THE STRUCTURE OF A NEW SESQUITERPENE — SIOL ACETATE FROM *Sium latifolium* L.*

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A new sesquiterpenic ester, a carotane derivative, was isolated from fruits of *Sium latifolium* (*Umbelliferae*). Its structure (*I*) was elucidated by spectroscopic and X-ray analysis.

Sesquiterpenic compounds with carotane skeleton have been recently isolated mainly from plants of the *Umbelliferae* family (for reviews see ref.[1,2]); some have been found also in *Compositae*[3] and *Cupressaceae*[4] family, in liverworts[5] and fungi[1]. In the course of our systematic studies of sesquiterpenic compounds from *Umbelliferae* plants we investigated the components of seeds of the perennial euroasiatic plant *Sium latifolium* L. Only the essential oil from its seeds has been studied previously[6]; its components being limonene, α,β-pinene, perilla aldehyde, β-bisabolene and α-curcumene.

We separated chromatographically the light petroleum extract and identified, in addition to paraffins (principal fraction C_{29}), limonene, α,β-pinene, camphene. myrcene, *p*-cymene, perilla aldehyde and also a trace amount of sesquiterpenic hydrocarbons. Finally, the more polar chromatographic fractions afforded, beside fats, a compound of the composition $C_{17}H_{26}O_4$.

The four oxygen atoms of this compound are accounted for by a tertiary OH ($3\,500\ cm^{-1}$, resistant to acetylation, ^{13}C NMR evidence), a keto group in a five-membered ring ($1\,740\ cm^{-1}$) and an ester group ($1\,720\ cm^{-1}$). ^1H NMR spectrum indicated the presence of an isopropyl group (δ 1·02 and 1·12, d, $J = 6\cdot5$, 3 H each), a methyl group on a quarternary carbon atom (δ 1·07, s, 3 H) a methyl group

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on a double bond (δ 1·76, s, long range coupling, 3 H), and acetoxy group (δ 1·97, sharp s, 3 H) an esterified secondary alcoholic function (δ 5·17, d, $J = 7\cdot5$, 1 H) and a trisubstituted double bond (δ 5·63, d, d, $J = 7\cdot5$, 1 H). Decoupling experiments demonstrated vicinal coupling between the last two protons as well as allylic coupling between the olefinic proton and the methyl on the double bond.
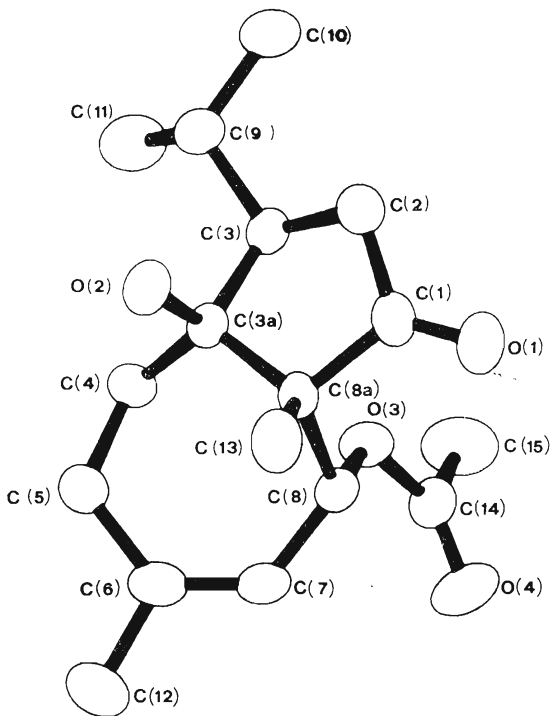

Fig. 1

Molecular structure of siol acetate (*I*) in a general orientation

^{13}C NMR spectrum showed the expected 17 lines whose multiplicities (five q, three t, four d, five s) confirmed the formula given above and strongly suggested — if a sesquiterpenic nature is supposed — formula *I* for siol acetate, in which the cyclopentanone function is allocated in position 1. This assignment is based on the high chemical shift for the adjacent angular methyl carbon atom and on the fact that none of the methylene groups present in the ^{13}C off-resinance spectrum gives a sharp triplet, as it would be expected for an isolated CH_2 group. The most known compounds of natural origin having such a skeleton are carotol (*II*) and daucol (*III*), earlier isolated from *Daucus carota*[6,8] (for structure elucidation see ref.[9-11]). In order to demonstrate the proposed structure in a classical way and presuming identical chiralities at the common centres, we planned to eliminate from *I* the carbonyl and the (esterified) alcoholic function using conventional chemical reactions. The compound, however, failed to react with hydrazine derivatives under mild conditions while under more drastic ones it suffered extensive decomposition.

