m-chloroperbenzoic acid in 15 ml of methylene chloride was added during 15 min to an ice-cold stirred solution of 0.900 g (3.54 mmol) of **4**[7] in 30 ml of methylene chloride. Stirring was continued in an ice bath for 1 hr and at room temperature for an additional 24 hr. Excess peracid was destroyed by the addition of 10% sodium sulfite until a test with starch–iodide paper was negative. The reaction mixture was washed with 5% sodium bicarbonate solution (3 × 50 ml), water (2 × 50 ml), and saturated sodium chloride solution (2 × 50 ml), and dried over anhydrous magnesium sulfate. Evaporation of the solvent provided an oil which was exhaustively evaporated of solvent at reduced pressure to give 0.900 g (89%) of **5**, which was recrystallized from pentane, mp 83–85°. The pmr spectrum is discussed in the text; ir (CCl_4) 2980, 1720, 1480, 1460, 1390, 1380, 1370, 1280, 1175, 1090, 1030, 1010, and 870 cm^{-1}; $\lambda_{max}^{C_6H_{12}}$ 316 nm (ϵ 200), 305 (340), 295 (330), 282 (260), 271 (465), 264 (510), 258 (300), 227 (5000).

Anal. Calcd for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20. Found: C, 79.89; H, 8.15.

Similarly, ***syn*-7,8-epoxy-1,3,3,7,8-pentamethyl-4-methyl-d_3-5,6-benzobicyclo[2.2.2]oct-5-en-2-one** (**6**) was prepared by epoxidation of 1,3,3,7,8-pentamethyl-4-methyl-d_3-5,6-benzobicyclo[2.2.2]octa-5,7-dien-2-one[7] and ***syn*-7,8-epoxy-1,3,3,4,8-pentamethyl-7-methyl-d_3-5,6-benzobicyclo[2.2.2]oct-5-en-2-one** (**7**) was obtained from 1,3,3,4,8-pentamethyl-7-methyl-d_3-5,6-benzobicyclo[2.2.2]octa-5,7-dien-2-one.[7]

General Photolysis Procedure.—All irradiations were carried out with a 450-W Hanovia Type L mercury lamp with the light filtered through a Corex glass sleeve. The solution to be irradiated was placed in a quartz test tube, sealed with a serum cap, and attached to the outside of a water-cooled immersion well, 2–3 cm from the center of the mercury lamp. This apparatus was then placed in a water bath, which maintained the temperature of the solution between 15 and 20° during irradiation.

For each of the irradiations reported, a control experiment showed that no reaction occurred under comparable conditions in the dark.

Irradiation of Epoxy Ketone 5.—A solution of 100 mg of **5** in 10 ml of diethyl ether was irradiated through a Corex filter. The photolysis was monitored by glpc (10 ft × 0.25 in. FFAP column; 215°; 60 ml/min of helium). Irradiation led to a progressive decrease in the concentration of **5** (retention time 22.6 min) and an increase in the concentration of a photoproduct with a retention time of 10.2 min. This photoproduct reached a maximum concentration after 225-min irradiation, and further irradiation for 75 min produced only a slight decrease in its concentration. After 5-hr irradiation, no more starting material remained. Glpc and pmr analysis with internal standards indicated that the photoproduct was obtained in *ca.* 95% yield. Purification of the photoproduct by glpc (above conditions) provided a colorless oil, epoxide **8**. The pmr spectrum is discussed in the text; ir (CCl_4) 2980, 2940, 1640, 1495, 1450, 1370, 1175, 1150, 1120, 1100, 1060, 1040, 900, and 870 cm^{-1}. The major peaks in the mass spectrum [*m/e* 242 (M^+)] are at 199 and 157.

Anal. Calcd for $C_{17}H_{22}O$: C, 84.25; H, 9.15. Found: C, 84.37; H, 9.17.

3,3,7,8-Tetramethyl-5,6-benzobicyclo[2.2.2]octa-5,7-dien-2-one (**9**).[8]—A solution of anthranilic acid (4.5 g, 33 mmol) in acetone (40 ml) was added during 1 hr to a solution of 3,4,6,6-tetramethyl-2,4-cyclohexadienone[11] (3.28 g, 21.8 mmol) and isoamyl nitrite (3.87 g, 33 mmol) in methylene chloride (80 ml). After an additional 1 hr at reflux, the solvent was evaporated and the residual brown oil was dissolved in ether (70 ml) and washed with 10% sodium hydroxide, then water, and finally dried over anhydrous sodium sulfate. Evaporation of the solvent provided an oil which was distilled to give 3.18 g (63%) of **9**, a pale yellow oil: bp 104–105° (0.5 Torr); pmr (CCl_4) three-proton singlets at τ 9.42, 8.86, 8.23, and 8.16, one-proton singlets at τ 6.60 and 5.98, and a four-proton aromatic multiplet centered at τ 2.88; ir (CCl_4) 1720, 1675, 1600, and 710 cm^{-1}; λ_{max}^{EtOH} 300 nm (ϵ 389), 273 (1100), 268 (1200), and 216 (8130). Treatment of **9** with hydroxylamine hydrochloride in ethanol–pyridine gave a crystalline oxime, mp 175–176° (from ethanol).

