o-methoxy group when compared with those of unsubstituted 10-phenylpyrido[3,2-*b*][1,4]benzothiazine (III). However, the largest differences observed are for the C atoms in the pyridine ring. This is supported by the conformation of the 10-(2-methoxyphenyl) substituent observed in the solid state. The *o*-methoxy group is tilted toward the pyrido ring as shown by the dihedral angles in Fig. 1 and the torsion angles about the N(10)—C(1′) bond in Fig. 3. Furthermore, all of the *ortho* ^{13}C—H couplings were too small to be observed in (III); however, the coupling constants in (I) have been observed and they are 3·10, 2·93, and 2·90 Hz, between C(8)—H(7), C(6)—H(7), and C(1)—H(2), respectively. These coupling changes indicate that there is an increase in the folding angle of the pyridobenzothiazine ring in (I) as compared to the unsubstituted 10-phenyl derivative (III). The crystal structure of (III) will be investigated to determine if the folding angle of (III) is smaller than that of (I) as predicted by NMR studies in solution.

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Thuriferin Monohydrate, $C_{21}H_{34}O_4.H_2O$

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Abstract. $M_r = 368\cdot52$, monoclinic, $P2_1$, $a = 7\cdot131\ (1)$, $b = 21\cdot310\ (3)$, $c = 7\cdot033\ (1)$ Å, $\beta = 110\cdot93\ (1)°$, $V = 998\cdot2\ (3)$ Å^3, $Z = 2$, $D_x = 1\cdot226$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·54178 Å, $\mu = 0\cdot697$ mm^{-1}, $F(000) = 404$, room temperature, $R = 0\cdot046$ for 1257 unique reflections with $I \geq 2\sigma(I)$. Thuriferin is a kaurane-type diterpene isolated from *Robinsonia thurifera* (Mol.) D.C. (tribe Senecioneae of family Compositae). It contains three six-membered rings in chair conformations, a five-membered ring in an envelope conformation, and an unusual methyl hemiacetal functionality.

Introduction. The concept of the tribe Senecioneae (Bentham, 1873) was generally accepted and remained basically unchanged for almost a century. During recent years there has been some disagreement concerning the number of subtribes, and a number of genera have even been shifted from tribes such as Helenieae into an expanded concept of Senecioneae (Nordenstam, 1977). Others have narrowed the concept and have excluded anomalous genera and even the entire subtribe Liabinae (Turner & Powell, 1977). In an attempt to provide chemical data for use as additional taxonomic markers, we have investigated *Robinsonia thurifera*. The genus *Robinsonia* contains approximately six species of rosette trees or epiphytic plants on tree ferns.

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Three species are found primarily on Juan Fernandez islands and in Chile (Nordenstam, 1977).

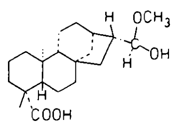
Experimental. Extracts of *Robinsonia thurifera* (collected on Masatierra, Juan Fernandez islands, February, 1980) yielded after SiO_2 column chromatography a transparent crystalline solid, m.p. 364–366 K. The compound exhibited a UV(EtOH)$_{max}$ 215 nm (ε,2700) and IR(Nujol)$_{max}$ at 2940, 2860, 1715, 1695, and 1660 cm^{-1}. The compound is difficult to crystallize, and a cluster of crystallites from the slow evaporation of a methanol:H_2O solvent mixture was cleaved to yield a fragment of dimensions 0·24 × 0·26 × 0·27 mm. Unit-cell dimensions obtained by least-squares refinement of angular data from 15 reflections; space group determined by systematic absences, $k = 2n+1$ for $0k0$. θ:2θ scan technique ($8{\cdot}3° \leq 2\theta \leq 114{\cdot}6°$), Syntex $P2_1$ diffractometer, variable scan rate, graphite-monochromated radiation. 1398 independent reflections ($0 \leq h \leq 7$, $0 \leq k \leq 21$, $-7 \leq l \leq 7$) collected (equivalent reflections were averaged), 1257 with intensities greater than $2\sigma(I)$. Check reflection showed no significant change in intensity. Lorentz–polarization corrections applied, no absorption correction. Direct methods (*MULTAN*78: Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) revealed positions of all 26 heavy atoms; 24 H atoms located in a difference Fourier map, the remaining H-atom positions calculated. Full-matrix least-squares refinement with heavy-atom thermal parameters anisotropic, H-atom positional parameters constrained (1·08 Å), and H-atom thermal parameters isotropic [except for H(O12)] yielded $R = 0{\cdot}046$, $R_w = 0{\cdot}051$ and $S = 2{\cdot}22$ for 269 parameters. $\sum w(|F_o| - |F_c|)^2$ minimized, where $w = 1/\sigma^2(F_o)$. $(\Delta/\sigma)_{max} = 0{\cdot}51$, $(\Delta/\sigma)_{avg} = 0{\cdot}13$. Largest peak in final difference Fourier map 0·12 e Å^{-3}. Calculations performed with *XRAY*76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). Atomic scattering factors for C and O from Cromer & Mann (1968), those for H from Stewart, Davidson & Simpson (1965).

