TERPENOIDS-LXXXIII

STRUCTURE OF β -BERGAMOTENE*

K. S. KULKARNI, S. K. PAKNIKAR and S. C. BHATTACHARYYA National Chemical Laboratory, Poona, India

(Received 12 December 1965)

Abstract— β -Bergamotene, in Indian valerian root oil, is a sesquiterpene analogue of β -pinene. Its structure has been established as I by application of physical methods and chemical degradations to known compounds, pinane (XXIX) and bicycloekasantalic lactone (XXXIII). The possible biogenesis of β -bergamotene and its relationship to other sesquiterpenes, such as α - and β - santalenes has been discussed and conclusions drawn regarding its stereochemistry by comparison of the NMR spectra of these related products.

EXAMINATION of European valerian root oil (*Valeriana officinalis*) has led to the isolation of a number of interesting compounds.¹⁻³ The preliminary examination of Indian valerian root oil (*Valeriana wallichi*),⁴⁻⁷ however, calls for more details.⁸ The present paper reports an investigation on the structure of β -bergamotene, a new sesquiterpene, occurring in Indian valerian root oil and its relationship with other related hydrocarbons, α -bergamotene, α - and β -santalenes, copaene, α -longipinene, ylangene etc.

Neutral fraction "N" of the Indian valerian root oil on stagewise chromatography over alumina led⁸ to the isolation of two sesquiterpenic hydrocarbons as the less polar components, one of which proved to be identical with calarene or β -gurjunene (II), the structure of which has been established by Büchi *et al.* and further confirmed by Sorm *et al.*⁹ The second hydrocarbon, named β -bergamotene, has a novel carbon skeleton which was suspected as early as 1960 and the structure III suggested by Sorm *et al.* for a sesquiterpene hydrocarbon isolated from bergamot oil and called bergamotene.¹⁰ In conformity with the accepted nomenclature of pinenes, the closely related bergamotene, examined by Sorm *et al.*, should be named as α -bergamotene. No chemical proof in support of the structure (III) was available before the appearance

* Communication NO. 865

From the National Chemical Laboratory, Poona-8, India.

- ^a A. Stoll, E. Seebeck and D. Stauffacher, Helv. Chim. Acta 40, 1205 (1957)
- ^a J. Kripinsky, V. Herout and F. Sorm, Coll. Czech. Chem. Comm. 24, 1884 (1959).
- ⁴ Tejsingh, Viswapal and K. L. Handa, Ind. Pref. 1, 55 (1957).
- ⁶ Tejsingh and K. L. Handa, Ind. Oil and Soap J. 25, 178 (1959).
- ^e K. Bullock, Pharm. J. 117, 152 (1926).
- ⁷ Sadgopal and B. C. Gulati, Soap Perf. Cos. 28, 1006, 1129, 1261 (1956).
- ⁸ C. S. Narayanan, K. S. Kulkarni, A. S. Vaidya, S. Kanthamani, G. Lakshmi Kumari, B. V. Bapat, S. K. Paknikar, S. N. Kulkarni, G. R. Kelkar and S. C. Bhattacharyya, *Tetrahedron* 20, 963 (1964).
- ⁹ G. Büchi, F. Greuter and T. Tokroyama, *Tetrahedron Letters* No. 18, 827 (1962); J. Vrkoc, J. Kripinsky, V. Herout and F. Sorm, *Ibid.* No. 4, 225 (1963).
- ¹⁰ V. Herout, V. Ruzicka, M. Vrany and F. Sorm, Coll. Czech. Chem. Comm. 15, 373 (1950).

¹ A. Stoll and E. Seebeck, Liebigs Ann. 603, 158 (1957).

of our preliminary communication on β -bergamotene.¹¹ Since then, isolation of α -bergamotene from two different sources has been reported.^{12,13} The structure of α -bergamotene rests mainly on the NMR data of Kovats. From the evidence recorded in this paper, β -bergamotene possesses the structure I and is related to β -santalene (IV), as β -pinene (V) is related to camphene (VI).



