, 3] and to have antifungal effects against phytopathogenic fungi belonging to the genera *Fomes*, *Cytospora*, *Pestalotiopsis* and *Ceratocystis* [4]. Moreover, it has been recently shown that the chloroform extract of *A. arvensis* is an inhibitor of seedling growth [5]. Previously, oleanane triterpenes [6], saponins [7] and flavones [8] have been found in this plant. The present paper deals with the isolation and the structure elucidation of a further oleanane triterpene for which we propose structure **1**.

RESULTS AND DISCUSSION

Compound **1** was isolated as an optically active crystalline solid from the chloroform extract of the whole plant by repeated silica gel column chromatographies followed by normal and reverse-phase HPLC.

The electron impact high resolution mass spectrum of **1** gave a parent ion at *m/z* 490.3615 corresponding to a molecular formula of $C_{30}H_{50}O_5$ requiring six sites of unsaturation. The fully decoupled ^{13}C NMR spectrum showed 30 distinct resonances attributable to seven methyls, nine methylenes, seven methines and seven non-protonated carbon atoms (from DEPT experiments), which accounted for 46 of the 50 protons of the molecule. The remaining four protons were part of hydroxyl functionalities as indicated by the following spectral evidences.

Four exchangeable protons were present in the low-field region of the ^1H NMR spectrum of **1** (Table 1). The IR spectrum exhibited a prominent hydroxyl absorbtion centred at 3410 cm^{-1}. The mass spectrum of **1** showed fragmentation peaks at *m/z* 472.3468, 454.3499, and 436.3282 due to the successive loss of three molecules of water from the $[M]^+$. Inspection of both ^1H and ^{13}C NMR spectra (Table 1) suggested that the fourth hydroxyl group, not lost as water in the mass spectrometer, was part of an hemiacetal function [^1H NMR: δ5.47 (1H, *s*); ^{13}C NMR: δ98.60 –$\underset{|}{C}$H and 87.50 (–$\underset{|}{\overset{|}{C}}$–)]. The



	R^1	R^2
1	H	H
2	Ac	H
3	*p*-IC_6H_4CO	H

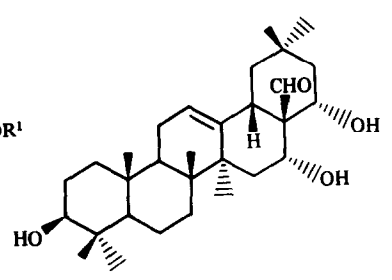


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Table 1. ^1H and ^{13}C NMR data for compound **1**[a]

