Ozonation of the Enol Acetate (VI). A mixture of ozone and oxygen was passed at −65 to −70°C through a solution of 170 mg of the enol acetate in 17 ml of ethyl acetate and 0.85 ml of pyridine until ozone appeared at the outlet of the reaction flask (25 min). The excess of ozone was eliminated by passing dry gaseous nitrogen through the solution, which was then poured into 30 ml of a 1% solution of NaOH and extracted with diethyl ether. The ethereal extract was washed with water, dried with anhydrous Na_2SO_4, and filtered, and the ether was distilled off. This gave 30 mg of a neutral fraction consisting of the enol acetate (VI).

The aqueous solution was acidified with 10% H_2SO_4 solution and extracted with diethyl ether. The ethyl extract was washed with water, dried, and filtered, and the ether was distilled off. This gave 125 mg of 8α-acetoxydriman-11-oic acid (VII), mp 144-145°C (from petroleum ether) $[\alpha]_D^{20}$ -39.74° (c 2.72). IR spectrum (cm^{-1}): 1240, 1720 (OAc), 1700 (>C=O), 2400-3550 (—C—OH), 1370, 1385 [$C(CH_3)_2$]. PMR spectrum (ppm): 0.75 (3H, s, CH_3-10), 0.82 (3H, s, CH_3-10), 0.82 (3H, s, CH_3-4), 1.08 (3H, s, CH_3-4), 1.6 (3H, s, CH_3-8), 1.82 (3H, s, $CH_3-\underset{|}{C}=O$), 10.35 (1H, s, CO_2H). Found %: C 68.82; H 9.92. $C_{17}H_{28}O_4$. Calculated %: C 68.88; H 9.52.

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INVESTIGATION OF THE PRODUCTS OF THE OZONOLYSIS OF SCLAREOL AND THE PATHWAYS FOR THEIR FORMATION

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It has been established that the main products of the ozonolysis of sclareol (I) under various conditions are "sclareol oxide" (III), 8α-hydroxy-14,15-bisnorlabdan-13-ome (IV), and the new compound (13R,14R)-14-hydroperoxy-13,14-epoxy-14-norlabdan-8α-ol (X), and structure of which has been shown on the basis of its transformations. The acid fraction of the ozonation products, the yield of which was low (<8%) included two compounds: sclareolic acid (85%) and 18α-hydroxy-14,15,16-trisnorlabdan-13-oic acid (3%). The mechanism for the formation of the above-mentioned compounds is discussed.

Continuing a series of studies on the products of the ozonolysis of readily available labdane diterpenoids, in the present communication, we give the results of an investigation of the ozonization of the labdanoid sclareol (I), which is of practical importance.

It must be mentioned that little attention has been devoted to the ozonization of sclareol. Janot [1] ozonized sclareol in carbon tetrachloride and decomposed the ozonide by heating with water, but the reaction products remained unidentified. When the reaction was performed in methanol and the reaction product was treated with ammonium chloride, Odinokov et al. [2] obtained an oxide compound of dimeric structure (II) with a yield of 80%.

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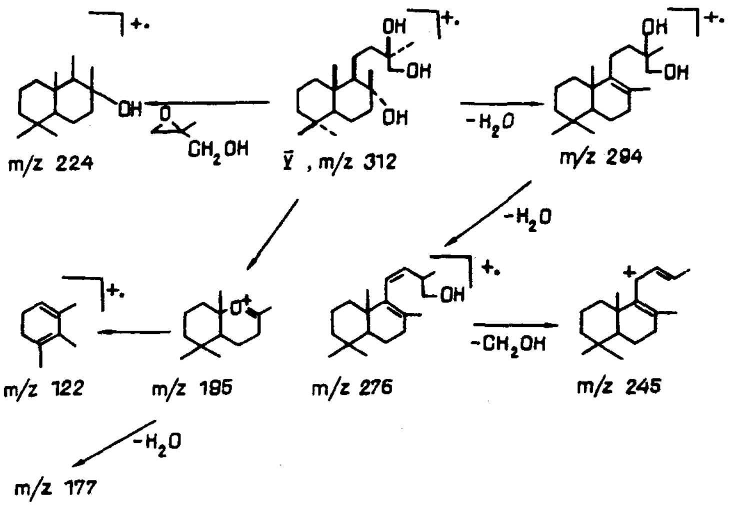
We have made a detailed study of the products of the ozonolysis of sclareol and also of the influence of the conditions of ozonization on their nature and ratio.

