Hydroboration of α-Gurjunene. A Rational Correlation with Cyclocolorenone[1,2]

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Hydroboration and oxidation of α-gurjunene (1) gives the expected tertiary alcohol **3**, the diol **7** resulting from 1:4 addition to the vinyl–cyclopropane system of **1**, and the secondary alcohol **5** resulting from prior isomerization of **1** to the nonconjugated "δ-gurjunene" **4**. This isomerization proceeds even at room temperature. The cyclocoloranol (**5**) has been converted, in turn, into cyclocoloranone (**6**), cyclocolorenone (**2**), and epicyclocolorenone (**18**), thus confirming an earlier, irrational correlation between α-gurjunene and cyclocolorenone.

We have recently assigned structure **1** to the tricyclic sesquiterpene α-gurjunene,[2b,3] a constituent of the balsam of many species of *Dipterocarpaceae*.[4] A correlation with α-terpineol has been achieved and used to define the configuration at C-7; the configuration at C-1 and C-10 was deduced from an oxidation to cyclocolorenone (**2**), of known structure[5] and stereochemistry.[6]

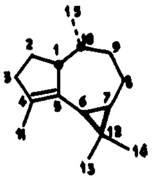
However, the methods used for the reaction **1** → **2** were not satisfactory. Autoxidation was effective only erratically, and the only reliable reagent found, sodium peroxide, is not one of those usually considered for allylic oxidations. It had been tried at random and gave reproducible, but very low yields.

We have now devised a rational correlation between α-gurjunene and cyclocolorenone, based on the following plan: α-gurjunene was to be hydrated by Brown's hydroboration–oxidation procedure in the hope that some of the tertiary alcohol **3** would be formed; this was to be dehydrated to the isomer **4** of α-gurjunene, which, again by Brown's procedure, could be hoped to give cyclocoloranol (**5**). Cyclocoloranone (**6**) would then be easily obtainable and could be dehydrogenated to cyclocolorenone (**2**), for example, through a bromination–dehydrobromination sequence.

As shown below, this plan was fulfilled, but some unexpected short cuts and side tracks lent additional interest to the results obtained. In particular, we shall describe a case of conjugate hydroboration, and the isomerization of a double bond by diborane under unusually mild conditions.

Hydroboration–Oxidation of α-Gurjunene.—Brown's method for the anti-Markovnikov hydration of olefins[7] is known to proceed by *cis* addition of the elements of water, and to give, at least at room temperature, products derived from attack on the double bond from its least hindered side. At higher temperatures, the hydroboration stage is reversible; hence the products are subject to thermodynamic control. Thus, the alcohol obtained may be derived from attack of the double bond from its more hindered side, or from initial isomerization of the double bond.

In the case of α-gurjunene (**1**), our expectation was that, at room temperature, diborane would attack the double bond from its α side, to give probably at least some of the tertiary alcohol **3** on oxidation.



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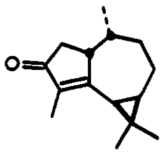

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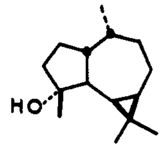

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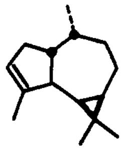

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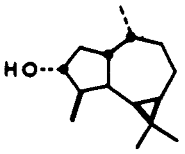

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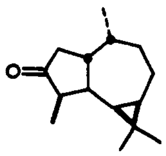

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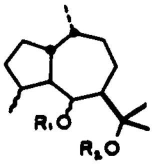
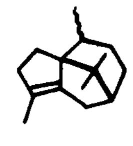


7 $R_1 = R_2 = H$
11 $R_1 = Ac$; $R_2 = H$
12 $R_1 = R_2 = Ac$



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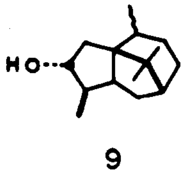

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In fact, when α-gurjunene was treated in tetrahydrofuran at room temperature by a current of diborane and then oxidized with alkaline hydrogen peroxide, three products were obtained and separated by chromatography over alumina. Two of these are isomers of the expected composition and the third one is a diol: A, $C_{15}H_{26}O$, m.p. 68–70°, $[\alpha]_D$ +16°; B, $C_{15}H_{26}O$, m.p. 89–90°, $[\alpha]_D$ +39°; and C, $C_{15}H_{28}O_2$, m.p. 113°, $[\alpha]_D$ +34°.