Anal. Calcd for $C_{16}H_{19}NO$: C, 79.63; H, 7.94; N, 5.80. Found: C, 79.90; H, 7.94; N, 5.80.

***syn*-7,8-Epoxy-3,3,7,8-tetramethyl-5,6-benzobicyclo[2.2.2]octa-5-en-2-one** (**10**).—Epoxidation of **9** with *m*-chloroperbenzoic acid, according to the procedure described in detail for **4** → **5**, gave epoxy ketone **10**, mp 85–86° (from pentane). The pmr spectrum is discussed in the text; ir (CCl_4) 2975, 2925, 1725, 1475, 1455, 1380, 1195, 1165, 1130, 1095, and 875 cm^{-1}.

Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.39; H, 7.44.

Irradiation of Epoxy Ketone 10.—A solution of 100 mg of **10** in 10 ml of diethyl ether was irradiated through a Corex filter. The photolysis was monitored by glpc (10 ft × 0.25 in. FFAP column; 210°; 60 ml/min of helium). Examination of the solution after 30-min irradiation showed a significant decrease in the concentration of **10** (retention time 25.9 min), the appearance of a main photoproduct (retention time 11.8 min), and a trace of another photoproduct (retention time 8.2 min). Continued irradiation led to a progressive decrease in the concentration of **10** and a progressive increase in the concentration of the photoproduct with retention time 11.8 min. A new photoproduct with retention time 6.2 min also appeared and further irradiation led to an increase in the concentration of this product at the expense of the compound with retention time 8.2 min. After 5-hr irradiation, no more starting material remained, and integration of the peak areas of the photoproducts showed their relative concentrations to be retention time 6.2 min (4.6%), 8.2 min (2.1%), and 11.8 min (93.3%). Pmr analysis with an internal standard of the photolysate indicated that the photoproduct with a retention time of 11.8 min was obtained in *ca.* 75% yield. This photoproduct was purified by glpc (above conditions) to provide a colorless oil, epoxide **11**. The pmr spectrum is discussed in the text; ir (CCl_4) 3075, 3010, 2970, 1640, 1495, 1450, 1385, 1245, 1170, 1145, 1080, 1010, 900, and 875 cm^{-1}.

Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 84.27; H, 8.49.

2,3-Epoxy-2,3-dimethyl-1,4-dihydronaphthalene (**12**).—Epoxidation of 2,3-dimethyl-1,4-dihydronaphthalene[10] with *m*-chloroperbenzoic acid, according to the procedure described in detail for **4** → **5**, gave **12**. The pmr spectrum is discussed in the text.

Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.84; H, 8.07.

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Registry No.—**4**, 17384-73-5; **5**, 41498-90-2; **8**, 41498-91-3; **9**, 22686-90-4; **9** oxime, 41498-21-9; **10**, 41498-92-4; **11**, 41498-93-5; **12**, 41498-22-0; 3,4,6,6-tetramethyl-2,4-cyclohexadienone, 14069-95-5; 2,3-dimethyl-1,4-dihydronaphthalene, 21564-72-7.

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Photosensitized Oxygenations of Some Derivatives of Kaurenes

A. K. BANERJEE, A. MARTÍN, AND T. NAKANO*[1]

Centro de Química, Instituto Venezolano de Investigaciones Científicas, Apartado 1827, Caracas, Venezuela

A. USUBILLAGA

Instituto de Investigación Química, Facultad de Farmacia, Universidad de Los Andes, Apartado 142, Mérida, Venezuela

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The dye-sensitized photooxygenation of organic compounds, which has been studied extensively by many workers,[2] provides a smooth method for the specific

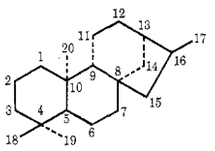
(1) Correspondence should be directed to this author.

(2) K. Gollnick and G. O. Schenck in "1,4 Cycloaddition Reactions," J. Hamer, Ed., Academic Press, New York, N. Y., 1967, p 255; K. Gollnick and G. O. Schenck, *Pure Appl. Chem.*, **9**, 507 (1964); E. J. Bowen, *Advan. Photochem.*, **1**, 23 (1963); G. O. Schenck, *Angew. Chem.*, **69**, 579 (1957); C. S. Foote, *Accounts Chem. Res.*, **1**, 104 (1968).

introduction of oxygen into their molecules. It has been elegantly employed in the synthesis, interconversion, and rearrangement of a number of natural products related to diterpenoids[3] and steroids[4] as a means of establishing their structural interrelationship and also as a model experiment for their biosynthetic pathways.

