

idic. No carboxylic acid could be detected when the alkaline solution was acidified. From the ether layer was obtained 0.130 g. of solid which was shown to be aldal by its infrared spectrum. One recrystallization from hexane-ether yielded 0.110 g. (55%) of VIII, m.p. 147-148.5°. The remainder of the starting material had been converted to water-soluble products (probably sulfonic acids) by the sulfuric acid.

In another, similar experiment, the white suspension which resulted when the sulfuric acid solution was poured onto ice was filtered directly, instead of being taken up in ether and treated with sodium hydroxide solution. The solid melted at about 65°, was very hygroscopic, and yielded an acidic oil on standing. Dilute alkali converted the solid to VIII. It seems likely that the solid was an oxonium salt of VIII or a sulfate ester of VII.

**x-Isopropyl-1-naphthoic Acid.**—Ethyl 1-naphthoate was alkylated with isopropyl bromide in carbon disulfide in the presence of aluminum chloride by the procedure of Gilman and Calloway.<sup>12</sup> The alkyl ester, b.p. 96-110° (0.2 mm.),  $n_D^{20}$  1.5772-1.5780, was saponified with sodium hydroxide. After chromatography and standing for three weeks, the oily acid crystallized. Recrystallization yielded a mixture of acids, probably the 5- and 6-isopropyl-naphthoic acids, which melted at 95-105° (3% yield); neut. equiv., 215; calcd. for  $C_{14}H_{14}O_2$ , 214.

(12) H. Gilman and N. O. Calloway, *THIS JOURNAL*, **55**, 4205 (1933).

A 0.35-g. sample of the acid was dissolved in cold, concentrated sulfuric acid and allowed to stand at 0° for 30 minutes. The mixture was then poured onto ice and worked up in the usual way to give 0.20 g. (57%) recovery of the acid (m.p. 128-133°, the infrared spectrum was virtually identical with that of the starting material). Only a trace of a neutral material was obtained and this did not give a dinitrophenylhydrazine derivative. There was, therefore, no evidence that an aldal had formed.

**Attempted Reaction of Cumene with Benzoyl Chloride.**—A solution containing 1.2 g. of cumene, 1.4 g. of benzoyl chloride and 3.5 cc. of stannic chloride in carbon disulfide was refluxed for 7 hours. No observable reaction occurred. The pale yellow solution was poured onto ice and hydrochloric acid, and the organic matter was taken up in ether. This solution was extracted with sodium bicarbonate solution and then washed with water and tested for the presence of carbonyl compounds with 2,4-dinitrophenylhydrazine reagent. There was no indication that any aldehydes or ketones were present. The ether layer was then extracted with dilute potassium hydroxide solution. Acidification of the combined alkaline extracts yielded 1.10 g. (90%) of benzoic acid. Evaporation of the ether left an oil which was shown by its infrared spectrum to be cumene contaminated with a very small amount of benzoyl chloride.

EVANSTON, ILL.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

## Terpenes. X.<sup>1,2</sup> The Constitution of Maaliol

BY G. BÜCHI, M. SCHACH V. WITTENAU AND DWAIN M. WHITE<sup>3</sup>

RECEIVED OCTOBER 13, 1958

The structure of maaliol, a tricyclic sesquiterpene alcohol, was shown to be LIII.

Maali resin is a soft cleni-like exudation from *Canarium samonense*, a tree endemic to the Samoan Islands. Chemical investigations on the resin were initiated by an anonymous chemist of Schimmel and Co.<sup>4</sup> who described a sesquiterpene alcohol, maaliol, m.p. 103-104°, and established the formula  $C_{15}H_{26}O$ . More recently, another substance of the same molecular composition, m.p. 102-103°, was isolated from *Valeriana officinalis* L. and the investigators suspected its identity with maaliol.<sup>5</sup> We have sent a sample of authentic maaliol to Dr. A. Hofmann, Sandoz A. G., Basel, and he has kindly informed us that the two specimens were indeed identical. The early researchers already established the presence of a tertiary hydroxyl group in maaliol by preparing a crystalline chromate ester  $(C_{15}H_{25})_2CrO_4$ . Furthermore, the natural product was reported to be stable to base, but on exposure to acids it was rapidly converted to a hydrocarbon  $C_{15}H_{24}$ . Some further relevant observations on the structure of maaliol are due to Hosking.<sup>6</sup> He found the compound to be stable to bromine and alkaline potassium permanganate and to be resist-

ant to catalytic reduction over platinum in neutral solvents. Maaliol was not affected by prolonged exposure to ozone and thus exhibited properties typical of saturated molecules. Treatment with hot formic acid produced a hydrocarbon  $C_{15}H_{24}$  which on catalytic hydrogenation absorbed almost two mole equivalents of hydrogen. Dehydrogenation of maaliol with selenium gave eudalene (VI) characterized by a picrate and a styphnate which were both compared with authentic samples. Hosking correctly concluded that this natural product is a saturated tricyclic sesquiterpene alcohol which may contain a cyclopropane ring.

We first eliminated the possibility that maaliol is identical with juniperol (macrocarpol)<sup>7</sup> ( $C_{15}H_{26}O$ ), m.p. 108°. A comparison of the infrared spectra of the two substances demonstrated their non-identity which was confirmed by mixture melting point determination.<sup>8</sup> Hosking<sup>6</sup> had shown previously by mixture melting point determination that maaliol is not identical with ledol<sup>9</sup> ( $C_{15}H_{26}O$ ), m.p. 105°.

In this paper it is shown that maaliol has structure I. In agreement with a previous finding<sup>6</sup> treatment of I with selenium gave eudalene (VI)

(1) Part IX, G. Büchi and K. Biemann, *Croatia Chem. Acta*, **29**, 133 (1957).

(2) A part of this investigation was published in a Communication to the Editor, G. Büchi and D. M. White, *THIS JOURNAL*, **79**, 750 (1957).

(3) National Institutes of Health Predoctoral Fellow 1955-1956.

(4) *Schimmel Reports*, 137 (1908).

(5) A. Stoll, E. Seebeck and D. Stauffacher, *Helv. Chim. Acta*, **40**, 1205 (1957).

(6) J. R. Hosking, deceased Oct. 14, 1916. We are indebted to Mrs. M. A. Hosking Wind for making these findings available to us in the form of an unpublished manuscript by J. R. H.

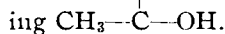
(7) H. Erdman and B. R. Thomas, *Chemistry & Industry*, 381 (1955).

(8) This comparison was kindly carried out by Dr. B. R. Thomas, Royal Institute of Technology, Stockholm.

(9) L. Dolejš, M. Šimeček, M. Horák and P. Šorm, *Chemistry & Industry*, 491 (1958); N. P. Kiryalov, *J. Gen. Chem. U.S.S.R.*, **23**, 1617 (1953), and earlier papers cited.

Dehydrogenation of the molecule in the gas phase<sup>10</sup> over a palladium catalyst produced eudalene (VI) again, but also a small amount of vetivalene (VII) (C<sub>15</sub>H<sub>18</sub>) which had been obtained previously from alantolactone.<sup>11,12</sup> These facts suggest that maaliol is a eudalene-type sesquiterpene and the small yield of vetivalene (VII) obtained indicates that the fifteenth carbon atom is located at C<sub>10</sub> rather than C<sub>1</sub> (cf. II) of the eudesmane skeleton. If this assumption is correct, we merely have to place the tertiary hydroxyl and one additional carbon-carbon bond to arrive at the complete structure.

The location of the hydroxyl group became clear from the following transformations. Acetylation of maaliol (I) with ketene, or more conveniently with acetic anhydride in boiling pyridine,<sup>13</sup> gave maaliacetate (VIII). That no skeletal rearrangement had occurred in this transformation was ascertained by reconversion to starting material with lithium aluminum hydride. Pyrolysis of maaliacetate (VIII) at 300° afforded a mixture of isomeric olefins C<sub>15</sub>H<sub>24</sub> which could be separated into pure compounds by fractional distillation. Strong absorption bands in the infrared at 885, 1637 and 2992 cm.<sup>-1</sup> suggested the presence of a high percentage of an olefin with a terminal methylene group. For more accurate characterization the olefin mixture was oxidized with osmium tetroxide and the products separated into β-maalidiol (XIX) (C<sub>15</sub>H<sub>26</sub>O<sub>2</sub>) (7.5% yield) and the isomeric γ-maalidiol (X) (>61% yield) which could also be prepared by permanganate oxidation of IX.<sup>14</sup> Further oxidation of X with lead tetraacetate yielded formaldehyde and normaaliolone (XI) (C<sub>14</sub>H<sub>22</sub>O), λ<sub>max</sub><sup>EIOH</sup> 280 mμ (ε 24.5), which could also be synthesized by ozonization of the olefin mixture just described. That this substance was a ketone rather than an aldehyde became clear from its infrared spectrum, which had a band at 1702 cm.<sup>-1</sup> but no peak characteristic of the aldehyde C-H stretching vibration. Furthermore, its 2,4-dinitrophenylhydrazone had λ<sub>max</sub><sup>EIOH</sup> 364 mμ (ε 21240) which is in good agreement with values reported for other ketone derivatives.<sup>15</sup> If it is assumed for the time being that the carbon skeleton was not altered in the pyrolysis of the acetate (VIII), maaliol must contain the grouping

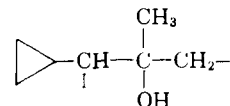


The spectral properties of the noraketone (XI) and its derivative demonstrate that the cyclopropane ring (if present) is not conjugated with the carbonyl group. Equilibration of XI with potassium deuteriooxide in deuterioethanol afforded a tri-

deuteroderivative which, when coupled with the fact that normaaliolone (XI) gave a negative iodoform test, demonstrated the presence of a —CH—CO—CH<sub>2</sub>— grouping. In agreement with this statement the band at 1430 cm.<sup>-1</sup> due to the deformation frequency of the methylene group adjacent to the carbonyl group present in the noraketone (XI) had disappeared in the deuterated substance.

Oxidation of normaaliolone (XI) with perbenzoic acid yielded a saturated lactone (XII) (C<sub>14</sub>H<sub>22</sub>O<sub>2</sub>) and the rapid rate of oxidation observed is in agreement with the behavior of cyclohexanones.<sup>16</sup> It then became necessary to develop a method for the conversion of this lactone (XII) to the ketocarboxylic acid XIV without cleaving the cyclopropane ring. After completion of experiments concerned with the conversion of thujone to thujaketocarboxylic acid (described in the Experimental Part) we adopted the following procedure. Mild hydrolysis of the lactone XII with aqueous sodium carbonate produced a hydroxycarboxylic acid (XIII) (C<sub>14</sub>H<sub>24</sub>O<sub>3</sub>) which, as anticipated for an ε-hydroxycarboxylic acid, did not relactonize. Further oxidation with chromium trioxide in pyridine solution gave a ketocarboxylic acid (XIV), λ<sub>max</sub><sup>EIOH</sup> 215 mμ (ε 2650) which possessed strong infrared bands (in CCl<sub>4</sub>) at 1709 (carboxyl), 1690 (carbonyl) and 1008 cm.<sup>-1</sup> (cyclopropane). Ring cleavage in the peracid oxidation had thus again occurred between the carbonyl group and the most highly substituted carbon atom. The spectral data of XIV are in good agreement with those of carone (XVI), λ<sub>max</sub><sup>EIOH</sup> 210 mμ (ε 3970),<sup>17</sup> infrared band (in CCl<sub>4</sub>) at 1685 cm.<sup>-1</sup>,<sup>18</sup> but not with dihydroumbellulone (XVII), λ<sub>max</sub><sup>EIOH</sup> 210 mμ (ε 2470), infrared peak at 1721 cm.<sup>-1</sup>,<sup>19-22</sup>

These findings can be summarized in the expression



Further verification of this part structure was forthcoming from the degradation of β-maalidiol (XIX). When it was oxidized with lead tetraacetate a diketone (XX) (C<sub>15</sub>H<sub>24</sub>O<sub>2</sub>) was formed which gave a positive iodoform test. β-Maalidiol (XIX) is thus not a stereoisomer of γ-maalidiol (X) but originated from β-maaliene (XVIII). In analogy to the previously reported pyrolysis of patchouly acetate<sup>23</sup> the thermal decomposition of VIII did not yield the terminal olefin exclusively. The spectral properties of the diketone XX, λ<sub>max</sub><sup>EIOH</sup> 214, 280 mμ (ε 2800, 68), strong infrared peaks (in CCl<sub>4</sub>) at 1704 (methylketone), 1681 (carbonyl con-

(10) Method of A. G. Anderson, J. A. Nelson and J. J. Tazuma, *THIS JOURNAL*, **75**, 4980 (1953).

(11) L. Ruzicka, P. Pieth, T. Reichstein and L. Ehmann, *Helv. Chim. Acta*, **16**, 268 (1933).

(12) We wish to thank Dr. A. Eschenmoser, ETH, Zürich, for an authentic sample of VII.

(13) This method for the acetylation of tertiary alcohols was developed by Y. R. Naves and P. Aridizio, *Ann. pharm. France*, **12**, 471 (1954).

(14) We have adopted the convenient isone-irone nomenclature for the designation of the isomeric maalienes. Thus, α-maaliene contains a trisubstituted, β-maaliene a tetrasubstituted and γ-maaliene a terminal double bond.

(15) J. D. Roberts and C. Green, *THIS JOURNAL*, **68**, 214 (1946); L. A. Jones, J. C. Holmes and R. B. Seligman, *Anal. Chem.*, **28**, 191 (1956).

(16) S. L. Friess, *THIS JOURNAL*, **71**, 2571 (1949).

(17) I. M. Klotz, *ibid.*, **66**, 88 (1944); A. E. Gillam and T. F. West, *J. Chem. Soc.*, 95 (1945).

(18) We are indebted to Dr. R. B. Bates for this determination.

(19) R. H. Eastman, *THIS JOURNAL*, **76**, 4115 (1954); R. H. Eastman and J. C. Selover, *ibid.*, **76**, 4118 (1954).

