1,3-oxazin-6-one nucleus to be present in the crystallographic literature. Particularly interesting is 2-(*m*-bromophenyl)-4-acetoxy-6*H*-1,3-oxazin-6-one (Ammon, Gordon & Ehrenkaufer, 1973). This molecule has the double bonds of the heterocycle ring much more localized than in the compounds which are studied here; in fact, the N(2)—C(3) and C(4)—C(5) bonds are 1·292 (5) and 1·331 (6) Å, respectively.

I wish to thank Professor A. Marchesini for providing crystals and for suggesting the investigation.

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# Structure of (−)-(6′*R*)-3′,6′-Epoxyaurapten

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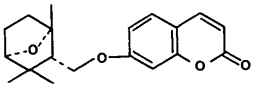
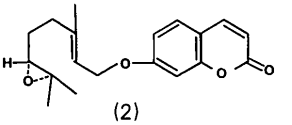
**Abstract.** 7-[(1,3,3-Trimethyl-7-oxabicyclo[2.2.1]heptan-2-yl)methoxy]-2*H*-1-benzopyran-2-one, $C_{19}H_{22}O_4$, $M_r = 314{\cdot}41$, orthorhombic, $P2_12_12_1$, $a = 7{\cdot}295$ (3), $b = 14{\cdot}926$ (8), $c = 15{\cdot}160$ (6) Å, $V = 1651$ (2) Å$^3$, $Z = 4$, $D_x = 1{\cdot}26$ Mg m$^{-3}$, Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, $\mu = 0{\cdot}04$ mm$^{-1}$, $F(000) = 608$, room temperature. Final $R = 0{\cdot}046$ for 1625 unique observed reflections, crystal growth from a solution by slow evaporation. The title compound was synthesized with the natural (−) absolute stereochemistry. The cohesion of this structure is due to van der Waals interactions. The characteristics of the lactone ring are consistent with an essentially aliphatic heterocyclic ring. The *syn* relationship between O2 and C9 postulated by other authors in this series is demonstrated unequivocally.

**Introduction.** In vegetable life, there are plants in which can be found compounds whose structure seems to stem from the joining of a coumarin and a terpenic heterocyclized chain, corresponding to a 2-alkyl-1,3,3-trimethylbicyclo[2.2.1]heptane, a structure which is rarely found.

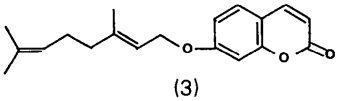
(−)-3′,6′-Epoxyaurapten (1) is the simplest representative, found in different species of Asters (Compositae) with (+)-epoxide (2) and the aurapten (3) (Bohlmann, Zdero & Kapteyn, 1968).



(1)



(2)



(3)

After studying various research reports on triterpene biogenesis, we feel that it is reasonable to agree that these three compounds are related, (−)-(1) resulting

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Table 1. *Fractional coordinates and equivalent isotropic temperature factors in (−)-(6′R)-3′,6′-epoxyaurapten (e.s.d.'s in parentheses)*

$B_{eq} = \frac{4}{3}\sum_i\sum_j\beta_{ij}(\mathbf{a}_i.\mathbf{a}_j)$ (Hamilton, 1959).