The IR spectrum (Fig. 1) of β -bergamotene indicates that one of the double bonds is of the methylenic type >C=CH₂ (3030, 1745, 1653, 875 cm⁻¹; typical of β -pinene or camphene) and the other one trisubstituted (832 cm⁻¹) in the form of an isopropylidene group (single peak at 1370 cm⁻¹).

On catalytic hydrogenation, β -bergamotene absorbs two moles of hydrogen to give the saturated hydrocarbon tetrahydro- β -bergamotene (VII), $C_{15}H_{28}$, thus showing the presence of two double bonds. Unlike the parent compound, the tetrahydro derivative does not give any colouration with tetranitromethane. Its IR spectrum (Fig. 1) is not identical with that of any satuated bicyclic sesquiterpenoid recorded in the literature, though it shows close similarity to that of bergamotane, on the basis of which the presence of the bergamotane skeleton was suspected.¹⁴

Dehydrogenation of β -bergamotene with selenium does not yield any naphthalenic or azulenic hydrocarbon, but gives a product containing a benzenoid system (λ_{max} 265 m μ , ν_{max} 1600, 1499, 815 cm⁻¹) indicating the presence of a six-membered ring in β -bergamotene. The GLC of the dehydrogenation products shows the presence of several components; however, one of the major peaks corresponds to that of dihydrocurcumene (VIII). In view of the fact that α - or β - pinene on dehydrogenation yields a mixture of *o*- and *p*-cymene, the presence of IX is also expected in the dehydrogenation products. This, however, could not be established with certainty.

The complete structure of the sidechain in β -bergamotene has been established by ozonolysis and other degradative experiments. Selective ozonolysis of β -bergamotene gives acetone and an unsaturated monoaldehyde (XV); v_{max} 2710, 1721;

- ¹² E. Sz. Kovats, Helv. Chim. Acta 46, 2705 (1963).
- ¹³ G. V. Pigulevski and A. V. Borovkov, Zh. Prikl. Khim. 36, 4, 926 (1963).
- ¹⁴ J. Pliva, M. Horak, V. Herout and F. Sorm, *The Terpenes, Coll. of Spectra and Physical constants* 1 (1960); Ref. 6, plate S193.

¹¹ K. S. Kulkarni, S. K. Paknikar, A. S. Vaidya, G. R. Kelkar, R. B. Bates and S. C. Bhattacharyya Tetrahedron Letters No. 8, 505 (1963).



1653, 875 cm⁻¹, due to —CHO and >C—CH₂ groupings. This suggests that one of the ethylenic linkages is of the type $\frac{CH_3}{CH_3}$ >C—CH— and is selectively cleaved during ozonolysis. The presence of the isopropylidene group is also indicated by the NMR spectrum (signals at 8.35 and 8.42 τ). Analogous results of ozonolysis have been reported in other instances; e.g. α -elemene (X), has been shown to give the α,β -unsaturated ketone (XI) on selective ozonolysis;¹⁵ neoabietic acid (XII) under similar conditions is converted to the α,β -unsaturated ketone (XIII).¹⁶ In support of the above findings, β -santalene (IV) gives bicycloekasantalal (XIV).

On oxidation with silver oxide,¹⁷ the aldehyde (XV) is converted to the corresponding acid (XVIa), characterized as its methylester (XVIb) which shows characteristics IR bands for the terminal methylene group (3060, 1653, 876 cm⁻¹). Catalytic hydrogenation of the ester results in the uptake of one mole of hydrogen to give the saturated ester (XVII), which shows characteristic IR absorption at 1730, 1190, 1166 cm⁻¹, due to the ester grouping, but no bands due to the methylene group. The ester XVII on treatment with phenylmagnesium bromide followed by dehydration of the resulting

¹⁵ S. K. Paknikar and S. C. Bhattacharyya, Tetrahedron 18, 1509 (1962).

¹⁴ G. C. Harris and T. F. Sanderson, J. Amer. Chem. Soc. 70, 339 (1948).