Position	δ_C[b]		δ_H[c] (mult., J)	$^1H/^{13}C$ Long-range correlation
1	39.57	H_{ax}	1.02 (*ddd*, 12.8, 12.8, 4.2)	H_3-25
		H_{eq}	1.74 (*bddd*, 12.8, 3.6, 3.6)	
2	28.37	H_{ax}	1.92 (*m*)[g]	H_{eq}-1
		H_{eq}	1.87 (*m*)[g]	
3	78.16		3.47 (*dd*, 10.4, 5.5)	
4	39.58			H_3-23
5	55.72		0.85 (*dd*, 11.0, 1.8)	H_3-23, H_3-24
6	18.33	H_{ax} and H_{eq}	1.56-1.43 (*m' s*)	
7	34.48	H_{ax}	1.66 (*m*)[g]	H_3-26
		H_{eq}	1.27 (*bddd*, 13.4, 3.0, 3.0)	
8	42.78[d]			
9	50.60		1.37 (*m*)[g]	H_{ax}-7, H_3-25, H_3-26
10	33.23			H_3-25
11	19.43	H_{ax}	1.89 (*m*)[g]	
		H_{eq}	1.53 (*m*)[g]	
12	33.54	H_{ax}	2.16 (*ddd*, 13.4, 13.4, 5.5)	H-9, H-18
		H_{eq}	1.64 (*ddd*, 13.4, 3.6, 3.6)	
13	87.52			H_{eq}-12, H-18
14	44.21[d]			
15	36.81	H_{ax}	2.25 (*dd*, 14.0, 6.1)	H_3-27
		H_{eq}	1.61 (*d*, 14.0)	
16	69.75		5.09 (*d*, 6.1)	H_{ax}-15, H_{eq}-15
17	52.91			H_{ax}-15, H_{eq}-15, H_α-19
18	47.40		2.22 (*dd*, 13.4, 3.7)	H_α-19, H_β-19
19	38.68	H_α	2.92 (*dd*, 14.6, 13.4)	H_3-29 (or H_3-30)
		H_β	1.37 (*m*)[g,h]	
20	37.32			H_α-19, H_3-29 (or H_3-30)
21	46 71	H_α	2.93 (*dd*, 12.2, 12.2)	H_3-29 (or H_3-30)
		H_β	1.91 (*dd*, 12.2, 5.5)	
22	68.08		5.06 (*dd*, 12.2, 5.5)	
23	28.70		1.22 (*s*)	H_3-24
24	16.40		1.04 (*s*)	H-5, H_3-23
25	16.59		0.95 (*s*)	H-9
26	18.76		1.41 (*s*)	H_{ax}-7, H-9
27	19.75		1.64 (*s*)	H_{ax}-15, H_{eq}-15
28	98.62		5.47 (*s*)	
29	33.79[e]		1.14 (*s*)[f]	H_α-19
30	26.03[e]		1.15 (*s*)[f]	H_α-19

[a] ^1H and ^{13}C NMR spectra were recorded in pyridine-d_5 at 400 and 100.1 MHz, respectively. For the ^1H NMR spectrum 15 mg of **1** were dissolved in 0.5 ml of pyridine-d_5.

[b] Pyridine-d_5 as internal reference = 135.5 ppm. Carbon multiplicities determined through DEPT experiments.

[c] Residual pyridine as internal reference = 8.71 ppm. Coupling constants are given in Hz.

[d–f] Assignments may be reversed.

[g] Overlapped with other signals. Values deduced from ^1H–^1H COSY spectrum.

[h] This signal appears as a broad double doublet (J = 14.5 and 3.5 Hz) in the spectrum recorded in CD_3OD.

NMR spectra also indicated the presence of three hydroxyl-bearing carbon methines showing, respectively, resonances at δ 78.20, 69.70 and 68.10, and 5.09 (1H, *d*, H-16), 5.06 (1H, *dd*, H-22) and 3.47 (1H, *dd*, H-3). Moreover, treatment of **1** with Ac_2O–pyridine gave a triacetyl-derivative (**2**).

The lack of olefinic and carbonyl resonances in the ^{13}C NMR spectrum of **1** indicated that rings had to account for all six sites of unsaturation in the molecule. The mass spectrum of **1** showed a fragmentation pattern characteristic of saturated pentacyclic triterpenes [9]. A strong ion peak at m/z 207.1740 was attributed to the fragment deriving from cleavage of the 9–11 and 8–14 bonds with concomitant hydrogen transfer to the uncharged right-hand part of the molecule. The mass spectrum also contained significant ion peaks at m/z 189.1651, due to the further loss of water from the m/z 207 ion [9] and 246.1623. The formation of these fragments suggested that the hemiacetal function and two hydroxyl groups were present in rings D/E, whereas one hydroxyl group was present in rings A/B. The latter hydroxyl group was assumed to be linked to C-3 from biogenetic considerations. On the basis of the above mass spectral evidences and from the inspection of the ^1H NMR spectrum of **1**, which included three-proton singlets at δ 0.95, 1.04, 1.13, 1.14, 1.22, 1.41 and 1.64 assignable to seven tertiary methyls, it was hypothesized that **1** is based on the oleanane carbon skeleton.