Assuming that such behaviour could be at least partially attributed to the allylic ester function, we decided to transform *I* into the (supposedly) more stable oxide analogue *IV* of daucol. The treatment with monoperphthalic acid, easily transforming carotol into daucol, however, was not successful and the reaction stopped at the stage of the epoxide *V* (in the ^{13}C NMR spectrum two signals at 62·9 and 61·5 due to carbon atoms of the epoxide ring were observed while in daucol the signals of six-membered oxide ring carbon atoms were found at 91·4 and 85·2). The epoxide nature of the introduced oxygen atom was confirmed also chemically by its easy LiAlH$_4$ opening to the tetraol *VI*.

Since also other attempted chemical transformations (elimination of the ester group or oxidation of the triol *VII* and removal of the keto groups in the diketone *VIII* via bis(ethylenethioketal)) did not lead to sufficient amounts of the desired compounds, we proved the assumed structure *I* by X-ray analysis.

The results of the X-ray study establish that siol acetate has the constitution and the relative stereochemistry shown by *I* (Fig. 1). No attempt has been made to determine the absolute configuration of the four chiral carbon atoms.

Concerning the stereochemistry, siol acetate resembles carotol[10,11] (*II*) in the following respects: The *cis*-junction of the cyclopentanone and the cycloheptene rings, the *cis*-arrangement of the isopropyl side-chain and the hydroxyl O(2), and finally the double bond between the C(6) and C(7) carbon atoms. The acetoxy group at C(8) is in *trans*-relation to the methyl group attached to C(8a). Because of the similarity with the three chiral centres of carotol, whose absolute configuration is known, siol acetate in figure 1 is shown in the same enantiomorphic form.

The fractional coordinates of siol acetate are listed in Table I. The interatomic bond distances and valence angles are reported in Table II for the heavy atoms only, while the mean distance involving hydrogen and carbon atoms is 0·97(7) Å, and the mean angles are 109(7)° and 116(5)° for the sp^3 and sp^2 carrier atoms, respectively.

Fractional coordinates with estimated standard deviations (in parentheses)