¹⁷ C. Enzell, Acta Chem. Scand. 15, 1303 (1961).



diphenyl carbinol (XVIII) yields the hydrocarbon (XIX), $C_{24}H_{28}$ (v_{max} 1600, 1488 cm⁻¹; λ_{max} 251 m μ).¹⁸ The position of the UV_{max} suggests the presence of the grouping Ph Ph > C = CHR and hence of the grouping $CH_3 > C = CH - CH_2$ in β -bergamotene. On ozonolysis the hydrocarbon (XIX) is converted to a mixture of the aldehyde (XX; v_{max} 2710, 1720 cm⁻¹) and benzophenone. The former on silver oxide oxidation is converted to the corresponding acid (XXIa), yielding the methyl ester (XXIb) with diazomethane. When this methyl ester is subjected to another Barbier-Wieland degradation, it yields a mixture of aldehyde (XXIII), v_{max} 2710, 1721 cm⁻¹ and benzophenone, via the intermediate (XXII), $C_{23}H_{26}$; v_{max} 1604, 1502 cm⁻¹, phenyl; λ_{max} 249.5 m μ .¹⁸ The tertiary nature of the aldehyde group in XXIII is confirmed by its conversion to the corresponding acid (XXIVa), the methylester (XXIVb) of which is resistant towards alkaline hydrolysis. It is, therefore, safe to conclude the presence of XXV in β -bergamotene. The presence of a three proton singlet at 9.05 τ in its NMR spectrum indicates that R₃ in the formula (XXV) may be a methyl group.*

The location of the methylene group in β -bergamotene is established by the following experiments. The unsaturated ester (XVIb) on reduction with LAH gives the corresponding unsaturated alcohol (XXVI), ozonolysis of which furnishes formaldehyde and a keto alcohol (XXVII) with the carbonyl group on a six membered ring (ν_{max} 1715 cm⁻¹). A band at 1420 cm⁻¹ indicates the presence of a --CO--CH₂--

• We are grateful to Prof. P. de Mayo for helpful discussion on this point and suggesting possibilities of an alternative structure while examining the Ph.D. thesis of one of the authors (K. S. K.).

¹⁸ J. D. Cocker and T. G. Halsall, J. Chem. Soc. 4262 (1956).



grouping and hence that of a $R-C-CH_2$ moiety in the six-membered ring of β -bergamotene, thus accounting for fourteen out of the fifteen carbon atoms.

Taking into consideration its bicyclic nature and assuming that β -bergamotene follows the isoprene rule, it can be represented by the structure I or XXVIII, the former being preferred because of the stability of tetrahydro- β -bergamotene (VII) towards anhydrous hydrogen chloride.

The presence of a cyclobutane ring in β -bergamotene is supported by its conversion to pinane. The mixture of the aldehyde (XXIII) and benzophenone obtained by

ozonolysis of the hydrocarbon (XXII), on Wolff-Kishner reaction is converted to pinane and diphenyl methane, identified by comparison of their retention times against authentic samples on a GLC column.

In view of the wellknown conversion of α - and β -pinenes via hydrochlorination and dehydrochlorination to camphene, it was anticipated that the unsaturated acid (XVIa) obtained by selective ozonization of β -bergamotene, followed by oxidation with silver oxide would furnish, by adopting a similar procedure, bicycloekasantalic acid (XXXII).¹⁹ Though a closely similar product was obtained with the expected IR bands at 1650 and 874 cm⁻¹ due to the terminal methylene group of the camphene system, it did not crystallize. However, when this product was treated with dilute sulphuric acid it yielded the highly crystalline lactone (XXXIII), identical in all respects with the product obtained by acid-catalysed cyclization of tricyclo or bicycloekasantalic acid.²⁰ Identity was established by undepressed mixed m.p. and superimposable IR spectrum with that of an authentic sample. The formation of the lactone (XXXIII) is consistent with the structure (I) proposed for β -bergamotene. The lactone could be formed by initial protonation and 1,2-methyl shift followed by lactonization as shown in chart 5.



NMR spectrum of β -bergamotene

The NMR spectrum of β -bergamotene¹¹ (Fig. 2) is in agreement with the proposed structure (I). It shows the presence of three vinyl protons (absorption at 5.43 and 5.24 τ for >C=CH₂; 4.95 τ >C=CH-), two vinyl methyl groups (signals at 8.42 and 8.35 τ) and one quaternary methyl group (singlet at 9.05 τ).