The oxygenation of olefins containing allylic hydrogen atoms in the presence of a suitable sensitizer and with visible light gives allylic hydroperoxides which are invariably accompanied by a shift of the double bond, a reaction analogous to the "ene" reaction. During the course of the isolation and structure determination[5] of the constituents of several species *Espeletia* (family *Compositae*), a fairly large amount of kaurene derivatives has been available. Thus photooxygenation of (−)-kaur-15-en-19-oic acid (**1a**),[6] (−)-kaur-16-en-19-oic

CHART I

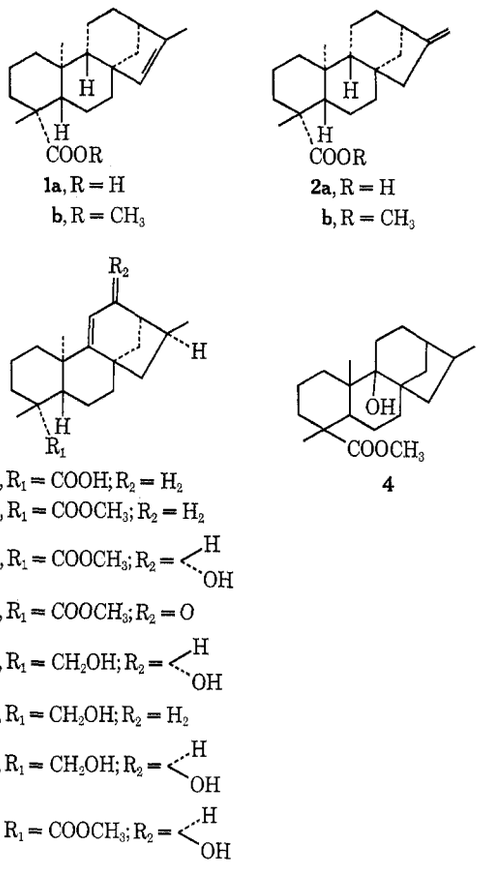


(−)-kaurane

acid (**2a**), and (−)-kaur-9(11)-en-19-oic acid (**3a**) appeared to offer an interesting problem, since thy may be the precursors of 15α-hydroxy-(−)-kaur-16-en-19-oic acid (**5a**),[5b] (−)-kaur-15-ene-17,19-diol (**6b**),[7] and methyl 9-hydroxykaur-19-oate (**4**),[8] respectively, and their conversion might occur *in vivo* by a process analogous to this sensitized photooxygenation.

Methyl (−)-kaur-15-en-19-oate (**1b**) in pyridine was irradiated with fluorescent tubes using haematoporphorin as a sensitizer. The resulting hydroperoxide was not isolated and was directly reduced in ethanol solution with sodium iodide and acetic acid. Chromatography of the product over silica gel afforded in 42% yield an allylic alcohol **5b**: *m/e* 332 (M^+); ir 3540 (OH) and 1727 cm^{-1} (ester C=O); nmr δ 0.85 (s, 3, tertiary methyl), 1.20 (s, 3, tertiary methyl), 3.66 (s, 3, carbomethoxy), 5.13 and 5.26[9] (broad m, 2, terminal methylene), and 3.83 (broad s, 1, proton[10] at C-15). Oxidation of **5b** with Jones reagent[11] at 0° afforded a keto methyl ester **5c**, which exhibited the characteristic absorption

CHART II



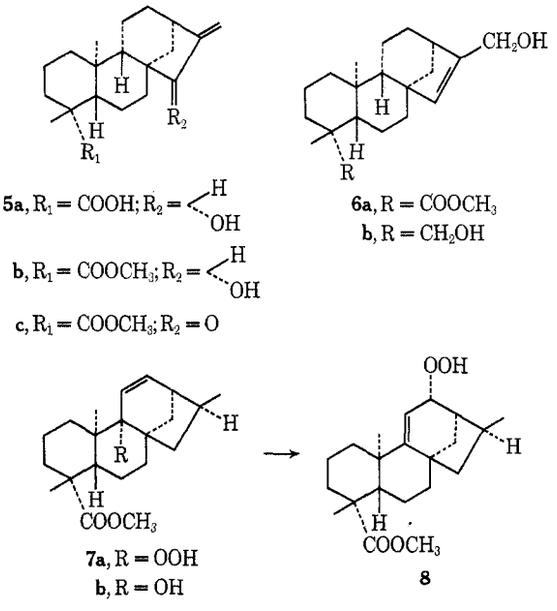
1a, R = H
b, R = CH_3

2a, R = H
b, R = CH_3

3a, R_1 = COOH; R_2 = H_2
b, R_1 = $COOCH_3$; R_2 = H_2
c, R_1 = $COOCH_3$; R_2 = H, OH
d, R_1 = $COOCH_3$; R_2 = O
e, R_1 = CH_2OH; R_2 = H, OH
f, R_1 = CH_2OH; R_2 = H_2
g, R_1 = CH_2OH; R_2 = H, OH
h, R_1 = $COOCH_3$; R_2 = H, OH