The ozonization of sclareol (I) under Janot's conditions led to a mixture of not less than eight compounds (TLC results), among which none predominated. The reaction also took place indeterminately in methanol with the reductive cleavage of the peroxide products by dimethyl sulfide: in this case, as well, a mixture was formed, with not less than six substances, among which, again there were no predominating products. On ozonization in ethyl acetate at -65 to -70°C in the presence of 5% of pyridine (by volume) (molar ratio of sclareol to pyridine 1:9.5) sclareol (I) gave a mixture of three substances, and these were separated by chromatography on a column of silica gel. The least polar substance proved to be "sclareol oxide" (III) (yield 37%). It was identified by comparison with an authentic sample. The second compound eluted from the column was 8α-hydroxy-14,15-bisnorlabdan-13-one (IV) (17%), which was likewise identified by comparison with an authentic sample.

The most polar compound eluted from the column consisted of an extremely unstable viscous liquid. It decomposed on chromatographic purification and even on brief storage in solution. It was therefore impossible to obtain an analytically pure sample of it for determining its elementary composition. This substance had a peroxide nature, since it liberated iodine from a solution of potassium iodide. In agreement with this, its IR spectrum contained a very strong band at 3100-3600 cm^{-1} with a maximum at 3475 cm^{-1}, which is characteristic for a hydroperoxy group [3]. In addition, in its IR spectrum there were maxima of a tertiary hydroxyl (1070 cm^{-1}) and of epoxide (1115 cm^{-1}) and keto (low intensity, 1716 cm^{-1}) groups.

It must, however, be mentioned that it was impossible to obtain reproducible IR and PMR spectra for the compound under investigation and its structure was therefore shown mainly on the basis of its chemical transformations. On being heated (170°C, 30 min) it decomposed with the formation of a complex mixture of substances the main one of which was the hydroxy ketone (IV). Lithium tetrahydroaluminate reduced it in good yield to a crystalline compound with the composition $C_{19}H_{36}O_3$. The IR spectrum of this compound contained the maxima of hydroxy groups, and its PMR spectrum the singlet signals of three methyl groups at quaternary carbon atoms and of two at tertiary carbinol carbon atoms, and the multiplet signal of five protons in the 3.25-4.25 ppm interval. When the spectrum was taken with the addition of deuterium oxide, a two-proton singlet signal of the $-C-CH_2OH$ grouping appeared at 3.35 ppm.

Thus, the substance under investigation contained two tertiary and one primary hydroxy groups. The facts given above led to the structure of 15-norlabdane-8α,13,14-triol (V). This was confirmed by its mass spectrum, which contained the peak of the molecular ion with m/z 312 of low intensity and the peaks of ions with m/z 294, 276, 245, 224 (100%), 195, 177, and 122. A possible route to their formation is shown in Scheme 1.