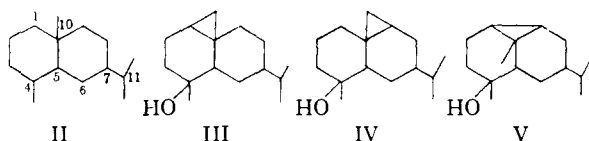
(20) G. Büchi and I. M. Goldman, *ibid.*, **79**, 4741 (1957).

(21) D. H. R. Barton, P. de Mayo and M. Shafig, *J. Chem. Soc.*, 140 (1958).

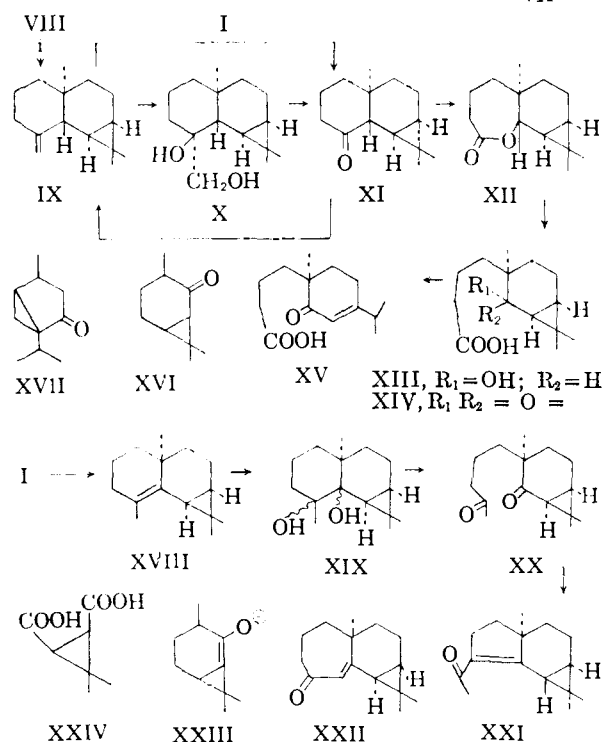
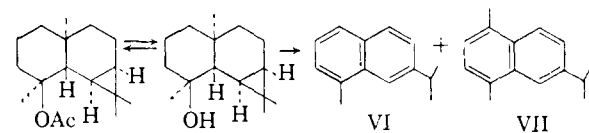
(22) D. Arigoni, H. Bosshard, H. Bruderer, G. Büchi, O. Jeger and L. J. Krebaum, *Helv. Chim. Acta*, **40**, 1732 (1957).

(23) G. Büchi and R. E. Erickson, *THIS JOURNAL*, **78**, 1262 (1956).

jugated with cyclopropane), 1013  $\text{cm}^{-1}$  (cyclopropane), are again in agreement with the part-structure proposed. Attempts to convert the diketone XX to the ketocarboxylic acid XIV by oxidation with sodium hypoiodite furnished mainly an unsaturated ketocarboxylic acid,  $\lambda_{\text{max}}^{\text{EtOH}}$  236  $\text{m}\mu$  ( $\epsilon$  10100) which we believe to be XV. Cleavage of the cyclopropane ring may well have taken place during the acid work-up of the reaction product. Equilibration of the diketone XX with potassium deuterioxide in deuterioethanol (0.5%) yielded a pentadeuteriodiketone. Under more drastic conditions a mixture of products was formed whose composition became clear from the mass spectrum.



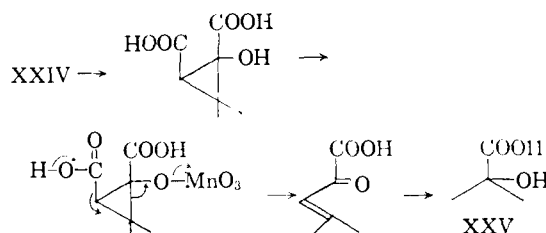
It contained (1) 20% of pentadeuteriodiketone, (2) 25% of hexadeuterodiketone, (3) 23% of a trideuterio derivative  $\text{C}_{15}\text{H}_{13}\text{D}_3\text{O}$ , and (4) 33% of a tetradeuterio compound  $\text{C}_{15}\text{H}_{13}\text{D}_4\text{O}$ . The infrared spectrum of this mixture had additional prominent peaks (in  $\text{CCl}_4$ ) at 1647 ( $\text{C}=\text{O}$ ) and 1618  $\text{cm}^{-1}$  (conjugated  $\text{C}=\text{C}$ ). Both findings suggest that the diketone XX had undergone partial conversion



to a tricyclic  $\alpha,\beta$ -unsaturated ketone which is most likely XXI, although the cycloheptenone formula XXII is not excluded. We can therefore exclude formulas III, IV and V for maaliol from further

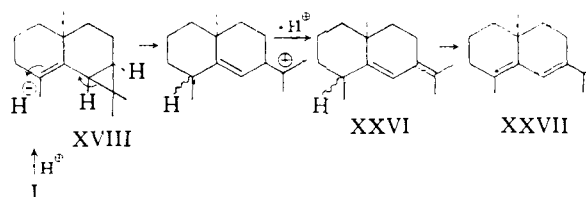
consideration. Structure I is in accord with the evidence presented if the cyclic carbonyl in XX can indeed enolize. Deuterium exchange on carone (XVI) confirmed the existence of the highly strained enol XXIII. In the presence of 20% NaOD in deuterioethanol XVI did exchange two hydrogens and reconversion to carone (XVI) proved that no structural change had taken place in the basic medium. The transformations so far discussed may now be illustrated in terms of formula I.

It was desirable to prove the presence of a cyclopropane ring in maaliol (I) by chemical methods. In principle, this problem can be solved by (a) degradation to a known derivative of cyclopropane or (b) by cleavage of the three nuclear carbon-carbon bonds.<sup>21,22,24</sup> Encouraged by the successful degradations of both car-3-ene and carone (XVI) to caronic acid (XXIV) by means of permanganate, we studied the effect of this oxidizing agent on maaliens. Under drastic conditions  $\alpha$ -hydroxyisobutyric acid (XXV) was the only isolable product. Whether it was formed by further oxidation of the anticipated caronic acid (XXIV) (*cf.* XXIV  $\rightarrow$  XXV) or by other processes is unknown. Its formation, however, left no doubt that maaliol



(I) possesses a geminal dimethyl group whose presence has so far been indicated only by the conversion to eudalene (VI). Attempts to degrade maaliene (IX) to caronic acid (XXIV) by oxidation with the same reagent under milder conditions produced only  $\gamma$ -maaliol (X) and the norketone (XI). We were thus forced to use the second more circuitous approach (b) to establish the presence of a cyclopropane ring.

When maaliol (I) was heated with concentrated formic acid a hydrocarbon  $\text{C}_{15}\text{H}_{24}$  (XXVII) was formed  $\lambda_{\text{max}}^{\text{EtOH}}$  241, 247, 256  $\text{m}\mu$  ( $\epsilon$  19000, 20000, 13500) which is undoubtedly identical with a substance described by previous investigators.<sup>4,6</sup> Catalytic reduction over Adams platinum catalyst confirmed the presence of two double bonds. If we assume that the change is initiated by dehydration of maaliol (I) to  $\beta$ -maaliene (XVIII) two bicyclic formulas, XXVI and XXVII, emerge.

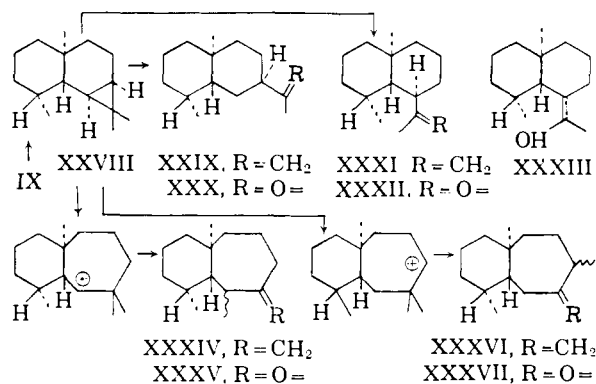


In harmony with both structures, the diene did not react with maleic anhydride and was not reduced by

(24) *E.g.*, E. P. Kohler and J. B. Conant, *This Journal*, **39**, 1404 (1917).

sodium in alcoholic solution. Structure XXVI is excluded on the following grounds: (a) neither ozonization nor periodate-permanganate<sup>25</sup> oxidation of the diene gave acetone; (b) the most intense ultraviolet absorption maximum observed is in better agreement with XXVII than with XXVI<sup>26</sup>; (c) the triple absorption is present in the spectra of other heteroannular dienes<sup>27</sup> but not in neoabietic acid.<sup>28</sup> The formation of eudalene (VI) in 60% yield by dehydrogenation of the diene is consistent with formula XXVII.

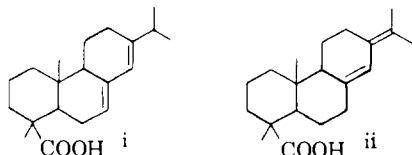
We now proceed to a discussion of the acid-catalyzed isomerization of maaliane (XXVIII). It can be prepared by catalytic hydrogenation of  $\gamma$ -maaliene (IX) over a supported palladium catalyst. In agreement with structure XXVIII a high resolution infrared spectrum of the carbon-hydrogen stretching region using a lithium fluoride prism showed no absorption bands characteristic of a methylene group on a three-membered ring.<sup>20,28-30</sup> The reliability of this method has recently been questioned<sup>31</sup> but it should be recognized that the measurements were taken on substances containing interfering functional groups rather than on saturated hydrocarbons. Isomerization of XXVIII with hydrogen chloride furnished an isomeric olefin containing a terminal methylene group with in-



frared bands at 880, 1629 and 3000 cm.<sup>-1</sup>. Its oxidation with osmium tetroxide led to a mixture of stereoisomeric glycols which was cleaved with lead tetraacetate to formaldehyde and a single crystalline norketone (XXXII) (C<sub>14</sub>H<sub>24</sub>O) which had an infrared band (in CCl<sub>4</sub>) at 1700 cm.<sup>-1</sup>. It did not react with hydroxylamine, semicarbazide and 2,4-

(25) R. U. Lemieux and E. v. Rudloff, *Can. J. Chem.*, **33**, 1701 (1955).

(26) Compare abietic acid (i),  $\lambda_{\max}$  241 m $\mu$ , and neoabietic acid (ii),  $\lambda_{\max}$  250 m $\mu$  (G. C. Harris and T. F. Sanderson, *THIS JOURNAL*, **70**, 339 (1948)).



(27) E. R. H. Jones and T. G. Halsall in L. Zechmeister, "Progress in the Chemistry of Organic Natural Products," Vol. XII, Springer, Wien, 1955, p. 53.

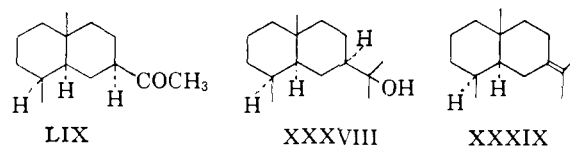
(28) A. R. H. Cole, *J. Chem. Soc.*, 3807, 3810 (1954).

(29) S. E. Wiberly and S. C. Bunce, *Anal. Chem.*, **24**, 623 (1952).

(30) We are indebted to Dr. M. Evans for these data.

(31) C. F. H. Allen, T. J. Davis, W. J. Humpblett and D. W. Stewart, *J. Org. Chem.*, **22**, 1291 (1957).

dinitrophenylhydrazine and gave a *negative* iodoform test (checked). The ketone afforded a maximum of 1.64 C-Me groups on Kuhn-Roth oxidation. On deuteration with both 0.5% and 7% NaOD in boiling deuterioethanol 2.98 D were introduced. Maaliane (XXVIII) could theoretically give rise to four olefins (XXIX, XXXI, XXXIV and XXXVI), whose genesis is outlined. The results of the deuterium exchange and the negative iodoform test led us initially to believe that the ketone is correctly represented by either XXXV or XXXVII and the non-Markownikoff ring opening was attributed to a conformational effect.<sup>2</sup> We were aware of the possibility that the ketone XXXII might not have enolized toward C<sub>6</sub> under the conditions of the deuterium exchange, but considered it unlikely because the scale model of the enol XXXIII did not appear to be *unduly strained*. New and definitive evidence in favor of a methyl ketone structure has now been adduced from the mass spectrum of this degradation product for which we are indebted to Drs. K. Biemann and J. Seibl, M.I.T.<sup>32</sup> The norketone gave a parent peak of (*m/e*) 208 and a strong peak of (*m/e*) 43 corresponding to a CH<sub>3</sub>CO<sup>+</sup> fragment, while the spectrum of the trideuterioketone exhibited a parent peak of (*m/e*) 211 and a high intensity peak of (*m/e*) 46 as demanded by a CD<sub>3</sub>CO<sup>+</sup> ion. It furthermore became clear that deuterium was introduced *only* on the methyl group because both the deuterated and the undeuterated ketones showed the (*m/e*) 165 ion corresponding to the molecule minus the methyl ketone group. This implies that the olefin contains an isopropenyl unit (XXIX or XXXI). A decision between the two remaining structures (XXX and XXXII) for the norketone seems possible on the following grounds: (a) compound XXX should give an iodoform test because the methyl ketone system is unhindered in both the axial and equatorial configurations; (b) the deuterium exchange experiment is incompatible with XXX, which should enolize toward C<sub>7</sub> as LIX indeed does and thus yield a tetradeuterio derivative. It must also be recalled that dihydroeudesmene (XXXIX) with *two space-demanding methyl groups* attached to the exocyclic double bond is formed with great ease by dehydration of the corresponding tertiary alcohol XXXVIII.<sup>33</sup> The



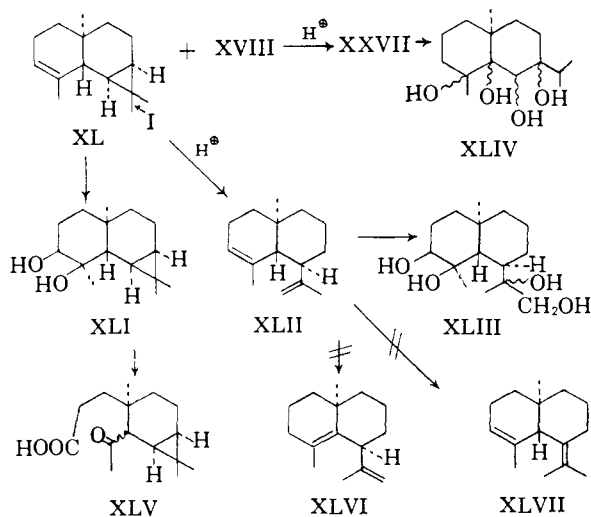
cleavages of the two cyclopropane bonds thus demonstrate the presence of C<sub>6</sub> → C<sub>11</sub> and C<sub>7</sub> → C<sub>11</sub> bonds in maaliol (I). The reality of the C<sub>6</sub> → C<sub>7</sub> bond in the molecule can hardly be questioned because it is retained in the dehydrogenation products.

