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THE STRUCTURES OF THE LACTONES FROM THE ACTION OF LEAD TETRA-ACETATE ON CAMPHENE, AND FROM ACID ON TRICYCLOEKASANTALIC ACID

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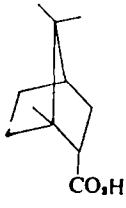
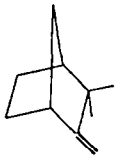
Abstract—Hot sulphuric acid (15 or 25%) or cold sulphuric acid (98%) converts tricycloekasantalic acid (VI) into a mixture of the *exo* and *endo* γ-lactones (IV) and (V) resp., and the δ-lactone (X), and not the pure *endo*-lactone (V) as reported in the literature. Formic acid converts VI into a mixture of IV and V. The action of lead tetra-acetate in acetic acid on camphene gives a mixture (ca. 4:1) of the lactones IV and V as a minor byproduct. A synthesis of pure *endo*-lactone (V) from (±)- and (+)-camphenilone is described and pure (+)-*exo*-lactone (IV) has been obtained indirectly from the mixture of lactones from tricycloekasantalic acid. The formation of *exo*-lactone (IV) from tricycloekasantalic acid *via* exclusive *exo*-methyl group migration in a 3,2-shift is established.

DURING an attempt to effect the oxidative decarboxylation of *endo*-2-carboxybornane (I) with lead tetra-acetate in acetic acid containing sodium acetate, the formation in a low yield of a product $C_{12}H_{18}O_2$, m.p. 101–103°, was observed. The IR spectrum of this compound showed the presence of a γ-lactone (1777 cm^{-1}) and a *gem*-dimethyl group (1386 and 1365 cm^{-1}) while its NMR spectrum revealed the presence of two tertiary methyl groups (overlapping singlets at τ 9·02). The absence of signals at lower field than 140 c/s showed that the ether oxygen of the lactone group must be attached to a carbon devoid of hydrogen atoms. As camphene (II) has been shown to be the major product from the action of lead tetra-acetate on *endo*-2-carboxybornane (I) in benzene,[1] the above product (later shown to be a mixture of epimers) was considered to have arisen from the addition of a ·CH_2COO· moiety (with no mechanistic implications) to the double bond camphene. Such a hypothesis seemed reasonable as Criegee[2] has observed the formation of the γ-lactone (III) by the addition of a ·CH_2COO· moiety to the double bond of oct-4-ene by the action of lead tetra-acetate.

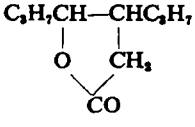
In a study of the action of lead tetra-acetate on camphene in acetic acid, Hückel and Hartmann[3] isolated a byproduct $C_{12}H_{18}O_2$, m.p. 101°, to which they were unable



I



II

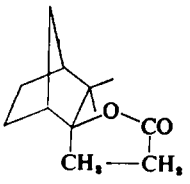


III

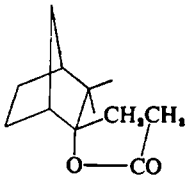
[1] G. E. Gream and D. Wege, unpublished work mentioned briefly in Ref. 13.
[2] R. Criegee, *Newer Methods of Preparative Organic Chemistry* (Edited by W. Foerst) Vol. 2; p. 378. Academic Press, New York (1963).
[3] W. Hückel and K. Hartmann, *Ber. Dtsch. Chem. Ges.* **70**, 959 (1937).

to assign a structure. Repetition of their work revealed that their product was identical with that obtained from 2-*endo*-carboxybornane.

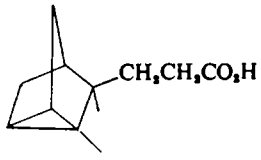
Working on the hypothesis that the ·CH_2COO· moiety would be added to the double bond of camphene from the less hindered *exo* side,[4] the unknown lactone was considered to be 3-(*exo*-2-hydroxy-3,3-dimethyl-2-norbornyl)propanoic acid lactone (IV) rather than the epimeric *endo*-lactone (V). Structure V was recently assigned by Bhati[5] to the lactone, m.p. 103–104°, obtained from tricycloekasantalic acid (VI) by the action of strong acids.[6] The assignment was based on an unambiguous synthesis of V, m.p. 103–104°, and a comparison of the IR spectra, m.p. and mixed m.p. of the synthetic lactone (V) with the lactone from VI.



IV



V



VI

The formation of the lactone from tricycloekasantalic acid (VI) appeared to involve certain interesting mechanistic features. In order to correlate this lactone with that from camphene, a new unambiguous synthesis of the *endo*-lactone (V) was carried out, and some aspects of the formation of the lactone from tricycloekasantalic acid were re-examined.

The synthesis of the *endo*-lactone (V) was achieved by the following route. Treatment of (±)-camphenilone (VII) with allylmagnesium chloride yielded the tertiary alcohol (VIII) in which the hydroxyl group must have the *endo* configuration.[7] Hydroboration-oxidation[8] of VIII gave the crystalline diol (IX, R = R′ = H), m.p. 68–69°, which was oxidized with Jones' reagent[9] to give the *endo*-lactone (V), m.p. 102–103°. Although capillary VPC showed that this lactone was homogeneous, its IR spectrum showed distinct differences in the "fingerprint" region when compared with the spectra of the lactones from *endo*-2-carboxybornane (I) and camphene. Examination of these lactones by capillary VPC revealed that they were in fact mixtures (ca. 4:1)

[4a] E. J. Corey, R. Hartmann and P. A. Vatakencherry, *J. Amer. Chem. Soc.* **84**, 2611 (1962), and Refs. therein; [b] J. A. Berson, *Molecular Rearrangements* (Edited by P. de Mayo) Part 1; pp. 125–135. Interscience, New York (1963); [c] R. Howe, E. C. Friedrich and S. Winstein, *J. Amer. Chem. Soc.* **87**, 379 (1965); [d] S. J. Cristol, T. W. Russell and D. I. Davies, *J. Org. Chem.* **30**, 207 (1965), and Refs. therein.