| | $x$ | $y$ | $z$ | $B_{eq}$(Å²) |
|---|---|---|---|---|
| O1 | −0·2458 (4) | 0·4305 (2) | 0·7035 (2) | 4·3 (2) |
| O2 | −0·5237 (3) | 0·1995 (2) | 0·8199 (2) | 4·2 (2) |
| O3 | 0·2268 (4) | 0·3682 (2) | 0·4950 (2) | 3·7 (2) |
| O4 | 0·4330 (4) | 0·3391 (2) | 0·3924 (2) | 6·3 (2) |
| C1 | −0·4886 (6) | 0·3389 (2) | 0·7529 (3) | 2·9 (2) |
| C2 | 0·1601 (5) | 0·4207 (2) | 0·5626 (2) | 2·9 (2) |
| C3 | 0·4342 (6) | 0·5107 (3) | 0·5549 (3) | 4·5 (3) |
| C4 | 0·3919 (6) | 0·3873 (3) | 0·4533 (3) | 4·2 (3) |
| C5 | −0·0836 (6) | 0·4466 (2) | 0·6641 (3) | 3·6 (2) |
| C6 | −0·0077 (6) | 0·3959 (3) | 0·5967 (3) | 3·3 (2) |
| C7 | −0·5048 (9) | 0·4353 (4) | 0·8933 (4) | 6·0 (3) |
| C8 | −0·6004 (5) | 0·2508 (2) | 0·7478 (3) | 3·2 (2) |
| C9 | −0·3263 (6) | 0·3432 (3) | 0·6922 (3) | 3·8 (3) |
| C10 | 0·2594 (6) | 0·4932 (2) | 0·5935 (3) | 3·3 (2) |
| C11 | −0·2457 (7) | 0·3285 (4) | 0·8767 (4) | 4·8 (3) |
| C12 | 0·4966 (7) | 0·4608 (3) | 0·4883 (3) | 4·6 (3) |
| C13 | −0·7944 (6) | 0·2700 (3) | 0·7814 (3) | 3·9 (3) |
| C14 | 0·0138 (7) | 0·5206 (3) | 0·6960 (3) | 4·2 (3) |
| C15 | −0·5915 (6) | 0·1966 (3) | 0·6631 (3) | 5·7 (3) |
| C16 | 0·1802 (7) | 0·5435 (3) | 0·6618 (3) | 4·3 (3) |
| C17 | −0·5561 (6) | 0·2651 (3) | 0·8876 (3) | 4·3 (3) |
| C18 | −0·4471 (5) | 0·3458 (3) | 0·8540 (2) | 3·3 (2) |
| C19 | −0·7645 (7) | 0·2774 (5) | 0·8816 (3) | 5·0 (3) |

from *in vivo* cyclization of (+)-(2), itself produced from (3) (Coates & Melvin, 1970; Van Tamelen & Coates, 1982).

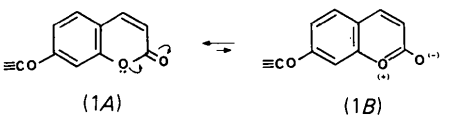
In the optically active series, we have verified that the electrophilic cyclization of (+)-(2) with $SnCl_4$ led effectively to (−)-(1), giving rise to the stereochemistry that is usually assumed but without any analytical evidence. In fact, the *exo* structure of this molecule could not be defined by NMR alone. The (+)-(2) epoxide itself has been obtained by the asymmetric epoxidation method (Katsuki & Sharpless, 1980). Then $SnCl_4$ was used to cyclize (+)-(2) into (−)-(6′*R*)-(1). In order to confirm the stereochemistry of (−)-(1) and allow the definition of structures of similar compounds, we decided to initiate an X-ray study of this molecule.

**Experimental.** Crystal specimens were obtained from an ether solution by slow evaporation of the solvent, giving rise to an elongated prismatic [(100), (011), (01$\bar{1}$)] crystal, 0·50 × 0·07 × 0·07 mm. Data collected on an automated four-circle Siemens AED2 diffractometer, $\omega$–2$\theta$ step-scan mode in $N$ steps of 0·035°, $N_{min} = 40$. Time per step: $t_{min} = 1{\cdot}0$ s, $t_{max} = 4{\cdot}0$ s. Profile-fitting data analysis (Clegg, 1981); isotropic line width $\omega = (0{\cdot}67 + 0{\cdot}63\tan\theta)°$. Aperture $D = 4{\cdot}0$ mm. Lattice constants based on 20 reflections. No absorption correction. Intensity measurement to $2\theta_{max} = 55°$ within range $-9 \le h \le +9$, $-19 \le k \le +19$, $0 \le l \le +19$. Standard reflections 013, 131, 231, intensity variation 1·1%. 5385 reflections measured; 2592 unique, $R_{int} = 0{\cdot}026$; 1625 reflections used for refinement [$|F| > 6\sigma(|F|)$]. $F$ magnitudes used in least-squares refinements: 348 parameters refined; mean $\Delta/\sigma = 0{\cdot}010$, max. $\Delta/\sigma = 0{\cdot}034$; secondary-extinction factor $x = 3{\cdot}0 \times 10^{-7}$; atomic scattering factors for C, O, H and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974); calculations with *SHELX*76 program (Sheldrick, 1976).