- ¹⁹ F. W. Semmler and K. Bode, Ber. Dtsch. Chem. Ges. 40, 1124 (1907); P. Rani Bai, S. Y. Kamat, B. B. Ghatge, K. K. Chakravarti and S. C. Bhattacharyya, Tetrahedron 21, 629 (1965).
- ²⁰ A. Bhati, *Perf. and Ess. Oil Rec.* 53, 15 (1962); J. Org. Chem. 27, 2135 (1962); Suryakumari Ramaswamy, S. K. Ramaswamy and S. C. Bhattacharyya, *Ibid.* 27, 2791 (1962).

A comparison of the NMR spectra* of β -bergamotene (I), tetrahydro- β -bergamotene (VII), α -santalene (XXXV), dihydro- α -santalene, β -santalene (IV) and tetrahydro- β -santalene, fully supports the structural assumptions for β -bergamotene. The chemical shifts of the terminal methyl groups on the side chain (8.42 and 8.35 τ) correspond closely in these related compounds. The positions of the main peaks (τ) and the assignments in the case of β -bergamotene, α -santalene and β -santalane are given in the Table 1.



In α -pinene, the unsplit methyl signals are observed at 9.17 and 8.74 T. In the NMR spectrum of α -bergamotene, a three proton singlet is located at 9.17 τ and coincides exactly with that of the methyl group in α -pinene which lies above the double bond. This observation and the occurrence of (-)- α -pinene in the same oil led Kovats¹² to propose the relative and absolute configuration of α -bergamotene as (-)- α -trans-bergamotene depicted in XXXVIII.

The position of the unsplit methyl signal in the spectrum of β -bergamotene deserves comment. The close resemblance of the NMR spectrum of β -bergamotene with that of β -pinene, affords information regarding the stereochemical relationship between the side chain and the portion containing the terminal methylene group of β -bergamotene. The two methylene protons (>C=CH₂) in β -bergamotene are not in the same magnetic environment as they are in β -pinene (V). The cyclobutane methyl peak in β -bergamotene is at 9.05 τ , half way between the two methyl peaks (9.28 and 8.77 τ) in the β -pinene spectrum. These differences would suggest that the conformation in the vicinity of the bicyclic ring system in β -bergamotene should be different

* We are extremely grateful to Prof. R. B. Bates for many of the NMR spectra, their interpretation and helpful discussion. He is also the co-author of our preliminary communication on β -bergamotene. from β -pinene. This would not be the case, if the former has the *trans*-configuration as in $(-)\alpha$ -*trans*-bergamotene. It is possible that the non-bonded steric interaction between the side chain and the unsaturated methylene link can modify the preferred conformation. A *cis*-conformation as shown in XL is therefore possible. In that context β -bergamotene isolated from V. wallichi may be (+)-cis- β -bergamotene and be represented by steroformula I or its mirror image. Confirmation of this will be published later.

It is interesting that the IR and NMR spectra of β -bergamotene (I) and β -santalene (IV) are strikingly similar.

Recently structures of α -longipinene,²¹ copaene,²² mustakone,²³ α -ylangene²⁴ and β -ylangene have been proposed. These sesquiterpenes also can be considered as pinene derivatives.

Biogenesis of β -bergamotene. A concerted type mechanism is unlikely for the



- ²¹ H. Erdtman and L. Westfelt, Acta. Chem. Scand. 17(8), 2351 (1963).
- ²² G. Büchi, S. H. Feairheller, P. de Mayo and R. E. Williams, Proc. Chem. Soc. 214 (1963).
- ²³ V. H. Kapadia, B. A. Nagasampagi, V. G. Naik and Sukh Dev, Tetrahedron Letters 1933 (1963).
- ³⁴ G. L. K. Hunter and W. B. Brodgen, J. Org. Chem. 29, 2100, 982 (1964).

formation of β -bergamotene having stereo-formula XL from *cis*-farnesol, since α - and β -bergamotenes formed by such a mechanism will have stereoformula XXXVIII and XXXIX or their mirror images.

