The use of the EPSRC X-ray Crystallographic Service at the University of Wales, Cardiff, and the assistance of Neil S. Stewart of the Cambridge Crystallographic Data Centre are gratefully acknowledged.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BM1103). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 31–37.

Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435–436.

Ansell, G. B. (1972). *J. Chem. Soc. Perkin Trans.* 2, pp. 841–843.

Darr, J. A., Drake, S. R., Hursthouse, M. B. & Malik, K. M. A. (1993). *Inorg. Chem.* **32**, 5704–5708.

Delage, C., Faure, F., Leger, J.-M., Raby, C. & Goursolle, M. (1990). *C. R. Acad. Sci. Ser.* 2, **311**, 781–784.

Karaulov, A. I. (1992). *ABSMAD. Program for FAST Data Processing*. University of Wales, Cardiff, Wales.

Karkhanis, D. W. & Field, L. (1985). *Phosphorus Sulfur*, **22**, 49–57.

Pflugrath, J. W. & Messerschmidt, A. (1989). *MADNES*. Version of 11 September, 1989. Distributed by Delft Instruments, Delft, The Netherlands.

Raper, E. S., Creighton, J. R., Oughtred, R. E. & Nowell, I. W. (1983). *Acta Cryst.* B**39**, 355–360.

Raper, E. S., Jackson, A. R. W. & Gardiner, D. J. (1984). *Inorg. Chim. Acta*, **84**, L1–L4.

Reynolds, J. E. F. (1993). *Martindale, The Extra Pharmacopoeia*, p. 531. London: The Pharmaceutical Press.

Schönerr, H.-J. & Wanzlick, H.-W. (1970). *Chem. Ber.* **103**, 1037–1046.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Sohal, B. (1996). Unpublished results.

Zsolnai, L. (1996). *ZORTEP. An Interactive ORTEP Program*. University of Heidelberg, Germany.

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2,2′:6′,2″-Terpyridinium Trifluoromethanesulfonate, [terpyH](CF_3SO_3)

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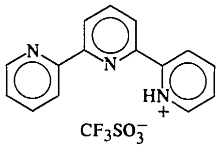
Abstract

In the title compound, $C_{15}H_{12}N_3^+.CF_3O_3S^-$, one terminal pyridine ring of the terpyridinium cation is protonated and forms an intramolecular N—H···N hydrogen bond of 2.646 (4) Å which stabilizes the *cis,trans* conformation in contrast to the *trans,trans* geometry of free terpyridine. An N—H···O hydrogen bond of 2.817 (5) Å connects the terpyridinium cations and the trifluoromethanesulfonate anions.

Comment

Terpyridine (terpy) is a well known tridentate ligand which forms numerous complexes with one, two or three terpyridines coordinated to the metal (Grdenić, Popović, Bruvo & Korpar-Čolig, 1991; Matković-Čalogović, Popović & Korpar-Čolig, 1995; Kepert, Patrick, Skelton & White, 1988). Only a few structures with terpy as a bidentate ligand have been published (for example, see Deacon, Patrick, Skelton, Thomas & White, 1984). The structure of free terpy was reported recently (Bessel, See, Jameson, Churchill & Takeuchi, 1992). A search of the Cambridge Structural Database (1996) (hereafter CSD) revealed no structure containing a free terpyridinium cation (terpyH). We report here the structure of terpyridinium trifluoromethanesulfonate, [terpyH](CF_3SO_3), (I).



(I)

The crystal structure consists of terpyridinium cations, since one terminal pyridine ring of terpy is protonated, and trifluoromethanesulfonate anions (Fig. 1). The numbering scheme of the terpyridinium cation is the same as that of free terpy. The H atom on the N11 atom is involved in a bifurcated hydrogen bond consisting of an intramolecular N11—H···N21 bond of 2.646 (4) Å [N—H 0.99, H···N 2.242 (3) Å and N—H···N 102.8 (2)°] and an intermolecular N11—H···O2 bond of 2.817 (5) Å [H···O 2.030 (3) Å and N—H···O 134.5 (2)°]. The pyridine rings in the terpy molecule are linked by C—C single bonds which enable rotation of the rings. Free terpy has a *trans,trans* configuration and upon coordination to a metal atom the rotation of the terminal pyridines results in the *cis,cis* geometry in the complexes. In terpyH, an intramolecular hydrogen bond stabilizes the *cis,trans* configuration. The deviation from coplanarity is small; the torsion angles N11—C12—C22—N21 and N21—C26—C32—N31 are 3.6 (5) and −172.9 (3)°, respectively (*cf.* 5.1 and 7.2° in the free terpy).

