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STUDIES IN SESQUITERPENES—LIV

OXIDOHIMACHALENE, A NOVEL SESQUITERPENOID FROM THE WOOD OF *CEDRUS DEODARA* LOUD†‡

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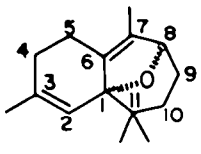
Abstract—Isolation and structure elucidation of oxidohimachalene, a minor constituent of the essential oil of *Cedrus deodara* Loud., is described. A biomimetic-type conversion of β-himachalene into oxidohimachalene employing photochemical hydroxylation or "copper peroxide" oxygenation is reported.

In continuation[1] of our investigations on the chemical composition of the essential oil from the wood of *Cedrus deodara* Loud., we describe the isolation of a novel β-himachalene-based ether, to which we assign the structure **1** and name it *oxidohimachalene*. The compound has been isolated from fractions[2] of the essential oil, immediately following himachalenes. With respect to β-himachalene (**2**) its GLC RRT is 3:1. (column: 180 × 0.6 cm, 5% diethyleneglycol polysuccinate on 60–80 mesh Chromosorb W; 140°) and RR_f is 0.37 (solvent: C_6H_6; 30°). It is present to the extent of ~0.1% in the essential oil. Structure **1** is based on spectroscopic data, biogenetic considerations, and key chemical transformations. A biomimetic-type synthesis from β-himachalene (**2**) has also been accomplished.



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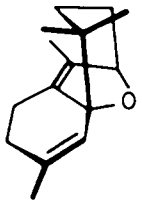

1a

Oxidohimachalene ($C_{15}H_{22}O$; M⁺, *m/e* 218) is clearly an ether from its IR spectrum, which displays no OH or C=O bands and, shows a number of strong absorptions in the 900–1050 cm⁻¹ region, where cyclic ethers (higher than oxirane) usually absorb.[3] Its PMR spectrum shows the following structural features: two $-\underset{|}{\overset{|}{C}}-Me$ (3H, s, 0.68 ppm; 3H, s, 1.09 ppm), two $-C=\underset{|}{C}-Me$ (3H, s, 1.68 ppm; 3H, d, 1.72 ppm, J = 1 Hz), $-\underset{|}{\overset{|}{C}}-O-\underset{|}{\overset{|}{C}}H$ (1H, unresolved m, 4.26 ppm, W_H = 6.5 Hz), $-C=\underset{|}{C}H-CH_2-$ (1H, unresolved m, 5.43 ppm, W_H = 5 Hz). From these structural features and its molecular formula, it is obvious that the new compound must be tricyclic—two carbocyclic rings and one ether ring.

The chemical shifts of the Me protons of the new ether are reminiscent of Me signals of β-himachalene (0.73, 0.97, 1.73, 1.73 ppm),[4] which is the major constituent of the *Cedrus deodara* essential oil and which could conceivably be the biogenetic precursor[5] of the new oxide. With this working hypothesis and noting (from PMR results) that one terminus of the ether bridge must be a quaternary C, and the only such position available on β-himachalene nucleus being C_1, one can write the partial structure **3**; conceivably, the other end of the oxide bridge can be any of the carbon atoms C_4, C_5, C_8, C_9 or C_{10}.

To gather evidence in favour (or against!) of the above working hypothesis and to possibly narrow down the alternatives inherent in **3**, the new ether was subjected to the action of Li in liquid NH_3, with the hope of reductive cleavage[6] of the ether terminus at C_1, which is allylic according to **3**. In practice, exposure of the oxide to Li in liquid NH_3 yielded a number of products in which a hydrocarbon (~15%) and an alcohol (~30%) predominated. From co-injection and PMR spectrum, the hydrocarbon was identified as β-himachalene. This observation not only confirms the part structure **3**, but also requires that the second terminus of the ether must also be allylic. Thus, structures with second terminus of the ether bridge at C_9 or C_{10} stand ruled out. The second major product of the Li-NH_3 reaction is an alcohol, m.p. 82–83°, $C_{15}H_{24}O$ (M⁺, *m/e* 220). IR: OH 3320, 1008 cm⁻¹. PMR: two $-\underset{|}{\overset{|}{C}}-Me$ (3H, s, 0.72 ppm; 3H, s, 1.00 ppm), two $-C=\underset{|}{C}-Me$ (6H, bs, 1.75 ppm), $HO\underset{|}{\overset{|}{C}}H-CH_2-$ (1H, t, 3.98 ppm, J = 8 Hz) $-C=CH-$ (1H, illresolved m, 5.35 ppm). From these characteristics and the co-formation of β-himachalene it is clear that this alcohol has β-himachalene base with a secondary OH function at C_4, C_5 or C_8, arising from the anticipated reductive cleavage of (one of the allylic C–O bond. From all this it is evident that the new ether is **1**, **4** or **5**.

