The x-ray spectral experiment was performed on Syntex $P2_1$ automatic four-circle diffractometer (λMoK_α, graphite monochromator, $\theta/2\theta$ scanning, $2\theta \leq 50°C$). The crystals were monoclinic, a = 9.206 (3), b = 7.987 (2), c = 19.487 (7) Å, β = 97.89°, d_{calc} = 1.23 g/cm³, Z = 4 ($C_{15}H_{22}NO_3$), sp. gr. $P2_1$.

In the calculations we used 2362 reflections with $I \geq 2\sigma$. The structure was interpreted by the direct method using the MULTAN-78 program [6] and was refined by the full-matrix MLS in the anisotropic approximation for nonhydrogen atoms by the SHELX-76 program [7]. The H atoms were assigned geometrically. All the calculations were performed on an ES-1022 computer. The final divergence factors were R = 0.081 and R_w = 0.092. The coordiantes of the non-hydrogen atoms are given in Table 3.

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SYNTHESIS OF BICYCLOHOMOFARNESANE DERIVATIVES FROM BIS(8α,13-EPOXY-14,15-BISNORLABD-12-EN-12-YL)METHANE — A PRODUCT OF THE OZONOLYSIS OF SCLAREOL

A. N. Aryku, M. N. Koltsa, P. F. Vlad, O. S. Kukovinets, V. N. Odinokov, and G. A. Tolstikov

UDC 547.659.1 728:542.943.5 951.92 942.6 953.2:543.422

A seven-stage method of obtaining a new odoriferous product with a strong amber odor analogous to ambroxide from sclareol has been developed. It includes odoriferous oxide compounds of the tetrahydrofuran series: (VIII), (IX), (XIII), and (XIV). The key stages in the synthesis of this product are the ozonolytic cleavage of sclareol with the formation of bis(8α,13-epoxy-14,15-bisnorlabd-12-en-12-yl)methane (II), its ozonolysis to bis(8α-acetyl-12-oxo-13,14,15,16-tetranorlabdan-12-yl)methane (III), and the alkaline cleavage of the latter.

Previously, in the investigation of the ozonolysis of sclareol (I) we [1] established that when the reaction was performed in methanol and the ozonolysis product was treated with anhydrous ammonium chloride an 80% yield was obtained of bis(8α,13-epoxy-14,15-bisnorlabd-12-en-12-yl)methane (II)

Institute of Chemistry, Academy of Sciences of the Moldavian SSR, Kishenev. Institute of Chemistry, Bashkir Scientific Center, Urals Branch, Academy of Sciences of the USSR, Ufa.

Translated from Khimiya Prirodnykh Soedinenii, No. 3, pp. 343-349, May-June, 1991. Original article submitted June 5, 1990.

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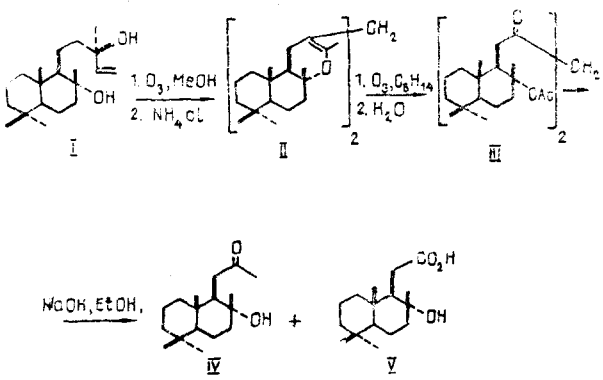
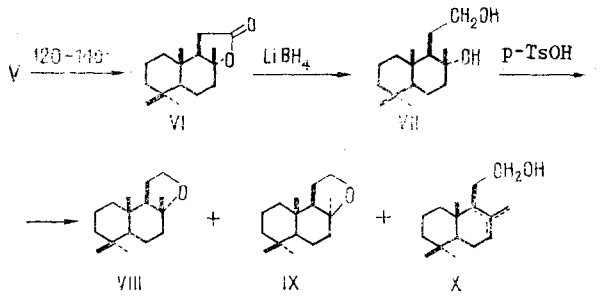


In the present communication we give information on the transformation of the dimer (II) into a mixture of homo- and bishomobicyclofarnesane compounds and describe the synthesis of an odoriferous product with a strong amber smell analogous to the well-known ambroxide (ambrox) [2].