Structure of the Alcohol A.—The alcohol A resisted chromic acid oxidation and was therefore probably tertiary. Its n.m.r. spectrum[8] was very informative.

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[1] Presented as a token of gratitude to Professor Louis F. Fieser by G. O., Harvard, 1950–1952.

[2] (a) α-Gurjunene. III. (b) Part II: J. Streith and G. Ourisson, *Bull. soc. chim. France*, 1960 (1963).

[3] (a) M. Palmade, P. Pesnelle, J. Streith, and G. Ourisson, *ibid.*, 1949 (1963); (b) preliminary communication, M. Palmade and G. Ourisson, *ibid.*, 886 (1958); J. Streith, P. Pesnelle, and G. Ourisson, *Tetrahedron Letters*, 677 (1962).

[4] A chemotaxonomic survey of this family is in progress; isolation from *Dipterocarpus dyeri.*[3a]

[5] R. E. Corbett and R. N. Speden, *J. Chem. Soc.*, 3710 (1958); R. E. Corbett and H. Young, *Australian J. Chem.*, **16**, 250 (1963).

[6] G. Büchi and H. J. E. Loewenthal, *Proc. Chem. Soc.*, 280 (1962).

[7] G. Zweifel and H. C. Brown, *J. Am. Chem. Soc.*, **86**, 393 (1964), and references quoted therein.

[8] N.m.r. spectra are measured on a Varian A-60 instrument, at 60 Mc. with solutions in deuteriochloroform, tetramethylsilane being the internal standard. The values quoted are δ.

It showed in particular, at 1.31 p.p.m., a singlet (3H) due to the system CH_3CO–; at 1.00 and 1.03 p.p.m., two singlets (3H) due to two methyl groups on fully substituted carbon atoms; at 0.93 p.p.m., a doublet (3H, J = 6 c.p.s.) due to a secondary methyl group; between 0 and 0.17 p.p.m., a multiplet (2H) attributed to two cyclopropane protons.[9]

Barring rearrangements, structure **3** is strongly suggested. The alcohol was dehydrated with phosphorus oxychloride in pyridine, giving a mixture of two hydrocarbons, easily separated by chromatography over silica gel impregnated with silver nitrate.[10] One of these hydrocarbons, the minor one (20%), is α-gurjunene, identified by its characteristic infrared and n.m.r. spectra; this confirms structure **3**. The second hydrocarbon, termed "δ-gurjunene",[11] was more strongly retained on the selective adsorbent, and its R_f (t.l.c.) time points to a trisubstituted double bond.[12] Its infrared spectrum ($\nu_{C=C}$ 1670 cm.$^{-1}$, δ_{CH} 790 cm.$^{-1}$) is indeed consistent with this deduction, which leads to **4** as a proposed structure. The n.m.r. spectrum of δ-gurjunene is entirely in agreement with this proposal. It shows, at 5.22 p.p.m., a multiplet (1H) assigned to the vinylic hydrogen of C-3; at 1.65 p.p.m., the signal (3H) due to the methyl group on the double bond, split into an ill-resolved multiplet (allylic couplings); at 1.13 p.p.m., the doublet (3H, J = 6 c.p.s.) due to the secondary methyl group at C-10; at 1.04 and 1.02 p.p.m., two singlets (3H) due to the methyl groups C-13 and C-14; between 0 and 0.16 p.p.m., a complex signal (2H) due to the cyclopropane protons.[9]

Structure **4** for δ-gurjunene will be confirmed below by its conversion into cyclocoloranol.

The stereochemistry of the alcohol A, as indicated in **3**, is deduced from the general rules summarized above holding for the addition of diborane. The α side is here definitely less crowded. The configuration is in agreement with the preferential dehydration of the alcohol **3** to δ-gurjunene, as a *cis* elimination is required to form α-gurjunene.