There are no significant differences in the bond lengths of the terpyH cation and free terpy. Some significant changes occur in the angles, the largest involving the protonated pyridinium ring, where an increase of the C12—N11—C16 angle and a decrease

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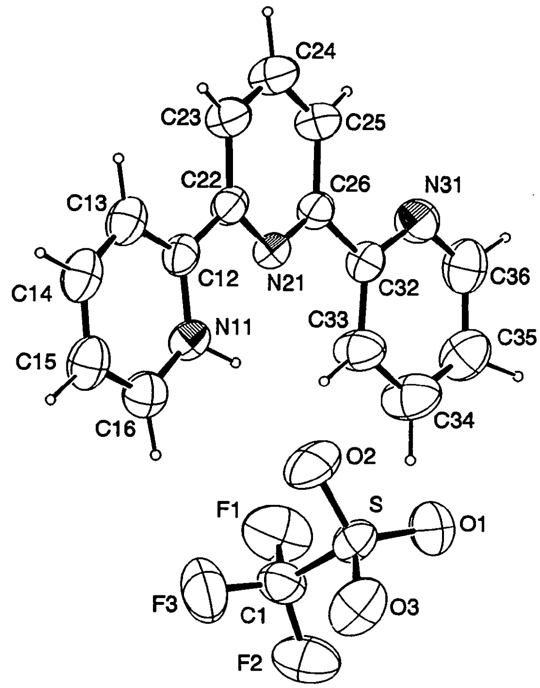

Fig. 1. An *ORTEP*II (Johnson, 1976) view of the ions of (I) with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

of the N11—C12—C13 angle is observed (by a mean value of 6.8 and 5.4°, respectively).

The CSD search for terpyH recorded only one hit, *i.e.* the structure of $[Ru(CO)_2(phen)(terpyH)](BF_4)_3.3H_2O$ (Thomas & Fischer, 1990). In this structure, the terpyridinium cation acts as a bidentate ligand since the protonated pyridine is not involved in coordination. To enable complexation, the terminal pyridine which is not protonated rotates into a *cis* position, while the protonated pyridine ring rotates to enable interaction with the carbonyl group. It does not form an intramolecular hydrogen bond to the N atom of the central pyridine moiety, which is involved in coordination. The resulting dihedral angles are quite different from those in the present structure; the dihedral angle of the protonated and central pyridine rings is 125.3°, while that involving the coordinated pyridine rings is −11.1°.

A structure containing the free diprotonated terpyH_2 cation has also been published recently, $(terpyH_2)_2[Tb(OH_2)_8]Cl_7.\frac{2}{3}H_2O$ (Kepert, Skelton & White, 1994). In this structure, the two independent terpyridinium cations have both terminal pyridine rings protonated, which then form two intramolecular hydrogen bonds that stabilize the molecules in the *cis,cis* conformation. Intermolecular hydrogen bonds with chlorine are also formed.

As a result of protonation, a significant increase in the C—N—C angle of the protonated pyridine ring is common in all of these structures. The decrease of the N(central)—C—C(terminal protonated pyridine) angle results from the intramolecular hydrogen bond.