The 400 MHz ^1H–^1H COSY 45 spectrum of **1** recorded both in pyridine-d_5 and pyridine-d_5–methanol-d_4 (9:1) and decoupling experiments performed both in these solvents and methanol-d_4 solution allowed the identification in the molecule of six independent scalar-coupled spin systems pertaining to one $-CH(OH)CH_2CH_2-$, two $-CH(OH)CH_2-$, two $>CHCH_2CH_2-$ and one $>CHCH_2-$ fragments.

The assembly of these subunits, as well as the positioning of the hemiacetal function and methyl groups, was achieved through a combination of data deriving from HETCOR [via ^2J and ^3J[10] (all the observed correlations are shown in Table 1)] and NOE difference experiments (Table 2) and supported by ^1H NMR spectral evidences. Such results allowed us to confirm the hypothesized oleanane nature of compound **1** and established the overall relative stereochemistry of the molecule as the one depicted in formula **1**. In particular, the correlations observed between C-5 and Me-23 and Me-24, and C-1 and Me-25, secured the C-4/C-5 and C-1/C-10 linkages (methyl resonances, apart from those relative to Me-29 and Me-30, had previously been assigned on the basis of NOE results) while the C-3/C-4 connection was indicated by a long-range (*W*) coupling between H-3 and Me-24 observed in the ^1H–^1H COSY spectrum **1**. This observation also indicated the axial orientation of the H-3 proton which was corroborated by the multiplicity and coupling constants of its signal which appeared at δ3.47 (*dd*, J = 10.4 and 5.5 Hz) in the ^1H NMR spectrum. Correlations between C-7 and Me-26 (and C-26 and H_{ax}-7) indicated that C-5/C-7 fragment had to be joined to C-8. The fragment C-9/C-12 was positioned with its C-9 terminal carbon between C-8 and C-10 because C-9 had correlation peaks with Me-25 and Me-26. Correlation peaks between C-12 and H-18 and between the quaternary carbon linked to oxygen at δ87.52 (C-13) and H_{eq}-12 and H-18 demonstrated the connections C-12/C-13 and C-13/C-18 and that the cyclic hemiacetal was located with its $-\overset{|}{\underset{|}{C}}-O$ carbon between C-12 and C-18. The connections C-19/C-20 and C-20/C-21 were secured by the correlations between C-18 and C-21 and one of the two geminal methyls at C-20 (Me-29 or Me-30). Furthermore, the quaternary carbon resonating at δ52.91 was seen to correlate with one of the C-19 protons (H_α-19) and both the C-15 protons. Thus, this carbon had to be linked both to the C-18/C-19 and C-15/C-16 fragments. Unfortunately, no information could be gained from the long-range heterocorrelation about the C-5/C-10, C-8/C-14, C-13/C-14 and C-17/C-22 linkages, and the position of the C-28 hemiacetal carbon. However, a strong positive NOE was induced in the H-18 signal when the H-22 proton was irradiated (and vice versa) indicating that there is a close spatial proximity between these protons. Moreover, positive NOE effects were registered between H-5 and H-3 and H-9, H-28 and H_{ax}-15 and H-16, H_α-19 and Me-27, and H_{ax}-15 and Me-26. These NOE results are consistent with structure **1** in which the hydroxyl groups at C-16 and C-22 are both α-oriented, the C-3 hydroxyl is β, and the hemiacetal hydroxyl is directed towards the E ring. That the C-16 hydroxyl group is axially disposed was also indicated by the strong pyridine-d_5 induced shifts of H_α-19, H_α- 21 and Me-27 in comparison with the values observed in the spectrum recorded in methanol-d_4 (H_α-19: $\Delta\delta$0.52; H_α-21: $\Delta\delta$0.75; Me-27: $\Delta\delta$0.36). The chirality at C-28 and C-22 is also supported by strong pyridine-induced shifts of the H-18 and H-22 protons ($\Delta\delta$ = 0.59 and 0.87, respectively), relative to methanol-d_4, which indicated a 1,3-diaxial-like arrangement of the hemiacetal hydroxyl group and both these protons.