When the dimer (II) was ozonized in hexane and the resulting ozonide was then decomposed in the presence of water, the unstable bis(8α-acetoxy-12-oxo-13,14,15,16-tetranorlabdan-12-yl)methane (III) was formed in quantitative yield but could not be purified either chromatographically or by recrystallization because of its rapid decomposition, and it was used in the following stage as such. It was characterized only spectrally. According to IR and PMR spectra, its molecule contained acetate and keto groups.

On cleavage with alcoholic alkali, the β-diketone (III) gave a product containing approximately equal amounts of neutral and acid fractions, each of which consisted of a practically individual compound – 8α-hydroxy-14,15,16-trinorlabdan-12-one (IV) [3] and 8α-hydroxy-13,14,15,16-tetranorlabdan-12-oic acid (V) [4], respectively. The latter, as is well known, is the starting material in the synthesis of ambroxide. For this purpose, it was converted by heating into norambreinolide (VI) [4, 5], which is reduced with lithium tetrahydroborate to dicyclohomofarnesane-8α,12-diol (VII) [6, 7], and this, on vacuum distillation in the presence of p-toluenesulfonic acid [8, 9], gives ambroxide, the composition of which includes compounds (VIII-X) [9].

In the light of the scheme given above, with the aim of developing a method for synthesizing an analogue of ambroxide from the diketone (III), we first investigated both the products of the reduction of the hydroxy ketone (IV) and also the products of the dehydration of the glycols formed in this process



The reduction of the hydroxy ketone (IV) by lithium tetrahydroborate obtained in situ [6], which is used in the production of ambroxide [7], led to a mixture of two crystalline substances with mp 146-147°C (the less polar) and 124.5-125.5°C (the more polar) which possessed fairly close chromatographic properties but were separated by careful chromatography on a column of silica gel. These compounds had the same composition ($C_{16}H_{30}O_2$) and similar IR and PMR spectra. According to the latter, each of their molecules contained two hydroxy groups – a secondary and a tertiary, three methyl groups at quaternary carbon atoms, a methyl group at a completely substituted carbon atom bearing a tertiary hydroxy group, and a methyl group on a carbon atom bearing a secondary hydroxy group. These facts showed that the substances under investigation were the 14,15,16-trinor-labdane-8α,12-diols (XI) and (XII) epimeric at $C_{(12)}$. We did not determine the configurations of these glycols at $C_{(12)}$ since during the performance of this work a publication by Ohloff et al. [10] appeared in which

a number of the substances which we had obtained were described, including the diasteromeric diols (XI) and (XII), and their configurations at the above-mentioned center were established. On comparing the physical and spectral characteristics of the glycols that we had synthesized with those given in [10] we came to the conclusion that the glycol (XI) with mp 146-147°C possessed the 12R configuration and the glycol (XII) with mp 124.5-125.5°C the 12S configuration. It must, however, be mentioned that in [10] there is no information on the method of establishing the configurations of these glycols.

When the glycol (XI) was dehydrated with p-toluenesulfonic acid under the conditions given in [8] that are used for the production of ambroxide [9], in the main, a single product was formed with a small amount of another. The predominating substance, which had a strong amber smell, was isolated in the individual state by chromatographing the reaction product on a column of silica gel impregnated with silver nitrate (SGSN). In its IR spectrum there were the three intense maxima in the 900-1100 cm^{-1} region that are characteristic for a THF ring. The PMR spectrum showed singlet signals of four methyl groups at quaternary carbon atoms, the doublet of a methyl group at a secondary carbon atom linked to an oxygen atom, and a multiplet signal of a single proton at the same carbon atom. These facts, in the light of the results of elementary analysis, agreed with structure (XIII) for the substance under investigation. Its properties coincided with those for (12S)-8α,12-epoxy-14,15,16-trinorlabdane (XIII) given by Ohloff et al. [10]. The impurity was, judging from TLC results, the epimer (XIV) of the oxide (XIII).