Structure of the Alcohol B.—The second alcohol isolated is secondary since it is oxidized with chromic acid to a ketone described below. We ascribe structure **5** to the alcohol B and structure **6** to the derived ketone; these will be confirmed in the sequel. The n.m.r. spectrum of B is in agreement with this proposal. It shows, at 4.00 p.p.m., the multiplet (1H) expected for the system $-CH_2CHOHCH-$; at 1.04 p.p.m., the doublet (3H, J = 6 c.p.s.) due to one secondary methyl group; at 1.02 and 0.93 p.p.m., two singlets (3H) due to the methyl groups C-13 and C-14; at 0.89 p.p.m., the doublet (3H, J = 6 c.p.s.) due to a second secondary methyl group.

The same alcohol B is also obtained by hydroboration–oxidation of δ-gurjunene. The stereochemistry indicated in **5** is the one deduced from the postulate of an α attack; this is however *not* necessarily valid here, as the differential hindrance introduced by the β substituents is certainly less marked at C-3–C-4 than at C-4–C-5.

The formation of the alcohol **5** from α-gurjunene *implies* a migration of the double bond, through the sequence described in other similar cases: addition of diborane, elimination, readdition of diborane, favored at equilibrium by the secondary nature of the alkyl borane formed. However, the present case is exceptional in that it occurs in a hydroboration run at room temperature. We have not been able to increase the yield of this "abnormal" product by running the hydroboration at reflux temperature in tetrahydrofuran, or at 160° in diglyme. We have, however, encountered another similar case in the hydroboration–oxidation of another tricyclic sesquiterpene cyperene, **8**,[13] giving exclusively, at room temperature, the secondary alcohol **9**.[14]

Structure of the Diol C.—In ether, this diol resisted attempts at oxidation with chromic acid. However, in acetic acid it is oxidized by the same reagent to a ketol **10**, m.p. 73°, and is therefore probably a secondary, tertiary diol.

This is borne out by the n.m.r. spectra of the diol itself, of its mono- and diacetates, obtained by treatment with acetic anhydride and pyridine at 110°, and of the ketol **10** (Table I).

TABLE I

Compd.	Me on fully substituted C atoms, $\underset{\mid}{\overset{\mid}{\text{MeCO–}}}$	Secondary methyl groups	$-\overset{\mid}{C}HOH$	CH_3CO_2
Diol **7**	1.25, 1.33	0.90, 1.07	4.05	. . .
Ketol **10**	1.21, 1.25	0.96, 1.03	. . .	. . .
Monoacetate **11**	1.11, 1.15	0.90, 1.08	5.06	2.01
Diacetate **12**	1.32, 1.38	0.90, 1.08	5.05	1.96, 2.00
	Singlets, 3H	Doublets, 3H, J = 6 c.p.s.	Multiplet, 1H	Singlets, 3H

These data led to **7** as the unique structural expression for the diol itself. The ketol **10** is a β-ketol and, as such, should be base sensitive, to give either an α,β-unsaturated ketone or the product of a ketol cleavage. As a matter of fact, simple filtration over alkaline alumina, or treatment with methanolic sodium hydroxide, *cleaves* the ketol **10** into acetone (characterized by its dinitrophenylhydrazone), and a saturated C_{12} ketone **13**. The infrared spectrum of this last compound shows the bands associated with the presence of the unstrained grouping $-COCH_2-$ ($\nu_{C=O}$ 1695 cm.$^{-1}$, δ_{CH_2} 1415 cm.$^{+1}$); its n.m.r. spectrum shows two doublets (0.96 p.p.m., J = 6 c.p.s.; 0.98 p.p.m., J = 6.5 c.p.s.) corresponding to the two secondary methyl groups. Its circular dichroism presents a very strongly positive Cotton effect; this is only compatible, in the light of an octant diagram,[15] with the *trans* ring junction, 1β,5α, shown in **10**. As this is the most stable configuration at C-5, it

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[9] This multiplet cannot be observed in the spectrum of **1** or **2**, in which the cyclopropane is conjugated, owing to interference of the methyl signals.

[10] B. de Vries, *Chem. Ind.* (London), 1049 (1962); C. B. Barrett, M. S. J. Dallas, and F. B. Padley, *ibid.*, 1050 (1962); A. S. Gupta and S. Dev., *J. Chromatog.*, **12**, 189 (1963).