| Atom	x/a	y/b	z/c	Beq (Å^2)[a]
O(1)	−0·3167(1)	−0·0319(6)	−0·2694(5)	4·19
O(2)	−0·3191(1)	−0·1243(5)	0·3199(5)	4·19
O(3)	−0·4083(1)	0·1322(5)	−0·0677(5)	3·33
O(4)	−0·4602(1)	0·1061(6)	−0·2913(6)	3·C0
C(1)	−0·3217(2)	−0·0027(8)	−0·1024(7)	3·01
C(2)	−0·2950(2)	0·1240(9)	0·0145(8)	3·63
C(3)	−0·3253(2)	0·1682(7)	0·1811(7)	2·81
C(3a)	−0·3488(1)	−0·0089(7)	0·2242(7)	2·51
C(4)	−0·3908(2)	0·0104(7)	0·3418(8)	3·01
C(5)	−0·4186(2)	−0·1558(8)	0·3626(8)	3·44
C(6)	−0·4465(2)	−0·2023(7)	0·1938(8)	3·25
C(7)	−0·4400(2)	−0·1559(7)	0·01C6(8)	3·05
C(8)	−0·4017(1)	−0·0591(6)	−0·C671(7)	2·50
C(8a)	−0·3563(1)	−0·0907(6)	0·0247(7)	2·47
C(9)	−0·3016(2)	0·2564(8)	0·3512(8)	3·43
C(10)	−0·2663(2)	0·3828(10)	0·2815(11)	4·43
C(11)	−0·3327(3)	0·3560(11)	0·4837(12)	5·26
C(12)	−0·4860(2)	−0·3145(10)	0·2453(11)	3·55
C(13)	−0·3475(2)	−0·2886(8)	0·0105(9)	3·12
C(14)	−0·4380(2)	0·1944(7)	−0·1897(7)	3·12
C(15)	−0·4403(2)	−0·3901(9)	−0·1819(14)	4·82
H(1)	−0·461(2)	−0·191(9)	−0·082(10)	2·90
H(2)	−0·398(2)	−0·092(9)	−0·211(9)	2·70
H(3)	−0·381(2)	0·036(9)	0·478(10)	2·90
H(4)	−0·406(2)	0·098(9)	0·287(10)	2·90
H(5)	−0·439(2)	−0·136(9)	0·481(10)	3·10
H(6)	−0·400(2)	−0·253(9)	0·394(10)	3·10
H(7)	−0·345(2)	0·244(9)	0·132(10)	2·90
H(8)	−0·283(2)	0·227(10)	−0·059(10)	3·60
H(9)	−0·268(2)	0·061(9)	0·051(10)	3·60
H(10)	−0·467(2)	0·424(11)	−0·232(12)	4·50
H(11)	−0·418(2)	0·435(11)	−0·230(13)	4·50
H(12)	−0·429(3)	0·434(11)	−0·058(12)	4·50
H(13)	−0·317(2)	−0·311(9)	−0·015(10)	3·60
H(14)	−0·352(2)	−0·324(10)	−0·132(10)	3·60
H(15)	−0·362(2)	−0·343(10)	0·097(11)	3·60
H(16)	−0·503(2)	−0·354(10)	0·112(11)	4·80
H(17)	−0·505(2)	−0·253(10)	0·334(11)	4·80
H(18)	−0·477(3)	−0·413(12)	0·314(12)	4·80
H(19)	−0·293(2)	0·161(10)	0·428(10)	3·40
H(20)	−0·245(2)	0·336(10)	0·209(12)	4·70

TABLE I
(Continued)

Atom	x/a	y/b	z/c	Beq $(\text{Å}^2)^a$
H(21)	−0·253(3)	0·444(10)	0·393(12)	4·70
H(22)	−0·278(2)	0·461(11)	0·198(12)	4·70
H(23)	−0·359(3)	0·290(12)	0·519(13)	5·50
H(24)	−0·349(3)	0·435(12)	0·417(13)	5·50
H(25)	−0·316(3)	0·405(11)	0·609(12)	5·50
H(26)	−0·319(2)	−0·099(9)	0·447(11)	3·50

^{a} Beq $= 8\pi^2(U_1 U_2 U_3)^{1/3}$, where U_i are the principal mean-square displacements.

As expected[12], the bond angles within the seven-membered ring are all larger than the ideal tetrahedral or triangular angles which is typical for a ring of this size[13]. The

I *II* *III*

IV *V* *VI*

VII *VIII*
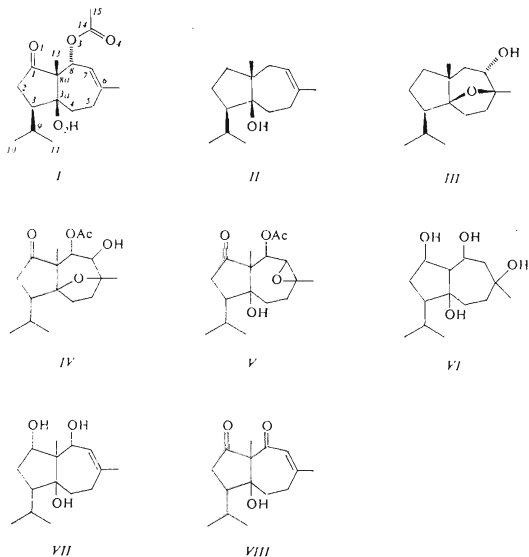
conformation of the molecule is described by the torsion angles reported in Table III.