We now wish to describe a reaction in which two cyclopropane bonds were ruptured competitively.

(32) These spectra were taken on a CEC 21-103 C mass spectrometer equipped with heated inlet system (135°) using an ionization potential of 70 V.

(33) L. Ruzicka, Pl. A. Plattner and A. Fürst, *Helv. Chim. Acta*, **25**, 1364 (1942).

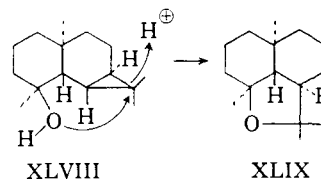
When maaliol (I) was treated with a catalytic amount of iodine a mixture of products was forthcoming which could be separated by chromatography into an olefin fraction and a crystalline product  $C_{15}H_{26}O$  isomeric with starting material. A partial separation of the olefin mixture was achieved by fractional distillation. The lower boiling portions had only strong terminal absorption in the ultraviolet region and the infrared spectrum with bands at 3000, 1630, 881 and 825  $cm^{-1}$  indicated the presence of olefins containing terminal and tri-substituted double bonds. The higher boiling distillation cuts had  $\lambda_{max}^{E_{1OH}^{OH}}$  245  $m\mu$  ( $\epsilon$  2420-10000) and the infrared spectra were in agreement with the presence of the conjugated diene XXVII. The exact composition of the olefin fraction was ascertained by oxidation with osmium tetroxide which furnished  $\beta$ -maaliol (XIX),  $\alpha$ -maaliol (XLI), a solid tetrol (XLIII) and a mixture of oily tetrols (XLIV). The structure of XLI was established by cleavage with lead tetraacetate to a ketoaldehyde and oxidation with silver oxide to a saturated ketocarboxylic acid (XLV) which gave iodoform on further oxidation with sodium hypiodite.  $\alpha$ -maaliene is thus XL. The solid tetrol XLIII consumed only two equivalents of sodium periodate and gave one equivalent of formaldehyde in 68% yield. The parent olefin is thus a non-conjugated diene for which we tentatively propose structure XLII. Isomerization of XLII to XLVII or a conjugated diene derived from XLVII does not seem possible because of steric interaction of the isopropylidene group with the methyl at  $C_4$ . Scale models also indicate that XLVI is prohibitively strained and the acid stability of XLII is thus explained. The formation of these four hydrocarbons (XVIII, XXVII, XL and XLII) can be rationalized as



The structure of the product  $C_{15}H_{26}O$  obtained by iodine catalysis must now be considered. Both the ultraviolet and the infrared spectra of the substance were in agreement with the presence of a saturated oxide. It was stable to 10% sulfuric acid and did not react with Brady 2,4-dinitrophenylhydrazine reagent<sup>34</sup> at reflux temperature. The

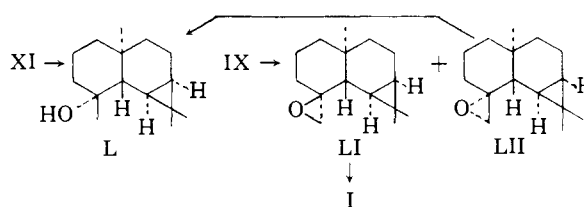
(34) O. L. Brady, *J. Chem. Soc.*, 756 (1931).

high stability of the oxide was also evidenced by its resistance to selenium at 300°. Since both epoxides and trimethylene oxides<sup>35</sup> may be expected to react with acids under the conditions quoted, the oxide must contain a larger hetero ring. Its genesis becomes rational if we assume cyclopropane bond cleavage again at  $C_7-C_{11}$  by a proton followed by bond formation with the tertiary hydroxyl at  $C_4$  (cf. XLVIII  $\rightarrow$  XLIX)



The formulation XLIX requires the presence of a geminal dimethyl system and the infrared spectrum does, in fact, possess strong bands of comparable intensity at 1360 and 1371  $cm^{-1}$ .<sup>36</sup>

We shall now discuss the configurations of the five asymmetric centers present in maaliol (I). The tertiary hydroxyl group is equatorial for the following reasons: (a) The C-O stretching absorption in the infrared spectrum of I occurs at 935  $cm^{-1}$  which is in good agreement with the values for 3 $\alpha$ -methylcholestan-3 $\beta$ -ol (940  $cm^{-1}$ )<sup>37</sup> and *epi*-patoulchouly alcohol (917  $cm^{-1}$ ).<sup>38</sup> (b) Dehydration of maaliol (I) with phosphorus oxychloride in pyridine gave a mixture of olefins which contained more than 70% of  $\gamma$ -maaliene (IX) as determined by gas-liquid partition chromatography. The mode of dehydration is characteristic of equatorial alcohols.<sup>1,37,39-41</sup> (c) Treatment of normalione (XI) with methylmagnesium bromide gave only *epi*-maaliol (L) (C-O stretch at 892  $cm^{-1}$ ). Unhindered cyclohexanones in general seem to yield mainly the methylcarbinols with axial hydroxyl groups.<sup>37,42</sup> (d) Epoxidation of  $\gamma$ -maaliene (IX) with perbenzoic acid led to a mixture of epoxides LI and LII which on reduction with lithium aluminum hydride gave maaliol (I) and *epi*-maaliol (L) in a ratio of



9:1, which also proves that no rearrangement had occurred in the acetate pyrolysis. Approach of the peracid should be more facile on the  $\beta$ -side of the

(35) G. Büchi, C. G. Inman and E. S. Lipinsky, *THIS JOURNAL*, **76**, 4327 (1954).

(36) We have not observed the appearance of a doublet in this region in any compound which includes the geminal dimethyl group on the cyclopropane ring; cf. the spectrum of car-3-ene, J. Pliva and V. Herout, *Coll. Czech. Chem. Comm.*, **15**, 160 (1950).

(37) D. H. R. Barton, A. da S. Campos-Neves and R. C. Cookson, *J. Chem. Soc.*, 3500 (1956), and references cited.

(38) G. Büchi, R. E. Erickson and N. Wakabayashi, to be published.

(39) H. Heusser, N. Wahba and F. Winternitz, *Helv. Chim. Acta*, **37**, 1052 (1954).

(40) M. Stoll, *ibid.*, **38**, 1587 (1955).

(41) J. D. Cocker and T. G. Halsall, *J. Chem. Soc.*, 4262 (1956).

(42) L. Ruzicka, N. Wahba, P. Th. Herzig and H. Heusser, *Ber.*, **85**, 491 (1952).

molecule (opposite the angular methyl group) and thus lead mainly to the epoxide LI. (e) The mass spectrum of maaliol has a low intensity parent peak (0.09% of total ion yield) of ( $m/e$ ) 222 like that of *epi*-patchouly alcohol (0.018%) which is definitely an equatorial alcohol.<sup>38</sup> The parent peaks in the spectra of *epi*-maaliol (L) (0.47%) and patchouly alcohol (3.46%), on the other hand, are intense and these substances therefore are axial alcohols. Whether this property must be ascribed to higher thermodynamic stability of the axial alcohols (less 1,3-diaxial interactions!) or to other factors is now being investigated by Dr. Biemann, who will report his findings in due course.

Maaliol is a *trans*-decalin as evidenced by the following observations. (a) The norketone XI was *not* epimerized in the presence of 10% sodium methoxide in methanol and therefore predominates at equilibrium. That the enol necessary for epimerization was actually formed is clearly evident from the previously described deuterium exchange experiment. The resynthesis of  $\gamma$ -maaliene (IX) from the norketone (XI) according to Wittig<sup>43</sup> demonstrated that XI and I have the same configuration at C<sub>5</sub>.<sup>44</sup> Maaliol (I) should thus be a *trans*-decalin because both the *trans-anti-cis* and the *trans-syn-cis* isomers have lower free energies than the corresponding *cis-syn-cis* and *cis-anti-cis* compounds.<sup>45</sup> (b) The formation of  $\beta$ -maaliene (XVIII) in the pyrolysis of maaliacetate VIII suggests that the acetyl group at C<sub>4</sub> and the hydrogen atom at C<sub>5</sub> are *cis*, although a partial isomerization of the  $\gamma$ -isomer IX to the  $\beta$ -isomer XVIII is not rigorously excluded. However, if this were the mode of formation of the  $\beta$ -isomer XVIII one would anticipate also the presence of the  $\alpha$ -isomer XL which we were unable to detect (*cf.* the iodine-catalyzed dehydration of maaliol). (c) The rotatory dispersion curve of the norketone XI provides some further evidence for a *trans- $\alpha$* -decalone.<sup>46</sup> It exhibits a positive single Cotton effect curve (see Experimental) which resembles that of (10-*R*)-*trans*-10-methyl-1-decalone, but is enantiomeric to that of cholestan-4-one.<sup>47</sup> If we assume that the cyclopropane ring in XI does not alter the rotatory dispersion curve drastically, maaliol (I) should have the opposite absolute configurations at C<sub>5</sub> and C<sub>10</sub> from those of eudesmol.<sup>48</sup> The absolute configuration at C<sub>7</sub>, however, is identical to that of eudesmol<sup>48</sup> and santonin.<sup>49</sup>

The configurations at C<sub>6</sub> and C<sub>7</sub> must be identical because a cyclopropane ring can be condensed with a cyclohexane ring only in a *cis* fashion. It is clear from the formation of the oxide XLIX that the potential isopropyl group at C<sub>6</sub> must have the equatorial ( $\beta$ ) configuration because oxide formation with the equatorial hydroxyl at C<sub>4</sub> is possible only in

(43) G. Wittig, *Angew. Chem.*, **68**, 505 (1956), and references cited.

(44) We are indebted to Dr. R. Albrecht for this experiment.

(45) *Cf.* the relative stability of perhydrophenanthrenes: W. S. Johnson, *THIS JOURNAL*, **75**, 1498 (1953), and also N. L. Allinger, *J. Org. Chem.*, **21**, 915 (1956).

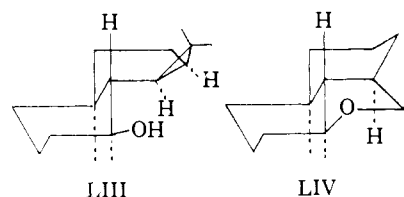
(46) We wish to thank Prof. C. Djerassi, Wayne State University, for this determination.

(47) C. Djerassi and D. Marshall, *THIS JOURNAL*, **80**, 3986 (1958).

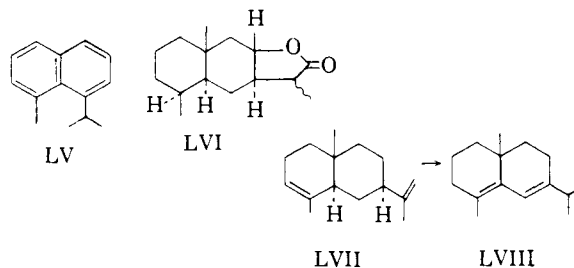
(48) B. Riniker, J. Kalvoda, D. Arigoni, A. Fürst, O. Jeger, A. M. Gold and R. B. Woodward, *ibid.*, **76**, 313 (1954).

(49) H. Bruderer, D. Arigoni and O. Jeger, *Helv. Chim. Acta*, **39**, 858 (1956).

this configuration. Scale models furthermore demonstrate that the formation of a tetrahydropyran ring (C<sub>4</sub>  $\rightarrow$  C<sub>7</sub>) is exceedingly unlikely if we are indeed dealing with a C<sub>4</sub>  $\beta$ -hydroxyl and a *trans*-decalin. The complete structure of maaliol is thus represented by LIII and that of the oxide by LIV.



It now seems possible to assign configurations to some of the degradation products already discussed. There is little doubt that both  $\alpha$ - (XLI) and  $\gamma$ -maaliol (X) are  $\beta$ -glycols which originated from  $\beta$ -attack of the oxidizing agent. Similarly, maaliene might be XXVIII and in support of this statement we may cite the configurations at C<sub>4</sub> of dihydroeudesmol (XXXVIII)<sup>50</sup> and tetrahydroalantolactone (LVI),<sup>51</sup> both of which are obtainable by catalytic reduction of the corresponding termi-



nal olefins. We now know that the acid-catalyzed isomerization of maaliene (XXVIII) results in the formation of XXXI with an equatorial isopropenyl group by cleavage of the "axial" C<sub>7</sub>  $\rightarrow$  C<sub>11</sub> bond. We should recall that dehydrogenation of maaliol (I) gave eudalene (VI) but none of the isomeric naphthalene (LV). This finding is no longer remarkable if we consider the steric interference between the bulky substituents at C<sub>6</sub> and C<sub>4</sub> in XXXI and XXXII. Molecular models suggest that such an interaction is augmented in the planar structure LV. In conclusion, we must consider the relationship between the diene XXVII and  $\delta$ -selinene prepared by isomerization of  $\alpha$ -selinene (LVII) with sulfuric acid.<sup>52</sup> The carbon skeleton of  $\delta$ -selinene was established by dehydrogenation to eudalene (VI) and catalytic reduction to a tetrahydroderivative indicated the presence of two double bonds. Because the diene was not reduced with sodium in ethanol, the authors supposed that the two double bonds were not conjugated. Mechanistically it is tempting to assume that  $\delta$ -selinene is LVIII and the known facts, including the resistance to sodium in alcohol, are in agreement with this proposal.<sup>53</sup> If this were correct  $\delta$ -selinene should be the enantiomer of the diene XXVII obtained from maaliol (I)

(50) D. H. R. Barton, *Chemistry & Industry*, 664 (1953); W. Klyne, *J. Chem. Soc.*, 3072 (1953).