A solution with 14 non-H atoms was found with the multisolution tangent direct method of *SHELX*76. Successive refinements and Fourier maps located 23 non-H atoms ($R = 0{\cdot}121$). Further refinements with anisotropic thermal parameters ($R = 0{\cdot}094$) allowed O and C atoms to be distinguished ($R = 0{\cdot}074$). H atoms were then found from a difference Fourier map. The residual decreased to $R = 0{\cdot}046$, $wR = 0{\cdot}035$, including refinement of coordinates and isotropic thermal parameters of 22 H atoms; C15, H6, H12 and H21 were constrained to form a methyl group. The absolute configuration could not be determined. Max. and min. heights in final difference map: 0·069 and −0·065 e Å$^{-3}$.

**Discussion.** The final atomic coordinates and equivalent isotropic temperature factors are listed in Table 1.*

An *ORTEP* plot (Johnson, 1965) of the molecule is given in Fig. 1. The coumarin part is almost flat. The deviation of the atoms, including H, from the mean plane is less than 0·08 Å. Intermolecular van der Waals interactions ensure the stability of the structure. The O···H distances are around 2·6 Å (Table 2). This corresponds to the sum of van der Waals radii as proposed by Bondi (1964) [$r$(H) = 1·20, $r$(O) = 1·50 Å]. The shortest distance between two molecules, 2·57 Å, is from atom O2 to atom H18. This H atom appears to be the most acidic owing to the polarized conjugated system C=C–C=O. The melting point of (1) (457 K) reflects the cohesion that is due to such interactions in three directions. The bond lengths in the lactonic ring confirm its non-aromatic character, suggesting that (1*A*) is more representative of (1) than the polar hybrid (1*B*).



(1*A*) (1*B*)

This is also consistent with the 1H NMR spectrum of (1) in which the signals from the protons H18, 6·92 p.p.m. and H11, 6·26 p.p.m. ($Me_4Si$, $CDCl_3$), and their coupling constant (9 Hz) are typical of a *cis* alkene

* Lists of structure factors, anisotropic thermal parameters and atomic coordinates, bond lengths and angles for H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44877 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Selected bond lengths* (Å) *and angles* (°) *in* (−)-(6′*R*)-3′,6′-*epoxyaurapten*

| | | | |
|---|---|---|---|
| C5–O1 | 1·347 (4) | C9–O1 | 1·440 (4) |
| C8–O2 | 1·447 (4) | C17–O2 | 1·438 (5) |
| C2–O3 | 1·378 (4) | C4–O3 | 1·390 (5) |
| C4–O4 | 1·210 (5) | C8–C1 | 1·549 (5) |
| C9–C1 | 1·501 (5) | C18–C1 | 1·567 (5) |
| C6–C2 | 1·380 (5) | C10–C2 | 1·385 (5) |
| C10–C3 | 1·427 (6) | C12–C3 | 1·334 (6) |
| C12–C4 | 1·438 (6) | C6–C5 | 1·387 (5) |
| C14–C5 | 1·399 (5) | C18–C7 | 1·521 (6) |
| C13–C8 | 1·531 (5) | C15–C8 | 1·519 (5) |
| C16–C10 | 1·403 (5) | C18–C11 | 1·531 (6) |
| C19–C13 | 1·538 (6) | C16–C14 | 1·364 (6) |
| C18–C17 | 1·530 (5) | C19–C17 | 1·534 (6) |
| C9–O1–C5 | 117·8 (3) | C17–O2–C8 | 96·6 (3) |
| C4–O3–C2 | 121·8 (3) | C9–C1–C8 | 114·9 (3) |
| C18–C1–C8 | 101·9 (3) | C18–C1–C9 | 116·4 (3) |
| C6–C2–O3 | 116·1 (4) | C10–C2–O3 | 120·8 (4) |
| C10–C2–C6 | 123·2 (4) | C12–C3–C10 | 120·9 (5) |
| O4–C4–O3 | 116·1 (4) | C12–C4–O3 | 116·7 (4) |
| C12–C4–O4 | 127·2 (5) | C6–C5–O1 | 125·4 (4) |
| C14–C5–O1 | 115·7 (4) | C14–C5–C6 | 118·9 (4) |
| C5–C6–C2 | 118·9 (4) | C1–C8–O2 | 102·0 (3) |
| C13–C8–O2 | 101·8 (3) | C13–C8–C1 | 108·1 (3) |
| C15–C8–O2 | 109·9 (3) | C15–C8–C1 | 118·1 (3) |
| C15–C8–C13 | 114·9 (4) | C1–C9–O1 | 106·7 (3) |
| C3–C10–C2 | 118·1 (4) | C16–C10–C2 | 116·9 (4) |
| C16–C10–C3 | 124·9 (4) | C4–C12–C3 | 121·5 (5) |
| C19–C13–C8 | 102·2 (4) | C16–C14–C5 | 121·3 (4) |
| C14–C16–C10 | 120·8 (4) | C18–C17–O2 | 102·3 (3) |
| C19–C17–O2 | 101·7 (4) | C19–C17–C18 | 113·7 (4) |
| C7–C18–C1 | 112·8 (4) | C11–C18–C1 | 113·2 (4) |
| C11–C18–C7 | 109·1 (4) | C17–C18–C1 | 99·9 (3) |
| C17–C18–C7 | 114·7 (4) | C17–C18–C11 | 106·9 (4) |
| C17–C19–C13 | 101·0 (4) | | |