The cyclopentanone ring is in the envelope conformation with C(3) displaced 0·59 Å out of the plane of the other four atoms, and with an approximate mirror plane passing through C(3) and the middle point of the C(1)—C(8a) bond. The C_s symmetry is slightly violated as the asymmetry parameter[16] is $\Delta C_s = 0·6°$. The

TABLE II

Interatomic distances (Å) and angles (deg.) with estimated standard deviations (in parentheses)

Bond lengths

O(1)—C(1)	1·204(6)	C(3a)—C(8a)	1·553(7)
O(2)—C(3a)	1·433(6)	C(4)—C(5)	1·540(8)
O(3)—(8)	1·484(6)	C(5)—C(6)	1·501(8)
O(3)—C(14)	1·335(6)	C(6)—(C7)	1·314(8)
O(4)—C(14)	1·195(7)	C(6)—C(12)	1·524(9)
C(1)—C(2)	1·512(8)	C(7)—C(8)	1·502(7)
C(1)—C(8a)	1·539(7)	C(8)—C(8a)	1·544(6)
C(2)—C(3)	1·528(7)	C(8a)—C(13)	1·549(8)
C(3)—C(3a)	1·567(7)	C(9)—C(10)	1·529(9)
C(3)—C(9)	1·552(7)	C(9)—C(11)	1·534(10)
C(3a)—C(4)	1·532(7)	C(14)—C(15)	1·507(9)

Valence angles

C(8)—O(3)—C(14)	116·6(4)	C(7)—C(6)—C(12)	119·9(5)
O(1)—C(1)—C(2)	125·5(5)	C(6)—C(7)—C(8)	128·4(5)
O(1)—C(1)—C(8a)	124·8(5)	O(3)—C(8)—3(7)	112·8(4)
C(2)—C(1)—C(8a)	109·7(4)	O(3)—C(8)—C(8a)	106·1(4)
C(1)—C(2)—C(3)	103·5(4)	C(7)—C(8)—C(8a)	117·1(4)
C(2)—C(3)—C(3a)	103·3(4)	C(1)—C(8a)—C(3a)	104·1(4)
C(2)—C(3)—C(9)	113·9(4)	C(1)—C(8a)—C(8)	107·6(4)
C(3a)—C(3)—C(9)	116·3(4)	C(1)—C(8a)—C(13)	106·0(4)
O(2)—C(3a)—C(3)	110·0(4)	C(3a)—C(8a)—C(8)	116·5(4)
O(2)—C(3a)—C(4)	109·5(4)	C(3a)—C(8a)—C(13)	115·5(4)
O(2)—C(3a)—C(8a)	105·4(4)	C(8)—C(8a)—C(13)	106·4(4)
C(3)—C(3a)—C(4)	113·7(4)	C(3)—C(9)—C(10)	111·0(5)
C(3)—C(3a)—C(8a)	104·2(4)	C(3)—C(9)—C(11)	113·4(5)
C(4)—C(3a)—C(8a)	113·6(4)	C(10)—C(9)—C(11)	108·1(6)
C(3a)—C(4)—C(5)	115·6(4)	O(3)—C(14)—O(4)	124·3(5)
C(4)—C(5)—C(6)	115·7(5)	O(3)—C(14)—C(15)	111·4(5)
C(5)—C(6)—C(7)	126·8(5)	O(4)—C(14)—C(15)	124·2(5)
C(5)—C(6)—C(12)	113·2(5)		

observed torsion angles are systematically smaller than the theoretical values[15], suggesting a certain degree of flattening of the five-membered ring.

TABLE III

Selected torsion angles (deg.) with estimated standard deviations in parentheses, according to the notation of Klyne and Prelog[14]

Cyclopentanone	obs.	theor. (ref.[15])
C(3a)—C(8a)—C(1)—C(2)	0·1(5)	0·
C(8a)—C(1)—C(2)—C(3)	— 23·5(6)	— 25·9
C(1)—C(2)—C(3)—C(3a)	37·2(5)	41·7
C(2)—C(3)—C(3a)—C(8a)	— 37·6(4)	— 41·7
C(3)—C(3a)—C(8a)—C(1)	22·8(4)	25·9