Electron-impact-induced fragmentation of oxidohimachalene generates base peak at *m/e* 161 and this is best rationalised in terms of structure **1** (see **8**). Clear support for structure **1** was obtained as follows.

Though, from the above considerations, structure **1** appeared most plausible, it was felt that it would be desirable to obtain more concrete evidence for the methine-terminus of the ether bridge. This could be

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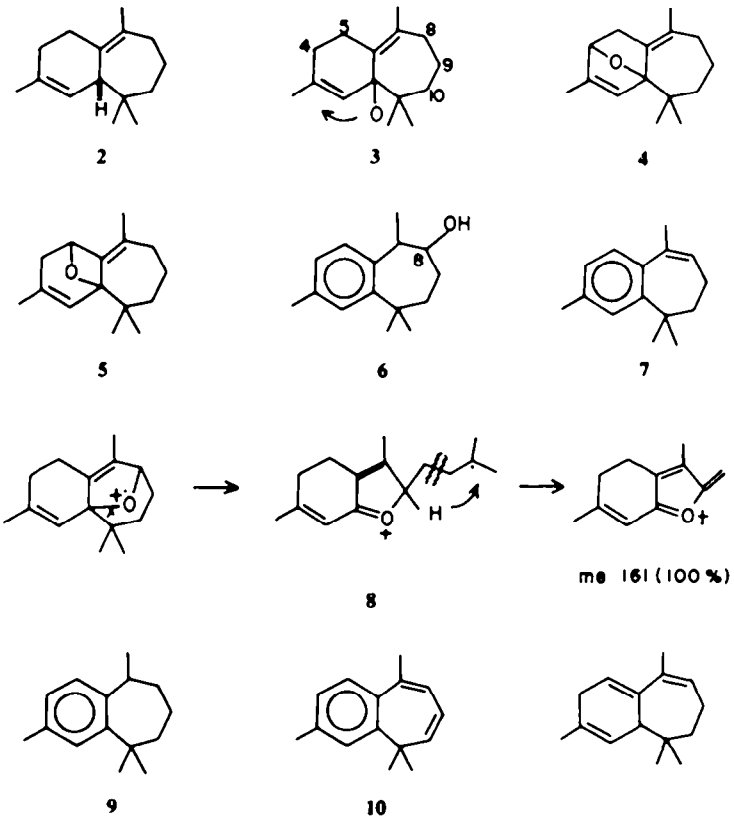


unexpectedly obtained as follows. While studying the hydrogenation of oxidohimachalene, it was found that over 5% Rh-C[a], the major product is an aromatic (IR: 1610, 1040 and 875 cm $^{-1}$. PMR: Ar-Me, 3H, s, 2.3 ppm; 2 Ar-H, A-B quartet, 6.97 ppm, J = 8 Hz; 1 Ar-H, s, 7.07 ppm) secondary alcohol (IR (liq): OH 3630, 3440, 1008 cm $^{-1}$. PMR: 1H, m, 3.42 ppm), which on the basis of previous considerations can *only* be **6**. This transformation is readily understood in terms of hydrogenolysis (**12a**) to **12b**, followed by isomerisation to **12c**, which is all-set for facile dehydrogenation to **6**.