[11] β-Gurjunene: see J. Streith, P. Pesnelle, and G. Ourisson, *Bull. soc. chim. France*, 518 (1963), and reference quoted therein. γ-Gurjunene is another constituent of *D. dyeri*, a guaiadiene: M. Palmade and Ch. Ehret unpublished results.

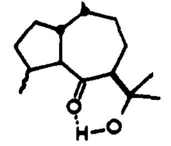
[12] We find, on silica gel impregnated with 20% silver nitrate, dried but not reactivated, using cyclohexane as eluent, for monoethylenic sesquiterpenes, with a tetrasubstituted double bond, R_f between 0.80 and 0.95; with a trisubstituted double bond, R_f between 0.60 and 0.75; with a methylene group, R_f between 0.25 and 0.40; for dienes, other eluents are used.

[13] B. Trivedi, O. Motl, J. Smolikova, and F. Sorm, *Tetrahedron Letters*, 1197 (1964).

[14] P. Pesnelle, unpublished results leading in particular to the definition of the partial stereochemistry indicated for cyperene.

[15] W. Moffit, R. B. Woodward, A. Moscowitz W. Klyne, and C. Djerassi, *J. Am. Chem. Soc.*, **83**, 4013 (1961).

is not possible to deduce from it any information regarding the stereochemistry of the ketol **10** or the diol **7**. Similarly, one can make no stereochemical use of the infrared spectrum of the diol **7**: in carbon tetrachloride, at high dilution, it shows the presence of free and associated OH bonds, separated by a frequency shift $\Delta\nu$ = 80 cm.$^{-1}$, in good agreement with values observed for other 1,3-diols by Schleyer.[16] Unfortunately, good intramolecular hydrogen bonding can take place in structure **7** whatever the configuration at C-5, C-6, or C-7. Diol **7** most probably arises through intermediate **14**. This is the result, at least formally, of a conjugate addition on the vinylcyclopropane system of α-gurjunene, in the sense of formula **15** (where we do *not* propose such a stereochemically improbable *concerted* bimolecular reaction but where the general picture of events follows the electronic changes indicated). A similar conjugate addition on the vinylcyclopropane system of α-gurjunene has been observed earlier, in the oxidation with peracid,[2b] **1** → **16**.



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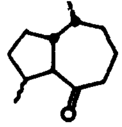

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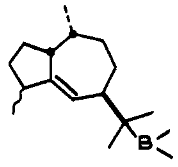

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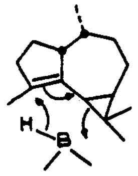

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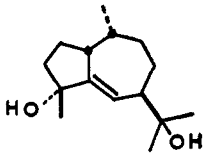

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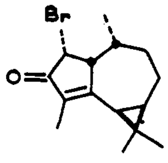

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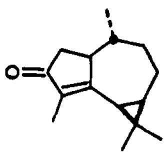

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Preparation of Cyclocolorenone and Epicyclocolorenone.—As mentioned above, the secondary alcohol **5** can be oxidized to the corresponding ketone **6**. This is a crystalline compound (m.p. 38–40°, $[\alpha]_D$ +173°). It is isomeric with, but different from, the two cyclocoloranones, of unknown configurations, obtained by Corbett[5] by catalytic hydrogenation, and by metal–ammonia reduction, of cyclocolorenone. The new cyclocoloranone **6** is brominated (phenyltrimethylammonium tribromide in tetrahydrofuran[17]) at room temperature and the crude bromo ketones obtained are at once dehydrobrominated by the dimethylformamide–lithium chloride–lithium carbonate procedure.[18] The major product of this sequence (over 50%) is cyclocolorenone (**2**), identified by its infrared, ultraviolet, and n.m.r. spectra, by its rotation, and by its 2,4-dinitrophenylhydrazone. Authentic samples of **2** and its derivative have been kindly given us by Dr. Corbett, and prepared by us earlier.[2b]

Cyclocolorenone thus obtained is contaminated by small amounts of unchanged cyclocoloranone **6** and of a monobromo ketone to which we ascribe structure **17**, on the basis of its spectral properties (*cf.* Experimental part).

Longer heating in the dehydrobromination stage, or short alkaline treatment of cyclocolorenone, lead to epicyclocolorenone **18**, identified in the same way.

These results confirm entirely, through the sequence of reactions initially planned, the correlation α-gurjunene–cyclocolorenone and therefore the configuration assigned to α-gurjunene.