[5] A. Bhati, *J. Org. Chem.* **27**, 2135 (1962).

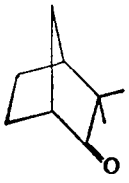
[6a] F. W. Semmler, *Ber Dtsch. Chem. Ges.* **40**, 1120 (1907); [b] L. Ruzicka and G. Thomann, *Helv. Chim. Acta* **18**, 355 (1935); [c] S. C. Bhattacharyya, *Science and Culture* **13**, 158 (1947).

[7] Although VPC analysis on two capillary columns indicated that VIII was homogeneous, the presence of some of the epimeric *exo*-alcohol was possible since the epimeric tertiary alcohol pair, camphene hydrate (XXII) and methylcamphenilol (XXI, H in place of $COCF_3$) could not be separated on these columns. Contamination of VIII by the *exo*-alcohol, however, would have been only slight since the addition of reagents to norbornan-2-ones unsubstituted in the *syn*-7 position is highly stereospecific, and occurs from the *exo* side.[4] That VIII was in fact contaminated by its epimer is shown later.[20]

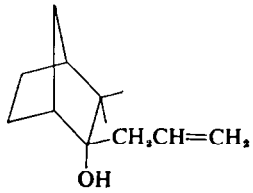
[8] H. C. Brown and B. C. Subba Rao, *J. Amer. Chem. Soc.* **81**, 6428 (1959).

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

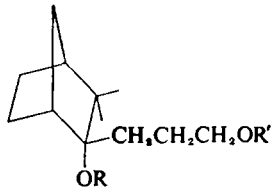
of two components. In both cases, the minor components had a retention time identical with that of the authentic *endo*-lactone (V).



VII



VIII



IX

The lactone from tricycloekasantalic (VI) was generated with sulphuric acid (15 and 25%) and formic acid. In each case, the "pure" product was shown by capillary VPC to be a mixture of the same lactones as from *endo*-2-carboxybornane and camphene (Table 1), with the *endo*-lactone (V) again being the minor component. When tricycloekasantalic acid was treated with sulphuric acid (98%) at $-10°$ for 25 min, the resulting lactone mixture contained a third component (56%). As the IR spectrum of this mixture showed carbonyl absorption of similar intensity at 1780 (γ-lactone) and 1745 cm^{-1}, the third component is believed to be a δ-lactone. Assuming that the δ-lactone would be formed by attack of the carboxyl group, or water (followed by lactonization of the intermediate hydroxy acid) on an intermediate carbonium ion from the *exo* side,[10] structures X and XI (from the ions XVI and XVII resp.,—Scheme 2) can be considered for the unknown lactone. Of these X, having the *cis* configuration for the lactone ring is preferred for the following reasons. First, as there is not apparent reason why the ion XVII should be formed in preference to XVI, it may be expected that X would be formed much more readily than XI since the latter possesses a highly strained *trans*-fused δ-lactone ring. Second, an attempt to isolate the hydroxy acid formed by alkaline hydrolysis of the unknown lactone was unsuccessful since the lactone was regenerated immediately upon acidification of the alkaline solution. Such facile lactone formation would not be expected for the hydroxy acid derived from XI. In support of structure X was the fact that the NMR spectrum of the mixture was similar to that of the lactone mixture from camphene, except for a sharp singlet at τ 8·76 which was assigned to the tertiary methyl group attached to the carbon bearing the ether oxygen atom of the lactone group in X. The alternative structures XII[14] (which can be formally derived from the ion XX—Scheme 2) and

[10] For kinetically controlled product formation, *exo* substitution would be expected. With the exception of one report,[11] *exo* substitution is characteristic of carbonium ion reactions of 2-norbornyl and substituted 2-norbornyl systems, even when the presence of *syn*-7 substituents causes the *exo* side to be the more hindered.[4c,12] For a recent review, see Gream.[13]

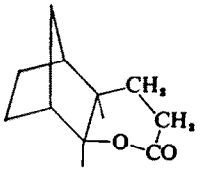
[11] W. Hückel and M. Heinzel, *Tetrahedron Letters* 2141 (1964).

[12a] H. C. Brown and H. M. Bell, *J. Amer. Chem. Soc.* **86**, 5006 (1964); [b] H. M. Bell and H. C. Brown, *Ibid.* **86**, 5007, (1964); [c] S. Winstein, E. Clippinger, R. Howe and E. Vogelfanger, *Ibid.* **87**, 376 (1965).

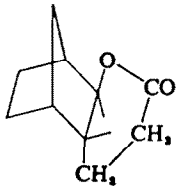
[13] G. E. Gream, *Rev. Pure Appl. Chem. Austral.* **16**, 25 (1966).

[14] J. L. Simonsen and D. H. R. Barton, *The Terpenes* (2nd Edition) Vol. III; pp. 103–105. University Press, Cambridge (1952).

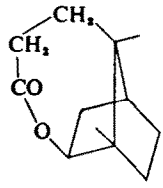
XIII (which can be formally derived from ions resulting from Wagner-Meerwein changes in the enantiomeric ions XVIII and XIX, or better, directly from the non-classical ion XXIX) were excluded owing to the absence of signals at lower field than 140 c/s in the NMR spectrum of the lactone mixture.