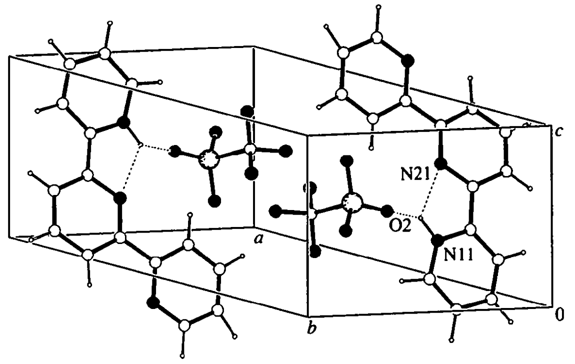

Fig. 2. The packing of the molecules in the unit cell. The N11—H···N21 and N11—H···O2 hydrogen bonds are shown by dashed lines.

Experimental

Trifluoromethanesulfonic acid reacts quantitatively with terpy to give a non-hygroscopic terpyridinium salt. This salt could be useful for identifying small amounts of the acid. An IR spectrum was recorded in the region 4000–450 cm^{-1} on a Perkin-Elmer 1600 FT spectrophotometer using a KBr disc. An accurate amount of trifluoromethanesulfonic acid (in a 1:1 stoichiometry) was added to an ethanolic solution of terpy. Transparent yellow needles of terpyridinium trifluoromethanesulfonate were obtained by slow evaporation of the solvent at room temperature. Analysis found: C 50.31, H 3.60%; calculated for $C_{16}H_{12}F_3N_3O_3S$: C 50.13, H 3.16%. IR max. (cm^{-1}): 3179 (*m*), 3100 (*m*), 1622 (*m*), 1607 (*s*), 1584 (*s*), 1563 (*m*), 1531 (*s*), 1458 (*m*), 1430 (*s*), 1298 (*s*), 1278 (*vs*), 1263 (*vs*), 1227 (*s*), 1217 (*s*), 1178 (*s*), 1162 (*vs*), 1144 (*vs*), 1094 (*m*), 1066 (*m*), 1032 (*vs*), 991 (*m*), 925 (*m*), 868 (*m*), 778 (*s*), 738 (*m*), 640 (*s*), 620 (*m*), 573 (*m*), 516 (*m*). Generally good correspondence between observed bands and those reported for $SO_3CF_3^-$ was found (Arduini, Garnett, Thompson & Wong, 1975; Dedert, Thompson, Ibers & Marks, 1982; Gramstad & Haszeldine, 1956).

Crystal data

$C_{15}H_{12}N_3^+.CF_3O_3S^-$
$M_r = 383.35$
Triclinic
$P\bar{1}$
$a = 12.155\,(2)$ Å
$b = 10.867\,(1)$ Å
$c = 6.415\,(1)$ Å
$\alpha = 77.50\,(1)°$
$\beta = 89.76\,(2)°$
$\gamma = 76.51\,(2)°$
$V = 803.5\,(2)$ Å^3
$Z = 2$
$D_x = 1.585$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 24 reflections
$\theta = 10.2$–$19.8°$
$\mu = 0.257$ mm^{-1}
$T = 293\,(2)$ K
Prism
0.33 × 0.17 × 0.15 mm
Colourless

Data collection

Philips PW1100 diffractometer updated by Stoe
$\theta/2\theta$ scans
Absorption correction: none
1915 measured reflections
1915 independent reflections
1885 observed reflections [$I > 2\sigma(I)$]
$\theta_{\max} = 29.97°$
$h = -16 \rightarrow 16$
$k = -14 \rightarrow 14$
$l = 0 \rightarrow 9$
3 standard reflections
  frequency: 120 min
  intensity decay: 5.9%