Discussion. Table 1 lists the atomic positional parameters and U_{eq} values for the heavy atoms.* Fig. 1 is an *ORTEP*II drawing (Johnson, 1971) of thuriferin (1). Table 2 gives bond distances, valence angles and torsion angles. The compound is a kaurane-type diterpene which contains a methyl hemiacetal functionality at C(17). Since the hemiacetal might be unstable relative to the aldehyde form, the exact nature of the naturally occurring material has not been demonstrated conclusively. The same functionality, but of opposite chirality at C(16) and C(17), is found in the diterpene phlebianorkauranol (2) isolated from the mycelium of the fungus *Phlebia strigosozonata* (Basidiomycete) (Lisy, Clardy, Anchel & Weinraub, 1975). Structural features of these molecules may protect the hemiacetal from hydrolysis during workup. Phlebianorkauranol contains additional O functionalities and exhibits antibacterial activity.

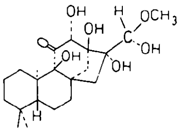
Table 1. *Atomic positional coordinates* (×10^4) *and* U_{eq} *values* (Å^2 ×10^3)

$$U_{eq} = \tfrac{1}{3}|U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{13}aca^*c^*\cos\beta + 2U_{23}bcb^*c^*\cos\alpha + 2U_{12}aba^*b^*\cos\gamma|.$$

	x	y	z	U_{eq}
C(1)	−3058 (7)	8432 (3)	−2622 (7)	57 (3)
C(2)	−3785 (7)	9065 (3)	−3626 (7)	58 (3)
C(3)	−2148 (8)	9403 (3)	−4153 (7)	62 (3)
C(4)	−208 (7)	9495 (3)	−2327 (7)	52 (2)
C(5)	491 (7)	8844 (3)	−1302 (6)	48 (2)
C(6)	2559 (6)	8830 (3)	442 (7)	54 (3)
C(7)	3270 (6)	8155 (3)	869 (7)	55 (3)
C(8)	1841 (6)	7734 (2)	1500 (6)	44 (2)
C(9)	−315 (6)	7804 (2)	−56 (7)	44 (2)
C(10)	−1107 (6)	8482 (2)	−699 (6)	42 (2)
C(11)	−1762 (6)	7362 (3)	566 (7)	55 (2)
C(12)	−1347 (7)	7320 (3)	2844 (7)	58 (3)
C(13)	887 (7)	7265 (3)	4094 (7)	50 (2)
C(14)	1933 (7)	7849 (2)	3696 (6)	49 (2)
C(15)	2532 (7)	7042 (3)	1664 (7)	53 (3)
C(16)	1879 (6)	6725 (2)	3321 (7)	48 (2)
C(17)	3637 (7)	6447 (3)	5024 (7)	55 (3)
C(18)	1405 (8)	9770 (3)	−3087 (8)	73 (3)
C(19)	−487 (7)	10001 (3)	−919 (7)	53 (2)
C(20)	−1667 (6)	8830 (3)	954 (6)	47 (2)
C(21)	4304 (8)	5876 (3)	8134 (8)	74 (3)
O(22)	4823 (4)	6038 (2)	4317 (5)	60 (2)
O(23)	2817 (4)	6112 (2)	6294 (5)	62 (2)
O(24)	1068 (5)	10094 (2)	739 (5)	69 (2)
O(25)	−2019 (5)	10317 (2)	−1304 (5)	62 (2)
O(w)	9013 (5)	6054	6897 (5)	65 (2)



(1)



(2)

The *A* and *B* rings of thuriferin are in regular chair conformations while ring *C* [C(8)C(9)C(11)C(12)-C(13)C(14)] is slightly distorted due to the fusion of the five-membered ring (a 1–3 ethylene bridge). The five-membered ring is in an envelope conformation with C(14) being the flap. The bond lengths and valence angles of the diterpene system are normal.

In the methyl hemiacetal functionality C(17)—O(22) = 1·422 (7), C(17)—O(23) = 1·422 (7) and O(23)—CH_3 = 1·439 (6) Å. The water molecule is involved in hydrogen bonding: O(w)···O(22) = 2·889 (4), O(w)—H(wb) = 1·08, H(wb)···O(22) = 1·87 Å, O(w)—H(wb)···O(22) = 155·7°; O(w)(x−1,y,z)···O(23) =

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* Lists of H-atom coordinates, anisotropic thermal parameters, additional valence angles and torsion angles, and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39541 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

2·894 (5), O(*w*)–H(*wa*) = 1·08, H(*wa*)···O(23) = 1·88 Å, O(*w*)–H(*wa*)···O(23) = 155·5°. There are additional close intermolecular contacts H(O22)···O(*w*) = 2·63 and H(O22)···H(*wb*) = 1·57 Å.