4

CHART III



5a, R_1 = COOH; R_2 = H, OH
b, R_1 = $COOCH_3$; R_2 = H, OH
c, R_1 = $COOCH_3$; R_2 = O

6a, R = $COOCH_3$
b, R = CH_2OH

7a, R = OOH
b, R = OH

8

of α,β-unsaturated ketones [uv max (MeOH) 234 nm (ϵ 7500) and ir 1700 (broad, unresolved ester and α,β-unsaturated C=O) and 1620 cm^{-1} (CH_2=C<)]. The identity of **5b** with methyl 15α-hydroxy-(−)-kaur-16-en-19-oate[12] was established by direct comparison

(3) M. F. Barnes, R. C. Durley, and J. MacMillan, *J. Chem. Soc. C*, 1341 (1970); R. A. Bell and R. E. Ireland, *Tetrahedron Lett.*, 269 (1963); M. F. Barnes and J. MacMillan, *J. Chem. Soc. C*, 361 (1967).

(4) (a) A. Nickon and J. F. Bagli, *J. Amer. Chem. Soc.*, **83**, 1498 (1961); A. Nickon, N. Schwartz, J. B. DiGiorgio, and D. A. Widdowson, *J. Org. Chem.*, **30**, 1711 (1965); (b) J. E. Fox, A. I. Scott, and D. W. Young, *J. Chem. Soc., Perkin Trans. 1*, 799 (1972).

(5) (a) A. Usubillaga and A. Morales Méndez, *Rev. Latinoamer. Quím.*, **1**, 128 (1970); (b) A. Morales Méndez, A. Usubillaga, A. K. Banerjee, and T. Nakano, *Planta Med.*, in press.

(6) The numbering and nomenclature of these diterpenoids follows a system recommended by R. McCrindle and K. H. Overton in "Advances in Organic Chemistry, Methods and Results," Vol. 5, R. A. Raphael, E. C. Taylor, and H. Wynberg, Ed., Interscience, New York, N. Y., 1965, p 47.

(7) H. A. Lloyd and H. M. Fales, *Tetrahedron Lett.*, 4891 (1967).

(8) L. A. Cuevas, F. García Jiménez, and A. Romo de Vivar, *Rev. Latinoamer. Quím.*, **3**, 22 (1972).

(9) These protons give broadened signals at about δ 4.70–4.80. See L. H. Briggs, B. F. Cain, R. C. Cambie, B. R. Davis, P. S. Rutledge, and J. K. Wilmskurst, *J. Chem. Soc.*, 1345 (1963), and G. Hugel, L. Lods, J. M. Mellor, D. W. Theobald, and G. Ourisson, *Bull. Soc. Chim. Fr.*, 2882, 2888 (1965).

(10) The β configuration of this hydrogen (hence the α configuration of the hydroxyl group) may be expected on the basis of attack of oxygen from the less hindered α side of the 15,16 double bond.

(11) A. Bowers, T. G. Halsall, E. R. H. Jones, and A. J. Lemin, *J. Chem. Soc.*, 2548 (1953).

(12) Reference 5b; C. H. Brieskorn and E. Pöhlmann, *Tetrahedron Lett.*, 5661 (1968); C. H. Brieskorn and E. Pöhlmann, *Chem. Ber.*, **102**, 2621 (1969). For the corresponding compound with the 15β-hydroxy group, see D. E. U. Ekong and A. U. Ogan, *J. Chem. Soc. C*, 311 (1968).

(melting point, mixture melting point, and ir spectrum) of both specimens.

Methyl (−)-kaur-16-en-19-oate (**2b**) was also photooxygenated under a similar condition and the resulting hydroperoxide, without isolation, was treated in the same way as above. Chromatography of the product over silica gel afforded in 30% yield an allylic alcohol **6a**: *m/e* 332 (M^+); ir 3300 (OH), 1730 (ester C=O), and 1680 cm^{-1} (C=C); nmr δ 0.85 (s, 3, tertiary methyl), 1.15 (s, 3, tertiary methyl), 3.63 (s, 3, carbomethoxy), 4.16 (s, 2, 17-allylic hydroxymethyl), and 5.35 (broad m, 1, 15-vinyl proton). Reduction of **6a** with lithium aluminum hydride in tetrahydrofuran gave a diol **6b**: mp 193–194°; $[\alpha]_D$ −11° (c 1.0, $CHCl_3$); *m/e* 304 (M^+); nmr δ 0.93 (s, 3, tertiary methyl), 1.00 (s, 3, tertiary methyl), 3.39 and 3.73 (AB q, 2, J = 12 Hz, 19α-hydroxymethyl), 4.16 (broad s, 2, allylic 17-hydroxymethyl), and 5.33 (broad m, 1, 15-vinyl proton). The spectroscopic as well as physical properties of this compound were completely consistent with those reported for (−)-kaur-15-ene-17,19-diol (**6b**).[13]