It is likely that β -bergamotene isolated from V. wallichi is biogenetically related to bisabolene. The cation (XXXIV) derived from bisabolene or cis-farnesol can be transformed into the intermediate (XXXV) by allowing the rotation around the bond between the carbon atoms marked by asterisks. The intermediate (XXXV) would then yield β -bergamotene having the stereoformula XL after cyclization and deprotonation. β -Bergamotene having stereoformula XL should be named cis- β -bergamotene, and α -bergamotene as cis- α -bergamotene (XLI).

It has been mentioned earlier that the IR spectrum of tetrahydro- β -bergamotene (VII) is similar to that of bergamotane (prepared from α -bergamotene) reported in the literature.¹⁴ Assuming the assigned stereochemistry to be correct, tetrahydro-*cis*- β -bergamotene (VII) obtained by hydrogenation of β -bergamotene should be different from the tetrahydro-*trans*- α -bergamotene (XLII) obtained by hydrogenation of α -bergamotene. A comparison of the NMR spectra of the two samples would be extremely helpful, but could not be carried out as no tetrahydro-*trans*- α -bergamotene was available.

EXPERIMENTAL

M.ps and b.ps are uncorrected. The b.ps unless otherwise stated, correspond to bath temp. Elemental analyses were performed by Mr. Pansare and colleagues in the microanalytical section of our laboratory. UV spectra were taken in alcoholic solution with Bechman DK-2 instrument and IR spectra on a Perkin-Elmer infracord. Optical rotations were determined in CHCl₃ at room temp (25-30°).

Isolation of β -bergamotene. The fraction Ni⁸ was chromatographed on alkaline grade I alumina (1:100). On extensive chromatography of the appropriate fractions pure β -bergamotene was obtained. The pure hydrocarbon gave a single peak on GLC analysis, b.p. 120–130°/1 mm, n_D^{37} 1.4949; d_4^{37} 0.8841; (α)_D + 35.8° (c, 4.0). IR bands at: 3030, 1745, 1653, 1370, 980, 925, 875 and 832 cm⁻¹ (Found: C, 88.16; H, 12.13. C₁₅H₃₄ requires: C, 88.16; H, 11.84%.)

Hydrogenation of β -bergamotene (I) to tetrahydro- β -bergamotene (VII). The hydrocarbon(1.09 g) in EtOH (30 ml) was hydrogenated in the presence of pre-reduced Adams catalyst (50 mg) until no further absorption took place (6 hr; 2 moles). The catalyst was removed and the solvent evaporated to yield the fully saturated hydrocarbon, tetrahydro- β -bergamotene, b.p. 125–130°/3.5 mm, n_{2}^{bb} 1.4683; (α)_D +27.13° (c, 4.0). IR bands at: 2941, 1468, 1383, 1366, 1330, 1217, 1170, 1099, 1064, 921 and 817 cm⁻¹. (Found: C, 86.90; H, 13.39. C₁₅H₁₈ requires: C, 86.46; H, 13.54%.)

Dehydrogenation of β -bergamotene. A mixture of the hydrocarbon (200 mg) and selenium (200 mg) was refluxed at about 300° in a N₂ atmosphere for 24 hr. After cooling, the product in pet. ether was filtered through grade II alumina to remove inorganic impurities and distilled (λ_{max} 265 m μ ; ν_{max} 1600, 1499, 815 cm⁻¹; characteristic of benzenoid system). One of the major peaks in GLC analysis corresponded to dihydrocurcumene (VIII).

Selective ozonolysis of β -bergamotene (I). β -Bergamotene (1 g) in chloroform (20 ml) was ozonized at 0° (0·2 g, ozone/hr) for exactly 15 min. The solvent was removed at 40° under vacuum. The ozonide was decomposed by heating with water for 2 hr, extracted with ether, dried and the ether removed. The product was filtered through gr. II neutral alumina (20 g). Pet. ether eluted the unreacted hydrocarbon (700 mg) and ether eluted the aldehyde (200 mg), b.p. 130–140°/0·5 mm, $n_{D}^{s_1}$ 1·4925; IR bands at: 2710, 1721, 1653, 875 cm⁻¹. (Found: C, 81·25; H, 10·80. C₁₈H₁₈O requires: C, 80·85; H, 10·18%.) The volatile part contained acetone, characterized through the iodoform test and DNP derivative, m.p. and mixed m.p. 124°.