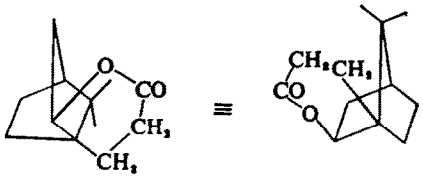
X



XI



XII



XIII

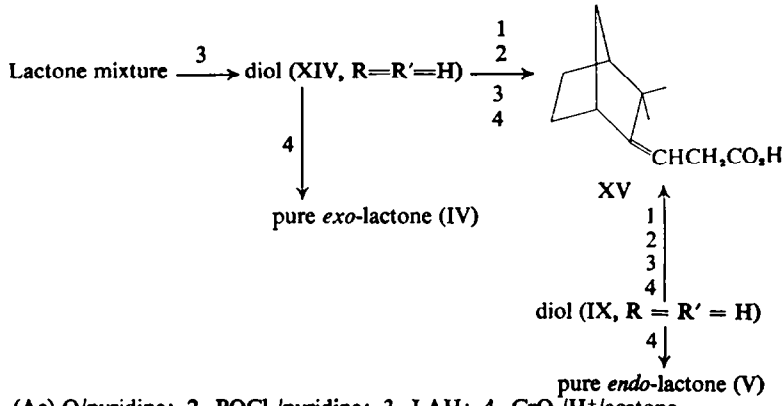
The lactone (X) was also present in small amounts (Table 1) in the crude products obtained from the action of hot sulphuric acid (15 and 25%) on tricycloekasantalic acid, but was readily removed during subsequent recrystallizations. It was absent, however, in the crude product formed by the action of formic acid on tricycloekasantalic acid. Three or four recrystallizations of the crude products gave "pure" compounds which were in fact mixtures (ca. 7:3) of the two γ-lactones, the minor component still being the *endo*-lactone (V).

Having established that the major component of these lactone mixtures is not the *endo*-lactone (V), the epimeric *exo* structure IV can be assigned to it on the basis of conversions described in this paper*. The relevant conversions are summarized in Scheme 1.

* The transformations of the lactone mixture from tricycloekasantalic acid described by Bhattacharyya *et al.*[15,16] to give the unsaturated acid (XV)[15] and a very low yield of camphenilone (VII)[16] do not give a conclusive proof for the structure of IV since the intermediate diol, m.p. 112°, must have been a mixture (ca. 1:1, based on the reported optical activity) of IX (R = R′ = H) and XIV (R = R′ = H). It could be argued that XV and VII arose from IX (R = R′ = H) alone. Bhati[5] has also converted the *endo*-lactone (V) and the lactone from tricycloekasantalic acid into XV. One step in his transformations, however, involved the use of methanolic hydrogen chloride. In view of the susceptibility of substituted norbornyl derivatives to undergo rearrangement in the presence of strong acids, the above step in Bhati's conversions would, in the absence of other evidence, have to be treated with caution.

[15] P. Rani Bai, S. Y. Kamat, B. B. Ghatge, K. K. Chakravarti and S. C. Bhattacharyya, *Tetrahedron* 21, 629 (1965).

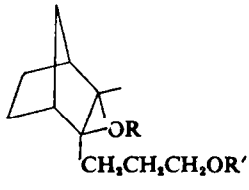
[16] S. Ramaswami, S. K. Ramaswami and S. C. Bhattacharyya, *J. Org. Chem.* 27, 2791 (1962).



1. $(Ac)_2O$/pyridine; 2. $POCl_3$/pyridine; 3. LAH; 4. CrO_3/H^+/acetone

Scheme 1. Conversions which prove the structure of IV.

In the present work, the lactone mixture (ca. 7:3) from tricycloekasantalic acid was reduced with LAH to give a crystalline diol (XIV, R = R′ = H), m.p. 133–134°, $[\alpha]_D$ +25. Significantly, this diol could be oxidized by Jones' reagent to the *exo*-lactone (IV), m.p. 119–120°, $[\alpha]_D$ +40, which was homogeneous as judged by capillary VPC, and whose retention time was identical with that of the major component in the lactone mixtures from tricycloekasantalic acid, *endo*-2-carboxybornane and camphene.



XIV

It is therefore clear that the lactone from tricycloekasantalic acid is a mixture of the *exo*-lactone (IV), $[\alpha]_D$ +40, and the *endo*-lactone (V) and that the latter must possess a negative specific rotation to account for the low rotations reported in the literature. The incorrect assignment of stereochemistry to the major component of the lactone mixture by Bhati[5] can be explained by the fact that the m.p. of the lactone mixture in admixture with the (±)*endo*-lactone (V) is not depressed. Contrary to Bhati's findings, however, infrared spectral differences between the two are distinct.

The unsaturated acid (XV) (called isobicyclo-ekasantalic acid[15]) which was obtained by Bhati[5] and Bhattacharyya *et al.*[15] from the lactone from tricycloekasantalic acid, and by Bhati[5] from the *endo*-lactone (V), and which both groups of workers claimed was converted back to the lactone (V) by the action of dilute sulphuric acid, has been synthesized in the present work. Successive treatments of the diol (IX, R = R′ = H) with acetic anhydride in pyridine, phorphorus oxychloride in pyridine, LAH, and Jones' reagent[9] yielded XV. Its NMR spectrum confirmed the structure assigned (Experimental). In hot sulphuric acid (25%), XV lactonized to give a mixture (68:32) of *exo*- and *endo*-lactones (IV) and (V) respectively.

TABLE 1. COMPOSITION OF LACTONE MIXTURES

Starting material	Reagent	Lactone purity	Lactone composition (%)		
			exo- (IV)	*endo*- (V)	δ-(X)
endo-2-Carboxybornane (I)	$Pb(OAc)_4$ in AcOH–NaOAc	Recryst. twice, m.p. 101–103°	79	21	—
Camphene (II)	$Pb(OAc)_4$ in AcOH–NaOAc	Recryst. twice, m.p. 101–103°	83	17	—
Tricycloekasantalic acid (VI)	98% H_2SO_4, −10°, 25 min	Recryst. once, m.p. 65–75°	32	12	56
Tricycloekasantalic acid	15% H_2SO_4, reflux 45 min	Crude, m.p. 75–100°	47	39	14
		Recryst. twice, m.p. 100–104°	73	27	—
Tricycloekasantalic acid	25% H_2SO_4, reflux 15 min	Crude, m.p. 85–95°	54	33	13
		Recryst. three times, m.p. 101–103°	69	31	—
Tricycloekasantalic acid	98% HCO_2H, reflux 30 min	Crude, m.p. 94–97°	62	38	—
		Recryst. four times, m.p. 101–103°	73	27	—
Unsaturated acid (XV)	25% H_2SO_4, reflux 10 min	Recryst. once, m.p. 97–99°	68	32	—