Experimental[19]

Hydroboration–Oxidation of α-Gurjunene.—A solution of α-gurjunene (**1**, 10 g.) in anhydrous tetrahydrofuran (150 ml.) was treated at 20° with diborane carried by a stream of dry nitrogen; diborane was prepared from boron trifluoride etherate (30 ml.) and a slurry of sodium borohydride (7 g.) in THF. After 12 hr., the solution was oxidized at room temperature by adding, with stirring, 3 *N* sodium hydroxide (50 ml.) followed by 30% hydrogen peroxide (50 ml.). After 5 hr., isolation was performed in the usual way and gave a colorless oil (11 g.), which was chromatographed on alumina (200 g.). After a small heterogeneous forerun (216 mg.), eluted with petroleum ether (b.p. 30–60°), three main crystalline fractions were eluted with a 3:1 petroleum ether–ether mixture: alcohol A (1.62 g.), alcohol B (1.14 g.), and diol C (3.39 g.). Intermediate fractions gave, by repeated chromatography, suitably monitored by t.l.c., additional crystalline material, raising the yields to about 25% A, 25% B, and 50% C. The three substances were purified by sublimation *in vacuo*.

5α-Cyclocoloran-4α-ol (alcohol A, 3) had m.p. 68–70°, $[\alpha]_D$ +16°; for the n.m.r. spectrum, see the text.

Anal. Calcd. for $C_{15}H_{26}O$: C, 81.02; H, 11.79. Found: C, 81.06; H, 11.79.

4α,5α-Cyclocoloran-3α-ol (alcohol B, 5) had m.p. 89–90°, $[\alpha]_D$ +39°; for the n.m.r. spectrum, see the text.

Anal. Found: C, 81.10; H, 11.70.

1β,4ξ,5ξ,αH,10βH-Guaia-6ξ,12-diol (diol C, 7) had m.p. 113°, $[\alpha]_D$ +34°; for the n.m.r. spectrum, see the text.

Anal. Calcd. for $C_{15}H_{28}O_2$: C, 74.95; H, 11.74. Found: C, 75.11; H, 11.96.

5α-Cyclocolor-3-ene (δ-Gurjunene, 4).—A solution of the alcohol **3** (700 mg.) in anhydrous ether (10 ml.) was cooled at 0° and treated with a mixture of thionyl chloride (1 ml.) and pyridine (4 ml.). The product, isolated in the usual way, was filtered through a column of alumina (20 g.). Petroleum ether eluates gave a hydrocarbon fraction (550 mg.), separated by chromatography over silica gel impregnated with 10% silver nitrate, into α-gurjunene (50 mg., identified by t.l.c. over SiO_2–$AgNO_3$ 20% and by n.m.r.), eluted with petroleum ether, and δ-gurjunene **4**, (380 mg.), eluted with petroleum ether containing 5% ether. δ-Gurjunene was only characterized by its infrared and n.m.r. spectra—infrared spectrum: 1180, 1125, 1010, 983, 880 cm.$^{-1}$ (neat); n.m.r. spectrum: $2CH_3C$, 1.01 and 1.04 p.p.m., $C\mathit{H}_3CH$–, 1.13 p.p.m.

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[16] P. von R. Schleyer, *J. Am. Chem. Soc.*, **83**, 1368 (1961).

[17] A. Marquet, M. Dvolaitzky, H. B. Kagan, L. Mamlok, C. Ouannes, and J. Jacques, *Bull. soc. chim. France*, 1822 (1961).

[18] R. Joly, J. Warnant, G. Nominé, and D. Bertin, *ibid.*, 366 (1958).

[19] Melting points were measured on a Kofler–Reichert microscope heating stage. Rotations measured with a Jouan automatic polarimeter, with solutions in chloroform (*ca.* 1% w./v.). Infrared spectra were measured in chloroform, with a Beckman IR-5A spectrophotometer. Ultraviolet spectra were measured in ethanol with a Beckman DK-2 instrument. For n.m.r. spectra, see footnote 8. Circular dichroisms were measured in dioxane, with a Jouan–Roussel Dichrograph. Analyses were performed by the Strasbourg branch of the Service Central de Micro-analyse (C.N.-R.S.). Adsorbents for chromatography are Merck (Darmstadt) products. The systematic nomenclature used is based upon the saturated tricyclic skeleton derived from α-gurjunene, for which we propose to use the name cyclocolorane to avoid ambiguities associated with the use of gurjunane.[11] The numbering is shown in formula **1**. The configurations of 1, 6, 7, and 10 are implied as indicated in **1**. Guaiane (formula **7**) implies no configuration; all centers must therefore be indicated, as is also the case for azulene (formula **13**). The configurational prefixes (α,β) are for the formulas oriented as presented in the structures.