Cycloheptene	obs.	theor. (ref.[16])
C(5)—C(6)—C(7)—C(8)	5·7(9)	7·8
C(6)—C(7)—C(8)—C(8a)	32·7(8)	27·9
C(7)—C(8)—C(8a)—C(3a)	— 72·7(6)	— 77·9
C(8)—C(8a)—C(3a)—C(4)	28·9(6)	43·1
C(8a)—C(3a)—C(4)—C(5)	52·3(6)	43·1
C(3a)—C(4)—C(5)—C(6)	— 78·5(6)	— 77·9
C(4)—C(5)—C(6)—C(7)	23·9(8)	27·9

Junction and side chains	
C(3)—C(3a)—C(8a)—C(8)	— 95·4(4)
C(3)—C(3a)—C(8a)—C(13)	— 138·6(4)
O(2)—C(3a)—C(8a)—C(1)	— 93·8(4)
O(2)—C(3a)—C(8a)—C(8)	148·8(4)
O(2)—C(3a)—C(8a)—C(13)	22·8(5)
C(4)—C(3a)—C(8a)—C(1)	147·1(4)
C(4)—C(3a)—C(8a)—C(13)	97·1(5)
O(3)—C(8)—C(8a)—C(1)	— 62·2(5)
O(3)—C(8)—C(8a)—C(3a)	54·2(5)
O(3)—C(8)—C(8a)—C(13)	— 175·3(4)
O(3)—C(8)—C(7)—C(6)	— 90·9(6)
C(14)—O(3)—C(8)—C(7)	— 70·6(5)
C(14)—O(3)—C(8)—C(8a)	160·0(4)
C(8)—O(3)—C(14)—O(4)	2·7(7)
C(8)—O(3)—C(14)—C(15)	— 177·2(5)
C(2)—C(3)—C(9)—C(10)	38·0(7)
C(2)—C(3)—C(9)—C(11)	159·9(6)
C(3a)—C(3)—C(9)—C(10)	157·9(6)
C(3a)—C(3)—C(9)—C(11)	— 80·1(6)

The conformation of the cycloheptene ring is approximately that of the twist conformation, as the ring torsion angles and their signs agree with the values calculated by Ermer and Lifson[17] for the unsubstituted cycloheptene ring; the approximate binary axis passes through C(3a) and the middle point of the C(6)—C(7) bond. Atoms C(5), C(6), C(12), C(7) and C(8) of the seven-membered ring are constrained to a nearly planar arrangement by the double bond, while C(3a), C(4) and C(8a) lie out of the plane (0·22, −0·65 and 0·83 Å, respectively). In this ring the deviation from the C_2 symmetry is larger, the asymmetry parameter being $\Delta C_2 = 14.8°$, while the dierences between the theoretical and experimental torsion angles have randomly distributed signs. It is noteworthy that the largest deviations from both the C_2 symmetry and the theoretical model values occur in the region of the junction of the seven-membered with the five-membered ring, namely along the the C(4)—C(3a)-C(8a) moiety.
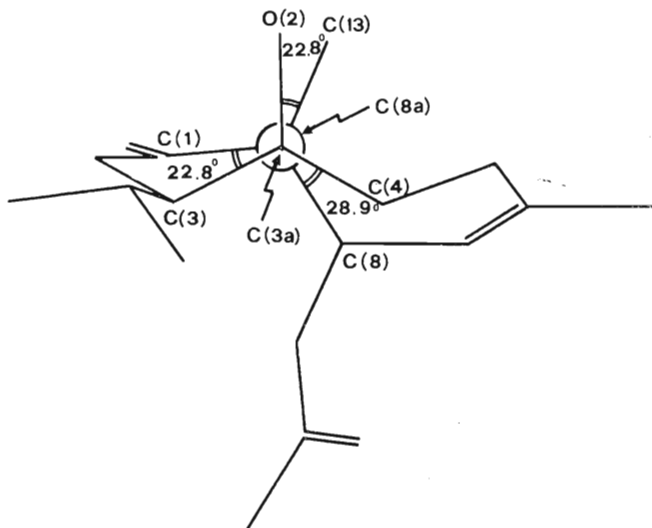

Fig. 2

Newman projection of the cyclopentanone-cycloheptene junction

Fig. 2 shows geometry of the fusion. Because of the *cis*-junction, the smaller torsion angle of the junction, C(8)—C(8a)—C(3a)—C(4), and consequently the larger torsion angle C(8a)—C(3a)—C(4)—C(5), are certainly due to the transmitted deformation by the cyclopentanone ring.