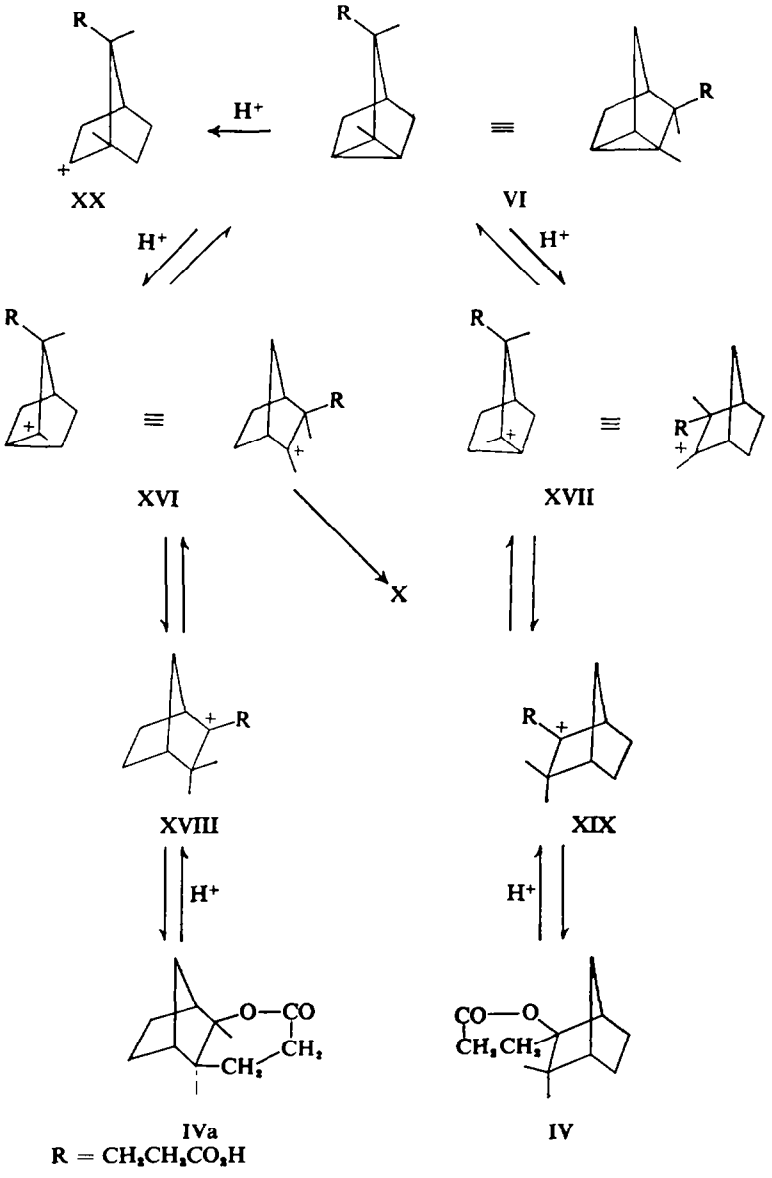
TABLE 2. COMPOSITION OF THE LACTONE MIXTURES FROM THE ACID CATALYSED EQUILIBRATION OF THE PURE *exo*- AND *endo*-LACTONES IV AND V RESPECTIVELY.

Lactone	Reagent	Reflux time (min)	Composition (%)	
			exo-	*endo*-
(±)-*endo*-	25% H_2SO_4	15	60	40
(±)-*endo*-	25% H_2SO_4	45	57	43
(+)-*endo*-	98% HCO_2H	90	60	40
(+)-*exo*-	15% H_2SO_4	45	66	34

Since mixtures of the γ-lactones were always formed in the acid catalysed reactions with tricycloekasantalic acid and the unsaturated acid (VX), each of the pure lactones (IV and V) was subjected to acid treatment and the results are summarized in Table 2. In all cases, it was found that the lactones underwent equilibration to give mixtures (ca. 60:40) of the lactones with the *exo*-lactone predominating.

For the formation of the lactone mixture from tricycloekasantalic acid (VI). two pathways can be envisaged (Scheme 2)*. Protonation and opening of the cyclopropane

* For simplicity only classical carbonium ion formulae are used in scheme 2 and 3 and in much of the discussion. This does not, however, *per se* imply, any bias against the possible intermediacy of non-classical ions at various stages in the transformations.



Scheme 2. Alternative pathways for conversion of tricycloekasantalic to *exo*-lactone (IV).

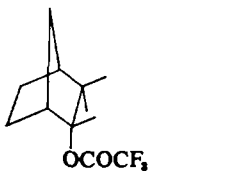
ring in VI can yield the tertiary ions XVI or XVII, or less likely the secondary ion XX. The cations XVIII and XIX can be derived by the migration of the *endo*-methyl group in XVI, and the *exo*-methyl group in XVII, respectively. Cyclization of XVIII and XIX, either directly by nucleophilic attack by the carboxyl group, or by water followed by cyclization of the intermediate hydroxy acid, would then yield the *exo*-lactones (IVa and IV), or very much less likely their corresponding *endo* counterparts.[10] It may be noted that the pairs of structures XVIII and XIX, and IVa and IV are non-superimposable mirror images. From the rotation studies of Ourisson[17] and the synthetic

[17a] G. Ourisson, *Chem & Ind.* 918 (1953). [b] G. Ourisson, *Bull. Soc. chim. Fr.* 895 (1955).

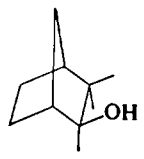
work of Corey *et al.*[18], the absolute configuration of (+)-tricycloekasantalic acid is represented by VI, and hence IVa and IV represent the absolute configurations of the *exo*-lactones derived by *endo* and *exo* methyl group migration respectively. Since IV is derived from (−)-camphenilone whose absolute configuration is represented by VII,[19] a configurational correlation of the *exo*-lactone from tricycloekasantalic acid with camphenilone should allow a distinction to be made between the two pathways outlined in Scheme 2.