Methyl (−)-kaur-9(11)-en-19-oate (**3b**) was rather resistant to photooxygenation. When it was irradiated for 120 hr and the resulting hydroperoxide was treated as before, there was isolated in 10% yield[14] an allylic alcohol, $C_{21}H_{32}O_3$, *m/e* 332 (M^+). At first it was assumed that this alcohol must be **7b**, derived from the attack of oxygen from the less hindered α side of the 9,11 double bond accompanied by an allylic shift of the double bond to the 11,12 position. However, the nmr spectrum of this alcohol did not exhibit signals corresponding to two olefinic protons, but instead one proton signal at δ 4.10 (multiplet), which could be assigned to the proton attached to the carbon bearing an allylic hydroxyl group, and one vinyl proton signal at δ 5.36 (doublet, J = 4.5 Hz), besides signals of two tertiary methyls at δ 0.95 (singlet) and 1.16 (singlet), one secondary methyl at δ 0.95 (doublet, J = 6 Hz), and one carbomethoxy group at δ 3.61 (singlet). This indicated that the original 9,11 double bond still exists at the same position. Furthermore, the fact that the 11-vinyl proton which appeared at δ 5.18 as a triplet (J = 3 Hz) in **3b** now resonates as a doublet (J = 4.5 Hz) suggested that substitution of one of the hydrogens at C-12, possibly with the hydroxyl group, had taken place. Therefore, this allylic alcohol must be **3c** and its mode of formation may be envisaged as follows. Photooxygenation of **3b** would first yield the unstable intermediate **9**α hydroperoxide **7a**,[15] which would then undergo an allylic rearrangement of the type observed in analogous systems[16] to the 12α hydroperoxide **8**. Subsequent reduction of **8** with potassium iodide would give rise to the allylic alcohol **3c**. The presence of the allylic hydroxyl function in **3c** was further verified by its oxidation with Jones reagent[11] at 0° to **3d**. The ketone **3d** displayed the characteristic α,β-unsaturated carbonyl absorption [ir 1722 (ester C=O) and 1666 cm^{-1} (α,β-unsaturated C=O); uv max (95% ethanol) 245 nm (ϵ 9734)].

Reduction of **3c** with lithium aluminum hydride in tetrahydrofuran afforded a diol **3e**. Its nmr spectrum revealed an AB quartet (δ 3.53 and 3.83, J = 11 Hz) that could be assigned to an axial 19α-hydroxymethyl group, a 12β-proton multiplet at δ 4.08, and an 11-vinyl proton at δ 5.30 (doublet, J = 4.5 Hz), in addition to two tertiary methyls at δ 0.93 (singlet) and 1.05 (singlet) and one secondary methyl at α 0.95 (doublet, J = 6.5 Hz).

Prolonged irradiation of **3b** did not improve the yield of the allylic alcohol **3c**. After photooxygenation for 15 days, followed by reduction of the resulting hydroperoxide with lithium aluminum hydride, the alcohol **3e** was obtained in 6% yield.[17]

In order to confirm the structure of **3c**, we then attempted to prepare it from **3b** *via* a different route. The allylic oxidation[18] of olefins with uv light in the presence of mercuric bromide or *N*-bromosuccinimide, or direct oxidation[19] of allylic methylene with *N*-bromosuccinimide to carbonyl with visible light, was recently reported. However, **3b** was found to be totally resistant to the oxidation of this type, and only starting material was recovered unchanged. Therefore, we turned to the usual chromic acid oxidation.[20] When **3b** was treated with chromium trioxide in acetic acid at room temperature for 2 days, the desired ketone **3d** was obtained in good yield. This ketone proved to be identical (ir, uv, nmr, and mass spectra) with the ketone obtained from the photooxygenation of **3b** followed by oxidation of the resulting allylic alcohol **3c**.

Reduction of **3d** with lithium aluminum hydride in tetrahydrofuran yielded a diol. The ir spectrum of this diol was very similar to, but not identical with, that of **3e**. Its nmr spectrum showed an AB quartet (δ 3.45 and 3.73, J = 10 Hz) attributable to the axial 19α-hydroxymethyl group. However, in comparison with the spectrum of the allylic alcohol **3e**, the corresponding 11-vinyl proton resonated as a doublet (J = 1.5 Hz) at δ 5.05 (0.25 ppm upfield) and the 12 proton as a multiplet at δ 4.51 (0.43 ppm downfield). The 12-hydroxyl group of this allylic alcohol must have the β configuration, since the attack of the hydride is expected from the less hindered α side[21] of the molecule. This alcohol is thus formulated as **3g**. Reduction of **3d** with sodium borohydride in 2-propanol also yielded from the same stereochemical grounds the 12β alcohol, which is formulated as **3h**. In its nmr spectrum, the 11-vinyl proton resonated as a doublet (J = 1.5 Hz) at δ 5.22 (0.14 ppm upfield) and the 12α proton as a multiplet at δ 4.62 (0.52 ppm downfield), as compared with those corresponding protons in **3c**.

