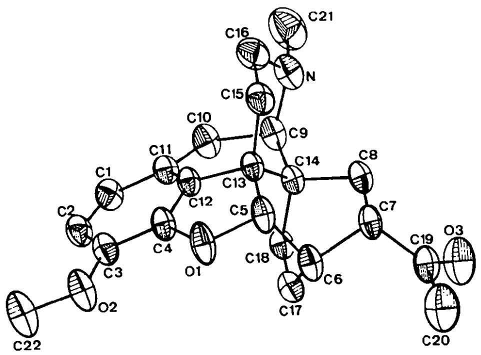

Fig. 1. *ORTEP* plot (Johnson, 1965) of the title compound. Boundary surfaces are drawn to enclose 50% probability.

Residual density in final difference Fourier map $<0\cdot16$ e Å^{-3}. All calculations performed with *XRAY72* (Stewart, Kruger, Ammon, Dickinson & Hall, 1972).

Discussion. The molecular structure is shown in Fig. 1 together with the atom numbering. The final atomic parameters are given in Table 1. Bond lengths and bond angles are listed in Table 2.

The acetyl substituent is in the 7α position of the 6,14-ethenoisomorphinan skeleton (2). This means that the Diels–Alder reaction of methyl vinyl ketone with (–)-6-demethoxythebaine (1) affords one isomer. Consequently, the reaction products of the title compound with different Grignard compounds will possess structure (3) with the alkyl methyl carbinol substituent also in the 7α position.

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Structure of 2-Methoxy-6-pentyl-1,4-benzoquinone (Primin), $C_{12}H_{16}O_3$

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Abstract. $M_r = 208\cdot26$, triclinic, $P\bar{1}$, $a = 4\cdot123$ (1), $b = 9\cdot759$ (4), $c = 14\cdot256$ (2) Å, $\alpha = 87\cdot07$ (2), $\beta = 87\cdot38$ (2), $\gamma = 79\cdot15$ (3)°, $V = 562\cdot2$ (5) Å^3, $Z = 2$, $D_x = 1\cdot230$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1\cdot54184$ Å, $\mu = 0\cdot722$ mm^{-1}, $F(000) = 224$, $T = 296$ K, R is 0·058 for 1518 unique reflections. The structure was solved after several trials by shifting the atomic positions of a correct model along the pentyl chain direction. The angle between the quinonoid ring plane and the pentyl chain plane is 13·4 (4)°. The average dimensions of the C_{sp^3}–C_{sp^3} distances and corresponding angles of the aliphatic chain are 1·523 (5) Å and 112·8 (3)°, those for the quinone ring are C–C 1·477 (4), C=C 1·338 (5), C=O 1·225 (4) Å, C–C–C 118·6 (3), C=C–C 121·1 (3), O=C–C 120·7 (3)°, the shortest intermolecular C···O distance being 3·33 (1) Å.

Introduction. In the course of our investigations on the relationship between chemical structure and allergenic potency of naturally occurring sensitizing 1,4-benzoquinones (Hausen & Schulz, 1977), X-ray structure analysis has been performed for primin (I), (*R*)-3,4-dimethoxydalbergione (II), (*R*,*S*)-4-methoxydalbergione (IV) and (*S*)-4,4′-dimethoxydalbergione (VII) (Schmalle, Jarchow, Hausen & Schulz, 1984), acamelin (V) (Schmalle & Hausen, 1980) and 2,6-dimethoxy-1,4-benzoquinone (VI) (Schmalle, Jarchow & Hausen, 1977). Elucidation of the structures of

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thymoquinone (III) and 2,5-dimethoxy-1,4-benzoquinone (VIII) is in progress. Primin (I) has proved to be the most potent sensitizer within the sequence (I)–(VIII) (Fig. 1) of naturally occurring quinones with diminishing allergenic power (Hausen, 1978, 1979).

Although very small crystals of the toxic and irritant principle of *Primula* species had been observed some 80 years ago (Nestler, 1904), the pure compound was not separated until 1927 by Bloch & Karrer and named primin. Finally, the chemical structure (I) was determined by Schildknecht, Bayer & Schmidt (1967) and synthesized by Schildknecht & Schmidt (1967). Cross-sensitization tests in primin-sensitive patients with synthetic primin and related quinones led to the question 'whether the relative lipid–water solubility of primin is optimal for cutaneous penetration, or whether the length of the side chain reflects the structure of the antibody' (Hjorth, Fregert & Schildknecht, 1969).