Oxidation of the aldehyde (XV) to the acid (XVIa). The aldehyde (0.5 g) and finely divided AgNO₄ (1 g) were dissolved in abs EtOH (25 ml) and a solution of NaOH (0.5 g) in aqueous EtOH (1.9; 10 ml) was added dropwise with good stirring. After 24 hr at room temp, the mixture was diluted with

water and acidified with ice cold 5% H₃SO₄ and extracted with ether. The ether layer was washed, dried and the ether removed to yield the acid (0.45 g) as a thick liquid. The methyl ester of the acid was prepared with diazomethane and distilled, b.p. 95-100°/0.5 mm, n_{21}^{21} 1.4865; (α)_D +21.58° (c, 3.89). IR bands at: 1730, 1653, 1186, 1170, 876 cm⁻¹. (Found: C, 75.56; H, 9.80. C₁₃H₃₀O₃ requires: C, 74.96; H, 9.68%.)

Catalytic hydrogenation of the ester (XVIb). The unsaturated ester (0.5 g) in EtOH (25 ml) was hydrogenated in the presence of Pd-C (5%) until no further adsorption took place (3 hr; 1 mole). The saturated ester was isolated in the usual way, b.p. 130-135°/4 mm, n_{D}^{st} 1.4765; (α)_D +25.32° (c, 7.2). IR bands at: 1730, 1190, 1166 cm⁻¹. (Found: C, 74.85; H, 10.64. C₁₃H₃₃O₃ requires: C, 74.24; H, 10.54%.)

Barbier-Wieland degradation of the ester (XVII). The saturated ester (1 g) in dry benzene (50 ml) was added to cooled (0°) Grignard reagent prepared from bromobenzene (8 g), Mg (3 g) and dry ether (100 ml). Subsequently dry benzene was added and the mixture heated to reflux for 4 hr. The product after decomposition with ice cold 5% H₃SO₄ was steam distilled to remove biphenyl. The non-volatile part was extracted with ether, dried and ether removed to yield (1.9 g) of diphenyl carbinol.

Dehydration of diphenylcarbinol (XVIII). The diphenyl carbinol (1.9 g) was refluxed with toluene (100 ml) and p-toluenesulphonic acid (100 mg) for 6 hr. The toluene was removed under suction and residue extracted with ether, washed with Na₂CO₂aq, water and dried. Evaporation of ether yielded the crude product (1.6 g), which after distillation gave a pure product (1.42 g), b.p. 160-200°/ 0.0009 mm, $\lambda_{max} 251 \text{ m}\mu$; log $\epsilon 4.24$; IR bands at: 1600, 1488 cm⁻¹. (Found: C, 90.14; H, 9.10. C₃₄H₃₅ requires: C, 91.08; H, 8.92%.)

Ozonolysis of the hydrocarbon (XIX). The hydrocarbon (1.3 g) was ozonized at 0° in CHCl_s (20 ml) for 30 min. The ozonide was decomposed and steam distilled to yield a mixture of XX and benzophenone (0.56 g) in the volatile part; v_{max} 2710, 1720 cm⁻¹ (aldehyde).

Ester (XXIb) from the aldehyde (XX). The mixture of XX and benzophenone was oxidized with Ag₂O. The acid formed was separated and converted to methyl ester with diazomethane, b.p. $135-140^{\circ}/20$ mm, IR bands at: 1729, 1163, 1124 cm⁻¹. (Found: C, 74.08; H, 10.25. C₁₂H₈₀O₂ requires: C, 73.43; H, 10.27%.)