Experimental Section

Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. Ir spectra were run on a Perkin-Elmer 337

(13) See ref 7. Direct comparison was not achieved because a comparison sample could not be obtained.

(14) Approximately 90% of the starting material was recovered unchanged.

(15) The attack of oxygen is expected from the less hindered α side of the 9,11 double bond of **3b**. For a similar case, see the hydroboration of **3b**: F. Piozzi, S. Passannanti, M. L. Marino, and V. Spiro, *Can. J. Chem.*, **50**, 109 (1972).

(16) G. O. Schenck, O.-A. Neumüller, and W. Eisfeld, *Justus Liebigs Ann. Chem.*, **618**, 202 (1958); ref 4b.

(17) After chromatography over silica gel, there was obtained the alcohol **3f** in 50% yield, besides **3e**.

(18) N. Friedman, M. Gorodetsky, and Y. Mazur, *Chem. Commun.*, 874 (1971).

(19) B. W. Finucane and J. B. Thomson, *Chem. Commun.*, 1220 (1969).

(20) **3b** was resistant to the selenium dioxide oxidation. Under varying conditions only starting material was recovered unchanged.

(21) Note that no epimeric 12α alcohol was obtained. Inspection of the molecular model indicated that the β side of the 12 carbonyl is severely sterically hindred by the β bridging of ring D as well as the β-methyl group at C-16.

spectrometer in KBr disks and uv spectra were measured with a Cary Model 15 spectrometer. Nmr spectra were obtained on a Varian A-60 instrument in deuteriochloroform and chemical shifts are reported in parts per million downfield from internal TMS (δ scale). Rotations were measured at 23° in chloroform with a Zeiss polarimeter (0.01°). Mass spectra were recorded on a Hitachi Perkin-Elmer RMU-6H at 70 eV using a direct inlet system. For column chromatography Merck standardized alumina, activity II–III, and Merck silica gel were used. For tlc Merck silica gel G was used and the spots were identified by exposure to iodine vapor. All organic extracts were dried over anhydrous magnesium sulfate and evaporated under reduced pressure below 40°. Microanalyses were carried out by A. Bernhardt Microanalytical Laboratory, 5521 Elbach über Engelskirchen, West Germany.

Photooxygenations were conducted in a vertical Pyrex tube irradiated externally along its length by two 33-W fluorescent bulbs mounted about 10 cm away. A fritted glass plate was near the bottom of the tube to disperse the oxygen, which was admitted at the bottom at a convenient rate and without interruption.

Photooxygenation of Methyl (−)-Kaur-15-en-19-oate (1b).[5a]—The methyl ester **1b** (0.28 g) and haematoporphorin (10 mg) were dissolved in dry pyridine (25 ml) and the deep brown solution was irradiated for 96 hr until no starting material had remained. The progress of the reaction was monitored by tlc. The solution was evaporated *in vacuo* and the resultant hydroperoxide (0.34 g) was treated at room temperature overnight with a solution of ethanol (30 ml) containing acetic acid (1 ml) and sodium iodide (2 g). The dark brown oil left after concentration of the solution *in vacuo* was taken up in ether and the ether solution was washed with aqueous sodium thiosulfate, then water, dried, and evaporated. The crude product (0.31 g) thus obtained was chromatographed over silica gel (30 g), and elution with hexane–ether (8:2) yielded methyl 15α-hydroxy-(−)-kaur-16-en-19-oate (**5b**) (0.12 g) which on recrystallization from ether–hexane showed mp 114–116°, $[\alpha]_D$ −95° (*c* 0.1). Direct comparison of this compound with an authentic sample[12] established its identity (melting point, mixture melting point, and ir spectrum).

Anal. Calcd for $C_{21}H_{32}O_3$: C, 75.86; H, 9.70. Found: C, 75.91; H, 9.85.

Oxidation of Methyl 15α-Hydroxy-(−)-kaur-16-en-19-oate (5b) with Jones Reagent.—The alcohol **5b** (40 mg) in acetone (10 ml) was oxidized at 0° with Jones reagent.[11] After usual work-up a gummy mass was obtained, which was purified in ether through alumina. The α,β-unsaturated ketone **5c** was crystallized from ether–hexane, mp 147–148°, $[\alpha]_D$ −92° (*c* 1.0). This ketone was identical (uv, melting point, mixture melting points, and ir spectrum) with an authentic sample.[12]

Anal. Calcd for $C_{21}H_{30}O_3$: C, 76.32; H, 9.15. Found: C, 76.22; H, 8.96.