In addition, an inspection of Dreiding models shows that the C_2 symmetry for the whole seven-membered ring should demand severe non-bonded transannular interactions between the hydrogens at the C(13) atom and the C(5) carbon atom. The arising repulsion acts in the same way as the torsional strain induced by the five-membered ring, tending to close the juction torsion angle of the more flexible cycloheptene ring.

The arrangement of the molecules in the crystal, viewed along the *b* axis, is shown in Fig. 3. The packing along the *a* and *b* axes involves only normal van der Waals interactions, the molecules being connected side by side through hydrogen bonds between the carbonyl O(1) and the hydroxyl O(2) oxygens of molecules related by unit cell translation along the *c* axis. Geometrical parameters of the hydrogen bond are the following: O(2)...O(1) = 2·971 Å, O(2)—H = 0·92 Å, H...O(1) = = 2·055 Å, O(2)—H...O(1) = 170° and C(3a)—O(2)—H = 109°.
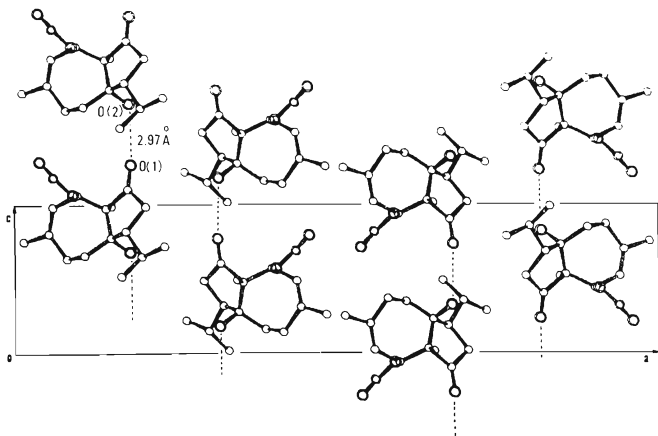

FIG. 3
Crystal packing of siol acetate (view down the *b* axis)

EXPERIMENTAL

Melting points were determined on a Kofler block and are uncorrected. Column chromatography was performed on a silica gel Merck (70—230 mesh), thin-layer chromatography was carried out on Fertigplatten Kieselgel 60 Merck. IR spectra were measured on a Perkin-Elmer 247 spectrometer, optical rotations were determined on a Roussel-Jouan type 71 polarimeter. Mass spectra were taken on an LKB-9000 instrument, NMR spectra were measured in deuteriochloroform on a Varian HA-100 (^{1}H) and Varian XL-100/15 (FT mode; ^{13}C) instruments with tetramethylsilane as internal standards; chemical shifts are given in ppm (δ scale), coupling constants in Hz; s singlet, d doublet, t triplet and q quartet.

Isolation and Identification of Compounds in the Light Petroleum Extract

Not completely ripe seeds of *S. latifolium* were collected in the vicinity of Houštka near Nymburk; the voucher of the plant is deposited in the National Museum Herbarium in Prague (PR). Dried and ground seeds (862 g) were exhaustively extracted with light petroleum (40—60°C), the obtained extract was taken down and the residue (48·3 g) was chromatographed on silica gel (1 500 g; deactivated with 11% water).

Paraffinic hydrocarbons: The first light petroleum fractions (4·43 g) were rechromatographed on silica gel, impregnated with silver nitrate. The mixture of saturated hydrocarbons was analyzed by gas-liquid chromatography on a Pye 104 chromatograph (1·5 m all-glass column of 4 mm internal diameter, 3% SE-30 on Gas-Chrom Q, 80—100 mesh) at 250°C, carrier gas nitrogen (50 ml/min). In the mixture of C_{25}—C_{31} hydrocarbons the C_{29} hydrocarbon was the principal constituent.