(51) K. Tanabe, *Pharm. Bull. (Tokyo)*, **6**, 218 (1958).

(52) L. Ruzicka and M. Stoll, *Helv. Chim. Acta*, **6**, 846 (1923).

(53) Other heteroannular dienes are known not to be reduced under these conditions (*cf.* abietic acid and XXXVII).

because the absolute configuration of  $\alpha$ -selinene (LVII) was established previously by conversion to  $\alpha$ -eudesmol.<sup>54</sup> The optical rotations of  $\delta$ -selinene ( $\alpha_D +194^\circ$ ) and diene XXVII ( $\alpha_D -191^\circ$ ) seem to confirm this relationship although a direct comparison of samples was not possible because no  $\delta$ -selinene was available to us.

**Acknowledgments.**—We are indebted to Firmenich and Co., Geneva, for generous financial support and to Dr. Alida Hosking-Wind for the maaliol which was made available to us by Prof. O. Jeger, ETH, Zürich.

### Experimental

Microanalyses by Dr. S. M. Nagy and associates, M.I.T. Deuterium analyses using the combustion method were carried out by Mr. J. Nemeth, Univ. of Illinois.

Melting points were taken on a Kofler hot-stage microscope and are corrected. All ultraviolet spectra were measured in ethanol solution on a Cary recording spectrophotometer, model 11. Infrared spectra, unless otherwise indicated, were measured on a Baird Associates recording spectrophotometer, model B, with a sodium chloride prism. The listings of infrared bands include those which are relevant to structural arguments and other strong bands. For all chromatograms carried out on alumina, unless otherwise indicated, Alcoa alumina (Grade F-20, 80–200 mesh), which had been neutralized by treatment with ethyl acetate followed by washing with water and methanol, was used. The activity of the alumina was determined by the absorption of dyes according to the procedure of Brockmann.<sup>55</sup>

**Maaliol (I).**—A resin extract of *Canarium samonense* containing approximately 10% maaliol was obtained from Prof. Jeger, ETH, Zürich. The resin extract (100 ml.) was dissolved in 200 ml. of ether, extracted with aqueous 5% sodium carbonate solution and aqueous 10% sodium hydroxide solution, washed with water and dried over anhydrous magnesium sulfate. The ether was removed by distillation and a portion of the concentrate (68 g.) was dissolved in petroleum ether and passed through a column containing 1350 g. of alumina (activity I). The material eluted with benzene (16.2 g.) was crystallized from ligroin (b.p. 90–100°); yield 7.5 g. Two recrystallizations yielded an analytical sample of maaliol, m.p. 103–104°, pure and mixed with an authentic sample obtained from J. R. Hosking. The infrared spectrum was identical with that of the authentic sample; infrared spectrum (KBr): 752, 791, 833, 869, 877, 900, 917, 935, 970, 1031, 1099, 1136, 1163, 1379, 1449, 2857, 3333 cm.<sup>-1</sup>. The compound gave a pale yellow color reaction when treated with tetranitromethane.

*Anal.* Calcd. for C<sub>15</sub>H<sub>26</sub>O: C, 81.02; H, 11.79. Found: C, 81.23; H, 11.65.

Maaliol was also isolated by distillation. Base-extracted resin (131 g.) was distilled through a modified Podbielniak column. The fraction boiling from 99–141° at 2.2–2.7 mm. (56 g.) crystallized partially on cooling. The crystals (12 g.) were recrystallized from ligroin to yield maaliol (10.4 g.). Chromatography of the filtrates afforded an additional 4.5 g. of I.

**Maali Acetate (VIII).** A. **Reaction of Maaliol with Ketene and Sulfuric Acid.**—Ketene was prepared by the pyrolysis of acetone in an apparatus described previously.<sup>56</sup>

Maaliol (4.44 g., 0.02 mole) dissolved in 75 ml. of anhydrous ether was added slowly to 200 ml. of anhydrous ether (cooled to -60°) containing ketene (0.2 mole). Ketene (0.05 mole) was bubbled through the reaction mixture for one hour. Concentrated sulfuric acid (0.1 ml.) dissolved in 10 ml. of anhydrous ether was added dropwise for 15 minutes and ketene (0.05 mole) was bubbled through for one hour. The mixture was allowed to stand at -15° overnight. The ether solution was washed with aqueous 10% sodium carbonate solution and dried over anhydrous magnesium sulfate. Removal of the ether afforded 5.26 g. of an oil which was chromatographed on alumina (activity I). Elution with hexane yielded a fraction containing ole-

fins (0.61 g.) which was followed by a fraction of semi-crystalline material (4.21 g.). Recrystallization from petroleum ether at -60° afforded 3.06 g. of maali acetate, m.p. 36.0–36.4°; infrared spectrum (CCl<sub>4</sub>): 1014, 1037, 1093, 1148, 1162, 1245, 1330 (wk), 1365, 1376, 1457, 1719, 2825, 2882, 2922 cm.<sup>-1</sup>. The compound gave a pale yellow color reaction with tetranitromethane.

*Anal.* Calcd. for C<sub>17</sub>H<sub>28</sub>O<sub>2</sub>: C, 77.22; H, 10.67. Found: C, 77.36; H, 10.60.

B. **Reaction of Maaliol with Pyridine and Acetic Anhydride.**<sup>13</sup>—A mixture of maaliol (4.44 g., 0.02 mole), acetic anhydride (23 ml.) and pyridine (7 ml.) was heated under reflux for five hours. The reaction mixture, after cooling to ice temperature, was poured into 100 ml. of water and treated slowly with powdered sodium carbonate (23 g.). After carbon dioxide evolution had ceased, the organic material was extracted with five portions of ether, washed with two portions of 1 N hydrochloric acid, one portion of 10% sodium carbonate solution and one portion of water and the combined ether extracts were dried over anhydrous magnesium sulfate. Removal of the ether and chromatography of the residue afforded 2.9 g. of maali acetate (VIII) and 1.4 g. of maaliene.

**Conversion of Maali Acetate (VIII) to Maaliol (I).**—Maali acetate (100 mg.) was dissolved in ether and slowly added to excess lithium aluminum hydride dissolved in ether. The mixture was shaken for 30 minutes and left at room temperature for 16 hours. Ethyl acetate followed by sodium hydroxide solution was added to destroy excess reagent. The ether layer was dried over anhydrous magnesium sulfate and evaporated to a crystalline residue which was recrystallized from petroleum ether to yield 50 mg. of maaliol, m.p. 102.5–103.0°, pure or mixed with an authentic sample.

**$\gamma$ -Maaliene (IX).**—Maali acetate (VIII) (5.6 g., 0.021 mole), in a 10-ml. one-neck round-bottom flask with a 20-cm. Vigreux column leading to an ice-cooled receiver, was heated in a Wood metal-bath to 295–315° for 10 minutes. Acetic acid was evolved readily and collected in the receiver. After cooling to room temperature, the product and the distillate were combined and dissolved in ether. The ether solution was washed with 10% sodium carbonate solution and water and dried over anhydrous magnesium sulfate. Removal of the ether yielded 4.06 g. of a colorless oil which on distillation through a modified Podbielniak column afforded only one fraction,  $\gamma$ -maaliene (3.71 g.), b.p. 120.5–121.0° (11 mm.),  $n_D^{20}$  1.5008; infrared spectrum (pure liquid): 752, 837, 857, 885, 961, 1012(wk), 1133, 1379, 1440, 1637, 2780–2870, 2992 cm.<sup>-1</sup>. The compound gave a yellow color reaction with tetranitromethane.

*Anal.* Calcd. for C<sub>15</sub>H<sub>24</sub>: C, 88.15; H, 11.85. Found: C, 87.75; H, 11.72.

$\gamma$ -Maaliene was also formed in small yield in the reaction of maaliol with ketene and sulfuric acid and in the reaction of maaliol with acetic anhydride and pyridine (see the preparation of maali acetate).

**$\gamma$ -Maalidiol (X).**—A solution of  $\gamma$ -maaliene (IX) (2.40 g., 17.6 mmoles) in 10 ml. of reagent pyridine was added slowly and with cooling (20°) to a solution of osmium tetroxide (3.0 g., 17.6 mmoles) in 15 ml. of pyridine and the mixture was allowed to stand for 11 days at 25° in the dark. Most of the pyridine was removed *in vacuo* and the brown residue taken up in a mixture of 50 ml. of ethanol and 50 ml. of benzene to which was added 21 g. of mannitol and a solution of 21 g. of potassium hydroxide in 50 ml. of water and 100 ml. of ethanol. The mixture was heated under reflux for 7 hours, allowed to cool to 25°, concentrated *in vacuo* to 50 ml. and extracted with three 150-ml. portions of ether. The combined ether extracts were washed with water and dried over anhydrous sodium sulfate. Removal of the solvent yielded a yellow oil which was dissolved in benzene and chromatographed on a column of alumina (activity III). Benzene eluted 0.33 g. of a semi-crystalline product. Recrystallization from petroleum ether at -60° followed by sublimation afforded  $\beta$ -maalidiol (XIX) (0.21 g.), m.p. 95.0–95.5°, pure and mixed with an authentic sample (see preparation of  $\beta$ -maalidiol). Ether containing 0.5% of ethanol (followed by methanol to remove the last traces) slowly eluted 1.69 g. of crystalline material. Recrystallization from diisopropyl ether followed by sublimation afforded  $\gamma$ -maalidiol (X), m.p. 139.4–139.7°; infrared spectrum (CCl<sub>4</sub>): 1015(wk), 1028, 1374, 1455, 2840, 3320 cm.<sup>-1</sup>.

*Anal.* Calcd. for C<sub>15</sub>H<sub>26</sub>O<sub>2</sub>: C, 75.58; H, 11.00. Found: C, 75.37; H, 10.94.

<sup>54</sup> E. Reicksa, A. H. Wind and D. R. Koolhaas, *Helv. Chim. Acta*, **14**, 1042 (1931).

<sup>55</sup> H. Brockmann and H. Schodder, *Ber.*, **74**, 73 (1941).

<sup>56</sup> W. L. H. Murray and J. C. Sauer, *Org. Reactions*, **3**, 132 (1946).

$\gamma$ -Maalidiol has also been prepared from  $\gamma$ -maaliene in low yield by oxidation with potassium permanganate (see permanganate oxidation of  $\gamma$ -maaliene).

**Normaalione (XI). A. Lead Tetraacetate Oxidation.**—A solution of  $\gamma$ -maalidiol (X) (1.19 g., 5 mmoles) in 15 ml. of reagent acetic acid was added to lead tetraacetate (2.22 g., 5 mmoles) in 10 ml. of reagent acetic acid and allowed to stand for 10 hours at 25°. The acetic acid was removed *in vacuo* and the residue triturated with petroleum ether. The petroleum ether was dried over anhydrous magnesium sulfate and the solvent removed to yield a liquid (0.72 g.,  $n_D^{20}$  1.5007) which crystallized on standing. Recrystallization from petroleum ether followed by sublimation afforded normaalione, m.p. 58.0–58.5°; infrared spectrum (CCl<sub>4</sub>): 945, 1018(wk), 1070, 1300, 1372, 1450, 1702, 2880 cm.<sup>-1</sup>; ultraviolet spectrum: 280 m $\mu$  ( $\epsilon$  24.5). The compound gave a pale yellow color reaction with tetranitromethane; R. D. in methanol (*c* 0.1) at 27°:  $[\alpha]_{790}^{27} +4^\circ$ ,  $[\alpha]_{589}^{27} +10^\circ$ ,  $[\alpha]_{510}^{27} +42^\circ$ ,  $[\alpha]_{450}^{27} +68^\circ$ ,  $[\alpha]_{400}^{27} +132^\circ$ ,  $[\alpha]_{350}^{27} +330^\circ$ ,  $[\alpha]_{270}^{27} +938^\circ$ ,  $[\alpha]_{210}^{27} +1478^\circ$ ,  $[\alpha]_{200}^{27} +1900^\circ$ ,  $[\alpha]_{170}^{27} +1085^\circ$ ,  $[\alpha]_{290}^{27} +170^\circ$ ,  $[\alpha]_{285}^{27} -760^\circ$ ,  $[\alpha]_{270}^{27} -2180^\circ$ ,  $[\alpha]_{257}^{27} -2135^\circ$ .

*Anal.* Calcd. for C<sub>14</sub>H<sub>22</sub>O: C, 81.50; H, 10.75. Found: C, 81.47; H, 10.82.

**B. Ozonolysis in Ethyl Acetate.**—A solution of  $\gamma$ -maaliene (IX) (1.00 g., 4.9 mmoles) in 50 ml. of reagent ethyl acetate at -15° was ozonized (8 mg. of ozone per minute) for 50 minutes. The solution was concentrated *in vacuo* to 10 ml., added to pre-reduced palladium-on-charcoal (10%) and hydrogenated until hydrogen uptake ceased. The reaction mixture was filtered and the solvent removed under reduced pressure leaving 1.17 g. of a residue. An ether solution of this residue was extracted with 10% sodium carbonate solution, washed with water and dried over anhydrous magnesium sulfate. Removal of the solvent left 0.58 g. of an oil which was dissolved in hexane and passed through a column containing 15 g. of alumina (activity I). Hexane eluted 0.18 g. of normaalione (XI), characterized by its 2,4-dinitrophenylhydrazone. Elution with benzene afforded oils which could not be crystallized.