Photooxygenation of Methyl (−)-Kaur-16-en-19-oate (2b).[22]—The methyl ester **2b** (0.35 g) and haematoporphorin (10 mg) in dry pyridine (25 ml) were irradiated for 120 hr. The solution was then evaporated *in vacuo* and the crude hydroperoxide, without isolation, was reduced, as before, in a solution of ethanol (35 ml) containing acetic acid (1 ml) and sodium iodide (2 g). The dark brown residue obtained after removal of the solvent was taken up in ether. The ether solution was washed with aqueous sodium thiosulfate, then water, dried, and evaporated. The residue (0.32 g) was chromatographed over silica gel (30 g), and elution with hexane–benzene (1:1) yielded the unchanged methyl ester **2b** (0.13 g). Further elution with hexane–ether (1:9) afforded methyl 17-hydroxy-(−)-kaur-15-en-19-oate (**6a**) (100 mg), which on recrystallization from ether–hexane had mp 125–126°, $[\alpha]_D$ −15° (*c* 1.0).

Anal. Calcd for $C_{21}H_{32}O_3$: C, 75.86; H, 9.70. Found: C, 75.67; H, 9.54.

Reduction of Methyl 17-Hydroxy-(−)-kaur-15-en-19-oate (6a) with Lithium Aluminum Hydride.—The methyl ester **6a** (80 mg) in dry tetrahydrofuran (20 ml) was reduced under reflux with lithium aluminum hydride (100 mg) for 4 hr. The complex was decomposed with alkali and the product was isolated in the usual way. (−)-Kaur-15-ene-17,19-diol (**6b**) (30 mg) was obtained and crystallized from chloroform to show mp 193–194°, ir 3250 cm^{-1} (OH). The physical constants (rotation, melting point, and nmr spectrum) were in perfect agreement with those reported in the reference.[7]

(22) The isolation and characterization of these related known diterpenoids are to be published somewhere.

Anal. Calcd for $C_{20}H_{32}O_2$: C, 78.89; H, 10.59. Found: C, 78.64; H, 10.33.

Photooxygenation of Methyl (−)-Kaur-9(11)-en-19-oate (3b).[22]

A.—The methyl ester **3b** (1.587 g) and haematoporphorin (25 mg) were dissolved in dry pyridine (25 ml) and the solution was irradiated for 120 hr. The solvent was then removed *in vacuo* and the resultant crude hydroperoxide was treated with a solution of ethanol (50 ml) containing potassium iodide (2.5 g) and acetic acid (0.75 ml) at room temperature for 24 hr. Water was added, the product was extracted with chloroform, and the chloroform extract was washed with aqueous sodium thiosulfate, then water, and dried. Evaporation of the chloroform left a dark brown residue which was chromatographed over silica gel (20 g). The methyl ester **3b** (1.25 g) was recovered unchanged from hexane–benzene and benzene fractions. Elution with chloroform containing methanol (1–5%) yielded methyl 12α-hydroxy-(−)-kaur-9(11)-en-19-oate (**3c**) as an amorphous powder (0.166 g) which could not be induced to crystallize: ir 3400 (OH) and 1730 cm^{-1} (ester C=O). The ir spectrum of this alcohol was different from that of the alcohol **3h** (see below) obtained by the reduction of **3d** with sodium borohydride.

Anal. Calcd for $C_{21}H_{32}O_3$: C, 75.86; H, 9.70. Found: C, 75.54; H, 9.46.

B.—The methyl ester **3b** (1.25 g) and haematoporphorin (25 mg) in dry pyridine (25 ml) was photooxygenated for 15 days. The solvent was removed *in vacuo* and the crude hydroperoxide was reduced in dry tetrahydrofuran (40 ml) under reflux with lithium aluminum hydride (3 g) for 4 hr. The complex was decomposed with alkali and the product (1.15 g) was isolated in the usual way and chromatographed over silica gel (30 g). Elution with benzene–chloroform yielded (−)-kaur-9(11)-en-19-ol (**3f**)[22] (0.6 g), mp 97–100° (from chloroform–hexane). Elution with chloroform afforded (−)-kaur-9(11)-ene-12α,19-diol (**3e**) (70 mg), mp 171–175° (from ether–hexane; see below).

C.—The methyl ester **3b** (0.963 g) and haematoporphorin (26 mg) in dry pyridine (30 ml) were irradiated for 20 days. The crude hydroperoxide was reduced with potassium iodide as before and the product (0.95 g) was obtained. Chromatography over silica gel (20 g) and elution with benzene yielded recovered methyl ester **3b** (0.698 g). Further elution with chloroform containing methanol (1–10%) yielded methyl 12α-hydroxy-(−)-kaur-9(11)-en-19-oate (**3c**) (46 mg).