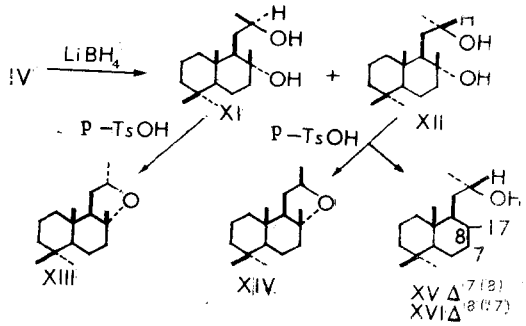
The dehydration of glycol (XII) under the same conditions led to an odoriferous product (with a yield of 88%), which was separated by chromatography on a column with SGSN. The least polar component of the dehydration product, eluted from the column first, proved to be an oxide compound. Its IR spectrum contained the maxima characteristic for a THF ring, while in the PMR spectrum there were the signals of four methyl groups at quaternary atoms and of a methyl group and one proton at a secondary carbon atom linked to an oxide oxygen. These spectra and the results of elementary analysis showed that the substance under investigation possessed the same structure as the oxide (XIII) and was its epimer at $C_{(12)}$. Its constants agreed with those of (12R)-8α,12-epoxy-14,15,16- trinorlabdane (XIV) given by Ohloff et al. [10].

In addition to the oxide (XIV), two other products of the dehydration of the glycol (XII) were eluted from the column. The IR spectrum of the first of them contained maxima characteristic for a trisubstituted double bond and a secondary hydroxy group, while its PMR spectrum contained the signals of three methyl groups at quaternary carbon atoms, of one double bond, and of one at a secondary carbon atom at which a hydroxy group was present, and also of one vinyl proton. It follows from the facts given that the substance was (12S)-14,15,16-trinorlabd-7-en-12-ol (XV). Judging from spectral characteristics, the second product was an isomer of the alcohol (XV) with a semicyclic double bond – (12S)-14,15,16-trinorlabd-8(17)-en-12-ols (XVI).

Thus, the dehydration of glycol (XII) took place less umambiguously than that of glycol (XI), and the yield of the oxide (XIV) was smaller than that of its epimer (XIII). The reason for this is the destabilizing action exerted by the mutual repulsion of the methyl groups at $C_{(8)}$ and $C_{(12)}$ in the oxide (XIV), which are present in the cis position on the β-side of the molecule.

Ohloff et al. [10] performed the dehydration of glycols (XI) and (XII) with mesyl chloride in pyridine and, as they considered, it took place with the reversal of the configuration at $C_{(12)}$. However, the dehydration of the glycols takes place in the same way under the action of p-toluenesulfonic acid (as mentioned above, on the dehydration of the glycol (XI) only traces of the oxide (XIV) were formed and the dehydration of the diol (XII) led to the oxide (XIV) and the alcohols (XV) and (XVI)). This is difficult to explain, since according to [11], on the dehydration of 1,4-secondary-tertiary glycols with p-toluenesulfonic acid the splitting out of the tertiary hydroxy group followed by attack of the carbocation formed by the secondary hydroxy group, with the retention of the configuration, should take place. (See scheme on following page.)

In view of the results obtained above and the existing method of producing ambroxide [7, 9], we performed the synthesis of an ambroxide analogue from the β-diketone (III) by the following scheme: this compound was subjected to alkaline cleavage and the product was heated at 135-140°C for 2 h in order to lactonize the hydroxy acid (V), the product was reduced with lithium tetrahydroborate obtained in situ from potassium tetrahydroborate and



lithium chloride, and the mixture of glycols so obtained was dehydrated by vacuum distillation in the presence of p-toluenesulfonic acid. The reaction product possessed a strong amber odor due to the presence of the oxides (VIII), (IX), (XIII), and (XIV), the amounts of which were, respectively, 31, 3, 18, and 16% of its weight or, taken together, 68%. We may note, in conclusion, that the yield of the ambroxide analog amounted to 48%, calculated on the sclareol (I), while the yield of ambroxide is only 30% [7, 9].