Table 2. NOE experiments on **1** performed in pyridine-d_5/CD_3OD (9:1)

Signal irradiated	Signal enhanced
H-28	H-16, H_{ax}-15
H-16	H_{ax}-15, H-28
H_β-21	H_α-21, H-22
H_α-19	H_3-27
H-3	H-5
H-18	H-22
H_3-29 and H_3-30	H-18, H_α-19, H_β-21, H-22
H-22	H-18, H_β-21
H-5	H-3, H-9, H_3-23
H_3-23	H-3, H-5, H_3-24
H_3-24	H_3-23, H_{ax}-2
H_{ax}-1	H-3, H-5, H_{eq}-1
H_3-25	H_3-26, H_{ax}-2

Finally, the positioning of the hemiacetal group was also indicated by a long-range coupling between H-28 and H_β-19 which are in a zig-zag arrangement. Long-range (*W*) couplings were also observed between H_α-21 and Me-29, Me-26 and Me-27, and Me-23 and Me-24 which agree with structure **1**.

Additional evidence in favour of the proposed structure was provided by acid hydrolysis of **1** performed at 60° which afforded the derivative **4** in good yield (70%). Spectral features of **4** (see Experimental) established a Δ^{12}-oleanene skeleton for this compound. Particularly, the mass spectrum of **4** exhibited prominent ion peaks at *m/z* 208 and 246 deriving from the retro-Diels–Alder fragmentation typical of this molecular structure [9]. The ^{13}C NMR spectrum exhibited resonances at δ124.8 (C-12) and 140.9 (C-13), which are diagnostic of the Δ^{12} double bond in this carbon skeleton [11], while the proton spectrum ($CDCl_3$) showed a somewhat downshifted methyl resonance at δ1.40 ($\Delta\delta$0.18 relative to the chemical shift value in **1**) attributable to the 27-methyl group which is situated in a homoallylic position.

To put the above conclusions on a firm basis an X-ray diffraction analysis was performed on the *p*-iodobenzoate derivative **3** prepared from **1** by reaction with *p*-iodobenzoylchloride in pyridine. Because of the severe crystal deterioration during X-ray exposure, the diffraction pattern was quantitatively limited and qualitatively poor, but sufficient to determine unambiguously the structure and the absolute stereochemistry of **3**, using the anomalous dispersion of the Cu radiation by the iodine atoms (Fig. 1). Bond lengths and valence angles show some anomalous departures from the standard values as a consequence of the poor quality of the experimental data. In the molecular skeleton it is possible to distinguish a corrugated platform formed by the four six-membered rings, A–D, fused through the *trans*-ring junctions A/B, B/C and C/D. The four rings are all in the chair conformation with small distortions increasing from A to D. The platform, from which the axial groups C-24, C-25, C-26, C-27 and O-7 protrude, ends, on one side, with the perpendicular fragment built of the six-membered E ring,

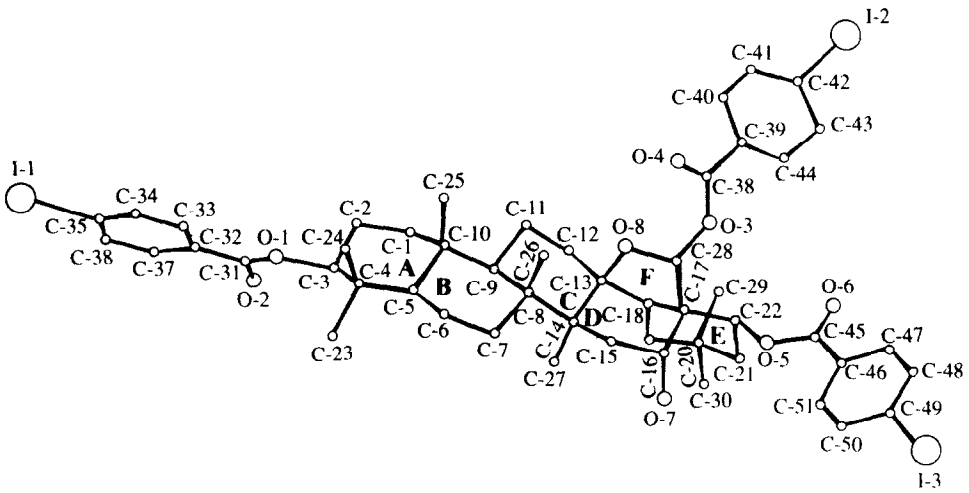

Fig. 1. Perspective view showing the X-ray absolute configuration of **3** together with the atom labelling scheme used in the crystallographic work. For sake of clarity H-atoms are omitted.