Refinement

Refinement on F
$R = 0.0448$
$wR = 0.0431$
$S = 0.646$
1885 reflections
227 parameters
H atoms refined using a common isotropic displacement parameter
Unit weights applied
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.252$ e Å^{-3}
$\Delta\rho_{\min} = -0.275$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
S	0.83587 (8)	0.38442 (9)	0.46732 (16)	0.0474 (3)
O1	0.8133 (3)	0.3899 (3)	0.2469 (4)	0.074 (1)
O2	0.8555 (3)	0.5015 (3)	0.5115 (5)	0.075 (1)
O3	0.9106 (2)	0.2665 (3)	0.5811 (5)	0.075 (1)
F1	0.6188 (2)	0.4745 (3)	0.4870 (5)	0.091 (1)
F2	0.6732 (2)	0.2676 (3)	0.5792 (5)	0.091 (1)
F3	0.7060 (3)	0.3852 (3)	0.7894 (4)	0.100 (2)
C1	0.7022 (4)	0.3774 (4)	0.5861 (6)	0.056 (2)
N11	0.8465 (3)	0.7195 (3)	0.6876 (5)	0.044 (1)
C12	0.8559 (3)	0.8428 (3)	0.6310 (6)	0.041 (1)
C13	0.9109 (3)	0.8892 (4)	0.7736 (6)	0.051 (1)
C14	0.9522 (3)	0.8096 (4)	0.9676 (7)	0.058 (2)
C15	0.9370 (3)	0.6852 (4)	1.0241 (6)	0.057 (2)
C16	0.8837 (3)	0.6409 (4)	0.8776 (6)	0.052 (2)
N21	0.7460 (2)	0.8564 (3)	0.3171 (4)	0.039 (1)
C22	0.8029 (3)	0.9184 (3)	0.4211 (6)	0.040 (1)
C23	0.8102 (4)	1.0460 (4)	0.3409 (7)	0.054 (2)
C24	0.7559 (4)	1.1102 (4)	0.1475 (7)	0.061 (2)
C25	0.6960 (4)	1.0483 (3)	0.0386 (6)	0.053 (2)
C26	0.6938 (3)	0.9199 (3)	0.1281 (6)	0.041 (1)
N31	0.5950 (3)	0.9057 (3)	−0.1858 (5)	0.052 (1)
C32	0.6361 (3)	0.8465 (3)	0.0125 (6)	0.042 (1)
C33	0.6291 (4)	0.7216 (4)	0.1059 (6)	0.060 (2)
C34	0.5798 (4)	0.6544 (4)	−0.0098 (8)	0.072 (2)
C35	0.5383 (4)	0.7130 (4)	−0.2145 (7)	0.066 (2)
C36	0.5465 (4)	0.8387 (4)	−0.2938 (6)	0.061 (2)

Table 2. *Geometric parameters (Å, °)*

S—O1	1.427 (3)	N21—C22	1.339 (5)
S—O2	1.433 (4)	N21—C26	1.337 (4)
S—O3	1.434 (3)	C26—C25	1.396 (5)
S—C1	1.803 (5)	C26—C32	1.483 (6)
F1—C1	1.327 (5)	C25—C24	1.381 (7)
F2—C1	1.330 (6)	C24—C23	1.371 (6)
F3—C1	1.327 (5)	C23—C22	1.394 (5)
N11—C12	1.342 (5)	N31—C36	1.334 (6)
N11—C16	1.339 (5)	N31—C32	1.335 (5)
C12—C13	1.378 (6)	C36—C35	1.377 (6)
C12—C22	1.478 (5)	C35—C34	1.370 (6)
C13—C14	1.373 (5)	C34—C33	1.373 (7)
C14—C15	1.377 (6)	C33—C32	1.382 (5)
C15—C16	1.372 (6)		
O3—S—C1	102.9 (2)	N11—C16—C15	119.6 (4)
O2—S—C1	102.3 (2)	C22—N21—C26	118.5 (3)
O2—S—O3	115.5 (2)	C12—C22—N21	115.2 (3)
O1—S—C1	103.8 (2)	N21—C22—C23	122.9 (4)
O1—S—O3	115.1 (2)	C12—C22—C23	121.9 (4)
O1—S—O2	114.7 (2)	C22—C23—C24	118.1 (4)
F2—C1—F3	107.6 (4)	C23—C24—C25	119.9 (4)
F1—C1—F3	107.0 (4)	C24—C25—C26	118.7 (4)
F1—C1—F2	107.2 (4)	N21—C26—C25	122.0 (4)
S—C1—F3	111.2 (4)	C25—C26—C32	120.9 (3)
S—C1—F2	111.8 (3)	N21—C26—C32	117.1 (3)
S—C1—F1	111.7 (3)	C32—N31—C36	117.1 (3)
C12—N11—C16	123.7 (4)	C26—C32—N31	116.7 (3)
N11—C12—C22	116.4 (3)	N31—C32—C33	122.5 (4)
N11—C12—C13	118.0 (3)	C26—C32—C33	120.8 (3)
C13—C12—C22	125.6 (3)	C32—C33—C34	119.1 (4)
C12—C13—C14	119.5 (4)	C33—C34—C35	119.2 (4)
C13—C14—C15	121.0 (4)	C34—C35—C36	117.9 (4)
C14—C15—C16	118.2 (4)	N31—C36—C35	124.1 (4)