EXPERIMENTAL

Melting points were determined on a Boëtius instrument. Specific rotations were measured on a Polamat S polarimeter in chloroform. IR spectra were taken on a Specord 71 IR instrument in CCl_4. PMR spectra were recorded on a Tesla BS-467 spectrometer (60 MHz) in CCl_4 with TMS as internal standard. Solutions of the substances in organic solvents were dried with anhydrous sodium sulfate. The petroleum ether used had bp 40-70°c. For columns we used silica gels L40/100 and 100/160 μ (Czechoslovakia) and silica gel impregnated with silver nitrate (SGSN) prepared as in [12]. For TLC we used silica gel plates prepared by ourselves that had been kept for a week at room temeprature the spots on which were revealed by spraying with concentrated sulfuric acid and heating in the flame of a gas burner, and also Silufol plates (Czechoslovakia), on which the spots were revealed in iodine vapor. The plates coated with silver-nitrate-impregnated silica gel were prepared by the method of Gupta and Dev [13], and were visualized by spraying with a 4% solution of potassium permanganate.

GLC analysis was performed on a Chrom-5 chromatogram with a flame-ionization detector using a 3 mm × 3.5 m glass column and the solid support Chromatom N-AW-HMDS, 0.16-0.20 mm, impregnated with 5% of the stationary phase XE-60 with a column temperature programmed from 160 to 200°C at the rate of 3 degrees/min, the carrier gas being helium at a rate of flow of 45 ml/min.

Ozonolysis of the Dimer (II). At −65 to −70°C, a mixture of ozone and oxygen was passed for 1.5 h (the productivity of the ozonizer being 4 mmole of O_3/h) through a solution of 2.7 g (5 mmole) of the dimer (II) obtained by the method of [1] in 150 ml of hexane until ozone appeared in the gas at the outlet from the reaction flask. The reaction mixture was purged with nitrogen and was kept at room temperature for 1 h, and then 50 ml of water was added and the mixture was heated at 70°C for 1 h. The hexane layer was separated off, dried, and filtered, and the solvent was distilled off. This gave 2.9 g of a reaction product containing, according to TLC, mainly the diketone (III) and consisting of a viscous glassy mass that decomposed rapidly on being dissolved in organic solvents or on chromatography. IR spectrum, cm^{-1}: 1250, 1728, 3480 (band) (acetate and diketone groups). PMR spectrum ($CDCl_3$; ppm); 6-H singlets at 0.71, 0.78, 0.81, and 1.13 (methyl groups at quaternary carbon atoms) and 2.18 (OAc). The product was used in the following stage without purification.

Alkaline Cleavage of the Diketone (III). The dimer obtained above was dissolved in 26 ml of a 10% solution of cautic potash in ethanol, and the solution was boiled under reflux for 1 h. The ethanol was distilled off, and the residue was treated with water and extracted with ether. The aqueous layer was acidified with 10% sulfuric acid and extracted with ether, the extract was washed with water to neutrality and was dried, and the ether was distilled off. This gave 1.29 g (yield 48%) of the hydroxy acid (V), mp 123.5-125.5°C (from a mixture of diethyl ether and petroleum ether), identical with an authentic sample.

The ethereal layer was washed with 10% sulfuric acid and with water to neutrality and was dried, and the ether was distilled off. The crystalline residue (the hydroxy ketone (IV) (1.24 g, 46% yield)) was recrystallized from petroleum ether: mp 65-66°C. It was identified by comparison with an authentic sample that we had obtained earlier [3].

(12R)- and (12S)-14,15,16-Trinorlabdane-8α,12-diols (XI) and (XII). The solution of 0.74 g (13.6 mmole) of potassium tetrahydroborate in 15 ml of isopropanol was treated with 0.82 g (13.6 mmole) of crystalline lithium chloride monohydrate. The mixture was stirred at room temperature for 1 h, and then a solution of 1.21 g (4.54 mmole) of the hydroxy ketone (IV) in 15 ml of isopropanol was added to it. The resulting reaction mixture was stirred at room temperature for 1 h and at 60°C for 2 h. The isopropanol was distilled off in a current of nitrogen, the residue was treated with water, and the mixture was acidified with 10% hydrochloric acid (5 ml) and was extracted with toluene (20 ml). The toluene layer was separated off, washed with water to neutrality, dried, filtered, and evaporated in vacuum. The residue (1.1 g), which gave two spots on TLC, was chromatographed on a column containing 48 g of silica gel L 100/160 μ deactivated by the addition of 10% of water.