Experimental. Naturally occurring primin from *Primula* species, separated by thin-layer chromatography, small yellow needle- and plate-shaped crystals grown by slow evaporation of different solutions (methanol, ethanol, chloroform, petroleum ether 40/60 °C), most of the crystals twinned, space-group determination from Weissenberg photographs; single crystals showed diffuse maxima on ($1kl$)-, ($3kl$)-layer Weissenberg photographs parallel to **b*** (polytypic structure), a trial of intensity measurement failed. Primin was synthesized (Faasch & König, 1983) for further experiments; two further attempts at data collection failed because the soft crystals were destroyed in glass capillaries; finally a plate-shaped single crystal (0·37 × 0·25 × 0·06 mm) was used without any capillary; cell dimensions measured on an Enraf–Nonius CAD-4 diffractometer by least-squares refinement of 25 reflections in the interval $18 < \theta < 54°$, intensities measured on the same diffractometer, graphite-monochromatized Cu $K\bar{\alpha}$ radiation, max. $\sin\theta/\lambda = 0·588$ Å^{-1}, θ–2θ scan, zig-zag mode, variable scan rate 0·24 to 20° min^{-1}, $-4 \le h \le 4$, $0 \le k \le 11$, $-16 \le l \le 16$; 11·6% loss of intensities in standard reflections 006 and $1\bar{3}0$ monitored at the beginning and every 2 h (35 times) during data collection; 2031 reflections measured, data reduction with program of CAD-4 structure-determination package, Lorentz–polarization correction, no absorption correction, $R_{\rm int} = 0·022$, 1908 unique reflections, 388 of these considered unobserved with $I < 3\sigma(I)$, $\sigma(I)$ based on counting statistics; structure solved by direct methods with *MULTAN* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); $\langle{\rm mod}(E)\rangle$, $\langle E^n\rangle$ and $N(Z)$ cumulative probability distribution values showed hypercentricity of the data; four parity groups (*ooo, ooe, eoe, eeo*) with E^2 values of approximately 1·0 and the four corresponding groups of 0·9 before rescaling. Several different *MULTAN* trials in space groups $P\bar{1}$ and $P1$ revealed solutions with two rings connected with a methoxy group and the pentyl chain; refinement stopped at $R = 0·33$ for all models. The partial $2/m$ symmetry of the molecule was taken into account: all atomic positions shifted by one half of the C(2)···C(6) distance of about 1·28 Å along the pentyl chain direction (Fig. 3), R dropped to 0·16; all H-atom positions determined from difference Fourier synthesis and refined isotropically, number of reflections in final least-squares cycle $m = 1518$ (because secondary extinction was suspected, reflections 001 and 011 omitted), $n = 184$ parameters refined, unit weight, $R = 0·058$, Δ/σ max. = 0·095 in final refinement cycle, max. and min. heights in final difference Fourier synthesis 0·20 and −0·20 e Å^{-3}; computer programs used: *MULTAN* (Main *et al.*, 1980), *SHELX* (Sheldrick, 1976), *XANADU* (Roberts & Sheldrick, 1975), *ORTEP* (Johnson, 1971), *ORFFE* (Busing, Martin, Levy, Brown, Johnson & Thiessen, 1971); atomic scattering factors from *SHELX*.

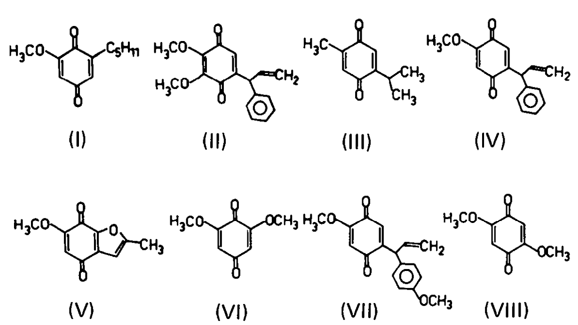

Fig. 1. Primin (I) and other naturally occurring 1,4-benzoquinones (II)–(VII) with diminishing sensitizing potency, (VIII) is non-allergenic.