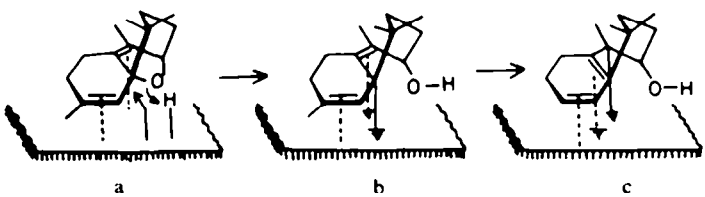
To further consolidate these results, alcohol **6** has been synthesised from β-himachalene. This was first converted to dehydro-*ar*-himachalene (**7**). The most efficient procedure involved the action of two molar equivalents of chloranil on β-himachalene, when **7** was formed in yields of 60–70%, other products obtained during this reaction were *ar*-himachalene (**9**; 15%)[8] and bis-dehydro-*ar*-himachalene (**10**; 12%).[9] This transformation (**2**→**7**) apparently proceeds via the triene **11**[8], as *ar*-himachalene failed to give significant quantities of **7**, on being exposed to chloranil in a variety of refluxing solvents (toluene, xylene, dioxane-t-BuOH[10]). Hydroboration of **7**, followed by oxidation yielded **6** identical (IR, PMR) with the product obtained from oxidohimachalene during attempted hydrogenation over Rh–C. This correlation, then, clearly settles the structure of oxidohimachalene as **1**. An examination of molecular models shows that structure **1** can have very few low-energy conformations and of these **1a** has least non-bonded interactions; conformation **1a** is consistent with the observed shielding of one of the geminal methyls in its PMR spectrum.

Conversion of β-himachalene into oxidohimachalene and its absolute stereochemistry

It is reasonable to assume that oxidohimachalene (**1**) arises from β-himachalene by some sort of biological allylic oxygenation.[11] Hence, it appeared of interest to subject β-himachalene to oxidation reagents with propensity for allylic attack. Of course, it is realised that selectivity would be poor as only species such as **13** are expected to lead to the ether-bridge formation.[12]

Metal ion-catalysed decomposition of organic peresters in the presence of olefinic substrates has been exploited for allylic substitution.[13] When β-himachalene was subjected to the action of t-butylperbenzoate in presence of cuprous bromide, oxidohimachalene (**1**) could be isolated in a yield of ~2%, based on unrecovered β-himachalene.

It was thought that "copper-peroxide"[14] might, like-



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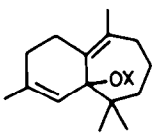

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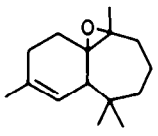

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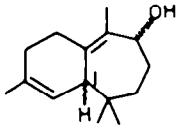

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wise, lead to some oxidohimachalene. Heating β-himachalene with copper peroxide yielded, besides unchanged himachalene (70%), an oxygenated product (30%), which was shown by programmed GLC (by co-injection) to contain ~8% oxidohimachalene (**1**) and ~16% mono-epoxide **14**. Similarly, action of Ag_2CO_3-celite[15] led to ~5% oxygenated product, containing (GLC) ~21% of **1** and ~19% of **14**.

Similar conversions were obtained by the action of 90% H_2O_2 in the presence of UV light. Hydrogen peroxide is known[16] to dissociate into hydroxyl radicals on irradiation with UV light. We have used such a system for the hydroxylation of cycloalkanes and alkenes.[17] When β-himachalene in EtOAc containing 90% H_2O_2 aq was irradiated, ~12% oxygenated products were formed. This material contained (GLC) oxidohimachalene (**1**) to the extent of ~13%. The required compound was isolated by column chromatography and identified (IR, PMR, Mass) as oxidohimachalene. This represents a yield of ~13%, based on unrecovered β-himachalene. The product is partly optically active, $[\alpha]_D$ +7.4 (natural product has $[\alpha]_D$ +20). This requires partial retention of configuration[18] during oxygenation and since, the sign of $[\alpha]_D$ is the same as that of natural oxidohimachalene, the absolute stereochemistry of (+)-oxidohimachalene should be as depicted in **1**, since the absolute stereochemistry of (+)-β-himachalene has been shown[19] to be **2**. This conclusion is in line with the Absolute Stereochemistry Biogenetic Rule,[3] as in biological hydroxylations the incoming OH is known[20] to have the same stereochemistry as the C–H bond substituted, and thus, (+)-β-himachalene (**2**) (accepting it as the immediate biological precursor of oxidohimachalene) should lead to **1**. The cleavage alcohol arising from Li-NH_3 reduction of oxidohimachalene, then, has structure **15**, with configuration at C_1, still undefined.