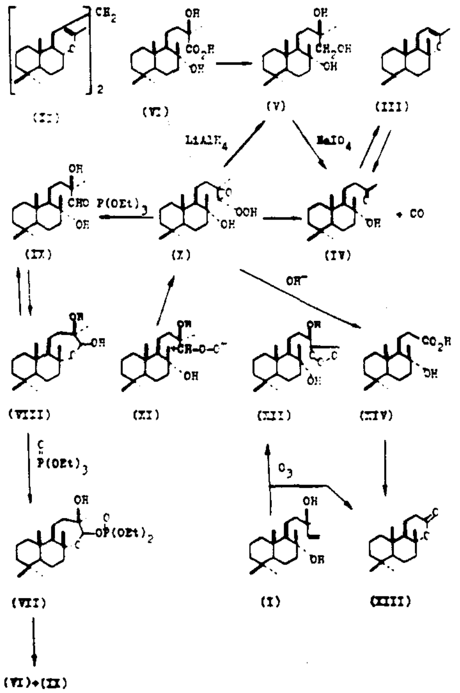


Scheme 1

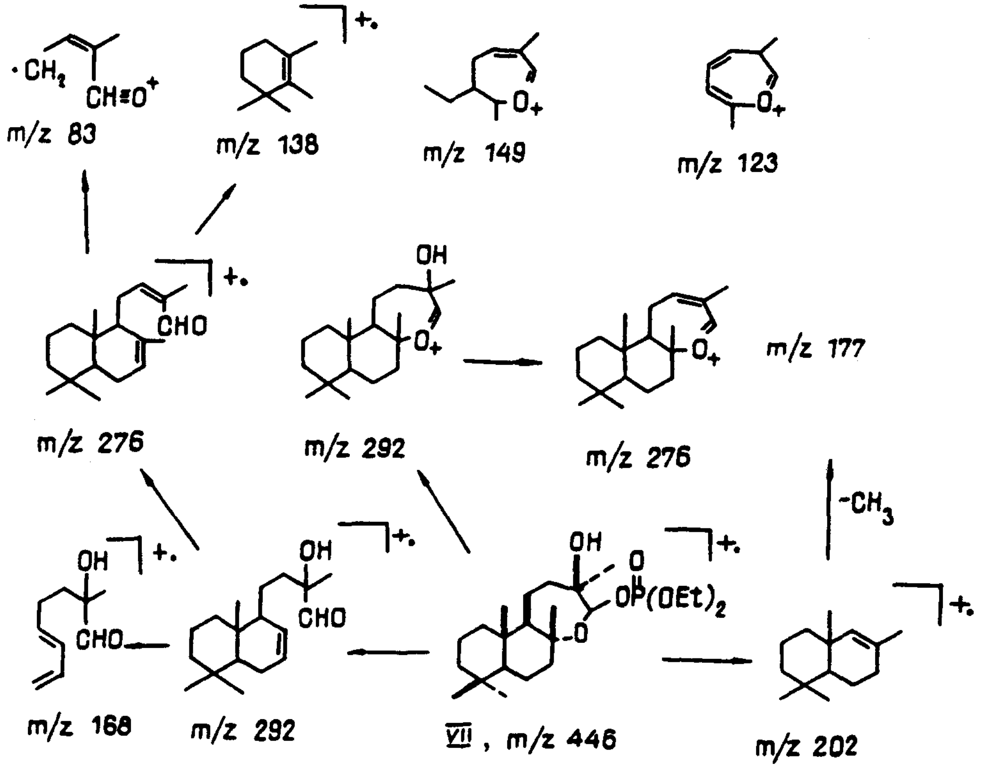
When the triol under investigation was oxidized with sodium periodate, the hydroxy ketone (IV) was formed, which also confirmed its structure. The triol (V) was identified definitively by its formation on the reduction of the known sclareolic acid (VI) [4] with lithium tetrahydroaluminate.

The hydroperoxide product of the ozonolysis of sclareol reacted slowly with ferrous sulfate and sodium sulfite to give complex mixtures of substances. However, it was reduced smoothly by triethyl phosphite using the method of Finugane and Thomson [5], which led with good yield to a crystalline product giving a positive reaction for phosphate with ammonium molybdate [6]. According to the results of elementary analysis it had the composition $C_{23}H_{43}O_6P$. Its IR spectrum contained intense bands of a hydroxy group at 3320 cm^{-1}, of a P—O—C group (1030, 1053 cm^{-1}), of a P=O group (1220 cm^{-1}), and of an oxide ring (1116 cm^{-1}) [7], while its PMR spectrum contained the singlet signals of three methyl groups at quaternary carbon atoms and of two at carbon atoms linked with oxygen atoms, a multiplet of methylene protons of two ethyl groups at 4.20 ppm, and a singlet signal at 5.16 ppm of a proton at C-14. The quartet signals of the methyl protons of the two ethyl groups were not clearly observed, since they overlapped one another and the signals of other protons.