Petroleum ether–diethyl ether (4:1) eluted from the column 573 mg (52.1%) of (12R)-14,15,16-trinorlabdane-8α,12-diol (XI), mp 146-147°C (from petroleum ether), $[\alpha]_D^{23}$ − 10.5° (c 0.77; CH_3OH). IR spectrum, cm^{-1}: 1380, 1390 [$C(CH_3)_2$], 1120, 3300 (band) (OH groups). PMR spectrum, ppm: 0.75 (3H, s, 10-CH_3), 0.78 (3H, s) and 0.88 (3H, s) [4-$(CH_3)_2$], 1.11 (3H, s, 8-CH_3); 1.13 (3H, d, J = 6 Hz, 12-CH_3); 3.56 (1H, m, 12-H); 4.93 (2H, s, OH groups). Found, %: C 75.97; H 12.07%. $C_{17}H_{32}O_2$. Calculated, %: C 76.10; H 11.90. According to the literature [10]: mp 147°C, $[\alpha]_D^{20}$ − 10.2°.

A mixture of the same solvents eluted from the column 526 mg (47.8%) of (12S)-14,15,16-trinorlabdane-8α,12-diol (XII), mp. 124.5-125.5°C (from petroleum ether), $[\alpha]_D^{23}$ + 16.1° (c 0.66; CH_3OH). IR spectrum, cm^{-1}: 1375, 1390 [$C(CH_3)_2$]; 1085, 1120, 3300 (band) (OH groups). PMR spectrum, ppm: 0.76 (3H, s, 10-CH_3); 0.80 (3H, s) and 0.90 (3H, s) [4-$(CH_3)_2$]; 1.10 (3H, d, J = 6 Hz, 12-CH_3); 1.16 (3H, s, 8-CH_3); 4.06 (1H, m, 12-H); 4.92 (2H, c, OH groups. Found, %: C 75.82; H 11.86. $C_{17}H_{32}O_2$. Calculated, %: C 76.10; H 11.90. According to the literature [10]: mp 125°C, $[\alpha]_D^{20}$ + 13.7° ($CHCl_3$).

Dehydration of the Diol (XI). A mixture of 0.65 g (2.4 mmole) of the diol (XI) and 0.052 g (0.29 mmole) of p-toluenesolfonic acid was heated in vacuum to 135°C and was distilled at 130-138°C (5 mm Hg). This gave 0.54 g of a product which was chromatographed on a column containing 26 g of SGSN. Petroleum ether eluted from the column 540 mg (89% yield) of (12S)-8α,12-epoxy-14,15,16-trinorlabdane (XIII), mp 38-39°C (from petroleum ether); $[\alpha]_D^{23}$ − 11° (c 2.21). IR spectrum, cm^{-1}: 1385, 1390 [$C(CH_3)_2$]; 905, 950, 1015, 1125 (THF ring). PMR spectrum 0.81 (6H, s, 4β- and 10-CH_3); 0.88 (3H, s, 4α-CH_3), 1.05 (3H, s, 8-CH_3); 1.10 (3H, d, J = 6.5 Hz, 12-CH_3), 4.06 (1H, m, 12-H). Found, %: C 81.78; H 12.14%. $C_{17}H_{30}O$. C 81.60; H 12.00%. According to the literature [10]: mp 39°C, $[\alpha]_D^{20}$ − 11.5°.

Then the same solvent eluted from the column a small amount of a substance (which was not investigated further) identical, according to TLC on silica gel, with the oxide (XIV).

