Table 6. *Selected cis-torsion angles* (°) *for the cyclooctadiene rings in three compounds compared to the theoretical values*

Bond	(1)*	(2)*	SP†	TBC‡	TB‡
C(4)—C(5)	−96·2	64·1	69·0	−94	5
C(5)—C(6)	90·8	−130·1	−125·3	85	−82
C(6)—C(7)	−52·7	34·9	29·7	−59	59
C(7)—C(8)	84·3	72·8	77·4	85	52
C(8)—C(9)	−103·0	−89·1	−89·4	−94	−92
C(9)—C(15)	10·3	−12·5	−20·1	6	2
C(15)—C(16)	54·9	28·3	42·5	54	42
C(16)—C(4)	−2·4	−7·2	−18·6	6	4

* E.s.d.'s ~ 0·2°.

† Values from Spencer & Flippen-Anderson (1981).

‡ Theoretical values for the twist-boat–chair, TBC, and twist-boat, TB, from Anet & Yavari (1978).

The dioxole rings are very close to the ideal cyclopentene envelope conformation given by Bucourt (1974). The slight distortions are probably related to the shorter C—O distances compared to C—C and a resultant flattening of the ring.

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Structure of Limonin

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Abstract. Limonoic acid 3,19:16,17-dilactone, $C_{26}H_{30}O_8$, $M_r = 470{\cdot}52$, orthorhombic, $P2_12_12_1$, $a = 17{\cdot}715\ (9)$, $b = 14{\cdot}520\ (8)$, $c = 8{\cdot}869\ (2)$ Å, $V = 2281\ (2)$ Å^3, $Z = 4$, $D_x = 1{\cdot}37$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 0{\cdot}109$ mm^{-1}, $F(000) = 1000$, $T = 290$ K, $R = 0{\cdot}065$ for 1929 observed reflections. The molecular structure of limonin, the bitter principle of citrus fruits, was determined by X-ray diffraction methods. The structure was essentially the same as epilimonol iodoacetate, the heavy-atom derivative of limonin. A structure energy calculation (*MMP*2) for limonin yields the same structure as that of the X-ray analysis.

Introduction. Limonin, the bitter principle of citrus fruits, has been focused upon for the biosynthesis of limonoid in citrus fruits (Hasegawa, Herman, Orme & Ou, 1986), the removal of bitterness from grapefruit (Show & Buslig, 1986), antifeedant activity against insects (Alford, Cullen, Storch & Bentley, 1987; Hassanali, Bentley, Ole Sitayo, Njoroge & Yatagai, 1986; Nakatani, Takao, Iwashita, Naoki & Hase, 1987, 1988), and inhibition of insect ecdysis (Kubo & Klocke, 1986).

After extensive chemical investigations (Arigoni *et al.*, 1960; Barton, Pradhan, Sternhell & Templeton, 1961), Arnott, Davie, Robertson, Sim & Watson (1961) determined the three-dimensional molecular structure of the heavy-atom derivative of limonin, epilimonol iodoacetate, by X-ray crystal analysis.

Since 1982 we have attempted the isolation of limonoids from *Evodia glauca* Miq. (Nakatani *et al.*, 1987, 1988) and produced a well shaped single crystal which was used for the X-ray analysis. An essentially identical structure to epilimonol iodoacetate was obtained. H atoms were found at all the

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Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* ($\times 10^3$) *with e.s.d.'s in parentheses*

$U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$.