In the mass spectrum of the substance under investigation the peak of the molecular ion was absent, but there were strong peaks of ions with m/z 245, 235, 203, 177, 168, 149, 138, 123, 111 and 83 (100%). Many of them are characteristic for labdane diterpenoids [8]. A possible route to the formation of the majority of them is shown in Fig. 2. The combination of the facts given above led to structure (VII) for the substance under investigation, i.e., it was the diethyl phosphate of the semiacetal form (VIII) of sclarealdehyde (IX). In agreement with this structure, it interacted with an alcoholic sulfuric acid solution of 2,4-dinitrophenylhydrazine with the formation, judging from elementary analysis, of a mixture of 2,4-dinitrophenylhydrazones of products of the degradation of sclarealdehyde. The phosphate ester (VII) was apparently formed as the result of the transesterification of triethyl phosphate - (the product of the oxidation of triethyl phosphite) obtained on the reduction of the hydroperoxide product of the ozonization of sclareol. The ease with which the transesterification reaction took place — under mild conditions in a neutral medium and giving the ester (VII) with a high yield (~70%) is surprising.



When the ester (VII) was saponified with alcoholic alkali under standard conditions, the main reaction product was sclareolic acid (VI) and a neutral substance, formed in small amount, which was unstable and readily underwent oxidation to sclareolic acid. Even when the ester (VII) was saponified in an atmosphere or argon, sclareolic acid predominated in the reaction product. Judging from its IR and PMR spectrum, the neutral compound was, as was to be expected, a mixture of sclarealdehyde (IX) and its cyclic semiacetal form (VIII). In actual fact, its IR spectrum contained the maxima characteristic for aldehyde (1715, 2710 cm^{-1}) and hydroxy (3380 cm^{-1}) groups and of an oxide ring (series of bands at 1110 cm^{-1}), and its PMR spectrum contained the signals of three methyl groups at quaternary carbon atoms, of a proton at a semiacetal carbon at 5.10 ppm, and of an aldehydic proton at 9.56 ppm. Judging from the integral intensities of the signals, the ratio of the aldehyde and semiacetal forms under the ordinary conditions was ~55:45.

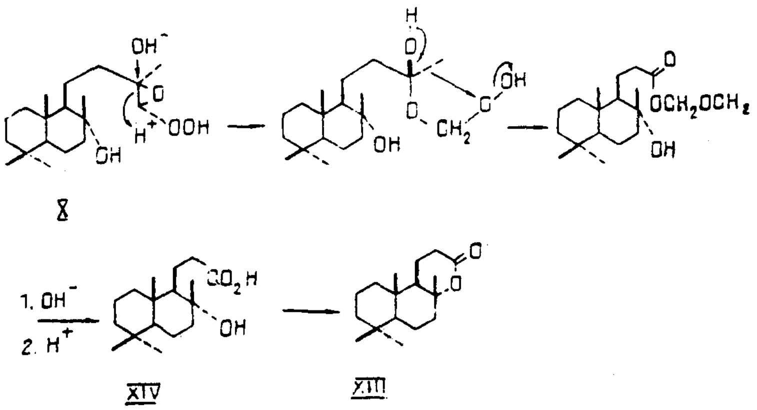


The above-given experimental facts relating to the transformation of the hydroperoxide product of the ozonization of sclareol (I), taken altogether, unambiguously led to the conclusion that it possessed the structure (X), i.e., it was (13R,14R)-14-hydroperoxy-13,14-epoxy-15-norlabdan-8α-ol. Its formation is in harmony with and confirmed the mechanism of the ozonization of allyl alcohols proposed by Everest et al. [3], according to which the zwitterion (XI) obtained from the primary sclareol ozonide (XII) is stabilized in the form of the epoxyhydroperoxide (X). On reduction, depending on the reagent, the latter gives either the triol (V) or the dihydroxy aldehyde (IX). In the absence of a reducing agent it is converted as the result of an intramolecular rearrangement into the hydroxy ketone (IV) and carbon monoxide. The formation of the latter both on the ozonization of sclareol and on the decomposition of the hydroperoxide (X) was shown by a qualitative reaction — the reduction of palladous chloride to metallic palladium — when the gaseous products issuing from the reaction vessels were passed through a dilute solution of palladous chloride [9].