EXPERIMENTAL

For General Remarks, see Part LIII of the Series.

Isolation of oxidohimachalene

A rectification cut,[2] collected after β-himachalene, but still containing ~60% β-himachalene contains ~12% oxidohimachalene. This material, b.p. 113–123°/4.5 mm, n_D^{25} 1.5150, $[\alpha]_D$ +85, was subjected to perparative GLC (10 × 1 ml injections; 2.7 m × 2.5 cm column, packed with 20% diethyleneglycol polysuccinate on Chromosorb W, 60–80 mesh; 180°; N_2) to get 0.8 g of oxidohimachalene, besides β-himachalene (~4 g) and other cuts. The required compound was redistilled: b.p. 101–103°/2.5 mm, n_D^{30} 1.5101, $[\alpha]_D$ +20.7 ($CHCl_3$; c, 1.3%). IR (liq): 1460, 1390, 1370, 1178, 1130, 1058, 1020, 995, 975, 940, 918, 850, 830 cm^{-1}. Mass: *m/e* 218 (M^+, 80%), 161 (100%), 147 (20%), 133 (7%), 119 (13%), 105 (10%), 91 (12%), 79 (5%), 77 (7%), 69 (6%), 55 (4%). (Found: C, 82.30; H, 10.29. $C_{15}H_{22}O$ requires: C, 82.51; H, 10.16%).

Lithium–ammonia reduction of oxidohimachalene

Li (1.0 g), cut in small pieces, was added in lots to liq. NH_3 (60 ml) during 20 min, under stirring and anhyd conditions. After stirring for an additional 20 min period, the above oxide (0.4 g), dissolved in dry ether (7 ml + 3 ml + 3 ml) was added, dropwise (20 min), with stirring. After stirring for another 1 hr, solid NH_4Cl (0.5 g) was added and NH_3 allowed to evaporate. To the residue, water (35 ml) was added and the product taken up in ether (12 ml × 3). The combined extract was washed with H_2O (10 ml × 4), brine (10 ml × 2) and dried (Na_2SO_4). Solvent was stripped off to yield a product (364 mg), which partly solidified. This material on TLC (solvent: 7% EtOAc in C_6H_6) showed two major spots, besides some unchanged oxidohimachalene (relative to **1**, these products had R_f 0.79 and 1.33). These products were separated by inverted-dry-column-chromatography[21] (SiO_2-gel/IIB, 25 cm × 2.0 cm; solvent, 7% EtOAc in C_6H_6).

Product (100 mg) with *RR*$_f$ 1.33 was a hydrocarbon mixture, with β-himachalene (co-injection of authentic sample; PMR) as the major component (GLC).

Product (135 mg) with *RR*$_f$ 0.79 was crystallised from CH_3CN aq. to give colorless needles (82 mg) of **15**: m.p. 82–83°, $[\alpha]_D$ +32.0 ($CHCl_3$; c, 3.2%). IR (KBr): 3320, 1468, 1445, 1380, 1360, 1182, 1170, 1158, 1022, 1008, 980, 870, 850, 812 cm^{-1}. Mass: *m/e* 220 (M^+, 2%), 202 (100%), 187 (24%), 159 (56%), 146 (37%), 131 (46%), 121 (18%), 105 (30%), 91 (48%), 77 (33%), 55 (50%) (Found: C, 81.43; H, 11.06. $C_{15}H_{24}O$ requires: C, 81.76; H, 10.98%).

8-Hydroxy-ar-himachalene (**6**)

(i) *By synthesis from β-himachalene.* A mixture of β-hinachalene (20.4 g, 0.1 mole), chloranil (48.0 g) and dry toluene (150 ml) was refluxed (N_2) for 12 hr. The mixture was cooled, the hydroquinone (45 g) filtered off, washed with light petrol and, the combined filtrate and washings washed with 10% KOH aq (200 ml × 2), 5% H_2SO_4 aq (100 ml × 2), water and dried (Na_2SO_4). Solvent was flashed off and the residue distilled to furnish a pale yellow liquid (16.0 g), b.p. 100–105°/1.5 mm. GLC (3% Carbowax on Chromosorb W, 180 cm × 0.6 cm; 130°; 60 ml H_2/min) showed it to consist of *ar*-himachalene (RRT, 1.0; 15%), dehydro-*ar*-himachalene (RRT, 1.13; 72%) and bis-dehydro-*ar*-himachalene (RRT, 2.18; 13%). This mixture could be used as such for the next step.