trans-fused with the five-membered heterocycle F. The ring E, which is intermediate between a chair and a half-chair, is *cis*-linked to the ring D, while the ring F, which is conformationally irregular, forms with the ring D the seven-membered ring C-13, C-14, C-15, C-16, C-17, C-28, O-8, which displays a boat conformation with O-8/C-28 as the stern and C-15 as the bow. The hydroxyl O-7 is involved in a bifurcated hydrogen bond. The first bond is intramolecular: O-7 . . . . . O(5) = 3.13 Å, H . . . . . O(5) = 2.21 Å, angle O(7)-H . . . . . O(5) = 139°. The second one is intermolecular and is directed towards the atom O(2) of the molecule at $1.5-x$, $-y$, $-0.5+z$: O(7) . . . . . O(2)′ = 3.07 Å, H . . . . . O(2)′ = 2.39 Å, angle O(7)-H . . . . . O(2)′ = 118°.

Although phytotoxicity tests showed that the fraction enriched in **1** markedly inhibited the growth of radish and lettuce seedlings, pure **1** showed no significant biological activity. This is likely to be due to the inactivity of compound **1**. However, the possibility that the biological activity may be due to a synergistic effect of different substances which separately are less active or active below the threshold level of toxicity [12], cannot be *a priori* ruled out. Studies are in progress to clarify this point and to isolate the possible active substance.

EXPERIMENTAL

General. FT-IR spectra were recorded as films. ^{1}H chemical shifts are referenced to the residual MeOH, $CHCl_3$ or pyridine signals (MeOH: 3.34 ppm; $CHCl_3$: 7.26 ppm; pyridine: 8.71 ppm). ^{13}C chemical shifts are referenced in pyridine-d_5 and $CDCl_3$ to the solvents (149.9 and 77.0 ppm, respectively). Nuclear Overhauser enhancement spectra were obtained at 400 MHz in degassed pyridine-d_5–CD_3OD (9:1) soln. HPLC was performed on an instrument equipped with a differential refractometer. Analytical TLC was carried out on silica gel 60 F_{254} and CC on silica gel 60, 0.063–0.20 mm.

Plant material. Anagallis arvensis L. was collected in May 1990 in the Naples Botanic Garden. A voucher specimen of the plant is on file at the herbarium of the Dipartimento di Biologia Vegetale dell 'Universita' di Napoli.

Extraction and isolation. Fresh plants (1.63 kg dry wt after extraction) were air-dried in the dark, cut into pieces and sequentially extd with $CHCl_3$, MeOH and H_2O in a Soxhlet. Phytotoxicity bioassays performed as previously reported [5] on lettuce (*Lactuca sativa* L. var. *capitata* 'Meraviglia d'inverno') and radish (*Raphanus sativus* L. 'Saxa') seedlings showed that only the $CHCl_3$ extract possessed biological activity. The $CHCl_3$ extract (19 g) was chromatographed on an open column of silica gel (450 g, 3 cm diameter) using eluents of increasing polarity from $CHCl_3$ to $CHCl_3$–MeOH (1:1). Frs of 250 ml were collected and those exhibiting similar TLC profiles were combined to give 13 frs which were tested to determine their biological activity.