	x	y	z	U_{eq}(Å^2)
O(1)	6176 (2)	5860 (2)	−6026 (3)	46 (1)
O(2)	7030 (2)	3706 (2)	−6310 (4)	81 (1)
O(3)	6983 (1)	4471 (2)	−4210 (3)	49 (1)
O(4)	5364 (2)	7561 (2)	−471 (3)	61 (1)
O(5)	4729 (2)	5269 (2)	1459 (3)	47 (1)
O(6)	3939 (2)	7141 (2)	3340 (3)	72 (1)
O(7)	3301 (2)	6318 (2)	1721 (3)	50 (1)
O(8)	1362 (2)	5805 (3)	−733 (4)	122 (2)
C(1)	5667 (2)	5298 (3)	−5165 (4)	39 (1)
C(2)	5838 (2)	4307 (2)	−5617 (4)	39 (1)
C(3)	6639 (3)	4119 (3)	−5466 (5)	49 (2)
C(4)	6468 (2)	6629 (3)	−5131 (4)	46 (2)
C(5)	6036 (2)	6536 (3)	−3703 (4)	35 (1)
C(6)	6267 (3)	7033 (2)	−2271 (4)	42 (1)
C(7)	5639 (3)	6912 (3)	−1113 (4)	39 (1)
C(8)	5410 (2)	5907 (2)	−821 (4)	36 (1)
C(9)	5222 (2)	5464 (2)	−2371 (4)	32 (1)
C(10)	5884 (2)	5513 (2)	−3498 (4)	36 (1)
C(11)	4763 (2)	4584 (3)	−2122 (4)	40 (1)
C(12)	3948 (2)	4863 (2)	−1633 (4)	37 (1)
C(13)	3909 (2)	5752 (2)	−639 (4)	37 (1)
C(14)	4671 (2)	5851 (3)	151 (4)	37 (1)
C(15)	4663 (2)	6240 (3)	1691 (5)	45 (1)
C(16)	3962 (2)	6604 (3)	2329 (4)	44 (2)
C(17)	3327 (2)	5579 (3)	620 (4)	47 (2)
C(18)	3708 (2)	6625 (3)	−1518 (4)	46 (2)
C(19)	6524 (2)	4862 (3)	−3026 (4)	43 (2)
C(20)	2518 (2)	5503 (3)	66 (4)	43 (1)
C(21)	2024 (3)	6226 (3)	−294 (5)	56 (2)
C(22)	2131 (2)	4714 (3)	−209 (5)	50 (2)
C(23)	1427 (2)	4897 (2)	−680 (4)	26 (1)
C(28)	6235 (3)	7504 (3)	−6011 (5)	63 (2)
C(29)	7294 (3)	6614 (3)	−5044 (5)	60 (2)
C(30)	6042 (2)	5431 (3)	49 (4)	49 (2)

expected positions. No abnormal bond lengths or bond angles were found throughout the whole molecule.

All structural parameters were almost the same as those found in epilimonol iodoacetate.

Structure energy analysis of limonin was also performed using the *MMP2* program (Allinger & Yuh, 1980) and the same structure as that in the crystal was obtained.

Experimental. A colorless needle-shaped crystal, 0·7 × 0·4 × 0·4 mm, Rigaku AFC-6 diffractometer, graphite-monochromated Mo $K\alpha$ ($\lambda = 0{\cdot}7107$ Å) at $T = 290$ K, the same cell constants as Arnott & Robertson (1959). Cell parameters by least squares on setting angles for 20 reflections, $8° < 2\theta < 30°$, 2336 unique reflections, of which 1929 were treated as observed in the refinement based on $I > 3\sigma(I)$, $2\theta_{max} = 60°$ ($0 < h < 21$, $0 < k < 17$, $0 < l < 10$), $\omega/2\theta$ scan mode, scan speed 4° min^{-1}, scan width (1·257 + 0·5tan θ)°, background measured for 5 s on each side of the peaks, three standard reflections monitored every 100 reflections, no significant variation in intensity, no absorption correction, structure solved by *MULTAN*87 (Debaerdemaeker, Germain, Main, Tate & Woolfson, 1987) on an INMOS T800 processor. In the final cycles of block-matrix least-squares refinement all non-hydrogen atoms anisotropic, all H atoms found by difference synthesis and refined isotropically, 398 parameters refined, $\sum w\Delta F^2$ minimized with $w = \sigma(F_o)^{-2}$. $R = 0{\cdot}065$, $wR = 0{\cdot}069$, $S = 1{\cdot}277$, $(\Delta/\sigma)_{max} = 0{\cdot}1$, $\Delta\rho_{max} = 0{\cdot}16$, $\Delta\rho_{min} = -0{\cdot}18$ e Å^{-3}, scattering factors from *International Tables for X-ray Crystallography* (1974).

No abnormally large thermal factors were found apart from the slightly larger U_{eq} values for the outer atoms of the molecule compared with the inner atoms.