Diborane ($NaBH_4$, 4.0 g; 20 ml BF_3-Et_2O; diglyme)[22] was slowly introduced (under slight N_2 pressure) into a soln of the above hydrocarbon mixture (15.0 g) in dry THF (30 ml) at room temp. (30°) under stirring during 1 hr. The mixture was next heated to 55–60° and 3N NaOH aq (75 ml) was added followed by 30% H_2O_2 aq (75 ml) introduced dropwise (30 min) with stirring, while maintaining the temp. at 55–60°. After stirring for an additional 1 hr, the mixture was cooled, the product taken up in ether (150 ml × 3). The combined extract was washed with 2N HCl aq (150 ml × 1), water, dried and freed of solvent. The product (14.0 g) was chromatographed over SiO_2-gel/IIB (80 × 3.5 cm) with TLC monitoring (solvent: 5% EtOAc in C_6H_6), using C_6H_6 and C_6H_6 containing increasing amounts of EtOAc as eluant. 5% EtOAc in C_6H_6 (200 ml × 3) eluted 8.0 g of the required product (**6**): m.p. 80–81° (CH_3CN); λ_{max}^{EtOH} (ε): 219 (6677), 260 (sh, 251), 268 (362) and 276.5 nm (347). IR (Nujol): 3330, 1610, 1460, 1420, 1375, 1358, 1332, 1300, 1250, 1210, 1172, 1120, 1072, 1040, 1010, 920, 890, 880, 845, 814 cm^{-1}. PMR (CCl_4): two $-\underset{|}{C}-\underline{Me}$ (3H, s, 1.34 ppm; 3H, s, 1.42 ppm), $-\underset{|}{C}H-\underline{Me}$ (3H, d, 1.40, J = 7 Hz), Ar $\underline{Me}$ (3H, s, 2.3 ppm), Ar $\underline{C}H$-Me (1H, m, 3.2 ppm), $\underset{|}{C}H\underline{O}H$ (1H, m, 3.42 ppm), 2 Ar-H (2H, AB/q, 6.97 ppm, J = 8 Hz), 1 Ar-H (1H, s, 7.07 ppm). Mass: *m/e* 218 (M^+, 100%), 187 (33%), 161 (43%), 157 (59%), 149 (66%), 145 (49%), 131 (39%), 128 (36%), 119 (43%), 105 (30%), 91 (26%). (Found: C, 82.77; H, 9.75. $C_{15}H_{22}O$ requires: C, 82.51; H, 10.16%).

(ii) *By hydrogenolysis of oxidohimachalene.* Oxidohimachalene

(18 mg) in EtOH (4 ml) was shaken over prereduced 5% Rh–C (60 mg) at room temp. (30°) and pressure (745 mm) in presence of H_2. There was practically no absorption of H_2 during 2 hr. Usual work-up gave a product (15 mg), which was chromatographed over 10% $AgNO_3$–silica gel (80 × 4 mm) using C_6H_6 and, C_6H_6 containing increasing proportions of EtOAc as eluant. 2% EtOAc in C_6H_6 eluted a gum (8 mg), identified (IR, PMR) as **6**.