A total of 2745 reflections with $I \leq 0$ were considered 'unobserved' and left out of the data set on which this analysis is based. All non-H atoms in the structure were found by direct methods. After anisotropic refinement, the difference electron-density synthesis revealed all of the H atoms, which were included in fixed positions. Final full-matrix least-squares refinement of the coordinates, anisotropic displacement parameters for non-H atoms and isotropic displacement parameters for H atoms, reduced R to 0.0448.

Data collection: *DIF*4 (Stoe & Cie, 1992*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1992*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1976) and *CRYSRULER* (Rizzoli, Sangermano, Calestani & Andreetti, 1987). Molecular graphics: *ORTEP*II (Johnson, 1976), *ORTEP*92 (Vicković, 1994) and *PLUTON* (Spek, 1993). Software used to prepare material for publication: *CSU* (Vicković, 1988).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SK1032). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Arduini, A. L., Garnett, M., Thompson, R. C. & Wong, T. C. T. (1975). *Can. J. Chem.* **53**, 3812–3819.

Bessel, C. A., See, R. F., Jameson, D. L., Churchill, M. R. & Takeuchi, K. J. (1992). *J. Chem. Soc. Dalton Trans.* pp. 3223–3228.

Cambridge Structural Database (1996). Version 5.11. Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, England.

Deacon, G. B., Patrick, J. M., Skelton, B. W., Thomas, N. C. & White, A. H. (1984). *Aust. J. Chem.* **37**, 929–945.

Dedert, P. L., Thompson, J. S., Ibers, J. A. & Marks, T. J. (1982). *Inorg. Chem.* **21**, 969–977.

Gramstad, T. & Haszeldine, R. N. (1956). *J. Chem. Soc.* pp. 173–180.

Grdenić, D., Popović, Z., Bruvo, M. & Korpar-Čolig, B. (1991). *Inorg. Chim. Acta*, **190**, 169–172.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Kepert, D. L., Patrick, J. M., Skelton, B. W. & White, A. H. (1988). *Aust. J. Chem.* **41**, 157–158.
Kepert, D. L., Skelton, B. W. & White, A. H. (1994). *Aust. J. Chem.* **47**, 391–396.
Matković-Čalogović, D., Popović, Z. & Korpar-Čolig, B. (1995). *J. Chem. Crystallogr.* **25**, 453–458.
Rizzoli, C., Sangermano, V., Calestani, G. & Andreetti, G. D. (1987). *J. Appl. Cryst.* **20**, 436–439.
Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination.* University of Cambridge, England.
Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures.* University of Göttingen, Germany.
Spek, A. L. (1993). *PLUTON93. Program for the Display and Analysis of Crystal and Molecular Structures.* University of Utrecht, The Netherlands.
Stoe & Cie (1992*a*). *DIF4. Diffractometer Control Program.* Version 7.09. Stoe & Cie, Darmstadt, Germany.
Stoe & Cie (1992*b*). *REDU4. Data Reduction Program.* Version 7.03. Stoe & Cie, Darmstadt, Germany.
Thomas, N. C. & Fischer, J. (1990). *J. Coord. Chem.* **21**, 119–128.
Vicković, I. (1988). *J. Appl. Cryst.* **21**, 987–990.
Vicković, I. (1994). *J. Appl. Cryst.* **27**, 437–437.