(J = 7 c.p.s.), $CH_3C=C$-, 1.65 p.p.m., $-CH=C$–, 5.22 p.p.m. (unresolved multiplet).

Hydroboration–Oxidation of δ-Gurjunene.—The procedure described for α-gurjunene was used with 280 mg. of δ-gurjunene. The crude product (300 mg., colorless oil) was chromatographed over alumina (15 g.). Petroleum ether with 30% ether gave 222 mg. of crystalline cyclocoloranol (**5**), identified by melting point infrared, and n.m.r. with the product described above (alcohol B).

4α,5α-Cyclocoloran-3-one (**6**).—The alcohol **5** (80 mg.) was oxidized in ether (5 ml.) with a solution of chromium trioxide (267 mg.) in water (1.4 ml.) and sulfuric acid (0.23 ml.). The addition of the oxidizing solution was stopped as soon as a t.l.c. control showed the absence of starting material. The crude product (80 mg., oily) was chromatographed over silicic acid. Crystalline cyclocoloranone (**6**) was eluted with petroleum ether containing 10% ether, and purified by sublimation; m.p. 38–40°; $[\alpha]_D$ +173°; infrared $\nu_{C=O}$ 1745 cm.$^{-1}$; δ_{CH_2CO} 1415 cm.$^{-1}$; C.D. $\Delta\epsilon_{315}$ +2.23, $\Delta\epsilon_{304}$ +3.69, $\Delta\epsilon_{295}$ +3.61; n.m.r. CH_3CH– 0.93 and 1.01 p.p.m., two 3H doublets, J = 6 c.p.s., CH_3C– 0.98 and 1.01 p.p.m.

Anal. Calcd. for $C_{15}H_{24}O$: C, 81.76; H, 10.98. Found: C, 81.70; H, 10.87.

2,4-Dinitrophenylhydrazone had m.p. 196–198° (recrystallized from ethyl acetate), $[\alpha]_D$ −11°, ultraviolet λ_{max} 363 mμ (ε 21,500); lit.[5] m.p. 191–193° and 201–202°, $[\alpha]_D$ −43 and −79°, respectively.

Cyclocolor-4-en-3-one (**Cyclocolorenone, 2**).—A solution of cyclocoloranone (**6**, 340 mg.) in THF (5 ml.) was treated with a solution of phenyltrimethylammonium tribromide (PTT, 640 mg.) in THF (5 ml.). The yellow color disappeared progressively. The solvent was then evaporated under reduced pressure without heating, and the residue was dissolved in ether and filtered over silicic acid. The solvent was again evaporated *in vacuo*, leaving 400 mg. of oil. This was taken up in dimethylformamide (5 ml.) and added to a slurry of lithium carbonate (600 mg.) and lithium chloride (520 mg.) in DMF (10 ml.). After 5 hr. on the steam bath, the product was isolated in the usual way; the yellowish oil (330 mg.) was chromatographed over silicic acid (20 g.). Elution was carried out with 4% ether in petroleum ether and gave successively 79 mg. of crystals, m.p. 38–40°, identified as starting material **6** by t.l.c. and infrared, then 90 mg. of crystals, m.p. 74–78°, identified below as **17**, and finally 150 mg. of cyclocolorenone (**2**), an oil, which was purified by distillation at 120° (0.1 mm.). There was practically no intermediate fraction; 40 mg. of heterogeneous cyclocolorenones was eluted later.

Cyclocolorenone was identified by infrared, ultraviolet, and n.m.r., and by rotation, with authentic material. Its dinitrophenylhydrazone was also prepared and identified by melting point, ultraviolet, and infrared.