Table 2. *Bond lengths* (Å) *and angles* (°) *of limonin*

O(1)—C(1)	1·436 (6)	O(1)—C(4)	1·464 (6)
O(2)—C(3)	1·183 (6)	O(3)—C(3)	1·369 (6)
O(3)—C(19)	1·444 (5)	O(4)—C(7)	1·204 (6)
O(5)—C(14)	1·439 (6)	O(5)—C(15)	1·430 (6)
O(6)—C(16)	1·189 (6)	O(7)—C(16)	1·354 (6)
O(7)—C(17)	1·452 (6)	O(8)—C(21)	1·379 (7)
O(8)—C(23)	1·324 (6)	C(1)—C(2)	1·524 (6)
C(1)—C(10)	1·559 (6)	C(2)—C(3)	1·451 (6)
C(4)—C(5)	1·486 (6)	C(4)—C(28)	1·547 (7)
C(4)—C(29)	1·465 (7)	C(5)—C(6)	1·517 (7)
C(5)—C(10)	1·521 (6)	C(6)—C(7)	1·524 (8)
C(7)—C(8)	1·537 (6)	C(8)—C(9)	1·554 (5)
C(8)—C(14)	1·570 (6)	C(8)—C(30)	1·526 (6)
C(9)—C(10)	1·543 (5)	C(9)—C(11)	1·531 (6)
C(10)—C(19)	1·534 (6)	C(11)—C(12)	1·561 (6)
C(12)—C(13)	1·565 (5)	C(13)—C(14)	1·528 (6)
C(13)—C(17)	1·541 (6)	C(13)—C(18)	1·530 (6)
C(14)—C(15)	1·478 (6)	C(15)—C(16)	1·463 (6)
C(17)—C(20)	1·519 (6)	C(20)—C(21)	1·404 (7)
C(20)—C(22)	1·357 (6)	C(22)—C(23)	1·342 (6)
C(1)—O(1)—C(4)	111·5 (3)	C(3)—O(3)—C(19)	119·2 (3)
C(14)—O(5)—C(15)	62·0 (3)	C(16)—O(7)—C(17)	117·8 (4)
C(21)—O(8)—C(23)	110·9 (4)	O(1)—C(1)—C(2)	105·8 (3)
O(1)—C(1)—C(10)	103·6 (3)	C(2)—C(1)—C(10)	112·9 (3)
C(1)—C(2)—C(3)	110·3 (3)	O(2)—C(3)—O(3)	116·3 (5)
O(2)—C(3)—C(2)	127·5 (5)	O(3)—C(3)—C(2)	116·1 (4)
O(1)—C(4)—C(5)	102·2 (3)	O(1)—C(4)—C(28)	105·0 (4)
O(1)—C(4)—C(29)	111·7 (4)	C(5)—C(4)—C(28)	111·5 (4)
C(5)—C(4)—C(29)	117·9 (4)	C(28)—C(4)—C(29)	107·8 (4)
C(4)—C(5)—C(6)	122·1 (4)	C(4)—C(5)—C(10)	106·4 (3)
C(6)—C(5)—C(10)	114·4 (4)	C(5)—C(6)—C(7)	108·2 (4)
O(4)—C(7)—C(6)	121·6 (5)	O(4)—C(7)—C(8)	123·8 (5)
C(6)—C(7)—C(8)	114·6 (4)	C(7)—C(8)—C(9)	107·5 (3)
C(7)—C(8)—C(14)	111·2 (3)	C(7)—C(8)—C(30)	108·8 (3)
C(9)—C(8)—C(14)	106·6 (3)	C(9)—C(8)—C(30)	114·7 (3)
C(14)—C(8)—C(30)	108·1 (3)	C(8)—C(9)—C(10)	113·0 (3)
C(8)—C(9)—C(11)	109·4 (3)	C(10)—C(9)—C(11)	122·4 (3)
C(1)—C(10)—C(5)	97·2 (3)	C(1)—C(10)—C(9)	114·7 (3)
C(1)—C(10)—C(19)	108·5 (3)	C(5)—C(10)—C(9)	104·9 (3)
C(5)—C(10)—C(19)	120·2 (3)	C(9)—C(10)—C(19)	110·9 (3)
C(9)—C(11)—C(12)	108·3 (3)	C(11)—C(12)—C(13)	114·3 (3)
C(12)—C(13)—C(14)	107·3 (3)	C(12)—C(13)—C(17)	107·7 (3)
C(12)—C(13)—C(18)	114·0 (3)	C(14)—C(13)—C(17)	105·9 (3)
C(14)—C(13)—C(18)	111·2 (3)	C(17)—C(13)—C(18)	110·4 (3)
O(5)—C(14)—C(8)	114·5 (3)	O(5)—C(14)—C(13)	112·2 (3)
O(5)—C(14)—C(15)	58·7 (3)	C(8)—C(14)—C(13)	119·3 (3)
C(8)—C(14)—C(15)	119·7 (4)	C(13)—C(14)—C(15)	116·9 (4)
O(5)—C(15)—C(14)	59·3 (3)	O(5)—C(15)—C(16)	118·8 (4)
C(14)—C(15)—C(16)	120·2 (4)	O(6)—C(16)—O(7)	118·1 (4)
O(6)—C(16)—C(15)	123·9 (4)	O(7)—C(16)—C(15)	118·0 (4)
O(7)—C(17)—C(13)	112·9 (3)	O(7)—C(17)—C(20)	104·0 (3)
C(13)—C(17)—C(20)	114·1 (3)	O(3)—C(19)—C(10)	117·4 (3)
C(17)—C(20)—C(21)	127·4 (4)	C(17)—C(20)—C(22)	126·6 (4)
C(21)—C(20)—C(22)	106·0 (4)	O(8)—C(21)—C(20)	105·3 (4)
C(20)—C(22)—C(23)	111·0 (4)	O(8)—C(23)—C(22)	106·8 (4)