rather than of an aryl ring. It can be seen also that the positive charge may migrate to C5 which explains the shortened length ($\pi$ character) of the O1–C5 bond *versus* the O1–C9 bond.

Finally, there is evidence of the *syn* relationship between the O2 bridge and the coumarin chain bonded to C1, a problem incompletely resolved until now by the nuclear Overhauser effect difference in NMR analysis. This verifies that anterior assignments based upon biogenetic pathways by Van Tamelen & Coates (1982) were correct.

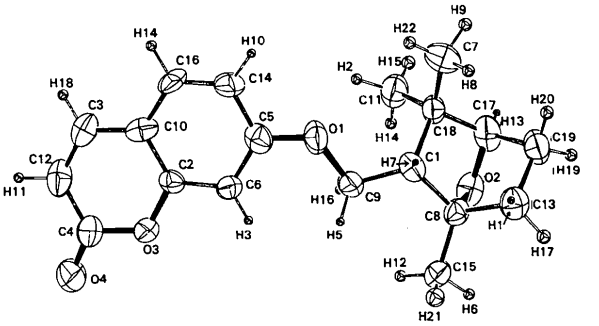



Fig. 1. *ORTEP* plot of the molecule of (−)-(6′*R*)-3′,6′-epoxyaurapten. For the sake of clarity, the isotropic thermal parameters of the H atoms were divided by ten.

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# Structure of the 1:1 Complex between 4-Amino-*N*-(4,6-dimethyl-2-pyrimidinyl)-benzenesulfonamide (Sulfadimidine) and 2-Hydroxybenzoic Acid (Salicylic Acid)

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**Abstract.** $C_{12}H_{14}N_4O_2S.C_7H_6O_3$, $M_r = 416{\cdot}46$, orthorhombic, *Pbca*, $a = 15{\cdot}7783\ (8)$, $b = 25{\cdot}3419\ (12)$, $c = 10{\cdot}2212\ (5)$ Å, $V = 4087{\cdot}0\ (4)$ Å$^3$, $Z = 8$, $D_m = 1{\cdot}360\ (5)$, $D_x = 1{\cdot}3535\ (2)$ Mg m$^{-3}$, $\lambda(\text{Cu } K\alpha) = 1{\cdot}5418$ Å, $\mu = 1{\cdot}69$ mm$^{-1}$, $F(000) = 1744$, $T = 293$ K, final $R = 0{\cdot}053$ for 2733 observed reflections. The molecular complex between sulfadimidine and salicylic acid is obtained as a result of two hydrogen bonds

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