Only fr. 9 (800 mg), eluted with $CHCl_3$–MeOH (47:3) showed significant biological activity. This fr. on standing deposited 10 mg of a crystalline material. The MeOH sol. portion from this material was further purified by normal and reverse-phase HPLC using Hibar LiChrosorb Si-60 (250 × 10 mm) and μBondapak RP-18 (250 × 10 mm) columns eluted with $CHCl_3$–MeOH (9:1) and MeOH–H_2O (9:1), respectively to give 6 mg of pure **1**. The mother liquors from the biologically active fr. were rechromatographed over silica gel (65 g) eluted with $CHCl_3$–MeOH (49:1) to give a fr. (110 mg) enriched in **1** which was obtained in pure form by HPLC as described above; 26 mg of pure **1** was obtained in this case.

Compound **1**. Mp 179–181° (MeOH). $[\alpha]_D$ −10.8 (pyridine; *c* 0.9). FTIR ν_{max} 3410 cm^{-1}. ^{1}H and ^{13}C NMR (see Table 1). EIHR-MS *m/z* 490.3615 ($[M]^+$, $C_{30}H_{50}O_5$ requires 490.3655), 472.3468 ($C_{30}H_{48}O_4$, $[M-H_2O]^+$), 454.3499 ($C_{30}H_{46}O_3$, $[M-2H_2O]^+$), 436.3282 ($C_{30}H_{44}O_2$), $[M-3H_2O]^+$ 246.1623 ($C_{16}H_{22}O_2$), 207.1740 ($C_{14}H_{23}O$), 189.1651 ($C_{14}H_{21}$, $[207-H_2O]^+$).

Acetylation. Compound **1** (2 mg) was acetylated overnight at room temp. with pyridine–Ac_2O (2:1). Usual work-up and purification by silica gel TLC petrol–Et_2O, 1:1) gave 2 mg of pure **2**. ^{1}H NMR (pyridine-d_5, 270 MHz) δ6.28 (1H, *s*, H-28), 2.14, 2.06, 1.98 (3H each, acetates), 1.56 (3H, *s*), 1.29 (3H, *s*), 1.13 (3H, *s*), 1.08 (3H, *s*), 0.87 (6H, *s*), 0.81 (3H, *s*).

Acid hydrolysis. To a soln of **1** (2 mg) in dioxane (two drops), 2 M HCl (one drop) was added and the soln kept at 60°. When the starting material disappeared (*ca* 1 hr, TLC monitoring) the reaction mixt. was taken to dryness and the crude product chromatographed by silica gel TLC ($CHCl_3$–MeOH, 17:3) giving 1.4 mg of pure **4**. FTIR ν_{max} 3400, 2850 and 1719 cm^{-1}.

^{1}H NMR ($CDCl_3$, 270 MHz) δ9.45 (1H, *s*, H-28), 5.47 (1H, *dd*, J = 3.8 and 3.8 Hz, H-12), 4.71 (1H, *br s*, $W_{1/2}$ = 9.4 Hz, H-16), 3.91 (1H, *dd*, J = 11.5 and 5.5 Hz, H-22), 3.22 (1H, *dd*, J = 10.2 and 4.7 Hz, H-3), 2.64 (1H, *dd*, J = 14.0 and 4.3 Hz, H-18), 2.29 (1H, *dd*, J = 13.7 and 13.7 Hz, H_{ax}-19), 1.90 (1H, *dd*, J = 8.5 and 3.8 Hz, H_a-11), 1.83 (1H, *dd*, J = 11.5 and 11.5 Hz, H_{ax}-21), 1.81 (1H, *dd*, J = 15.4 and 5.5 Hz, H_{ax}-15 or H_{eq}-15), 1.61 (1H, *m*, overlapped to other signals, H_b-11), 1.47 (1H, *dd*, J = 15.4 and 2.6 Hz, H_{eq}-15 or H_{ax}-15), 1.40 (3H, *s*, H_3-27), 1.20 (1H, *ddd*, J = 13.7, 4.7 and 2.1 Hz, H_{eq}-19), 0.98 (6H, *s*), 0.95, 0.91, 0.77 and 0.74 (3H each, *s*'*s*). ^{13}C NMR ($CDCl_3$, 100.1 MHz) δ207.2 (C-28), 140.9 (C-13), 124.8 (C-12), 78.9 (C-3), 69.2 (C-16 or C-22), 68.4 (C-22 or C-16), 55.5, 55.1, 46.5, 46.2, 43.7, 41.7, 40.9, 39.7, 38.7. 38.5, 36.9, 34.7, 33.0, 32.9, 31.2, 28.1, 27.1, 26.6, 24.7, 23.4, 18.2, 17.1, 15.6 and 15.5; EILR-MS *m/z* 472 ($[M]^+$), 454 ($[M-H_2O]^+$), 436 ($[M-2H_2O]^+$), 408 ($[M-2H_2O-CO]^+$), 407 ($[M-2H_2O-HCO]^+$), 246 (fragment ion comprising D and E rings deriving from the molecular ion through retro-Diels–Alder fragmentation of ring C and loss of H_2O), 228 ($[246-H_2O]^+$).