The sodium carbonate washings of the crude product after acidification with hydrochloric acid yielded 0.58 g. of organic material that could not be crystallized.

**C. Ozonolysis in Methanol.**<sup>17</sup>—A solution of  $\gamma$ -maaliene (IX) (0.50 g., 2.45 mmoles) in 30 ml. of reagent methanol and 5 ml. of reagent carbon tetrachloride at -60° was ozonized (5 mg. ozone per minute) for one hour. The solution was treated with 3 g. of sodium iodide in 10 ml. of glacial acetic acid and 20 ml. of methanol. The yellow coloration which gradually developed was removed by addition of aqueous 1 *N* sodium thiosulfate solution. After concentration *in vacuo* to a volume of 10 ml., the organic material was taken up in ether. The ether was washed with aqueous 10% sodium carbonate solution and water and dried over anhydrous magnesium sulfate. Removal of the ether afforded 0.54 g. of an oil which was passed through a column containing 15 g. of alumina (activity I). Elution with petroleum ether yielded 308 mg. of normaalione (XI).

Normaalione has also been prepared in low yield by permanganate oxidation of  $\gamma$ -maaliene (see permanganate oxidation of  $\gamma$ -maaliene).

**Normaalione 2,4-Dinitrophenylhydrazone.**—Addition of normaalione in ethanol to a 10% excess of weakly acidic 2,4-dinitrophenylhydrazine reagent (2.5 g. of 2,4-dinitrophenylhydrazine and 4 ml. of hydrochloric acid per 100 ml. of methanol) resulted in immediate precipitation of yellow crystals. Three recrystallizations from ethanol yielded crystals with a constant melting point of 166.5–167.0°; ultraviolet spectrum: 364 m $\mu$  ( $\epsilon$  21240) in C<sub>6</sub>H<sub>5</sub>OH.

*Anal.* Calcd. for C<sub>20</sub>H<sub>26</sub>N<sub>4</sub>O<sub>4</sub>: C, 62.16; H, 6.78; N, 14.50. Found: C, 62.15; H, 6.79; N, 14.35.

**Reaction of Normaalione (XI) with Sodium Methoxide.**—A solution of normaalione (115 mg., 0.56 mmole) in 5 ml. of 10% sodium methoxide in methanol was allowed to stand at 25° for one day. Water was added and the mixture extracted with three portions of ether. The ether extracts were combined, washed with water and dried over anhydrous sodium sulfate. Removal of the ether afforded a quantitative yield of normaalione, identical with an authentic sample.

**Deuterium Exchange of Normaalione (XI).**—A mixture of normaalione (103 mg., 0.5 mmole); 20 mg. of potassium

deuterioxide, 1 ml. of deuterium oxide and 3 ml. of deuterioethanol was heated under reflux in a nitrogen atmosphere for 10 minutes. After the reaction mixture had been cooled to 25°, the solvent was removed *in vacuo*. Three additional exchanges were carried out by the following procedure: 3 ml. of deuterioethanol and 0.5 ml. of deuterium oxide were added, the mixture refluxed for 10 minutes and the solvent removed *in vacuo*. After the final exchange deuterium oxide was added and the organic material removed with two portions of ether. The ether fractions were combined, dried over anhydrous magnesium sulfate and the ether removed. Sublimation of the crystalline residue (93 mg.) afforded pure deuterionormaalione, m.p. 58.0–58.5°.

*Anal.* Calcd. for C<sub>14</sub>H<sub>18</sub>D<sub>3</sub>O: 13.64 atom % D. Found: 13.42 atom % D.

**Epimaaliol (L).**—A solution of normaalione (XI) (102 mg., 0.5 mmole) in 4 ml. of anhydrous ethyl ether was added slowly to a solution of 400 mg. of methylmagnesium iodide in 4 ml. of anhydrous ethyl ether. The solution was heated under reflux for 22 hours, cooled in an ice-bath and a saturated solution of ammonium chloride in water was added dropwise. The ether layer was separated, washed with water and dried over anhydrous magnesium sulfate. Removal of the ether left a crystalline residue which upon recrystallization from petroleum ether afforded pure epimaaliol (L), m.p. 59.1–59.5°; infrared spectrum (KBr): 885, 910, 953, 1014(wk), 1050, 1103, 1137, 1170, 1240, 1290, 1461, 3000, 3530 cm.<sup>-1</sup>.

*Anal.* Calcd. for C<sub>12</sub>H<sub>22</sub>O: C, 81.02; H, 11.79. Found: C, 81.12; H, 11.71.

**Lactone (XII) from Normaalione (XI).**—To a solution of normaalione (927 mg., 4.5 mmoles) in 50 ml. of reagent chloroform at 20° a mixture of perbenzoic acid (820 mg., 5.9 mmoles) and 10 mg. of *p*-toluenesulfonic acid in 23 ml. of benzene was added dropwise. After allowing the solution to stand at 25° for 6.25 hours, the solution was extracted with two portions of 10% sodium carbonate solution, washed with water and dried over anhydrous magnesium sulfate. Removal of the solvent under reduced pressure afforded 1.0 g. of an oil, which was passed through a column containing 10 g. of Davison silica gel. Benzene eluted 464 mg. of normaalione (identified by melting point and mixed melting point with an authentic sample). Ether eluted 492 mg. of a crystalline product. Recrystallization from ethanol and water followed by sublimation afforded the lactone (XII), m.p. 113.2–114.0°; infrared spectrum (CCl<sub>4</sub>): 1022, 1490, 1690, 1140, 1180, 1290, 1234, 1279, 1324, 1354, 1441, 1719, 2840 cm.<sup>-1</sup>.

*Anal.* Calcd. for C<sub>14</sub>H<sub>22</sub>O<sub>2</sub>: C, 75.63; H, 9.97. Found: C, 75.67; H, 9.79.

A variety of reagents and experimental conditions were tried before the above procedure was developed. Initial experiments involving perbenzoic acid in chloroform with times varying from 3 to 24 hours gave yields of 10–25% with little recovered starting material. Peroxytrifluoroacetic acid in methylene chloride yielded no lactone. Perbenzoic acid and *p*-toluenesulfonic acid in benzene gave yields of 50%, but no starting material could be recovered. The yield based on recovered starting materials for the procedure finally used was 89%.

**Hydroxycarboxylic Acid (XIII).**—A solution of the lactone (492 mg., 2.21 mmoles) in 5 ml. of dioxane and 20 ml. of 10% sodium carbonate solution was heated under reflux for 3 hours. The solution was cooled, extracted with two portions of ether and acidified with a saturated aqueous tartaric acid solution until the pH was 2–3. The insoluble organic material was taken up in ether and the ether washed with water and dried over anhydrous magnesium sulfate. Removal of the ether left 440 mg. of crystalline residue. Recrystallization from cold ether afforded the hydroxycarboxylic acid (XIII), m.p. 127–121°; infrared spectrum (KBr pellet): 953, 1030(wk), 1041, 1058, 1081, 1111, 1214, 1250, 1273, 1289, 1394, 1322, 1363, 1401, 1427, 1464, 1486, 1702, 2560, 2940, 3460 cm.<sup>-1</sup>.

*Anal.* Calcd. for C<sub>13</sub>H<sub>18</sub>O<sub>3</sub>: C, 69.96; H, 10.07. Found: C, 70.06; H, 10.07.

**Ketocarboxylic Acid XIV.**—A solution of the hydroxycarboxylic acid XIII (145 mg., 0.6 mmole) in 3.5 ml. of reagent pyridine was added dropwise to a pyridine–chromium trioxide complex formed by adding chromium trioxide (96 mg., 0.96 mmole) to 1.8 ml. of reagent pyridine with tem-



perature maintained between 10 and 15°. The mixture, which darkened quickly, was agitated with a mechanical stirrer for 17 hours at 27°. After the addition of water, the organic material was removed by extraction with three portions of ether and the combined ether extracts were dried over anhydrous magnesium sulfate. Removal of the ether left 138 mg. of semi-crystalline material which was passed through a column of silica gel (Davison). Benzene containing 10% ether and later pure ether eluted 100 mg. of a liquid which crystallized when scratched. Three recrystallizations from petroleum ether-ether afforded pure ketocarboxylic acid XIV, m.p. 64.0–64.5°; infrared spectrum (CCl<sub>4</sub>): 1008, 1100, 1225, 1260, 1690, 1709, 2700- (broad), 2950 cm.<sup>-1</sup>; ultraviolet spectrum: 215 mμ (ε 2650).

*Anal.* Calcd. for C<sub>14</sub>H<sub>20</sub>O<sub>3.1/2</sub>H<sub>2</sub>O: C, 67.98; H, 9.37. Found: C, 68.41; H, 9.54.

**Maaliene (XXVIII).**—A solution of γ-maaliene (IX) (4.95 g., 0.024 mole) in 100 ml. of absolute ethanol was catalytically reduced at 1 atm. and 27° with 0.1 g. of pre-reduced 10% palladium-on-charcoal catalyst. After two hours 0.022 mole of hydrogen was absorbed. Continued treatment for 15 hours resulted in no further hydrogen uptake. The ethanolic solution was filtered and the solvent removed under reduced pressure to yield 4.53 g. of liquid. The liquid was distilled through a modified Podbielniak column,<sup>58</sup> b.p. 109–110° (7 mm.), *n*<sub>D</sub><sup>25</sup> 1.4876; infrared spectrum (pure liquid): 823, 954, 972, 1020, 1122, 1152, 1228, 1371, 1450, 2780–2880 cm.<sup>-1</sup>. A high resolution spectrum of the carbon-hydrogen stretching frequency region using a lithium fluoride prism showed no absorption bands characteristic of a methylene group on a three-membered ring.

**Isomerization of Maaliene (XXVIII).**—Anhydrous hydrogen chloride was bubbled through pure maaliene (3.50 g., 0.017 mole) at ice-bath temperature for 75 minutes. The product was allowed to stand at 0° for 20 hours, dissolved in petroleum ether, washed with 10% sodium hydroxide solution and water and dried over anhydrous magnesium sulfate. Removal of the petroleum ether yielded 3.2 g. of liquid which was distilled through a modified Podbielniak column. Two fractions were collected: (1) 0.84 g., b.p. 112–115° (7 mm.), *n*<sub>D</sub><sup>25</sup> 1.4931; (2) 2.08 g., b.p. 115–118° (7 mm.), *n*<sub>D</sub><sup>25</sup> 1.4947. The infrared spectrum of (1) was identical with the spectrum of (2) except that the bands due to a terminal olefin (3000, 1629 and 880 cm.<sup>-1</sup>) were more intense in (2) than in (1). Thus fraction 2 corresponded to a pure sample of XXXI; infrared spectrum (pure liquid): 880, 955, 1017, 1050, 1122, 1149, 1227, 1371, 1452, 1629, 2782–2900, 3000 cm.<sup>-1</sup>.

*Anal.* Calcd. for C<sub>13</sub>H<sub>18</sub>: C, 87.30; H, 12.70. Found: C, 87.39; H, 12.52.

**Oxidation of XXXI with Osmium Tetroxide.**—The olefin XXXI was oxidized with osmium tetroxide by the procedure used for the oxidation of γ-maaliene (see the preparation of γ-maaliol). In a typical run 2.50 g. (0.012 mole) of XXXI yielded 1.65 g. of diols. A second product (0.30 g.) was identified as β-maaliol (XIX), m.p. 92.0–92.5°, pure or mixed with an authentic sample which must have originated from XVIII present in XXVIII; infrared spectrum (CCl<sub>4</sub>): 1035, 1370, 1456, 2840, 3300 cm.<sup>-1</sup>.

**Norketone XXXII.**—A solution of the above diol (0.740 g., 3.1 mmoles) and lead tetraacetate (1.507 g., 3.5 mmoles) in 15 ml. of glacial acetic acid was allowed to stand at 25° for 10 hours. The solution was concentrated *in vacuo* to a volume of 1 ml., 20 ml. of 10% sodium carbonate solution was added and the organic material taken up in three portions of petroleum ether. The petroleum ether extracts were combined and dried over anhydrous sodium sulfate. Removal of the solvent yielded 0.55 g. of oil which was passed through a column containing 15 g. of alumina (activity III). Petroleum ether eluted 0.43 g. of liquid which crystallized from aqueous methanol. Recrystallization afforded the norketone XXXII, m.p. 33.2–33.4°; infrared spectrum (CCl<sub>4</sub>): 1140, 1160, 1185, 1271, 1348, 1456, 1700, 2860 cm.<sup>-1</sup>; C-methyl determination: 4 hours oxidation, 1.35 C-Me; 8 hours oxidation, 1.64 C-Me; 12 hours oxidation, 1.59 C-Me. The compound did not form a derivative when treated with 2,4-dinitrophenylhydrazine, hydroxylamine and semicarbazide.

(58) J. Cason and H. Rapoport, "Laboratory Text in Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1950, p. 237.

*Anal.* Calcd. for C<sub>14</sub>H<sub>20</sub>O: C, 80.71; H, 11.61. Found: C, 81.17; H, 11.81.

**Deuterium Exchange on Norketone XXXII.**—The active hydrogen atoms in XXXII were exchanged with deuterium by the procedure used for the exchange on normaaliene. In the reaction 172 mg. of XXXII yielded 127 mg. of sublimed deuterioketone, m.p. 33.2–33.8°.

*Anal.* Calcd. for C<sub>14</sub>H<sub>21</sub>D<sub>3</sub>O: 12.50 atom % D. Found: 12.41 atom % D.

Repetition of the exchange using 7% of NaOD in EtOD gave the same result.

**Iodine Dehydration of Maaliol (Preparation of β-Maaliene (XVIII), α-Maaliene (XL), Maalidienes (XXVII and XLII) and Maali Oxide (XLIX)).**—Pure maaliol (12 g., 0.054 mole) was heated to melting (103°) and several crystals of iodine were added. After an initial vigorous effluence of water the reaction mixture was gradually heated over a period of 75 minutes to 120°. The product was cooled to 25°, dissolved in petroleum ether and passed through a column containing 250 g. of alumina (activity I).