It is interesting to note that, in spite of the fact that the reduction of the hydroperoxide (X) by triethyl phosphite formed the cyclic semiacetal (VIII), the stabilization of the zwitterion (XI) took place only through the participation of the hydroxy group at C-13, even though this produced the strained α-epoxy hydroporoxide (X), while the hydroxy group at C-8 did not interact with the zwitterion.

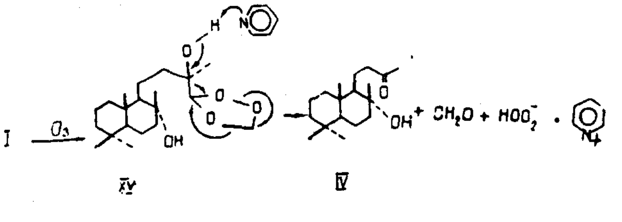
The yield of the acid fraction of the product of the ozonization of sclareol was small (~8%) by weight of the ozonization product. It included sclareolic acid (VI) (yield 6.8%) and traces of ambreinolide (XIII) (yield 0.35%) (the composition of the acid fraction was: 85% of scareolic acid and 3% of ambreinolide.

The decomposition of the hydroperoxide (X) in an alcoholic solution of alkali at the ordinary temperature took place quite differently. In this case, the acid fraction consisted wholly of the hydroxy acid (XIV), which lactonized into ambreinolide (XIII). The neutral fraction of the product gave, on TLC, a continuous band with no clearly formed spots. When it was chromatographed on a column of silica gel it was possible to isolate only a small amount of ambreinolide. Its total yield amounted to 34%. In this case, the decomposition of the hydroperoxide (X) apparently took place by the mechanism shown in scheme 3.



As can be seen from Table 1, when sclareol (I) was ozonized in ethyl acetate the temperature and method of working up the ozonization products had little effect on the ratio of the ozonolysis products (experiments 3-5). Since, when the solvent was distilled off in vacuum, the hydroxy ketone (IV) was converted completely into the oxide (III), subsequently, in the separation of the neutral part of the ozonolysis product, the fractions containing the hydroxy ketone (IV) and the oxide (III) were combined, the solvent was distilled off, and the oxide (III) was obtained in the yields shown in Table 1. When ozonization was performed in the presence of pyridine in ethyl acetate, methanol, and methylene chloride, the solvent again had only a slight influence on the composition of the ozonolysis product (experiments 3, 4, and 6-8).

It was shown by special experiments that pyridine did not reduce the hydroperoxide (X). If the ozonization of sclareol (I) took place by the mechanism suggested by Everest et al. [3], the presence of pyridine in the reaction mixture should not have affected the yield and the ratio of compounds (III) and (X). However, the investigation showed that this was not the case (compare experiments 8-10 in Table 1). This apparently indicates that the ozonization of sclareol takes place in part by Criegee's mechanism [10, 11] with the formation of sclareol ozonide (XV) and its decomposition with the participation of pyridine, possibly, as shown in Scheme 4, the degree of occurrence of the reaction by this mechansim depending to a certain degree on the solvent used (Table 1, experiments 3, 4, and 6-10).



EXPERIMENTAL

For the general part, see [2].

Ozonolysis of Sclareol (I) in Ethyl Acetate in the Presence of Pyridine. A mixture of ozone and oxygen was passed through a solution of 1 g of sclareol (I) in 50 ml of ethyl acetate and 2.5 ml of dry pyridine at −65 to −70°C until the initial sclareol had disappeared (monitoring by TLC).

The reaction mixture was purged with nitrogen, allowed to assume room temperature, treated with 20 ml of 10% sulfuric acid solution, and extracted with ether. The ethereal extract was washed with water, with 2% sodium hydroxide solution, and with water again, and

TABLE 1. Influence of the Conditions for the Ozonization of Sclareol (I) on the Yields of Reaction Products*