p-*Iodobenzoylderivative.* To a soln of **1** (10 mg) in pyridine (2 ml), *p*-iodobenzoylchloride (20 mg) was added and the mixt. kept at room temp. for 1 hr. The soln was taken to dryness and the residue purified by silica gel TLC (petrol–Et_2O, 7:3) giving 15 mg of pure **3** (^{1}H NMR analysis).

X-Ray analysis. Crystal data and relevant details of the structure determination are presented in Table 3. A crystal obtained by slow evapn of a $CHCl_3$ soln and sealed in a Lindemann capillary tube was mounted on an Enraf-Nonius CAD4 diffractometer. Data collection was done at room temp. with the ω/θ scan technique. Three monitoring reflections showed a crystal decay of *ca* 50% at the end of data collection. In addition to the usual corrections for Lorentz and polarization factors, a linear correction for the crystal decay and an empirical correction for the absorption effects according to North *et al.* [13] were applied. The structure was solved by direct methods using the program MULTAN80 [14]. The structure was refined by full-matrix least-squares procedure, minimizing the quantity $\Sigma W(\Delta F)^2$ with $W = 1/\sigma^2$ (F_0). Owing to the small number of observed reflections, anisotropic temperature factors were used only for the I atoms. The H atoms were generated at their expected positions and included, but not refined, in the last refinement cycles with the thermal parameters of the carrier atoms. The absolute configuration was determined on the basis of the Hamilton's test [15] on the conventional and weighted R and R_w indices for the two enantiomorphous structures. Atomic scattering factors and anomalous dispersion corrections were taken from International Tables for X-ray Crystallography [16]. Lists of final atomic coordinates, structure factors, anisotropic thermal parameters and H-atom parameters have been deposited at the Cambridge Crystallographic Centre.

Table 3. Summary of crystal data of compound **1**

Crystal dimensions, mm	0.14 × 0.19 × 0.56
Formula	$C_{51}H_{59}O_8I_3$
Formula weight	1180.7
Space group	$P2_12_12_1$
a, Å	7.923(2)
b, Å	24.768(6)
c, Å	26.771(60)
V, Å^3	5253(1)
Z	4
D_x, g/cm^3	1.49
λ Cu Kα, Å	1.5418
θ_{max} (°)	60
Absorption coefficient (μ), cm^{-1}	145.5
No. indep. refl.	4396
No. refl. above 3σ (I)	1923
No. variables	264
R	0.084
R_W	0.094
R$^-$(inverted struc.)	0.106
R^-_W (inverted struc.)	0.121

Acknowledgements—This work was supported by the Ministero della Pubblica Istruzione (Italy) and by C.N.R. The mass spectral data were provided by the Servizio di Spettrometria di Massa del C.N.R. e dell'Universita' di Napoli. Throughout the crystallographic work the facilities of the Centro di Metodologie Chimico-fisiche dell'Universita' di Napoli were used; assistance of the staff is gratefully acknowledged. Thanks are also due to Miss Rita Carolla for the skilful technical assistance.

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