For the configurational studies, syntheses of the optically active lactones (IV and V) from optically active camphenilone were initially desired. (+)-Camphenilone (80% optically pure) was converted into the (+)-*endo*-lactone (V), m.p. 114–115°, $[\alpha]_D$ +32, by the sequence already outlined for the synthesis of (±)-V.[20]

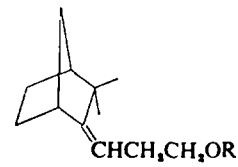
As the solvolysis of methylcamphenilyl trifluoroacetate (XXI) in aqueous acetone containing calcium carbonate yields camphene (28%) and camphene hydrate (XXII, 72%),[1] it was thought that a similar solvolysis of the optically active di-trifluoroacetate



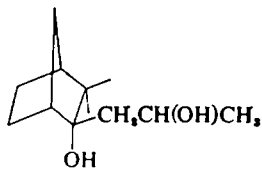
XXI



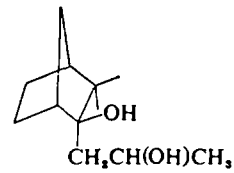
XXII



XXIII



XXIV



XXV

(IX, R = R′ = $COCF_3$) would yield optically active *exo*-diol (XIV, R = R′ = H) which could then be oxidized to optically active *exo*-lactone (IV). The product of solvolysis, however, was the unsaturated alcohol (XXIII, R = H). At this stage, attempts to synthesize optically active IV were abandoned as the unsaturated alcohol from the solvolysis was readily oxidized by Jones' reagent to the unsaturated acid (XV), m.p. 100–102°, $[\alpha]_D$ +95, which served as a very satisfactory reference compound for the configurational correlations.

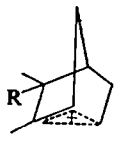
[18] E. J. Corey, S. W. Chow and R. A. Scherrer, *J. Amer. Chem. Soc.* **79**, 5773 (1957).

[19] J. A. Berson, J. S. Walia, A. Remanick, S. Suzuki, P. Reynolds-Warnhoff and D. Willner, *J. Amer. Chem. Soc.* **83**, 3986 (1961).

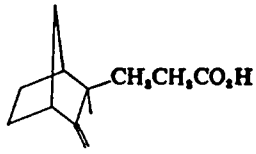
[20] As well as the desired diol (IX, R = R_1 = H), two other isomeric diols (XXIV) and (XXV) were isolated from the product obtained by hydroboration-oxidation of the (+)-tertiary alcohol (VIII). While the basic structures of the diols were defined by their NMR spectra (see Experimental), the configurations of the tertiary hydroxyl groups were assigned as being *endo* in XXIV, the isomer formed in the higher yield and which was less strongly retained on silica gel, and *exo* in XXV for the following reasons: (1) the isomer having the *endo* hydroxyl group should be less hydrogen bonded than its *exo* epimer,[21] and so should be less strongly retained on silica gel, and (2) the yield of the *endo* epimer should be higher than the *exo* compound since the precursor hydroxy olefin (VIII) should contain only a small quantity of the *exo* epimer as contaminant.[7]

[21] Ref. 4(b), pp. 127–130.

By the sequence of steps already described for the preparation of the unsaturated acid (XV) from the (±)-*endo*-diol (IX, R = R′ = H), the (+)-diol (XIV, R = R′ = H) from the lactone mixture from (+)-tricycloekasantalic acid was converted into the unsaturated acid (XV), m.p. 95–96°, $[\alpha]_D$ −118. The calculated specific rotation of optically pure XV is +119 since the observed value was +95 when the acid was synthesized from (+)-camphenilone of 80% optical purity. The sign and magnitude of the rotation of XV obtained from the *exo*-lactone (IV) therefore proves that the latter is derived by the exclusive migration of the *exo*-methyl in the classical ion XVII, or much more likely its non-classical counterpart XXVI. This finding is in accord with the general observation that 3,2-hydrogen or alkyl shifts in the substituted norbornyl cations appear to occur only when the migrating group is *exo*.[13,22] The highly stereospecific nature of 3,2-shifts has been rationalized in terms of non-classical cationic intermediates in which attack by nucleophile (in this case the migrating group) can only occur from the *exo* direction.[22]

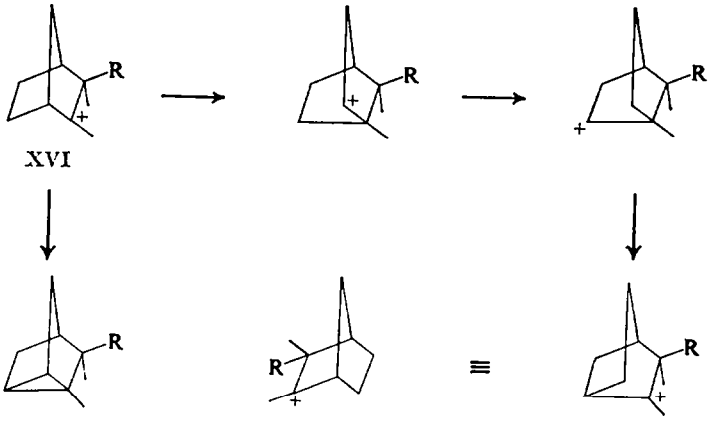


XXVI



XXVII

It is interesting to note that the action of formic acid on bicycloekasantalic acid (XXVII) has been reported[6b] to give the same lactone as does tricycloekasantalic acid. Protonation of XXVII would yield the carbonium ion XVI in which the methyl

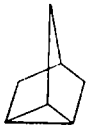


R = $CH_2CH_2CO_2H$

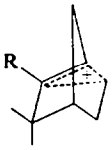
Scheme 3. Alternative pathways for conversion of bicycloekasantalic acid (XXVII) to *exo*-lactone (IV).