Second Barbier-Wieland degradation. The ester (XXIb; 210 mg) was subjected to another Barbier-Wieland degradation. The diphenyl carbinol after dehydration yielded a hydrocarbon (320 mg), b.p. $160^{\circ}/0.0001$ mm, λ_{max} 249.5 m μ ; IR bands at: 1604, 1502 cm⁻¹. (Found: C, 91.60; H, 8.80. C₃₂H₃₅ requires: C, 91.33; H, 8.67%.)

Ozonolysis of the hydrocarbon (XXII). The hydrocarbon (300 mg) was ozonized at 0° in CHCl_a (20 ml). The ozonide was decomposed and the steam distilled to give a mixture of aldehyde and benzophenone. The above mixture was oxidized with Ag_aO to furnish XXIVa (92 mg). The acid was characterized by preparing its methyl ester with diazomethane; IR bands at: 1729, 1274 and 1163 cm⁻¹.

Saponification of methyl ester (XXIVb). The ester (80 mg) and alcoholic KOH (5%, 15 ml) were refluxed for 1 hr. After usual work up, the neutral portion (71 mg) was obtained with IR band at 1730 cm^{-1} .

Pinane (XXIX) from aldehyde (XXIII). The mixture (85 mg) of aldehyde (XXIII) and benzophenone obtained by the ozonolysis of XXII, diethylene glycol (20 ml), hydrazine hydrate (0.5 ml) and KOH (0.3 g) were heated at 150° for 3 hr. After usual work up, the crude product (72 mg) was chromatographed on gr. II neutral alumina (20 g). The pet. ether fraction after evaporation furnished a mixture of hydrocarbons (12 mg) identified as pinane and diphenylmethane by GLC analysis and comparison with authentic reference compounds.

Reduction of ester (XVIb) by lithium aluminium hydride. The ester (500 mg) was added to a solution of LAH (200 mg) in dry ether (150 ml) at 0° under stirring. The mixture was refluxed for 4 hr. After usual work up, XXVI (288 mg) was obtained, b.p. $140^{\circ}/0.6$ mm, (α)_D +11.0° (c, 4.2); IR bands at: 3500, 1661, 1053 and 875 cm⁻¹. (Found: C, 79.95; H, 11.36. C₁₂H₁₀O requires: C, 79.94; H, 11.18%.)

Ozonolysis of unsaturated alcohol (XXVI). The alcohol (200 mg) was ozonized at 0° in CHCl_s solution. Decomposition of the ozonide and extraction with ether yielded XXVII (150 mg), b.p. $160^{\circ}/0.3$ mm; IR bands at: 3448, 1715, 1414 and 1053 cm⁻¹. (Found: C, 72.08; H, 9.39. C₁₁H₁₈O₈)

requires: C, 72.49; H, 9.96%.) The volatile part gave formaldehyde, characterized by the dimedone derivative, m.p. and mixed m.p. 189°.

Hydrochlorination of the unsaturated ester (XVIb). Dry HCl gas was passed through a solution of XVIb (500 mg) in dry ether (50 ml) for 2 hr and was left at the room temp for 24 hr. It was then poured into cold water, extracted with ether, washed and dried. Removal of ether furnished the hydrocyloride (0.45 g).

Dehydrochlorination. The hydrochloride (0.45 g), fused AcONa (1 g) and AcOH (20 ml) were refluxed for 2 hr. The mixture was poured into cold water, and extracted with ether. Removal of ether furnished the dehydrohalogenated ester (0.42 g). The crude ester was saponified with 10% alcoholic KOH. The crude acid (0.3678 g) was distilled to yield pure XXXII (0.2484 g), b.p. $150^{\circ}/0.5$ mm.

Lactone XXXIII from acid XXXII. The acid (XXXII; 200 mg) was refluxed with 15% H₂SO₄ (50 ml) for 3 hr. The solution after cooling was extracted with ether. Acidic and neutral portions were separated. The neutral part gave a solid lactone (85 mg) which was crystallized from pet. ether, m.p. 103°; IR bands at: 1754, 1263, 1163, 1020, 961 and 917 cm⁻¹. Its identity was confirmed by comparison of IR spectra and mixed m.p. determination with an authentic sample prepared from tricycloekasantalic acid.