Reduction of Methyl 12α-Hydroxy-(−)-kaur-9(11)-en-19-oate (3c) with Lithium Aluminum Hydride.—The methyl ester **3c** (0.107 g) in dry tetrahydrofuran (40 ml) was refluxed with lithium aluminum hydride (0.5 g) for 4 hr. Water was added to decompose the excess reagent and the complex was treated with 5% aqueous sodium hydroxide (5 ml). The product was isolated in the usual way and purified through silica gel (10 g). Elution with chloroform yielded (−)-kaur-9(11)-ene-12α,19-diol (**3e**) (60 mg), which after recrystallization from ether–hexane showed mp 170–175°; *m/e* 304 (M^+); ir 3340 cm^{-1} (OH).

Anal. Calcd for $C_{20}H_{32}O_2$: C, 78.89; H, 10.59. Found: C, 78.61; H, 10.33.

Oxidation of Methyl 12α-Hydroxy-(−)-kaur-9(11)-en-19-oate (3c) with Jones Reagent.—The methyl ester **3c** (60 mg) in acetone (10 ml) was treated with Jones reagent[11] at 0°. The product was isolated by extraction with chloroform in the usual way, and methyl 12-oxo-(−)-kaur-9(11)-en-19-oate (**3d**) (55 mg) was obtained as a semisolid, *m/e* 330 (M^+).

Anal. Calcd for $C_{21}H_{30}O_3$: C, 76.32; H, 9.15. Found: C, 76.61; H, 8.93.

Oxidation of Methyl (−)-Kaur-9(11)-en-19-oate (3b) with Chromium Trioxide in Acetic Acid.—The methyl ester **3b** (0.203 g) in acetic acid (10 ml) was treated with chromium trioxide (0.12 g) and the solution was stirred at room temperature for 4 hr. An additional amount (0.13 g) of chromium trioxide was then added and the solution was stirred at room temperature for 2 days. After addition of water the product was extracted with chloroform and the chloroform extract was washed with water, dried, and evaporated to afford a crude product (0.19 g). This oxidation was repeated using the methyl ester **3b** (0.4 g), chromium trioxide (0.3 g), and acetic acid (15 ml), and the combined products (0.58 g) were chromatographed over alumina (20 g), and methyl 12-oxo-(−)-kaur-9(11)-en-19-oate (**3d**) (0.26 g) was obtained by elution with hexane–benzene (1:1): $[\alpha]_D$ +121° (*c* 1.1). This ketone was identical (ir, uv, nmr, and mass spectra) with the ketone obtained by the oxidation of **3c** with Jones reagent.

Anal. Calcd for $C_{21}H_{30}O_3$: C, 76.32; H, 9.15. Found: C, 76.11; H, 8.82.

Reduction of Methyl 12-Oxo-(−)-kaur-9(11)-en-19-oate (3d) with Lithium Aluminum Hydride.—The ketone **3d** (0.107 g) in dry tetrahydrofuran (40 ml) was treated with lithium aluminum hydride (0.4 g) and the solution was refluxed for 2 hr. The excess reagent was decomposed with water and the complex was treated with 5% aqueous sodium hydroxide (5 ml). After addition of anhydrous magnesium sulfate, the solution was filtered and evaporated. The crude product was chromatographed over silica gel (20 g) and elution with benzene–chloroform (1:1) and chloroform afforded (−)-kaur-9(11)-ene-12β,19-diol (**3g**) (50 mg), mp 160–165° (from ether-hexane), $[\alpha]_D$ +48° (*c* 0.9), *m/e* 304 (M^+). The ir spectrum of this diol was very similar to, but different from, that of the diol **3e**.

Anal. Calcd for $C_{20}H_{32}O_2$: C, 78.89; H, 10.59. Found: C, 78.61; H, 10.31.

Reduction of Methyl 12-Oxo-(−)-kaur-9(11)-en-19-oate (3d) with Sodium Borohydride.—The ketone **3d** (80 mg) in 2-propanol (10 ml) was treated with sodium borohydride (90 mg) and the solution was left under stirring at room temperature for 4 days. Water was then added and the product (92 mg) was isolated by extraction with chloroform. This reduction was repeated using the ketone **3d** (80 mg) and the combined products (0.15 g) were chromatographed over silica gel (20 g). Elution with benzene yielded methyl 12β-hydroxy-(−)-kaur-9(11)-en-19-oate (**3h**) (0.14 g) as an amorphous powder, *m/e* 332 (M^+), $[\alpha]_D$ +46° (*c* 1.3). The ir spectrum of this alcohol was different from that of the alcohol **3c** obtained from the photooxygenation of **3b**.

Anal. Calcd for $C_{21}H_{32}O_3$: C, 75.86; H, 9.70. Found: C, 75.55; H, 9.46.

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Registry No.—**1b**, 18671-79-9; **2b**, 41473-15-8; **3b**, 41473-16-9; **3c**, 41473-17-0; **3d**, 41473-18-1; **3e**, 41473-19-2; **3f**, 41473-20-5; **3g**, 41473-21-6; **3h**, 41473-22-7; **5b**, 22343-41-5; **5c**, 22376-47-2; **6a**, 35030-39-8; **6b**, 41473-26-1.