[22a] C. J. Collins, Z. K. Cheema, R. G. Werth and B. M. Benjamin, *J. Amer. Chem. Soc.* **86**, 4913 (1964); [b] J. A. Berson, R. G. Bergman, J. H. Hammons and A. W. McRowe, *Ibid.* **87**, 3246 (1965); [c] J. A. Berson, J. H. Hammons, A. W. McRowe, R. G. Bergman, A. Remanick and D. Houston, *Ibid.* **87**, 3248 (1965).

group at the migration origin has the *endo* configuration, and its migration is therefore prohibited. Before migration can occur, rearrangement to the ion XVII must occur either *via* tricycloekasantalic acid (as in Scheme 2) or *via* the Wagner-Meerwein rearrangements and 6,2-hydrogen shift oultined in Scheme 3. Of these pathways, the latter seems more likely even through the conversion of a tertiary into a secondary carbonium ion is involved,* since the formation of nortricyclene (XXVIII) or substituted nortricyclene derivatives as intermediates from 2-norbornyl or substituted 2-norbornyl cations has been shown to be unlikely by labelling experiments.[22a,24]



XXVIII



XXIX

As already mentioned,[10] *exo* substitution is characteristic of carbonium ion reactions of 2-norbornyl and substituted 2-norbornyl derivatives. Although Brown[25] has attempted to explain this stereospecificity of substitution by the "windshield wiper effect" involving rapidly equilibrating classical ions, the general consensus of opinion seems to favour the intermediacy of non-classical species as offering the better explanation. In the present work, it is believed that the *exo*-lactone (IV) is the kinetically controlled product derived from the non-classical ion XXIX by *exo* attack by either the carboxyl group or water (followed by lactonization of the intermediate hydroxy acid). As the *endo*-lactone (V) is unlikely to be derived from XXIX since the *endo* side of the latter is protected from nucleophilic attack by the partial covalency, the classical tertiary ion XIX is most probably its precursor. Detailed studies of the acid catalysed equilibration of 2-norbornyl and substituted 2-norbornyl derivatives have received scant attention, although a study of the equilibration of the 2-norbornyl acetates was recently reported.[26] The formation of *endo* substituted norbornyl derivatives under these conditions presumably involves the classical norbornyl cation, for which the energy barrier for capture by nucleophile is likely to be less than that for capture of the more stable non-classical ion.[26] In the case of the lactones, the ca. 60:40 *exo*:*endo* composition observed is presumably that of the equilibrium mixture.

EXPERIMENTAL

The m.ps were determined on a Reichert micro hot stage, and are uncorrected. Routine IR spectra were recorded with a Perkin–Elmer Infracord 137, while the spectra of the lactones (IV and V) and their mixtures, including those containing X, were recorded with a Perkin–Elmer 237 grating spectrometer. IR spectra for liquids were determined with liquid films, and for solids in CCl_4 solution. The characteristics of the IR bands are expressed in the text as follows: (s), strong; (m), medium;

* Such a change is well known in the norbornyl series, e.g., in the conversion of camphene hydrochloride to isobornyl chloride.[23]

[23] Ref. 4(b), pp. 113–121.

[24] A. Nickon and J. H. Hammons, *J. Amer. Chem. Soc.* **86**, 3322 (1964).

[25a] H. C. Brown, in *The Transition State* (Special Publication No. 16) pp. 177–178. The Chemical Society, London (1962); [b] H. C. Brown, K. J. Morgan and F. J. Chloupek, *J. Amer. Chem. Soc.* **87**, 2137 (1965).

[26] H. L. Goering and C. B. Schewene, *J. Amer. Chem. Soc.* **87**, 3516 (1965).

(w), weak; (sh), shoulder; (b), broad. VPC analyses were carried out with a Perkin–Elmer 800 apparatus equipped with a flame ionization detector. The carrier gas (N_2) flow rate was 40 ml/min for the conventional columns, and 2 ml/min for the capillary columns. For quantitative analyses, peaks were approximated to triangles, and the areas were determined from (peak height) X (peak width at ½ peak ht). NMR spectra were determined in CCl_4 solution containing TMS as internal standard with a Varian DP60 spectrometer operating at 60 Mc/s. Analyses were performed by the Australian Microanalytical Service, Melbourne.

Light petroleum refers to the fraction, b.p. 40–60°. All organic solvent extracts were dried over $MgSO_4$.

VPC *analysis of the lactone mixtures*

The lactone mixtures (consisting of IV, V and sometimes X) were analysed using a 3′ Apiezon column. The samples (dissolved in benzene) were injected (injector temp 260°) with the column temp at 170°, and 1 min after injection, the column temp was programmed to 210° at 10°/min. Under these conditions, the following retention times were observed: *endo*-lactone (V), 6 min; *exo*-lactone (IV), 6 min 15 sec; δ-lactone (X), 7 min. Because the peaks from IV and V overlapped, the reported compositions (normalized peak areas) (Tables 1 and 2) are regarded as being accurate to ca. ±4%. Several mixtures of IV and V were analysed on a 150′ Apiezon capillary column at 190° (injector temp 260°). Under these conditions, the retention times of IV and V were 13 min 0 ± 5 sec, and 14 min 0 ± 5 sec, respectively, but slight "tailing" of the peaks occurred. The compositions of several mixtures were in good agreement (±2%) with those determined on the 3′ Apiezon column.

Attempted oxidative decarboxylation of endo-2-*carboxybornane* (I)

The method was based on that described by LeBel and Huber.[27]

A solution of *endo*-2-carboxybornane, m.p. 74–75°, (1·80 g, 0·01 mole) and freshly fused AcONa (1·00 g, 0·012 mole) in glacial AcOH (40 ml) was warmed to 60°. Lead tetra-acetate (5·1 g. 0·0115 mole) was added and the temp of the stirred solution was slowly raised to 116–118° over a period of 1 hr. During this time, evolution of CO_2 was not observed. After being kept at this temp for 1½ hr and then at room temp overnight, the solution was poured into water, and the AcOH was neutralized with K_2CO_3. (The acid, I, was relatively insoluble in potassium carbonate solution, and was readily extracted by ether after the neutralization.) The mixture was extracted with ether, and the ether extract was washed with dil KOHaq (acidification of this extract followed by ether extraction yielded unchanged I(1·0 g), m.p. 73–75°), water and dried ($MgSO_4$). Removal of the ether left a semi-solid residue (0·40 g) which from light petroleum yielded colourless plates (0·11 g), m.p. 97–100°. A second recrystallization raised the m.p. to 101–103°. VPC analysis showed that this product was a mixture (79:21) of IV and V, ν_{max} 1777 (s), 1465 (m), 1421 (m), 1386 (m), 1366 (m), 1297 (m), 1282 (m), 1261 (s), 1250 (s), 1201 (w), 1185 (m), 1171 (s), 1147 (m), 1131 (m), 1121 (m), 1072 (w), 1065 (w), 1026 (m), 1014 (m), 975 (w), 970 (m), 951 (w), 917 (m), 910 (m, sh) cm^{-1}; NMR τ 9·02 (overlapping singlets, 6H), 8·88–7·57 (complex, 12H). (Found: C, 74·35; H, 9·2. $C_{18}H_{18}O_2$ requires: C, 74·2; H, 9·3%.)