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Table 2. *Interatomic distances* (Å), *selected valence angles* (°) *and selected torsion angles* (°)

C(1)–C(2)	1·525 (8)	C(9)–C(10)	1·558 (6)
C(1)–C(10)	1·559 (5)	C(9)–C(11)	1·570 (7)
C(2)–C(3)	1·526 (9)	C(10)–C(20)	1·547 (7)
C(3)–C(4)	1·527 (6)	C(11)–C(12)	1·524 (7)
C(4)–C(5)	1·561 (8)	C(12)–C(13)	1·524 (6)
C(4)–C(18)	1·546 (9)	C(13)–C(14)	1·527 (8)
C(4)–C(19)	1·524 (8)	C(13)–C(16)	1·548 (8)
C(5)–C(6)	1·545 (5)	C(15)–C(16)	1·555 (5)
C(5)–C(10)	1·555 (7)	C(16)–C(17)	1·511 (6)
C(6)–C(7)	1·519 (9)	C(17)–O(22)	1·422 (7)
C(7)–C(8)	1·537 (7)	C(17)–O(23)	1·422 (7)
C(8)–C(9)	1·543 (5)	C(19)–O(24)	1·306 (5)
C(8)–C(14)	1·542 (6)	C(19)–O(25)	1·228 (7)
C(8)–C(15)	1·546 (8)	C(21)–O(23)	1·439 (6)
C(2)C(1)C(10)	113·1 (4)	C(14)C(8)C(15)	100·3 (3)
C(1)C(2)C(3)	111·5 (4)	C(8)C(9)C(10)	117·5 (3)
C(2)C(3)C(4)	113·5 (4)	C(8)C(9)C(11)	109·4 (3)
C(3)C(4)C(5)	108·6 (5)	C(1)C(10)C(5)	108·1 (4)
C(4)C(5)C(6)	116·1 (5)	C(5)C(10)C(9)	108·3 (4)
C(4)C(5)C(10)	115·0 (4)	C(9)C(11)C(12)	115·3 (4)
C(6)C(5)C(10)	111·0 (4)	C(11)C(12)C(13)	112·4 (4)
C(5)C(6)C(7)	109·4 (4)	C(12)C(13)C(14)	108·0 (4)
C(6)C(7)C(8)	113·6 (4)	C(14)C(13)C(16)	103·1 (4)
C(7)C(8)C(9)	109·5 (5)	C(8)C(14)C(13)	101·8 (3)
C(7)C(8)C(14)	113·6 (4)	C(8)C(15)C(16)	107·3 (4)
C(7)C(8)C(15)	110·6 (4)	C(13)C(16)C(15)	103·7 (4)
C(9)C(8)C(14)	111·7 (4)		
C(1)C(2)C(3)C(4)	−55·9 (6)	C(8)C(9)C(11)C(12)	38·9 (6)
C(2)C(3)C(4)C(5)	53·9 (6)	C(9)C(11)C(12)C(13)	−42·9 (7)
C(3)C(4)C(5)C(10)	−54·4 (6)	C(11)C(12)C(13)C(14)	60·4 (6)
C(4)C(5)C(10)C(1)	53·7 (5)	C(12)C(13)C(14)C(8)	−71·8 (5)
C(5)C(10)C(1)C(2)	−53·0 (6)	C(13)C(14)C(8)C(9)	71·0 (4)
C(10)C(1)C(2)C(3)	55·2 (6)	C(14)C(8)C(9)C(11)	−54·5 (5)
C(5)C(6)C(7)C(8)	−59·7 (5)	C(8)C(15)C(16)C(13)	−1·8 (4)
C(6)C(7)C(8)C(9)	51·0 (5)	C(15)C(16)C(13)C(14)	−27·2 (4)
C(7)C(8)C(9)C(10)	−47·0 (6)	C(16)C(13)C(14)C(8)	46·6 (4)
C(8)C(9)C(10)C(5)	49·7 (5)	C(13)C(14)C(8)C(15)	−46·4 (4)
C(9)C(10)C(5)C(6)	−55·3 (5)	C(14)C(8)C(15)C(16)	29·5 (4)
C(10)C(5)C(6)C(7)	61·7 (6)	O(22)C(17)O(23)C(21)	64·0 (5)

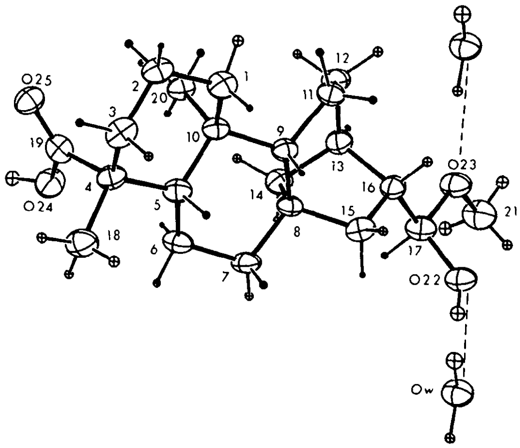

Fig. 1. *ORTEP*II drawing of thuriferin. Thermal ellipsoids are drawn at the 35% probability level.

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