Petroleum ether eluted 7.62 g. of liquid which was fractionally distilled through a modified Podbielniak column. Five fractions were collected: (1) 0.83 g., b.p. 110–112° (8 mm.), *n*<sub>D</sub><sup>25</sup> 1.5036; (2) 2.63 g., b.p. 112–113° (8 mm.), *n*<sub>D</sub><sup>25</sup> 1.5038; (3) 1.95 g., b.p. 113–115° (8 mm.), *n*<sub>D</sub><sup>25</sup> 1.5035; (4) 1.22 g., b.p. 115–118° (8 mm.), *n*<sub>D</sub><sup>25</sup> 1.5058; (5) 0.35 g., b.p. 118–120° (8 mm.), *n*<sub>D</sub><sup>25</sup> 1.5152. Each fraction gave an intense brown color reaction with tetranitromethane. Infrared spectra (pure liquid): fractions 1 through 4 had almost identical spectra with bands at 772, 825, 881, 892, 955, 1065, 1132, 1159, 1191, 1224, 1368, 1441, 1630, 2780–2890 cm.<sup>-1</sup>; fraction 5 had bands at 876, 953, 1050, 1150, 1223, 1365, 1442, 1610, 1630–1650, 2780–2890 cm.<sup>-1</sup>; ultraviolet spectra: fractions 1 through 4 had only end absorption; fraction 5 had a maximum at 245 mμ (ε 2420).

Petroleum ether-benzene (1:1) eluted 2.94 g. of crystalline material. Recrystallization from methanol-water afforded maali ether, m.p. 66.5–67.5°; infrared spectrum (CCl<sub>4</sub>, CS<sub>2</sub>): 959, 1058, 1136, 1300, 1371, 1440, 1457, 3160 cm.<sup>-1</sup>.

*Anal.* Calcd. for C<sub>13</sub>H<sub>20</sub>O: C, 81.02; H, 11.79; mol. wt., 222. Found: C, 80.73; H, 11.62; mol. wt., 219.

Maali oxide (XLIX) did not react with 2,4-dinitrophenylhydrazine even when refluxed in Brady reagent,<sup>54</sup> and gave no color reaction with tetranitromethane.

**Catalytic Reduction of the Olefins from the Maaliol-Iodine Reaction.**—A solution of maaliene (fraction 2 from the iodine dehydration of maaliol; 0.41 g., 0.002 mole) was added to 40 mg. of pre-reduced 10% palladium-on-charcoal catalyst and reduced at 1 atm. and 27°. Hydrogen uptake was very rapid during 10 minutes until 20% of the calculated volume for one double bond had been absorbed, steady for 5 hours until 48% of the calculated volume had been absorbed, but then further uptake ceased. (In a second experiment 17% of the calculated volume of hydrogen was absorbed readily with the total volume absorbed being 47% of the calculated volume.) Filtration of the reaction mixture and removal of the solvent at reduced pressure afforded 0.41 g. of a liquid product; infrared spectrum (pure liquid, CCl<sub>4</sub>): 774, 955, 967, 1014(wk), 1065, 1133, 1224, 1358, 1443, 2940 cm.<sup>-1</sup>.

**β-Maaliol (XIX).**—A solution of 4.31 g. of crude β-maaliene (XVIII) (from the partial reduction of the olefins produced by iodine dehydration of maaliol; corresponding to 2.46 g., 0.012 mole, of pure β-maaliene calculated from the reduction data) in 15 ml. of reagent pyridine (distilled from barium oxide) was oxidized with osmium tetroxide (3.00 g., 0.018 mole) by the procedure described for the oxidation of γ-maaliene (see preparation of γ-maaliol). The crude product (3.8 g.) was passed through a column containing 120 g. of alumina (activity III). Elution with petroleum ether yielded two fractions: (1) 1.16 g. of colorless liquid that gave a red-brown color reaction with tetranitromethane; (2) 0.56 g. of yellow liquid that gave a pale yellow color with tetranitromethane. Elution with petroleum ether-benzene (9:1) yielded 0.29 g. of yellow liquid that gave a negative color reaction with tetranitromethane. Further elution with benzene and later with ether yielded 1.43 g. of a liquid which crystallized on cooling. Recrystallization from hexane afforded β-maaliol (XIX), m.p. 95–96°; infrared

spectrum (CCl<sub>4</sub>): 931, 971, 1007 (wk), 1032, 1050, 1332, 1371, 1456, 2900, 3384-3520 cm.<sup>-1</sup>.

*Anal.* Calcd. for C<sub>15</sub>H<sub>26</sub>O<sub>2</sub>: C, 75.58; H, 11.00. Found: C, 75.37; H, 11.14.

Elution with ether-methanol (49:1) yielded 0.60 g. of liquid. The material gave a pale yellow color reaction when treated with tetranitromethane. Elution with methanol yielded a trace of yellow material which gave no color reaction with tetranitromethane.

$\beta$ -Maalidiol (XIX) has been prepared also by osmium tetroxide oxidation of the olefin mixture from iodine dehydration of maaliol (I) (see preparation of  $\alpha$ -maalidiol (XLI)) and maalitretol (XLIII) and as a side product in the osmium tetroxide oxidation of  $\gamma$ -maaliene (IX) and of XXXI.

**Diketone XX.**—A solution of  $\beta$ -maalidiol (XIX) (536 mg., 2.25 mmoles) and lead tetraacetate (1.10 g., 2.47 mmoles) in 30 ml. of reagent glacial acetic acid was allowed to stand at 25° for 8 hours. Removal of the acetic acid *in vacuo* left a residue which was triturated with four portions of petroleum ether. The petroleum ether fractions were combined and concentrated to 550 mg. of liquid which was dissolved in petroleum ether and passed through a column containing 20 g. of alumina (activity III). Petroleum ether eluted 231 mg. of colorless liquid. Distillation through a semi-micro distillation apparatus afforded the diketone XX, *n*<sub>D</sub><sup>25</sup> 1.4858. Elution with benzene afforded an additional portion (131 mg.), *n*<sub>D</sub><sup>25</sup> 1.4855 (infrared spectrum identical to that of the petroleum ether fraction); infrared spectrum: 885, 952, 990, 1013, 1124, 1163, 1220, 1316, 1351, 1408, 1681, 1704 cm.<sup>-1</sup>; ultraviolet spectrum: 214.5  $\mu$  ( $\epsilon$  2800), 280  $\mu$  ( $\epsilon$  68).

*Anal.* Calcd. for C<sub>15</sub>H<sub>24</sub>O<sub>2</sub>: C, 76.22; H, 10.24. Found: C, 76.15; H, 10.31.

Oxidation of the diketone XX with alkaline sodium hypiodite afforded iodoform which was recrystallized from ethanol, m.p. 122.0-122.5°, pure and mixed with an authentic sample.

The diketone XX gave no color reaction when treated with fuchsin-aldehyde reagent. It reacted with 2,4-dinitrophenylhydrazine reagent to give two crystalline products which could be separated by trituration with ethanol. The ethanol-soluble compound crystallized from solution on cooling, m.p. 87-90°, ultraviolet maximum at 360  $\mu$  ( $\epsilon$  24500). The ethanol-insoluble derivative was recrystallized from ethyl acetate-ethanol, m.p. 143.9-144.6°, ultraviolet maximum at 360  $\mu$  ( $\epsilon$  28150).

**Deuterium Exchange of the Diketone XX.**—The active hydrogen atoms in XX were exchanged with deuterium by the procedure used for the exchange of normalone (XI). In the reaction 172.7 mg. of diketone yielded 131 mg. of distilled deuteriodiketone, b.p. 120° (bath, 0.1 mm.), *n*<sub>D</sub><sup>25</sup> 1.4821.

*Anal.* Calcd. for C<sub>15</sub>H<sub>18</sub>D<sub>8</sub>O<sub>2</sub>: 20.83 atom % D. Found: 21.05 atom % D.

The results obtained when the exchange was carried out under more drastic conditions are described in the Discussion section.

**$\alpha$ -Maalidiol (XLI) and Tetrol XLIII.**—A solution of olefins from iodine dehydration of maaliol (4.82 g., 0.0236 mole) in 25 ml. of pyridine (distilled from barium oxide) was oxidized with osmium tetroxide (6.00 g., 0.0236 mole) by the procedure described for the oxidation of  $\gamma$ -maaliene (IX). The crude product (5.28 g.) was passed through a column containing 180 g. of alumina (activity III).

Elution with petroleum ether-benzene (2:1) yielded 0.8 g. of a pale yellow liquid which was distilled through a semi-micro-distillation apparatus to give a colorless liquid, b.p. 167° (bath, 7 mm.), *n*<sub>D</sub><sup>25</sup> 1.5090. The infrared spectrum was almost identical with that of starting material.

Further elution with petroleum ether-benzene (2:1) followed by elution with petroleum ether-benzene (1:1) yielded 0.78 g. of crystalline material. Recrystallization from petroleum ether afforded  $\beta$ -maalidiol (XIX), m.p. 94.0-94.5°, pure and mixed with an authentic sample.

Further elution with petroleum ether-benzene (1:1) followed by elution with benzene-benzene-ether (9:1) ether-ether-methanol (99:1) yielded 0.9 g. of a viscous oil which could not be crystallized; infrared spectrum (CCl<sub>4</sub>): 689, 915, 954, 1014, 1043, 1062, 1115, 1132, 1316, 1341, 1360, 1457, 2870, 3450 cm.<sup>-1</sup>.

Elution with ether-methanol (99:1) yielded 1.37 g. of semi-crystalline material. Crystallization from benzene

afforded 0.20 g. of fine needles of  $\alpha$ -maalidiol (XLI), m.p. 129.0-129.2°. A mixed melting point determination with  $\gamma$ -maalidiol (X) gave a marked depression, 120-130°; infrared spectrum (KBr pellet): 997, 1020, 1039, 1057, 1150, 1181, 1370, 1447, 2860, 3360 cm.<sup>-1</sup>.

*Anal.* Calcd. for C<sub>15</sub>H<sub>26</sub>O<sub>2</sub>: C, 75.58; H, 11.00. Found: C, 75.30; H, 11.09.

Elution with methanol yielded 1.06 g. of semi-crystalline material. Crystallization from petroleum ether-benzene and from benzene afforded 0.30 g. of a tetrol (XLIII), m.p. 145.6-146.0°; infrared spectrum (KBr pellet): 890, 964, 1006, 1030, 1072, 1121, 1148, 1212, 1295, 1371, 1454, 2860, 3260 cm.<sup>-1</sup>.

*Anal.* Calcd. for C<sub>15</sub>H<sub>28</sub>O<sub>4</sub>: C, 66.14; H, 10.36. Found: C, 66.26; H, 10.15.

The infrared spectrum of the mother liquors suggested the presence of XLIV which was obtained by oxidation of XXVII with osmium tetroxide.

**Ketocarboxylic Acid XLV.**—A solution of  $\alpha$ -maalidiol (XLI) (56.7 mg., 0.24 mmole) and lead tetraacetate (116 mg., 0.26 mmole) in glacial acetic acid was allowed to stand at 23° for 6 hours. Removal of the acetic acid *in vacuo* left a residue which was triturated with three portions of ether. The ether portions were combined and concentrated to an oil (53 mg.). The oil was dissolved in 2 ml. of ethanol, 2 ml. of water and treated with 1 ml. of 1.4*N* sodium hydroxide solution and 123 mg. of silver nitrate. After shaking the mixture for 15 minutes and allowing the reaction to stand for 12 hours at 23°, the mixture was filtered through Filter-cel and the Filter-cel washed with water and then with ether. The washings were added to the filtrate and the ether layer separated. The aqueous layer was washed with two portions of ether. The ether extracts were combined, dried over anhydrous magnesium sulfate and concentrated to an oil (4 mg.). The aqueous layer was acidified with tartaric acid and extracted with three portions of ether. The combined ether extracts were dried over anhydrous magnesium sulfate and concentrated to an oil (57 mg.). The product, XLV, could not be crystallized. It gave a positive iodoform test; infrared spectrum (CCl<sub>4</sub>): 1164, 1218, 1296, 1351, 1380, 1418, 1449, 1690, 2630, 2870 cm.<sup>-1</sup>.

**Oxidation of the Tetrol XLIII with Sodium Periodate.**—To a slurry of tetrol XLIII (34.5 mg., 0.127 mmole) in 4 ml. of hot water in a distillation pot was added 18 ml. of sodium periodate solution (0.04 *M* in 1 *N* sulfuric acid) and allowed to stand at room temperature for one hour. After 10 ml. of water had been added to the pot, the solution was distilled and the first 10 ml. of the distillate collected in a small ice-cooled flask. A second 10-ml. fraction was collected after addition of another 10 ml. of water to the distillation pot. The trace of iodine present in the distillation fractions was removed by adding a small amount of sodium thiosulfate. Dimedone solution (100 mg. in 2 ml. of water and 2 ml. of ethanol) was added to each flask and the flasks were allowed to stand for 24 hours. Filtration yielded crystalline material from both fractions, 32.6 mg. (m.p. 146-175°) and 47.2 mg. (m.p. 145-150°), respectively. Recrystallization from ethanol afforded pure formaldehyde derivatives, 15 mg. (m.p. 190-191°) and 10 mg. (m.p. 191.0-191.3°), respectively. There was no melting point depression on mixture with an authentic sample. The total yield of derivative was 25 mg. (68%). An identical analysis performed on mannitol (25.9 mg.) yielded 66 mg. (80%) of formaldehyde derivative, m.p. 190.5-191.0°.