Action of lead tetra-acetate on camphene in acetic acid (cf. Ref. 3)

A solution of (±)-camphene (5·0 g, 0·038 mole), fused AcONa (3·3 g, 0·040 mole) and lead tetra-acetate (18·0 g, 0·040 mole) in glacial AcOH (50 ml) was stirred at 100–110° for 75 min and then kept at room temp overnight. The mixture was poured into excess of water and after ether extraction yielded an oil (6·2 g) which was distilled to give a small hydrocarbon fore-run and a main acetate fraction (3·1 g), b.p. 112–122°/15 mm. The distillation residue (1·4 g), after being freed from further volatile material by distillation at 100° (bath)/2 mm, was diluted with light petroleum. The solid material (0·16 g) was collected and recrystallized twice from light petroleum to give colourless plates (0·040 g), m.p. 101–103° (lit.[3] m.p. 101°), undepressed in admixture with the product from the oxidative decarboxylation of *endo*-2-carboxybornane. A sample in admixture with pure (±)-*endo*-lactone (V) melted at 101–102°. Capillary VPC analysis showed that the product was a mixture (83:17) of IV and V.

[27] N. A. LeBel and J. E. Huber, *J. Amer. Chem. Soc.* **85**, 3193 (1963).

Camphenilone (VII)

Camphenilone was prepared by ozonolysis of camphene.[28] (+)-Camphenilone, $[\alpha]_D^{18}$ +61 (*c* 2·46, benzene) was obtained from camphene, $[\alpha]_D$ +107. The calculated optical purity of the camphenilone was 80%, using the value $[\alpha]_D$ +76·1 (benzene) for optically pure camphenilone.[29]

Tertiary alcohol (VIII)

To a slurry of allylmagnesium chloride[30] (0·10 mole) in ether maintained in an atm of N_2 was added a solution of (±)-camphenilone (6·0 g, 0·043 mole) in ether over a period of 10 min. After the mixture had been stirred at room temp for 1 hr, then heated under reflux for 4 hr and finally kept at room temp overnight, sat NH_4Claq was added. The ether layer was separated by decantation and the inorganic residue washed thoroughly with ether. The combined ether extract was washed with water and dried. Removal of the ether and distillation of the residue yielded a colourless oil (6·8 g, 87%), b.p. 68–71°/1 mm. VPC analysis (150′ Apiezon and 300′ Ukon capillary columns) indicated >99% purity. For analysis, a sample was redistilled. (Found: C, 80·2; H, 11·2. $C_{13}H_{20}O$ requires: C, 79·9; H, 11·2%.) Optically active VIII, $[\alpha]_D^{18}$ +44·4 (*c* 1·90, benzene) was obtained in similar yield from (+)-camphenilone, $[\alpha]_D^{18}$ +61.

Hydroboration-oxidation of the tertiary alcohol (VIII)

(a) A cooled solution of VIII (2·3 g, 0·014 mole) and $NaBH_4$ (1·5 g, 0·040 mole) in dry diglyme (50ml), maintained in an atm of N_2, was treated dropwise with BF_3-etherate (5·0 g, 0·035 mole). When the addition had been completed, the mixture was stirred at room temp overnight, and then oxidized by the addition of 3N NaOH (10 ml) and 30% H_2O_2 (10 ml). The mixture was stirred at 50–60° for 2 hr, cooled, diluted with water, and extracted with ether. After the ether extract had been washed with water and dried, the ether was removed to give a colourless viscous oil (2·5 g) which on trituration with light petroleum yielded colourless plates (1·1 g, 42%), m.p. 66–67°. Two recrystallizations from light petroleum gave IX(R = R′ = H), m.p. 68–69°. (Found: C, 72·9; H, 11·15. $C_{13}H_{22}O_2$ requires: C, 72·7; H, 11·2%.)

(b) A reaction was carried out under similar conditions using optically active VIII(7·0 g), $NaBH_4$ (4·6 g) and BF_3-ethereate (7·1 g) in diglyme (100 ml). The product obtained from the alkaline peroxide oxidation was distilled to yield a viscous oil (6·1 g), b.p. 125–130°/0·5 mm, which would not crystallize. TLC (silica gel, ether–hexane (1:1)) revealed the presence of two components (R_f 0·15 and 0·13) other than the desired diol (R_f 0·09). Part of the product (3·30 g) was chromatographed on silica gel (50 g) in ether–hexane (1:1). Elution with ether–hexane (7:3) gave a fraction (0·42 g), m.p. 79–81° which consisted mainly of the component having R_f 0·15. Two crystallizations from hexane gave XXIV as colourless needles, m.p. 83–84°. (Found: C, 73·0; H, 11·2. $C_{13}H_{22}O_2$ requires: C, 72·7; H, 11·2%.) NMR τ 9·07 (6H, overlapping singlets, 2 tertiary CH_3), 8·93–8·15 (12H, complex, —CH_2—, —CH—, —CH(OH)CH_3), 7·67 (1H, broad singlet, bridgehead —CH—C(OH)—), 7·00–6·20 (2H, broad, 2XOH) and 5·87 (1H, complex, —CH_2—CH(OH)CH_3). Further elution with ether–hexane (7:3) yielded a fraction (0·58 g) shown to be a mixture of the components having R_f 0·15 and 0·13. This material was rechromatographed on silica gel (15 g) and elution with ether–hexane (1:1) yielded a further quantity of XXIV, followed by material (0·060 g) having R_f 0·13. Recrystallization of the latter from hexane gave XXV as colourless needles, m.p. 94–95°. (Found: C, 72·6; H, 11·2. $C_{13}H_{22}O_2$ requires: C, 72·7; H, 11·1%.) NMR τ 9·02 and 8·98 (each 3H, singlets, 2 tertiary CH_3); 8·93–8·00 (12H, complex, —CH_2—, —CH—, and —CHOH—CH_3), 7·92 (1H, broad singlet, bridgehead —CH—C(OH)—), 6·36 (2H, broad, 2XOH) and 5·89 (1H, complex, —CH_2—CH(OH)CH_3).