The coordinates and equivalent isotropic thermal parameters are given in Table 1. Bond lengths and bond angles are shown in Table 2.* An *ORTEP*II (Johnson, 1976) drawing of limonin is given in Fig. 1.

The structure energy of limonin was calculated by the *MMP*2 (Allinger & Yuh, 1980) program to give the energy-minimized conformation in an isolated molecule. Using the crystal structure as the starting conformation, *MMP*2 energy minimization gave an almost identical molecular structure to that in the crystal (Fig. 2).

* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates, bond lengths, bond angles and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52347 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

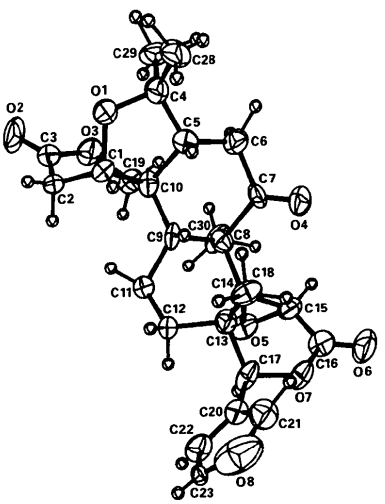

Fig. 1. *ORTEP* drawing of limonin with thermal ellipsoids at the 30% probability level. H atoms are shown as spheres of arbitrary radius.

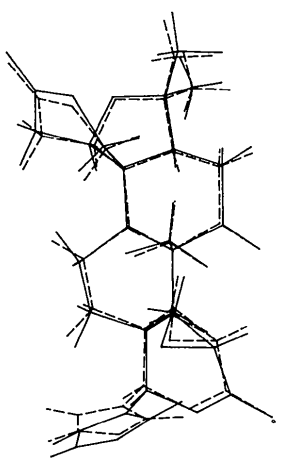

Fig. 2. Superimposed view of limonin molecules determined by X-ray analysis (solid line) and by energy minimization (broken line).

Discussion. Bond lengths, bond angles and torsion angles were compared between Arnott's and the present data. The epoxy ring [O(5)—C(14), O(5)—C(15) and C(14)—C(15)] of limonin is somewhat smaller. The bond lengths of the two carbonyls of limonin, O(2)—C(3) 1·18 and O(6)—C(16) 1·19 Å, are slightly shorter than that of epilimonol iodoacetate (1·27 and 1·29 Å, respectively). Slight differences of bond lengths around C(9) were found between the two molecules. The torsion angle around the single bond which connects the furan ring to the rest of the molecule also differs slightly between them.

The fact that an *MMP*2 energy-minimization calculation of limonin yields the same molecular structure in the crystal means that the structure in the crystal is in one of the local energy minima of an isolated molecule, and intermolecular interactions in the crystal do not produce conformational deformations in limonin. It is confirmed that a set of *MMP*2 parameters is able to reproduce the correct conformation of limonin.

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