Experiment No.	Solvent	Method of working up the ozonization products	Temperature, °C	Yield, %		Proportion of the acid fraction in the ozonolysis
				"sclareol oxide" (III)	hydroperoxide (X)	
1	CCl_4	H_2O, Δ	0		Mixture of eight substances	
2	CH_3OH	$(CH_3)_2S$	0		Mixture of six substances	
3	$CH_3CO_2C_2H_5$	5% C_5H_5N	−65 ÷ −70	54	42	8
4	-	-	18−20	52	42	7
5	-	H_2O, Δ	18−20	50	48	2
6	CCl_4	5% C_5H_5N	0	36	57	5
7	CH_3OH	5% C_5H_5N	18−20	44	43	6
8	CH_2Cl_2	5% C_5H_5N	18−20	46	49	4
9	CH_2Cl_2	2% C_5H_5N	18−20	45	46	8
10	CH_2Cl_2	10% C_5H_5N	18−20	52	30	14

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*The amount of sclareol was 1 g, the volume of solvent 50 ml, and the time of ozonization 60 min; the solvent was used dry.

it was dried with anhydrous sodium sulfate and filtered, and the solvent was distilled off in the vacuum of a water pump. This gave 900 mg of neutral fraction. The alkaline extract was acidified with 10% sulfuric acid solution and extracted with ether, the extract was washed with water to neutrality, dried with sodium sulfate, and filtered, and the solvent was distilled off. This gave 80 mg of acid fraction.

The neutral fraction was chromatographed on a column containing 20 g of silica gel. Petroleum ether eluted 315 mg (37% yield) of "sclareol oxide" (III), mp 46-47°C (from petroleum ether), which was identified by a chromatographic and spectral comparison with an authentic sample. Petroleum ether—diethyl ether (9:1) eluted 152 mg (17% yield) of the hydroxy ketone (IV), mp 87-88°C (from acetonitrile), which was identified by comparison with an authentic sample. Petroleum ether—diethyl ether (8:2) eluted 402 mg (42% yield) of (13R,14R)-14-hydroperoxy-13,14-epoxy-15-norlabdan-8α-ol (X), a viscous extremely unstable liquid which decomposed on chromatography and on storage on solution. IR spectrum (cm^{-1}): 3100-3600 (intense band) with a maximum at 3475 (—OOH) [3], 1070 (tert. OH), 1115 (epoxy group), 1716 (C=O).

The products of the ozonization of sclareol under different conditions (see Table 1) were worked up similarly.

Thermal Decomposition of the Hydroperoxide (X). Hydroperoxide (X) (100 mg) was heated at 170°C for 30 min. Acording to TLC, a mixture of substances, with the hydroxy ketone (IV) predominating, was formed.

Reduction of the Hydroperoxide (X) with Lithium Tetrahydroaluminate. A solution of 500 mg of the hydroperoxide (X) in 10 ml of absolute ether was carefully treated with 120 mg of lithium tetrahydroaluminate and the mixture was boiled under reflux for 2 h. The excess of hydride was decomposed with ethyl acetate, and the mixture was acidified with 10% sulfuric acid solution and was extracted with ether. The extract was worked up in the usual way, and the product was crystallized from acetone. This gave 350 mg (70% yield) of (13R)-15-norlabdane-8α,13,14-triol (V), mp 150-151°C. IR spectrum (cm^{-1}): 1040, 3100-3600 (band), 3360 (max.) (OH). PMR spectrum (ppm): 0.78 (6H, c) [$C-(CH_3)_2$, 0.86 (3H, s, CH_3 at C-10), 1.08 (3H, s, CH_3 at C-8), 1.15 (3H, s, CH_3 at C-13), 3.35 (2H, s, $-C-CH_2OH$), 3.25-4.25 (3H, m, OH groups). Mass spectrum, m/z (%): 312 (M^+, 3), 294(22), 279(6), 277(11), 276(22), 264(10), 263(16), 262(7), 261(13), 256(9), 246(25), 245(93), 243(6), 238(7), 237(20), 236(13), 233(8), 228(6), 225(20), 224(100), 222(15), 220(9), 219(18), 218(7), 209(6), 207(10), 205(20), 204(9), 203(6), 202(8), 200(10), 199(9), 195(33), 194(7), 193(10), 192(13), 191(16), 190(6), 189(16), 185(10), 179(7), 178(13), 177(78), 176(12), 175(11), 166(11), 163(9), 162(20), 160(8), 153(6), 152(12), 150(13), 149(9), 148(39), 146(9), 140(7), 138(24), 137(10), 136(44), 135(13), 134(22), 132(7), 128(10), 126(16), 125(8), 124(40), 123(18), 122(69), 121 (10), 120(22), 118(8), 114(10), 112(16), 110(11), 109(44), 108(8), 107(20), 99(6), 98(13), 97(51), 96(25), 95(16), 94(40), 93(11), 92(7), 86(7), 84(17), 83(11), 82(20), 81(25), 80(28), 72(9), 71(9), 70(31), 69(8), 68(29), 67(6), 59(9), 56(17), 54(6). Found, %: C 72.95; H 11.64. $C_{19}H_{36}O_3$. Calculated, %: C 73.07; H 11.54.