2α-Bromocyclocolor-4-en-3-one (**17**) had m.p. 74–78°; Beilstein test positive; infrared $\nu_{C=O}$ 1705 cm.$^{-1}$, $\nu_{C=C}$ 1620 cm.$^{-1}$; ultraviolet λ_{max} 271 mμ (ε 14,500); n.m.r. CH_3CH–, 0.90 p.p.m., doublet, 3H, J = 7 c.p.s., $2CH_3C$–, 1.00 and 1.25, $CH_3C=C$–, 1.76, doublet, J = 2 c.p.s., –C*H*Br–, 3.96 p.p.m., doublet, J = 3.5 c.p.s.[20]

2,4-Dinitrophenylhydrazone had m.p. 183–184°, ultraviolet λ_{max} 398 mμ (ϵ_{max} 31,000), Beilstein test positive.

1α-Cyclocolor-4-en-3-one (**18, Epicyclocolorenone**).—A solution of cyclocolorenone (**2**, 60 mg.) in 0.5 *N* ethanolic potassium hydroxide (4 ml.) was boiled under nitrogen for 1 hr. The product isolated as usual was chromatographed over silicic acid (5 g.) and gave crystalline epicyclocolorenone (**18**, 50 mg.), purified by sublimation and identified by melting point, $[\alpha]_D$, infrared ultraviolet, and n.m.r., and by the melting point and ultraviolet of its dinitrophenylhydrazone.

The same substance was obtained when the bromination-dehydrobromination sequence described above was followed by refluxing the DMF solution before isolation.

12-Hydroxy-1β,4ξ,5ξ,αH,10βH-guaian-6-one (**10**).—The diol **7** (100 mg.) was oxidized with CrO_3 in acetic acid at room temperature. The product was chromatographed over 5 g. of silicic acid. With 10% ether in petroleum ether, the crystalline β-ketol **10** (40 mg.) was eluted. It was purified by sublimation *in vacuo;* m.p. 72–73°; $[\alpha]_D$ −95°; for the n.m.r. see the text.

Anal. Calcd. for $C_{15}H_{26}O_2$: C, 75.58; H, 11.00. Found: C, 75.34; H, 10.83.

4ξ,10α-Dimethyl(1β,5ξ)azulan-6-one (**13**).—The ketol **10** (100 mg.) was warmed on the steam bath with 0..5 *N* methanolic potassium hydroxide (8 ml.). After neutralization with dilute sulfuric acid, water (10 ml.) was added, and the mixture was boiled with condensation of the distillate into 1 ml. of Brady's DNPH solution; acetone dinitrophenylhydrazone, identified by melting point and mixture melting point, was collected. The solution after distillation was extracted, and gave the saturated ketone **13** (50 mg.), which was evaporated *in vacuo* for purification, $[\alpha]_D$+5°, infrared $\nu_{C=O}$ 1695 cm.$^{-1}$.

2,4-Dinitro phenylhydrazone had m.p. 159–160°.

Anal. Calcd. for $C_{18}H_{24}N_4O_4$: C, 59.98; H, 6.71; N, 15.55. Found: C, 59.88; H, 6.79; N, 15.70.

Mono- and Diacetate of the Diol 7 (**11 and 12**).—The diol **7** (1 g.) was dissolved in pyridine (25 ml.) and acetic anhydride (5 ml.) and heated under reflux during 5 hr. Isolation in the usual manner gave 1.2 g. of crude product, which was chromatographed over alumina (25 g.). Two substances, homogeneous in t.l.c., were eluted successively: the diacetate **12** (490 mg.), characterized as such in particular by n.m.r., and the monoacetate **11** recrystallized in cyclohexane (m.p. 74–75°) (670 mg.); for the n.m.r. see the text.

The monoacetate had $[\alpha]_D$ +12°.

Anal. Calcd. for $C_{17}H_{30}O_3$: C, 72.30; H, 10.71. Found: C, 72.59; H, 10.46.

The diacetate had $[\alpha]_D$ +16°.

Anal. Calcd. for $C_{19}H_{32}O_4$: C, 70.33; H, 9.94. Found: C, 71.44; H, 9.91.

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[20] This splitting is attributed to interaction with the hydrogen of C-1 (β), and this value of J is then only compatible with the 2α configuration for the bromine atom.