Oxygenation of β-himachalene

(i) *With t-butyl perbenzoate.* A mixture of β-himachalene (5.7 g) and CuBr (1.0 g) was maintained at 85–90° (N_2) and t-butyl perbenzoate (5.2 g) was added (30 min) under stirring. The blue mixture was stirred at that temp. for an additional 2 hr period, when practically all per ester had disappeared (IR: disappearance of 1775 cm^{-1} absorption). The mixture was cooled (25°), diluted with EtOAc (100 ml), washed with 10% $NaHCO_3$ aq (50 ml × 4), water and dried. Solvent was flashed off and the residue passed through a column of silica gel/IIA (75 × 3 cm). Light petrol (1000 ml) eluted hydrocarbon (4.3 g, essentially β-himachalene), while EtOAc (1000 ml) yielded a polar cut (1.7 g). The polar fraction was saponified (10% KOH–MeOH, 50 ml; reflux, 8 hr, N_2) and the product (0.78 g) chromatographed on 10% $AgNO_3$–SiO_2 gel (75 × 1.5 cm) with TLC monitoring (solvent: C_6H_6) of the fractions obtained with light petrol and, light petrol containing increasing quantities of C_6H_6 (5–50%). 20% C_6H_6 in light petrol (80 ml × 2) eluted 30 mg of a liquid, identified (IR, PMR, Mass) as oxidohimachalene.

(ii) *With "copper peroxide".* To a cooled (−10°) soln of $Cu(NO_3)_2 \cdot 3H_2O$ (2.0 g) in MeOH (20 ml) was added dropwise an ether soln of H_2O_2 (50 ml, 30% H_2O_2 aq extracted successively with ether, 20 ml × 3) under stirring and cooling. The brown ppt was filtered and washed successively with dry MeOH (100 ml) and dry ether (100 ml). The ppt was dried *in vacuo* at room temp. for 15 min, yield 0.5 g (*Caution*: dry reagent may explode on heating!)

β-Himachalene (1.4 g) was stirred with the above reagent (0.3 g) at 80° for 12 hr (N_2). The mixture was cooled and worked up with ether and separated on a SiO_2-gel column into hydrocarbon (1.0 g) and oxygenated cuts (0.5 g), as above. Programmed GLC (column: 300 × 0.6 cm, 5% DEG polysuccinate on 60–80 mesh Chromosorb W; 150–200°, 6°/min; 90 ml H_2/min) of the oxygenated material showed at least 20 components, in which **1** and **14** were major and were identified by co-injection technique.

(iii) *With Ag_2CO_3–celite.* Freshly prepared[14] Ag_2CO_3–celite (7.5 g), C_6H_6 (100 ml) suspension was distilled to collect 50 ml of C_6H_6 (and some water), cooled, β-himachalene (2.04 g) added and the whole refluxed (24 hr, N_2). The reaction mixture was cooled, filtered to remove the catalyst and the filtrate freed of solvent. The residue was processed as above.

(iv) *With 90% H_2O_2 and light.* To β-himachalene (102 g), a soln of 90% H_2O_2 aq (20 ml) in EtOAc (300 ml) was added and the clear soln irradiated with a 250-W Hanovia high pressure Hg vapour lamp in an immersion-type water-cooled set-up; the immersion well was of clear quartz and a Corex filter sleeve was used. A steady, minute flow of N_2 (O_2-free!) was maintained through the soln. After all the H_2O_2 had been consumed (30 hr), the reaction mixture was washed with 10% $NaHCO_3$ aq (300 ml × 3), water and dried. The solvent was removed and the residue passed through a column of Al_2O_3/III (Brockmann) (90 × 6 cm). Light petrol (1000 ml × 5) eluted unchanged himachalene (88 g), while EtOAc (1000 ml × 5) eluted a polar cut (5.8 g), b.p. 100–120°/1.5 mm.

The above polar product (12 g) was chromatographed over SiO_2-gel/IIB (100 × 6 cm), using C_6H_6 and, C_6H_6 containing increasing quantities of EtOAc (10–20%) as eluant. After the first C_6H_6 cuts (150 ml × 14), the later fractions with the same solvent (150 ml × 18) gave a product (2.7 g) rich in the required oxide. EtOAc containing fractions yield a complex mixture of alcohols, which was not examined further. The oxide-rich cut was purified further by chromatography over 10% $AgNO_3$–SiO_2-gel (110 × 3 cm) to furnish the required oxide (1.2 g): b.p. 120–125° (bath)/2.5, $[\alpha]_D$ + 7.44 ($CHCl_3$; *c*, 0.43%). (Found: C, 82.02; H, 10.10. $C_{15}H_{22}O$ requires: C, 82.51; H, 10.16%).

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