Table 1. *Final atomic coordinates* ($\times 10^4$) *and* B_{eq} *values for primin with e.s.d.'s in parentheses*

$$B_{\rm eq} = 4[(b_{11}/a^{*2})(b_{22}/b^{*2})(b_{33}/c^{*2})]^{1/3}.$$

	x	y	z	$B_{\rm eq}$(Å^2)
O(1)	1663 (7)	4490 (2)	2146 (2)	4·7 (1)
O(2)	3056 (7)	3722 (2)	420 (2)	4·3 (1)
O(4)	−600 (8)	−472 (3)	1348 (2)	5·6 (2)
C(1)	990 (8)	3374 (3)	1956 (2)	3·3 (2)
C(2)	1808 (9)	2820 (3)	994 (2)	3·4 (2)
C(3)	1265 (10)	1555 (4)	797 (3)	3·8 (2)
C(4)	−105 (10)	698 (4)	1506 (2)	3·9 (2)
C(5)	−1062 (10)	1264 (4)	2439 (2)	3·8 (2)
C(6)	−595 (8)	2519 (3)	2670 (2)	3·2 (1)
C(7)	−1577 (10)	3163 (4)	3598 (2)	3·6 (2)
C(8)	−2533 (10)	2170 (4)	4377 (2)	3·7 (2)
C(9)	−3556 (10)	2891 (4)	5297 (2)	3·7 (2)
C(10)	−4348 (11)	1891 (4)	6092 (3)	4·2 (2)
C(11)	−5392 (14)	2616 (5)	7007 (3)	5·3 (2)
C(12)	3820 (12)	3319 (5)	−541 (3)	4·7 (2)

Discussion. Final atomic coordinates and equivalent isotropic temperature factors are given in Table 1. The atom numbering scheme and bond distances and angles are presented in the *ORTEP* drawing of Fig. 2. The projection of the crystal structure viewed along **a** is shown in Fig. 3. The 1,4-quinone ring as well as the pentyl chain are each essentially planar: torsion angles C(1)–C(2)–C(3)–C(4) 0·0 (4), C(3)–C(4)–C(5)–C(6) −2·7 (4) and C(8)–C(9)–C(10)–C(11) 180·0 (4)°, the angle between the quinone ring and the aliphatic chain being 13·4 (4)°, calculated with *XANADU*.

Many 1,4-benzoquinone structures have been determined since the three-dimensional X-ray analysis of 1,4-benzoquinone itself was extensively described (Trotter, 1960). Owing to the *mmm* symmetry of the non-substituted 1,4-benzoquinone (BQ), the values of the four C_{sp^2}–C_{sp^2} single bonds, the two C=C and the C=O double bonds are equal. For the same reason there are only three different valence angles.* In the centrosymmetric molecule of 2,3,5,6-tetrahydroxy-1,4-benzoquinone (THQ), however, all quinone ring angles are approximately 120°, and the two different C–C distances are similar: 1·476 (5) and 1·480 (5) Å (Klug, 1965).

The loss of symmetry of 1,4-benzoquinones is observed as an effect of hydrogen bonding between different molecules, *e.g.* in the benzoquinone–hydroquinone complex (BQ–HQ); the C–C bonds of the benzoquinone being 1·447 (8) and 1·487 (8) Å (Sakurai, 1965). Another example is shown in the resorcinol–quinone complex (RBQ), the C–C bond lengths also being different in the quinone molecule: 1·468 (9) and 1·485 (9) Å (Ito, Minobe & Sakurai, 1970). Further examples of loss of symmetry are observed in 2,5-substituted benzoquinones with equal ligands as well as in benzoquinones with different ligands (Fig. 1). In 2,5-dimethyl-1,4-benzoquinone (2,5-DMBQ), the C–C bond lengths are 1·482 (2) and 1·502 (2) Å (Hirshfeld & Rabinovich, 1967). The 2,5-bis(aziridinyl)-1,4-benzoquinone (EBQ) exhibits stability of the quinone ring system because the crystal structures (measured at 300, 240 and 140 K) are essentially the same at different temperatures (Ito & Sakurai, 1973); the C–C bond lengths at 300 K being 1·448 (2) and 1·520 (5) Å, the C=C–C angles being 123·0 (3)° and 119·4 (3)°.* Asymmetric bond distances and angles of quinone rings are observed in primin (I) and other sensitizing 1,4-benzoquinones (Fig. 1) and agree with other differently substituted 1,4-benzoquinone derivatives.

The position for the hapten–protein coupling by Michael-type addition (Byck & Dawson, 1968) is assumed to be C(3) for primin. Remarkably, most of the 2,6-substituted 1,4-benzoquinones are sensitizers while a great number of 2,5-substituted 1,4-benzoquinones exhibit no or only weak sensitizing properties. The length of the aliphatic chain too is of importance for the allergenic power (Hjorth *et al.*, 1969). The average dimensions of the C_{sp^3}–C_{sp^3} distances and the corresponding angles of the pentyl chain are 1·523 (5) Å and 112·8 (3)°. These values are consistent with those observed in aliphatic chain structures measured at room temperature (Hospital, 1971; Hybl & Dorset, 1971; Sjöberg, Österberg & Söderquist, 1973).