Monoterpenic hydrocarbons: Further light petroleum fraction (12·4 g) was distilled at 1·3 kPa up to b.p. 90°C and analyzed by gas-liquid chromatography (Perkin-Elmer F-11, 2 m all-glass column of 2·2 mm internal diameter, packed with 10% CW 400 on Chromosorb (80—100 mesh)). The distillation residue (10 mg) contained compounds of M 204.

Fats: Fractions, eluted with light petroleum-ether (95 : 5) contained fats as the major component (band at 1 752 cm^{-1} in the IR spectrum).

Perilla aldehyde: Distillation of the middle fat-containing chromatographic fractions at 0·13 kPa afforded a liquid which was purified by TLC. IR spectrum, cm^{-1}: 1 690 (C=O), 1 646 (C=C), 2 715, 2 805 (aldehyde C—H), 1 377, 1 395 (isopropyl), 895, 920, 1 166, 1 308 (CH$_2$=).

Siol acetate (*I*): The more polar fractions, eluted with light petroleum-ethyl acetate (96 : 4) were rechromatographed on a fifty-fold amount of silica gel (deactivated with 11% water), yielding a compound of m.p. 130—131°C, $[\alpha]_D^{20}$ −252° (*c* 0·28, CHCl$_3$). Mass spectrum: M$^+$ 276, 1 722, for $C_{17}H_{26}O_4$ calculated 276, 1 725. For $C_{17}H_{26}O_4$ (276·1) calculated: 69·36% C, 8·90% H; found: 69·40% C, 8·99% H. IR spectrum, cm^{-1}: 3 500, 1 740, 1 720 sh. ^{1}H NMR spectrum: 5·63 (d, *J* = 7·5, 1 H, collapsing to s on irradiation at 5·17), 5·17 (d, *J* = 7·5 with further fine splitting, 1 H, collapsing to s on irradiation at 5·63), 1·95 (s, 3 H), 1·65, 1·15 (s, 3 H), 1·15 (s, 3 H), 1·12 and 1·02 (both d, *J* = 6·5, 3 H each). ^{13}C NMR spectrum: 220·3 (s), 169·2 (s), 146·5 (s), 119·3 (d), 82·3 (s), 76·0 (d), 60·3 (s), 51·7 (d), 38·9 (t), 37·3 (t), 29·2 (t), 26·6 (d), 26·1 (q), 24·8 (q), 21·3 (q), 21·1 (q) and 18·1 (q).

Epoxide *V*

A solution of *I* (140 mg) in diethyl ether was mixed at room temperature with an ethereal solution (10 ml; 14 mg/ml) of monoperoxyphthalic acid. The usual work-up procedure afforded

100 mg of V, m.p. 211—213°C (benzene); $[\alpha]_D^{20}$ —44° (c 0·15, CHCl₃). ¹H NMR spectrum: 5·01 (d, $J = 6·5$, 1 H), 3·18 (d, $J = 6·5$, 1 H), 2·0 (s, 3 H), 1·1 (s, 3 H) and 1·0 (d, $J = 6·5$, 6 H). ¹³C NMR spectrum: 219·0, 170·1, 82·44, 75·34, 62·91, 58·5, 50·8, 38·4, 31·1, 27·4, 24·8, 24·0, 21·2, 20·5 and 16·5. Mass spectrum: M⁺ 310 m/e.

Tetraol VI

The compound V (50 mg) was treated with a large excess of LiAlH₄ in ether affording amorphous VI (40 mg). IR spectrum: 3 500 cm⁻¹, no bands in the carbonyl region. ¹³C NMR spectrum: 89·8, 85·1, 78·1, 71·3, 51·5 (probably two overlapping lines), 50·5, 42·4, 38·6, 31·5, 29·7, 24·1, 23·1, 22·9 and 21·6.