**Eudalene (VI) from Maaliol (I).**—Maaliol (1.00 g., 4.5 mmoles) was heated with selenium (1.0 g.) for 36 hours at 290-315°. The reaction mixture was cooled to 25° and treated with ether. The ether extract was filtered, washed with 10% potassium hydroxide solution and then with water and dried over anhydrous magnesium sulfate. Removal of the ether left 0.77 g. of an oil which was dissolved in petroleum ether and passed through a column containing 100 g. of alumina (activity I). Hexane eluted 0.69 g. of a colorless liquid which was distilled through a semi-micro distillation apparatus. A portion of the distillate, b.p. 149° (bath, 5 mm.), *n*<sub>D</sub><sup>25</sup> 1.5774, when treated with picric acid, afforded eudalene picrate, m.p. 92-93°; infrared spectrum of VI (CCl<sub>4</sub>, CS<sub>2</sub>): 752, 826, 876, 1370, 1455, 1590 (wk), 1619 (wk), 2850, 2962 cm.<sup>-1</sup>; ultraviolet spectrum of VI: 228  $\mu$  ( $\epsilon$  74100), 274  $\mu$  ( $\epsilon$  4190), 280  $\mu$  ( $\epsilon$  4460), 290  $\mu$  ( $\epsilon$  3490), 306  $\mu$  ( $\epsilon$  470), 314  $\mu$  ( $\epsilon$  240), 321  $\mu$  ( $\epsilon$  265).

**Eudalene (VI) and Vetivalene (VII) from Palladium Dehydrogenation.**—Molten maaliol (7.0 g., 0.0315 mole) was added dropwise for a period of 8 hours to a column containing 2 g. of 10% palladium-on-charcoal and 2 g. of acid-washed asbestos. The column was heated by refluxing a motor oil cut which provided a temperature of 336–338° at the center. Benzene (4 ml.) was passed through the column to remove any residual products. The products were dissolved in petroleum ether, water was separated with a separatory funnel and the organic layer was dried over anhydrous magnesium sulfate. Removal of the solvent yielded 5.27 g. of liquid, which was dissolved in petroleum ether and passed through a column containing 250 g. of Merck acid-washed alumina (activity I). Petroleum ether eluted two olefinic fractions: (1) 1.30 g.,  $n_{D}^{20}$  1.4786; (2) 0.71 g.,  $n_{D}^{20}$  1.4941. Petroleum ether-benzene eluted (3) 0.56 g.,  $n_{D}^{20}$  1.5032. Petroleum ether-benzene (49:1) eluted (4) 0.49 g.,  $n_{D}^{20}$  1.5530. Petroleum ether-benzene (19:1) eluted (5) 1.85 g.,  $n_{D}^{20}$  1.5740. Benzene eluted (6) 0.16 g.,  $n_{D}^{20}$  1.5780.

Fraction (5) distilled through a Holzman column in one fraction, 1.53 g., b.p. 122° (7 min.),  $n_{D}^{20}$  1.5800, was treated with an ethanolic solution of picric acid to yield eudalene picrate, m.p. 92–93°, pure and mixed with an authentic sample.

A solution of 0.14 g. of fraction 4 in ethanol was added to 4.7 ml. of 4% picric acid in ethanol, heated to boiling and then cooled. Four crystalline fractions were obtained by concentration of the mother liquors. The first fraction, 21 mg., m.p. 102–105°, was recrystallized twice from ethanol to yield vetivalene picrate, m.p. 113–114°, pure and mixed with an authentic sample. The three other fractions consisted of eudalene picrate, 76 mg.

**Partial Synthesis of Maaliol (I) and Epimaaliol (L).**—To a solution of  $\gamma$ -maaliene (IX) (380 mg., 1.8 mmoles) in 5 ml. of chloroform was added with cooling to 20° a solution of perbenzoic acid (290 mg., 2.1 mmoles) in 8.1 ml. of benzene and the solution allowed to stand at 25° for 22 hours. The reaction mixture was extracted with 10% sodium carbonate solution, washed with water, dried over anhydrous sodium carbonate and concentrated to 0.49 g. of liquid epoxides (LI and LII). The entire product was dissolved in 15 ml. of anhydrous ether and added dropwise to a slurry of lithium aluminum hydride (70 mg., 1.8 mmoles) in 15 ml. of anhydrous ether. The mixture was stirred at 25° for 3 hours and 2 ml. of water followed by 10 ml. of 6 *N* sodium hydroxide was added. The ether layer was separated and the aqueous layer extracted with two portions of ether. The ether solutions were combined, dried over anhydrous magnesium sulfate and concentrated to 384 mg. of oil, which was dissolved in 10 ml. of petroleum ether and passed through a column containing 15 g. of alumina (activity III). Petroleum ether eluted 189 mg. of oil. Petroleum ether-benzene (9:1) and later benzene eluted 118 mg. of crystalline maaliol (I), which was recrystallized from ligroin, m.p. 102–103°, pure and mixed with an authentic sample.

The oil eluted with petroleum ether was redissolved in petroleum ether and passed through a column of very active alumina (heated at 220° at 25 mm. for one day). Petroleum ether-benzene (9:1) eluted an oil (19 mg. after distillation). Benzene eluted 15 mg. of liquid which crystallized when seeded with epimaaliol (L). The material was sublimed and found to be identical with epimaaliol (L).

**Permanganate Oxidation of  $\gamma$ -Maaliene (IX).**—To a solution of  $\gamma$ -maaliene (0.95 g., 4.65 mmoles) in 70 ml. of acetone at  $-10^{\circ}$  was added dropwise with stirring a solution of potassium permanganate (0.88 g., 5.57 mmoles) in 22.5 ml. of acetone and 7.5 ml. of water. The solution was maintained at  $-10^{\circ}$  for 3 hours, then gradually warmed for a period of 2 hours to  $10^{\circ}$ . The solution was filtered and poured into 300 ml. of water. The mixture was extracted with three portions of ether, the ether washed with water and dried over anhydrous magnesium sulfate. Removal of the solvent left 1.25 g. of semi-crystalline material which was dissolved in benzene and passed through a column containing 40 g. of alumina (activity I). Benzene eluted 490 mg. of starting material. Benzene-ether (9:1) and later ether eluted 0.66 g. of a liquid. Ethanol eluted 200 mg. crystalline material. Recrystallization from diisopropyl ether afforded  $\gamma$ -maaliol (X), m.p. 135.5–136.5°, mixed with an authentic sample.

The fraction eluted with benzene-ether and ether was rechromatographed on 15 g. of alumina (activity III).

The sample was put on the column in benzene and came through in the first fraction. The eluate (0.49 g.) was distilled through a semi-micro distillation apparatus and afforded 0.45 g. of distillate, b.p. 180° (bath, 0.3 mm.); infrared spectrum (CCl<sub>4</sub>): 935(wk), 957(wk), 1038, 1077, 1121, 1194, 1282, 1366, 1416, 1466, 1579(wk), 1600(wk), 1721, 2890 cm.<sup>-1</sup>; ultraviolet spectrum: 227 m $\mu$  ( $\epsilon$  5980), 276 m $\mu$  ( $\epsilon$  928).

*Anal.* Calcd. for C<sub>13</sub>H<sub>18</sub>O<sub>4</sub>: C, 65.53; H, 7.61. Calcd. for C<sub>10</sub>H<sub>14</sub>O<sub>3</sub>: C, 65.91; H, 7.94. Found: C, 65.53, 65.81; H, 7.50, 7.71.

The compound did not react with 2,4-dinitrophenylhydrazine reagent and gave a negative test with ferric chloride. Treatment with tetranitromethane afforded a very pale yellow color reaction.

**Permanganate Oxidation of a Mixture of Maalienes. A.**

—To the olefin fraction from the pyridine-acetic anhydride acetylation of maaliol (10.35 g., 0.05 mole) in a 2-l. flask with stirrer, condenser and dropping funnel, 1000 ml. of aqueous 5% potassium permanganate solution was added over a 3-hour period while the temperature was gradually raised from 25 to 100°. To the refluxing solution 112 g. of powdered potassium permanganate was gradually added during 45 hours. Only a trace of volatile material was obtained from steam distillation of the reaction mixture. The flask was cooled in an ice-bath and sulfur dioxide passed over the reaction mixture until all the manganese dioxide was reduced. The reaction mixture was acidified with sulfuric acid, saturated with sodium chloride and extracted with eight 100-ml. portions of ether. The ether layer was extracted with sodium carbonate solution until all the acidic material was removed. Evaporation of the ether left 0.5 g. of liquid. The aqueous basic extract was acidified with sulfuric acid, saturated with sodium chloride and extracted with five 100-ml. portions of ether. The extract was dried over anhydrous magnesium sulfate and the ether evaporated leaving 0.5 g. of liquid, which was dissolved in ether and treated with diazomethane. The solution was dried over anhydrous magnesium sulfate and concentrated to a liquid (0.51 g.). Saponification of the product by heating for 90 minutes with 2 ml. of 10% potassium hydroxide in methanol yielded 0.45 g. of acidic material which could not be crystallized.

The aqueous acidic oxidation medium was concentrated to 800 ml. and continuously extracted with ethyl acetate for 48 hours. The ethyl acetate was washed with 10% sodium hydroxide solution and water. The ethyl acetate washings of the aqueous layer were added to the ethyl acetate extract, dried over anhydrous magnesium sulfate and concentrated to a trace of liquid. The sodium hydroxide extract was acidified, saturated with brine and extracted with ethyl acetate, which was dried over anhydrous magnesium sulfate. Removal of the solvent left 1.5 g. of liquid which was dissolved in ether and passed through a column containing 40 g. of silica gel (Davison). Ether eluted 0.8 g. of oil from which on heating in a sublimation apparatus at 15 mm. a crystalline material (50 mg.) sublimed. Recrystallization from ether-petroleum ether afforded  $\alpha$ -hydroxyisobutyric acid (XXV), m.p. 78–79°, pure and mixed with an authentic sample.

*Anal.* Calcd. for C<sub>4</sub>H<sub>8</sub>O<sub>3</sub>: C, 46.13; H, 7.75; neut. equiv., 104. Found: C, 45.97; H, 7.41; neut. equiv., 102.

**B.**—When the above procedure was used on a solution of maaliene (10 g., 0.049 mole) in 10 ml. of acetone under milder oxidation conditions (the temperature was maintained at 35° for 20 hours, then raised to 65° for 25 hours), starting material and normaaliene (XI) were isolated (2.6 g.). The acids isolated could not be induced to crystallize.

**Conversion of the Diketone XX to the Ketocarboxylic Acid XXV.**—To a solution of the diketone XX (164 mg.) in 0.8 ml. of dioxane, 0.2 ml. of water and 0.4 ml. of 10% potassium hydroxide solution was added iodine-potassium iodide solution until the reaction mixture was a pale yellow for one minute. It was then heated to 60° for three minutes and more iodine-potassium iodide solution was added until the yellow color persisted. The mixture was cooled, 2 ml. of water added and the mixture centrifuged to remove the iodoform that crystallized from the solution. The supernatant was treated with 10% sodium bisulfite solution, acidified with hydrochloric acid and extracted with three portions of ether. The ether then was dried over anhydrous magnesium sulfate and evaporated leaving 90 mg. of a

liquid. The product was dissolved in ether and extracted into sodium hydroxide solution. The dried ether after evaporation left 8.5 mg. of oil. The sodium hydroxide extract was acidified with hydrochloric acid and the organic material extracted into ether, which was dried over anhydrous magnesium sulfate. Removal of the solvent left a liquid product which was chromatographed on silica gel. The reaction yielded 68 mg. of acidic material which was eluted from the column with ether; infrared spectrum ( $\text{CCl}_4$ ): 885, 925, 1110, 1205, 1275, 1412, 1452, 1656, 1696, 2858  $\text{cm}^{-1}$ ; ultraviolet spectrum: 236  $\text{m}\mu$  ( $\epsilon$  10100).

The product formed an oily 2,4-dinitrophenylhydrazone; ultraviolet spectrum: 376  $\text{m}\mu$  ( $\epsilon$  22000).

**Treatment of the Diketone XX with Sodium Methoxide.**—To a solution of the diketone XX (43.4 mg., 0.18 mmole) in 3 ml. of reagent methanol at 0°, 3 ml. of 10% sodium methoxide in methanol was added and the solution was allowed to stand at 0° for 20 minutes and 25° for one hour. Water (15 ml.) was added and the mixture was extracted with three portions of ether, which were combined and dried over anhydrous magnesium sulfate. Removal of the ether left 38.3 mg. of liquid, which was passed through a column of alumina (activity III) in petroleum ether and treated with 2,4-dinitrophenylhydrazine reagent to form a derivative (40 mg.) which was recrystallized from ethanol, m.p. 147.0–147.5°, pure and mixed with a sample of the 2,4-dinitrophenylhydrazone of XX.

**Treatment of Maali Oxide (XLIX) with Selenium.**—A mixture of XLIX (523 mg., 2.36 mmoles) and 525 mg. of selenium was heated to 290–330° for one day in a Wood metal-bath. The reaction mixture was cooled to 25° and triturated with ether. The ether was filtered, extracted with two portions of 10% sodium hydroxide solution, washed with water and dried over anhydrous magnesium sulfate. Removal of the ether left 0.47 g. of a brown oil which was dissolved in petroleum ether and passed through a column of alumina (very high activity, heated at 220° and 25 mm. for one day).

Petroleum ether eluted 122 mg. of a liquid which after distillation weighed 81.5 mg., b.p. 70–80° (bath, 0.04 mm.),  $n_D^{20}$  1.5093; infrared spectrum ( $\text{CCl}_4$ ): 1370, 1460, 2950  $\text{cm}^{-1}$ . The ultraviolet spectrum indicated the absence of naphthalenes.

Further elution with petroleum ether yielded 254 mg. of liquid, of which 208 mg. was distilled (yield 176 mg.), b.p. 65–75° (bath, 0.04 mm.),  $n_D^{20}$  1.5035. The compound did not form a picrate when treated with 4% ethanolic picric acid. After the distillate had set for several days crystals formed which were identical with starting material.

Ether eluted 42 mg. of a brown oil which was distilled (17 mg.), b.p. 80° (bath, 0.04 mm.). After cooling, the distillate crystallized partially. The crystals were identical with starting material.