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An 18-Chloro-4α-hydroxy Derivative of 19-Acetylteupolin IV: a Neo-clerodane Diterpenoid of Biological Interest

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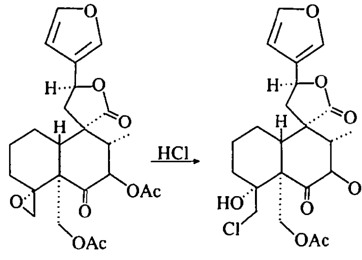
Abstract

The title compound, (12*S*)-7β,19-diacetoxy-18-chloro-15,16-epoxy-4α-hydroxy-6-oxo-neo-cleroda-13(16),14-dien-20,12-olide {systematic name: 4′a-(acetoxymethyl)-5′-(chloromethyl)-5-(3-furyl)-5′-hydroxy-2′-methyl-2,4′-dioxodecahydrospiro[furan-3(2*H*),1′(2′*H*)naphthalen]-3′-yl acetate; $C_{24}H_{29}ClO_9$}, is of interest on account of its biological activity as an insect antifeedant. The fused six-membered rings of the molecule have similar chair conformations. The crystal contains dimeric molecules which are formed *via* bifurcated (intra- and intermolecular) O—H···O hydrogen bonds.

Comment

A large number of diterpenoids with the clerodane skeleton have been isolated from plants in the past few years (Merritt & Ley, 1992). Interest in these compounds has been stimulated by their biological activity as antitumoural, antimicrobial and antifungal agents, and particularly as antifeedant agents against some economically important lepidopterous pests (Merritt & Ley, 1992; Simmonds & Blaney, 1992). The richest source of this kind of compound has been plants belonging to the genus *Teucrium* of the family Labiatae, from which about 170 clerodanes have been isolated (Merritt & Ley, 1992; Piozzi, 1994; Rodriguez *et al.*, 1994). Some years ago a new neo-clerodane (Rogers *et al.*, 1979), 19-acetylteupolin IV, (1), was isolated (De la Torre, Piozzi, Rizk, Rodriguez & Savona, 1986) and its structure and absolute configuration [(12*S*)-7β,19-diacetoxy-4α,18;15,16-diepoxy-6-oxo-neo-cleroda-13(16),14-dien-20,12-olide] were established by spectroscopic (^{1}H and ^{13}C NMR, CD) means and by comparison with closely related compounds. Compounds possessing 7β-acetoxy-6-oxo functional groups, however, are not usual among the natural neo-clerodanes (Merritt & Ley, 1992; Piozzi, 1994; Rodriguez-Hahn, Esquivel & Cardenas, 1994; Davies-Coleman, Hanson & Rivett, 1994) and in our opinion the structure attributed (De la Torre *et al.*, 1986) needed further support.



(1) (2)

Attempts at obtaining suitable crystals of (1) for X-ray diffraction analysis were unsuccessful. Treatment of the natural diterpenoid (1) with hydrochloric acid (Rodriguez *et al.*, 1994) gave the chlorohydrin (2) in almost quantitative yield.

Rings *A* and *B* (Fig. 1) have very similar chair conformations with the following Cremer & Pople (1975) parameters: q_2 = 0.035 (5), q_3 = 0.586 (5) Å, φ_2 = −116 (7) and θ_2 = 3.4 (5)° for ring *A*; q_2 = 0.021 (4), q_3 = 0.501 (4) Å, φ_2 = 178 (28) and θ_2 = 2.4 (5)° for ring *B*. The γ-lactone ring (*C*) has an envelope conformation, with the C11 atom deviating by −0.304 (4) Å from the plane defined by the other four atoms [maximum deviation of −0.029 (4) Å for atom C20]. Ring *D* is planar (all deviations are less than 0.004 Å). All interatomic distances and angles have normal values. The crystal packing involves an inter- and intramolecular bifurcated hydrogen bond through the H70 atom; O7···O5 2.946 (4) Å, O7—H70···O5 127.4 (3)°, O7···O5^{i} 3.030 (4) Å and O7—H70···O5^{i} 142.0 (3)° [symmetry code: (i) $1-x, y, 1-z$]. This links pairs of molecules through a twofold axis (Fig. 1).

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