Oxidation of the Triol (V) with Sodium Periodate. A solution of 2 g of sodium periodate in 16 ml of water was added to a solution of 400 mg of the triol (V) in 16 ml of ethanol and 8 ml of a saturated solution of potassium carbonate. The reaction mixture was kept at room temperature for 48 h and was then diluted with water and was extracted with ether. The ethereal extract was worked up in the usual way, giving 338 mg of reaction product, which was chromatographed on a column containing 8 g of alumina. Petroleum ether—diethyl ether (9:1) eluted 300 mg (83% yield) of the hydroxy ketone (IV), mp 87-88°C (from acetonitrile) identical with an authentic sample.

Reduction of Sclareolic Acid (VI) with Lithium Tetrahydroaluminate. To a solution of 60 mg of sclareolic acid (VI) in 5 ml of absolute diethyl ether was carefully added 42 mg of lithium tetrahydroaluminate, and the mixture was boiled under reflux for 2 h. After the usual working up, 55 mg (95%) of the triol (V) was obtained with mp 150-151°C (from acetonitrile), identical with the triol formed on the reduction of the epoxyhydroperoxide (X) with lithium tetrahydroaluminate.

Reduction of the Epoxyhydroperoxide (X) with Triethyl Phosphite [5]. At —10°C, 150 mg of triethyl phosphite was added to a solution of 140 mg of compound (X) in 5 ml of ethyl acetate, and the mixture was stirred until its temperature had risen to that of the room, and it was then diluted with water and extracted with ether. After the usual working up of the ethereal extract, 158 mg of product was isolated which was chromatographed on a column containing 5 g of alumina. Diethyl ether—ethanol (1:1) eluted from the column 121 mg (62% yield) of the phosphate ester (VII), mp 127-128.5°C (from acetone).

IR spectrum (cm^{-1}): 3320 (OH), 1030, 1053 (P—O—C), 1220 (P═O), 1116 (oxide ring). PMR spectrum (ppm): 0.78 (6H, s) [C—$CH_3)_2$], 0.85, (3H, s, CH_3 at C-10), 1.07 (3H, s, CH_3 at C-8), 1.18 (3H, s, CH_3 at C-13), 4.20 (4H, m, P—($OC_2H_5)_2$, 5.16 (1H, s, H at C-14). Mass spectrum, m/z (%): 292(10), 276(7), 263(11), 256(11), 253(13), 246(9), 245(30), 240(9), 236(6), 235(24), 219(11), 211(9), 204(7), 203(7), 202(24), 201(14), 200(16), 196(6), 195(13), 193(8), 192(9), 191(12), 178(12) 177(24), 176(7), 175(7), 168(23), 167(13), 165(7), 164(5), 163(13), 161(7), 153(9), 151(11), 150(8), 149(25), 147(10), 141(7), 140(18), 138(30), 137(17), 136(21), 135(20), 134(6), 133(9), 127(15), 126(7), 125(19), 124(18), 123(52), 122(11), 121 (24), 120(6), 119(11), 115(10), 113(17), 112(13), 111(88), 110(20), 109(58), 108(10), 107 (21), 106(18), 104(13), 100(11), 98(15), 97(39), 96(27), 95(64), 94(21), 93(42), 92(12), 91(16), 87(12), 85(27), 84(17), 83(100), 82(39), 81(76), 77(15), 74(13), 73(27), 72(8), 71 (70), 70(15), 69(94), 68(18), 67(33), 66(21), 65(57), 63(9), 62(24), 61(8), 60(30), 57(55), 56(16), 55(21), 54(18), 53(10), 52(15), 46(12), 43(15), 42(19), 41(18), 40(5). Found, %: C 61.74; H 10.06. $C_{23}H_{43}O_6P$. Calculated, %: C 61.86; H 9.70. The substance gave a positive qualitative reaction for phosphrous by the method of [6]. 2,4-Dinitrophenylhydrazone, mp 148-150°C (from methanol).