Dehydration of the Diol (XII). A mixture of 0.6 g (2.23 mmole) of the diol (XII) and 0.048 g (0.27 mmole) of p-toluenesulfonic acid was heated to 135°C, the product was distilled off at 130-138°C (5 mm Hg), and the distillate (0.49 g) was chromatographed on a column containing 25 g of SGSN. Petroleum ether eluted 330 mg (59%) of (12R)-8α,12-epoxy-14,15,16-trinorlabdane (XIV), mp. 59-60°C (from petroleum ether): $[\alpha]_D^{24}$ − 32° (c 2.6). IR spectrum, cm^{-1}: 1385, 1390 [$C(CH_3)_2$] 901, 990, 1015, 1120 (THF ring). PMR spectrum, ppm: 0.81 (6H, s, 4β- and 10-CH_3); 0.86 (3H, s, 4α-CH_3), 1.06 (3H, s, 8-CH_3), 1.2 (3H, d, J = 6.5 Hz, 12-CH_3); 4.00 (1H, m, 12-H). Found, %: C 81.59; H 12.32. $C_{71}H_{30}O$. Calculated, %: C 81.60; H 12.00.

The same solvent then eluted from the column 66 mg (11.8% yield) of (12S)-14,15,16-trinorlabd-7-en-12-ol (XV), mp 116-117°C (from acetonitrile); $[\alpha]_D^{23}$ + 12.6° (c 0.97). IR spectrum, cm^{-1}: 1375, 1380 ([$C(CH_3)_2$], 830, 1670 (tetrasubstituted double bond); 1120, 3450, 3600 (OH). PMR spectrum, ppm: 0.73 (3H, s, 10-CH_3); 0.88, 6H, s, [4-$(CH_3)_2$], 1.16 (3H, d, J = 6 Hz, 12-CH_3); 1.63 (3H, s, 8-CH_3); 3.85 (1H, m, 12-H), 5.45 (1H, m, 7-H). Found %: C 81.59; H 12.32. $C_{17}H_{30}O$. Calculated, %: C 81.60; H 12.00.

The same solvent then eluted from the column 96 mg (17.1% yield) of (12S)-14,15,16-trinorlabd-8(17)-en-12-ol (XVI), mp 82-83°C (from acetonitrile), $[\alpha]_D^{24}$ + 12.2° (c 1.08). IR spectrum, cm^{-1}: 1375, 1385 [$C(CH_3)_2$]; 890, 1640, 3080 (semicyclic double bond); 1120, 3450 (band), 3600 (OH). PMR spectrum, ppm: 0.66 (3H, s, 10-CH_3); 0.81 (3H, s) and 0.90 (3H, s) [4-$(CH_3)_2$], 1.15 (3H, d, J = 7 Hz, 12-CH_3), 3.75 (1H, m, 12-H), 4.41 (1H, s) and 4.83 (1H, s) (> $C=CH_2$). Found, %: C 81.56; H 12.02. Calculated, %: C 81.60; H 12.00.

Synthesis from Sclareol (I) of a New Odoriferous Product Analogous to Ambroxide. Sclareol (I) (4 g) was ozonized by the method of [1], giving 2.72 g (80%) of dimer (II), mp 190-191°C. It was ozonized as described above, and 2.9 g of the diketone (III) was isolated and was then subjected to alkaline cleavage by boiling with 26 ml of 10% caustic potash solution (see above). The reaction product (2.7 g) was heated at 120-130°C for 2 h [5], and the residue (2.68 g) was reduced with lithium tetrahydroborate obtained from 1.23 g of potassium tetrahydroborate and 1.4 g of lithium chloride monohydrate in 27 ml of isopropanol as reported in [6, 7]. The reaction product (2.35 g) was heated and distilled, as described for the dehydration of the diol (VII), in the presence of 0.2 g of p-toluenesulfonic acid [9], giving 2.15 g of an odoriferous product with an amber smell analogous to ambroxide, which, according to GLC, included: ambroxide (VIII) (31%), isoambroxide (IX) (3%), the oxides (XIII) (18%) and (XIV) (16%), and a mixture of bicyclohomofarnesols (X) and of bicyclobishomofarnesols (XV) and (XVI) (32%).

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