**Dehydration of Maaliol (I) to the Diene XXVII.**—Maaliol (I) (2.0 g.) was dissolved in 20 ml. of anhydrous formic acid and the mixture heated on the steam-bath for 5 hours. The material was then poured on ice-water and the hydrocarbon extracted with five portions of petroleum ether. The organic layer was washed repeatedly with aqueous sodium bicarbonate solution and with water and was then filtered through 20 g. of alumina (activity I).

After the solvent had been removed by evaporation the residue was distilled and had b.p. 118–120° (8 mm.) (1.13 g.),  $n_D^{20}$  1.5238,  $[\alpha]_D^{20}$   $-231^\circ$  ( $c$  2.97,  $\text{CHCl}_3$ ),  $\alpha_D$   $-191^\circ$ ,  $\lambda_{\text{max}}^{\text{OH}}$  241, 247, 256  $\text{m}\mu$  ( $\epsilon$  19000, 20000, 13500). Vapor phase chromatography indicated the presence of only one substance; infrared spectrum (neat) 876, 955, 995, 1030, 1065, 1175, 1215, 1270, 1295, 1375, 1385, 1450–1470, 1620, 1645, 2900 (broad)  $\text{cm}^{-1}$ .

*Anal.* Calcd. for  $\text{C}_{15}\text{H}_{24}$ : C, 88.16; H, 11.84. Found: C, 88.16; H, 11.78.

The diene XXVII did not react with maleic anhydride in boiling benzene (28 hr.) and was not reduced by sodium in boiling ethanol nor in boiling 1-pentanol.

**Catalytic Reduction of XXVII.**—The diene XXVII (14.7 mg., 0.072 mmole) was dissolved in 1 ml. of glacial acetic acid and reduced over Adams platinum catalyst in a microhydrogenator. The uptake of hydrogen ceased after 3.14 ml. (0.14 mmole) of hydrogen had been absorbed.

**Oxidation of the Diene XXVII to a Mixture of Tetrols XLIV.**—The diene XXVII (2.54 g.) was dissolved in pyridine (64 g.). After the addition of osmium tetroxide (6 g.) the reaction mixture was allowed to stand in the dark for 13

days. The pyridine was then removed *in vacuo* and the residue dissolved in a mixture of 100 ml. of ethanol and 100 ml. of benzene. Forty grams of mannitol and potassium hydroxide (42 g.) were then added and the mixture allowed to reflux for 7.5 hours. After the organic material had been isolated by the conventional method it was further purified by chromatography over 60 g. of alumina (activity III). Ether eluted 2.69 g. of a colorless material which could not be crystallized. Both the infrared and ultraviolet spectra indicated the absence of unsaturation and the substance gave a negative color reaction with tetranitromethane. Oxidation of this mixture of tetrols XLIV with sodium periodate gave an oily substance which was treated with 2,4-dinitrophenylhydrazine. Paper chromatographic analysis of the crude derivatives indicated the absence of acetone and formaldehyde.

**Ozonization of the Diene XXVII.**—The diene (204 mg.) was dissolved in ethyl acetate (10 ml.) and ozonized at  $-60^\circ$ . The solution was then mixed with 20 ml. of water and heated to reflux. The distillate was treated with 800 mg. of 2,4-dinitrophenylhydrazine in 30 ml. of methanol. After the addition of water, crystals separated which were filtered. Analysis by paper chromatography demonstrated the absence of the derivatives of acetone and formaldehyde.

**Conversion of the Diene XXVII to Eudalene (VI).**—The diene (0.858 g.) was mixed with selenium (0.79 g.) and heated to reflux for 20 hours. The reaction mixture was extracted with ether and the ether washed consecutively with aqueous potassium hydroxide solution and water. After drying, the ether was removed *in vacuo*, the oily residue (0.61 g.) dissolved in petroleum ether and passed through a column of 5 g. of alumina (activity I). The eluate had an infrared spectrum which was superimposable on that of eudalene (VI). The picrate had m.p. 93.5° (from ethanol) and the styphnate m.p. 118–121° (from ethanol). Neither derivative gave a melting point depression when mixed with an authentic sample.

**Dehydration of Maaliol (I) with Phosphorus Oxychloride.**—Maaliol (1 g.) was dissolved in a mixture of pyridine (15 ml.) and phosphorus oxychloride (1.85 g.) and the solution allowed to stand at room temperature for 18 hours. The pyridine hydrochloride which had separated was removed by filtration and the filtrate diluted with water and extracted with petroleum ether. The organic layer was washed subsequently with aqueous sodium bicarbonate solution and water. After the solvent had been dried with sodium sulfate it was removed by evaporation *in vacuo* and the oily residue chromatographed in hexane solution over 35 g. of alumina (activity I). The eluate was concentrated and distilled through a Hickman flask. It had strong infrared bands at 871, 1637 and 2990  $\text{cm}^{-1}$  and contained over 70% of  $\gamma$ -maaliene (IX) ascertained by gas-liquid partition chromatography.

**Juniperol.**—A sample of juniperol, obtained from B. R. Thomas, Kungl. Tekniska Högskolan, Stockholm, Sweden, was recrystallized, m.p. 103–106°, and used for a mixed melting point determination with maaliol, mixed m.p. 74–84°; infrared spectrum (KBr pellet): 970, 1010, 1021, 1043, 1114, 1170, 1240, 1282, 1360, 1452, 3020, 3190  $\text{cm}^{-1}$ .

**Thujalactone.**—Thujone (4.6 g., 0.03 mole) was added to a mixture of peroxytrifluoroacetic acid (0.032 mole, prepared by the method of Sager and Duckworth<sup>59</sup>) and trifluoroacetic acid in an ice-bath at a rate sufficient to maintain the temperature at 10–15°. The reaction mixture was diluted with 10 ml. of chloroform and made basic with 6 g. of sodium carbonate in 30 ml. of water. The two layers were separated and the aqueous layer extracted with chloroform. The chloroform solutions were combined and dried over anhydrous magnesium sulfate. Removal of the solvent left 4.4 g. of liquid which was distilled through a modified Podbielniak column. The fraction boiling at 152–155° (31 mm.), 1.3 g., partially crystallized on cooling. The crystals were filtered and washed with cold petroleum ether (yield 0.70 g.). Recrystallization afforded thujalactone, m.p. 60.2–60.4°.

*Anal.* Calcd. for  $\text{C}_{10}\text{H}_{16}\text{O}$ : C, 71.39; H, 9.59. Found: C, 71.32; H, 9.65.

In another oxidation the above procedure was altered by using chromatography over alumina (activity II) instead

(59) W. F. Sager and A. Duckworth, *THIS JOURNAL*, **77**, 188 (1955).

of fractional distillation to isolate the product. The yield of recrystallized product was 38%.

**Thujaketonic Acid.**—A solution of thujalactone (500 mg., 3 mmoles), chromium trioxide (220 mg., 2.2 mmoles), two drops of concentrated sulfuric acid and three drops of water in 6.5 ml. of glacial acetic acid was allowed to stand at 27° for 5 hours. Sodium carbonate was added to neutralize the sulfuric acid and the solvent was removed *in vacuo* to yield a viscous liquid which was dissolved in ether and extracted with 10% sodium carbonate solution. The ether layer was washed with water and dried over anhydrous magnesium sulfate. Removal of the solvent afforded 0.30 g. of starting material. The basic aqueous layer was acidified with hydrochloric acid and extracted with ether, which was dried over anhydrous magnesium sulfate. Removal of the ether left 0.18 g. of liquid. When seeded with a crystal of thujaketonic acid (prepared from thujone by permanganate oxidation<sup>60</sup>) the product crystallized. Recrystallization from benzene-petroleum ether afforded thujaketonic acid, m.p. 74.5–75.3°; infrared spectrum (CCl<sub>4</sub>): 944, 1022(wk), 1092, 1172, 1220, 1380, 1684, 2880 cm.<sup>-1</sup>.

The product formed a 2,4-dinitrophenylhydrazone which was recrystallized from ethanol, m.p. 161–162°; ultraviolet spectrum: 368 mμ ( $\epsilon$  22000).

Several other methods for the preparation of thujaketonic acid were attempted but the yields were low. These methods consisted of: (1) base hydrolysis of thujalactone followed by chromium trioxide-pyridine oxidation, (2) base hydrolysis of thujalactone followed by sodium hypobromite oxidation and (3) chromium trioxide oxidation of thujalactone at 15–20° in acetic acid.<sup>61</sup>

**Conversion of Normaaliene (XI) to  $\gamma$ -Maaliene (IX).**—A 0.9 M solution of *n*-butyllithium (3.15 ml.) in anhydrous ether was added under vigorous stirring to a suspension of methyl-triphenylphosphonium bromide (1.02 g.) in 12 ml. of ether. After 2 hours at room temperature normaaliene (0.5 g.) in 15 ml. of ether was added and the solution stirred overnight. Tetrahydrofuran (50 ml.)<sup>62</sup> was added and the

(60) F. Tiemann and F. W. Semmler, *Ber.*, **30**, 429 (1897).

(61) Method of E. J. Corey and J. J. Ursprung, *THIS JOURNAL*, **78**, 5041 (1956).

(62) Modification of F. Sondheimer and R. Mechoulam, *ibid.*, **79**, 5029 (1957).

ether removed by distillation. After 6 hours at reflux the solution was poured in water, extracted with petroleum ether and the organic layer washed with water and then dried with sodium sulfate. The solvent was removed by evaporation and the residue chromatographed over 15 g. of alumina (Woelm, neutral, act. I). Hexane eluted 400 mg. (80%) of an oil which after distillation had an infrared spectrum identical with that of highly purified  $\gamma$ -maaliene (IX) prepared by pyrolysis of maaliacetate (VIII).

**Deuterium Exchange of Carone (XVI).**—Sodium (0.149 g.) was dissolved in EtOD (3 ml.). After the addition of carone (0.9 g.) the solution was allowed to reflux for 20 minutes and the deuterioethanol removed by evaporation. Three additional exchanges were carried out using 2 ml. of EtOD each time. After the last exchange the residue was taken up in petroleum ether, the organic phase washed with D<sub>2</sub>O and dried. The deuterated carone was purified by distillation, b.p. 95–105° (3.8 mm.) (bath temperature measured). Its mass spectrum indicated the presence of 80% dideuteriocarone and 20% monodeuteriocarone. The above exchange was repeated using deuteriocarone and ethanol. The product obtained had an infrared spectrum identical with that of carone.<sup>63</sup>

**Deuterium Exchange of LIX.**<sup>64</sup>—Dihydroeudesmol<sup>65</sup> (230 mg., m.p. 85–86°) was dehydrated by means of POCl<sub>3</sub> in pyridine.<sup>67,64</sup> Ozonolysis of the mixture of olefins (–60° in methanol-carbon tetrachloride solution) and work-up in the usual way<sup>67</sup> afforded an oil, the active hydrogens of which were exchanged with deuterium (*cf.* procedure used on normaaliene (XI)). Distillation of the deuterated material in a micro-distillation apparatus afforded 138 mg. of colorless oil which, upon mass-spectral analysis, showed mass peaks at 212 (tetra-deuterated nor-ketone LIX), 194 (tetra-deuterated LIV minus -CD<sub>2</sub>), 184 (tetra-deuterated trisnor-ketone derived from XXXIX) and 46 (CD<sub>3</sub>CO- group).

(63) We are indebted to Dr. T. Matsuura for these experiments.

(64) We wish to thank Dr. I. M. Goldman for this experiment.

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## Experiments with 2-Arylidene-3(2H)-thianaphthenone-1,1-dioxides. II. Reactions of *p*-Thiocresol and of Grignard Reagents with 2-Arylidene-3(2H)-thianaphthenone-1,1-dioxides

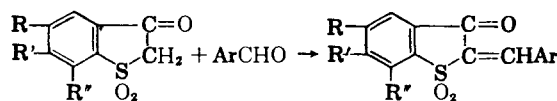
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The condensation reaction of substituted 3(2H)-thianaphthenone-1,1-dioxides (I) with aromatic aldehydes now has been further investigated. Oxidation of 2-arylidene-3(2H)-thianaphthenone and its substituted derivatives (IIIa-e) with hydrogen peroxide proved to be a general method for the preparation of 2-arylidene-3(2H)-thianaphthenone-1,1-dioxide and its substituted derivatives (*cf.* IIa,b,g,i,k). 2-Arylidene-3(2H)-thianaphthenone-1,1-dioxides (II) undergo an addition reaction with *p*-thiocresol, yielding the thiol adducts believed to have structure V. Conjugate addition, without any indication of cleavage, now has been observed when substances of type II are allowed to react with arylmagnesium halides, yielding colorless reaction products, believed to have structures VII.

Recently<sup>1,2</sup> the condensation of 3(2H)-thianaphthenone-1,1-dioxides (I) with aromatic aldehydes has been reported; *e.g.*, 3(2H)-thianaphthenone-1,1-dioxide (Ia) condenses with benzaldehyde to give 2-benzylidene-3(2H)-thianaphthenone-1,1-dioxide (IIa). We now have extended the study of this condensation reaction and have obtained a number of new arylidene derivatives (IIc-f,h,j,l). Oxidation of 2-arylidene-3(2H)-thianaphthenone

and its substituted derivatives (IIIa-e, respectively) with hydrogen peroxide also leads to the formation of the corresponding 2-arylidene-3(2H)-thianaphthenone-1,1-dioxides (IIa,b,j,i,k) in good yield.



(1) A. Mustafa and S. M. A. D. Zayed, *THIS JOURNAL*, **79**, 3500 (1957).

(2) W. Asker, A. F. A. Shalaby and S. M. A. D. Zayed, *J. Org. Chem.*, **23**, 1781 (1958).

Ia, R = R' = R'' = H  
b, R' = R'' = H; R = CH<sub>3</sub>  
c, R = R'' = H; R' = CH<sub>3</sub>  
d, R = R' = H; R'' = CH<sub>3</sub>