Saponification of the Phosphate Ester (VII). The ester (VII) (200 mg) was added to a solution of 52 mg of potassium hydroxide in 1 ml of methanol, and the solution was kept at room temperature in an atmosphere of argon for 1 h. The reaction mixture was worked up in the usual way, giving 109 mg of an acid fraction consisting of sclareolic acid (VI), mp 152-153°C (from acetone) and 57 mg of a neutral fraction consisting of a mixture of sclarealdehyde (IX) and its cyclic semiacetal form (VIII). IR spectrum (cm^{-1}): 1715, 2710 (CHO), 3380 (OH), 1100 (oxide ring). PMR spectrum (ppm): 0.78 (6H, s) [C($CH_3]_2$], 0.86 (3H, s, CH_3 at C-10), 1.13 (3H, s, CH_3 at C-8), 1.19 (3H, s, CH_3 at C-13), 5.10 (1H, s, OH), 9.56 (1H, s, CHO).

Determination of Carbon Monoxide [9]. Sclareol (3 g) was ozonized as described above, and the gases issuing from the reaction flask were passed through receivers connected in series, the first two of which were filled with a saturated solution of potassium iodide to absorb ozone and the last with a 1% solution of palladous chloride. After the end of the reaction metallic palladium had deposited on the bottom and walls of the last flask. The same reaction took place when the epoxyhydroperoxide (X) was decomposed under the action of alkali.

Composition of the Acid Fraction of the Product of the Ozonization of Sclareol. According to TLC, this fraction consisted of two components. The acid fraction (80 mg) obtained on the ozonization of sclareol (see above) was dissolved in diethyl ether, and the solution was boiled under reflux for 3 h, after which it was treated with a 1% solution of potassium hydroxide and was separated into acid (72 mg) and neutral (3 mg) fractions. The neutral fraction (mp 140-142°C (from petroleum ether)) consisted of ambreinolide, which was identified by comparison with an authentic sample. The acid fraction was crystallized from a mixture of petroleum ether and diethyl ether, giving sclareolic acid (VI), mp 152-153°C.

Interaction of the Epoxyhydroperoxide (X) with Alkali. A solution of 600 mg of the epoxyhydroperoxide (X) in 1 ml of ethanol was treated with 2.5 ml of a 10% solution of caustic potash, and the mixture was kept at room temperature for 6 h and was then worked up in the usual way. This gave 257 mg of neutral and 233 mg of acid fractions. The acid fraction was chromatographed on a column containing 7 g of silica gel. Petroleum ether eluted 152 mg of ambreinolide (XIII), mp 140-142°C. On TLC, the neutral fraction gave a continuous band. When it was chromatographed on a column containing 7 g of silica gel, 30 mg of ambreinolide (XIII) was isolated. Its total yield was 34%.

Ozonolysis of Sclareol in Ethyl Acetate with Decomposition of the Ozonide by Water. A mixture of ozone and oxygen was passed through a solution of 1 g of sclareol (I) in 50 ml of ethyl acetate at 18-20°C until the reaction was complete (monitoring by TLC). The solution was purged with nitrogen, and then 50 ml of water was added to the reaction mixture and it was kept at room temperature for 1 h and at 60°C for 5 h. The products were worked up as described above, and 1.01 g of neutral and 16 mg of acid fractions were obtained. The neutral fraction was chromatographed on a column containing 20 g of silica gel. Petroleum ether—diethyl ether (9:1) eluted 498 g of a mixture of the oxide (III) and the hydroxy ketone (IV). It was distilled in vacuum at 174-176°C/10 mm, giving 429 mg (50%) of "sclareol oxide" (III). An 8:2 mixture of the same solvents eluted 460 mg (46%) of the epoxy hydroperoxide (X).

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