Intermolecular distances were calculated up to 3·6 Å with *ORFFE* (Busing *et al.*, 1971). The shortest C···O distance observed is 3·33 (1) Å, O(4)···H(3) being 2·47 (1) Å, the C(3)–H(3)···O(4) angle being 156 (1)°.

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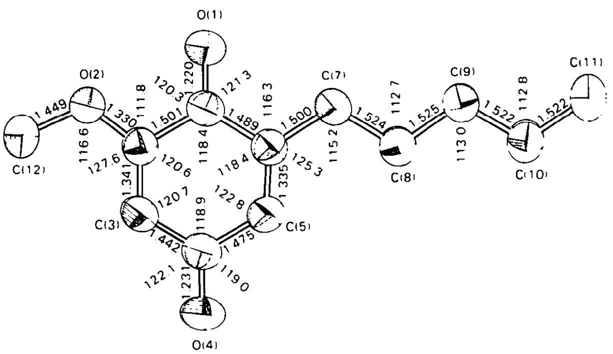

Fig. 2. *ORTEP* drawing of primin with bond distances (Å) and angles (°). The standard deviations range from 0·004 to 0·006 Å, for all bond angles 0·3°. C and O atoms are 65% probability ellipsoids.

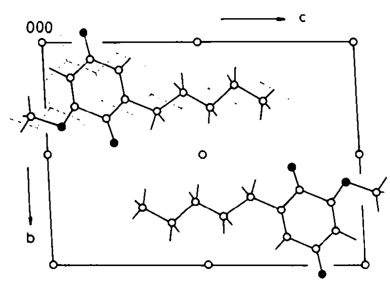

Fig. 3. *bc* projection of the crystal structure. Filled circles represent O atoms and open circles C atoms. The broken lines indicate the position of the *MULTAN* solution model.

* Lists of structure factors, anisotropic thermal parameters of the C and O atoms, bond lengths including H atoms, positional and isotropic thermal parameters of the H atoms and mean values of bond distances and angles of quinone structures cited in this paper have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39281 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of (*R*,*S*)-4-Methoxydalbergione,* $C_{16}H_{14}O_3$

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Abstract. $M_r = 254\cdot29$, monoclinic, $P2_1/n$, $a = 6\cdot701\,(1)$, $b = 38\cdot826\,(1)$, $c = 5\cdot365\,(1)$ Å, $\beta = 109\cdot56\,(1)°$, $V = 1315\cdot3\,(6)$ Å^3, $Z = 4$, $D_x = 1\cdot284$ Mg m^{-3}, Cu $K\alpha$ radiation, $\lambda = 1\cdot5418$ Å, $T = 296$ K, $F(000) = 536$, $\mu = 0\cdot728$ mm^{-1}, final $R = 0\cdot053$ for 1449 observed reflections. The quinone ring is almost planar with a maximum out-of-plane deviation of $-0\cdot031\,(3)$ Å for C(2). The average dimensions of the C_{sp^3}–C_{sp^2} distances and corresponding angles are 1·508 (4) Å and 112·5 (3)°; those for the quinone ring are C–C = 1·477 (4), C=C = 1·333 (4), C=O = 1·220 (4) Å, C–C–C = 118·2 (3), C=C–C = 120·9 (3) and O=C–C = 121·0 (3)°. The methylene distance is 1·279 (5) Å. The structure consists of discrete molecules; the shortest O···O and C···O contacts are 3·28 (1) and 3·41 (1) Å respectively.

* IUPAC name: (*R*,*S*)-2-methoxy-5-(1-phenylallyl)-1,4-benzoquinone.

Introduction. The group of dalbergiones as naturally occurring compounds in South American commercial timbers (*Dalbergia* sp.) has been discovered and their structures elucidated by spectroscopic methods. They represent a new class of 4-arylchroman-type quinones for which the name neoflavanoids has been suggested (Eyton, Ollis, Sutherland, Gottlieb, Taveira Magalhães & Jackman, 1965).

Cases of contact dermatitis due to Brazilian rosewood (*Dalbergia nigra* All.) have been reported since 1922 and to African blackwood (*Dalbergia melanoxylon* Guill. & Perr.) since 1924; important cases are summarized in the manual *Woods Injurious to Human Health* (Hausen, 1981). The sensitizing power of the dalbergiones from *Dalbergia* species has been established by Schulz, Garbe, Hausen & Simatupang (1979) and the following sequence of diminishing allergenic potency has been revealed: (*R*)-3,4-dimethoxydalbergione (*R*-3,4-DMD) > (*R*)-

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