Triol VII

Compound I (150 mg) in ether was reduced with a large excess of lithium aluminium hydride for 2 h. After decomposition with a few drops of ethyl acetate, the mixture was filtered, the filtrate washed with dilute hydrochloric acid, dried over sodium sulfate and taken down. The dry residue (60 mg) consisted of nearly pure VII and was crystallized from hexane; m.p. 123—125°C; $[\alpha]_D$ —57° (c 0·2, CHCl₃). ¹H NMR spectrum: 5·58 (d, $J = 7$, 1 H), 4·30 (d, $J = 7$, 1 H), 3·98 (broad d, 1 H), 1·74 (s, 3 H), 1·04 and 0·94 (both d, $J = 6·5$, 3 H each) and 0·96 (s, 3 H). ¹³C NMR spectrum: 142·6, 124·2, 83·7, 73·1, 57·2, 53·7, 35·4 (probably two overlapping lines), 30·0, 26·3, 25·9, 24·3, 21·9 and 21·2.

Diketone $VIII$

A solution of the triol VII (100 mg) in dichloromethane was treated with pyridinium dichromate (100 mg) and the mixture was refluxed in nitrogen atmosphere for 12 h. The filtered solution was purified by silica gel column chromatography and gave 22 mg of a foamy compound for which structure $VIII$ is suggested. ¹H NMR spectrum: 5·72 (m, 1 H), 1·95 (d, $J = 1·0$, 3 H), 1·37 (s, 3 H) and 1·01 (d, $J = 6·5$, 6 H).

Structure Solution and Refinement

Suitable single crystals of I were grown at room temperature from aqueous ethanol. Space group and preliminary cell dimensions were determined from oscillation and Weissenberg photographs. The crystal data are: $C_{17}H_{26}O_4$, $M = 294·3944$, space group $P2_12_12_1$, $a = 30·470$ (17), $b = 7·687$ (3), $c = 7·023$ (4) Å, $V = 1\,645$ Å, $D_0 = 1·19$ g cm⁻³ for $Z = 4$, $\mu(Mo—K_\alpha) = 0·9$ cm⁻¹. Accurate lattice constants were determined and intensities were measured on an automatic Syntex $P2_1$ diffractometer with Mo—K$_\alpha$ radiation (0·71069 Å) monochromatized by graphite crystal. Cell parameters were refined by the least-squares method from the values of selected 15 high-order reflections. The intensities were collected within the range of $2·5 \leqq 2\vartheta \leqq 55·0°$ by ω-scan technique, over a range of 0·9° with a scan speed in the interval 0·8—29·8° min⁻¹. Of the 2 225 reflections measured with a crystal of $0·15 \times 0·3 \times 0·7$ mm, the intensities of 1 314 with $I_0 \geqq 2·5\sigma(I_0)$ were considered observed. Three standard reflections monitored after every 100 remained essentially constant, showing that the crystal suffered no X-ray damage. Lorentz and polarization factors, but no absorption corrections, were applied.

The structure was solved by direct methods using 200 reflections, with normalized structure factors $|E| \geqq 1·63$, processed by MULTAN (ref.[18]). An E map computed with the phases of one of the best sets revealed a chemically significant molecular fragment with 20 maxima. The remaining atomic position was recognized after the first structure factors and Fourier synthesis

calculations. The structure was refined by block-diagonal (9×9) least-squares calculation up to an R value of 0.07. A difference Fourier synthesis showed significant maxima in feasible positions for all the hydrogen atoms and these were included in the final refinement with a fixed B value equal to that of the carrier atoms. The final cycles of refinements were run in block-diagonal approximation, with two blocks, one for all the positional parameters and the other for the thermal ones, and the scale factor, minimizing the function $\sum w(|F_o| - |F_c|)^2$, where $w = (a + + |F_o| + b|F_o|^2)^{-1}$ with $a = 10$ and $b = 0.01$. The weighing parameters were selected so to keep constant the mean of $w \, \Delta F^2$ in the whole range of $|F_o|$ and sin ϑ/λ values. The final R and R_w are 0.053 and 0.074, respectively, for all the observed reflections. Scattering factors were taken from International Tables for X-Ray Crystallography[19]; all the calculations[20] were carried out on the HP 1000 minicomputer of the C.N.R. Research Area.

Lists of the observed and calculated structure factors and of the anisotropic thermal parameters are available on request from the authors.

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