Elution of the first column with ether gave IX(R = R′ = H) as an oil (2·20 g) which slowly crystallized. Recrystallization from light petroleum gave colourless plates (1·10 g), m.p. 54–56°, $[\alpha]_D^{18}$ +23·1 (*c* 1·58, EtOH).

3-(endo-2-*Hydroxy*-3,3-*dimethyl*-2-*norbornyl*)*propanoic acid lactone* (V)

(a) A stirred solution of IX(R = R′ = H; 0·40 g) in acetone (100 ml) was treated dropwise with Jones' reagent[8] until the colour of the reagent persisted. The mixture was stirred at room

[28] P. S. Bailey, *Chem. Ber.* **88**, 795 (1955).
[29] W. R. Vaughan and R. Perry, *J. Amer. Chem. Soc.* **75**, 3168 (1953).
[30] M. S. Kharash and C. F. Fuchs, *J. Org. Chem.* **9**, 359 (1944).

temp for 1 hr, after which the excess of oxidizing agent was destroyed by the addition of EtOH. After the addition of water to the solution, the mixture was concentrated under reduced press. The aqueous residue was extracted with ether and the ether extract washed with water and dried. Removal of the ether gave V(0·38 g, 95%), m.p. 98–102°, raised to 102–103° (lit.[5] 103–104°) after a further recrystallization from light petroleum. Capillary VPC analysis showed that the lactone was homogeneous; ν_{max} 1780 (s), 1465 (s), 1447 (m), 1420 (m), 1387 (m), 1365 (m), 1325 (w), 1295 (m), 1280 (s), 1258 (sh), 1253 (s), 1203 (s), 1185 (s), 1170 (s), 1155 (s), 1135 (w), 1095 (w), 1065 (s), 1045 (m), 1025 (s), 1006 (m), 997 (s), 975 (s), 920 (s), 913 (s) and 880 (m) cm^{-1}. (Found: C, 74·2; H, 9·4. Calc. for $C_{12}H_{18}O_2$: C, 74·2; H, 9·3%.)

(b) (+)-Diol (IX, R = R′ = H; 0·40 g) was oxidized as described in (a) to give the crude lactone (0·39 g), m.p. 110–114°. Recrystallization from hexane gave colourless plates (0·22 g), m.p. 114–115°, $[\alpha]_D^{18}$ +32·0 (*c* 2·04, $CHCl_3$). This lactone was homogeneous as judged by VPC, and its IR spectrum was identical with that of the (±)-lactone described in (a).

Unsaturated acid (XV)

This synthesis was modelled on recent work of Büchi *et al.*[21]

Ac_2O (5 ml) was added to a cooled solution of IX(R = R′ = H; 0·45 g) in pyridine (ca. 40 ml). After being kept at room temp overnight, the mixture was poured into water and after ether extraction yielded IX(R = H, R′ = $COCH_3$; 0·47 g), ν_{max}^{film} 3550, 1740 and 1240 cm^{-1}. This crude product was dissolved in pyridine (ca. 50 ml), cooled to 0°, and then treated dropwise with $POCl_3$ (10 ml). After being kept at room temp for 1 hr, the mixture was warmed on a steam bath for 1 hr, cooled, poured into iced water and acidified with dil HCl. Ether extraction yielded XXIII(R = $COCH_3$; 0·40 g), ν_{max}^{film} 1730 and 1220 cm^{-1}. This acetate was heated under reflux with excess LAH in ether for 1 hr, and yielded XXIII(R = H; 0·34 g) as an oil, ν_{max}^{film} 3350 cm^{-1}. The crude alcohol was dissolved in acetone (50 ml), treated dropwise with an excess of Jones' reagent, and stirred at room temp for 1 hr, yielding a crystalline acid fraction (0·19 g), m.p. 80–90°. Successive recrystallizations from aqueous MeOH and light petroleum gave XV as colourless plates, m.p. 104–105° (lit.[5] m.p. 105–106°). NMR τ 8·97 and 8·93 (3H, each, singlets, 2 tertiary CH_3), 8·86–7·90 (7H, complex, saturated —CH_2— and —CH—), 7·09 (1H, broad, —CH—C=C—), 6·98 (2H, doublet J 7 c/s, =CH CH_2—CO_2H), 4·95 (1H, triplet J 7 c/s, —C=CH—CH_2—) and −1·90 (1H, singlet, —CO_2H). (Found: C, 74·25; H, 9·3. Calc. for $C_{12}H_{18}O_2$: C, 74·2; H, 9·3%.)

(b) Optically active XV was prepared as follows. A solution of IX(R = R′ = H ; 0·80 g) in anhydrous ether (25 ml) was treated with trifluoroacetic anhydride (6 ml) and kept at room temp for 30 hr. The solution was poured into dil $NaHCO_3$aq, and the ether layer was separated, washed with water and dried. Evaporation of the ether gave a colourless oil (IX, R = R′ = $COCF_3$) whose IR spectrum lacked OH absorption and showed strong trifluoroacetate absorption at 1780 and 1240–1130 cm^{-1}. This product was stirred with $CaCO_3$ (2·0 g) in aqueous acetone (50% V/V, 100 ml) at room temp for 40 hr, and then the mixture was heated under reflux for 4 hr. Ether extraction yielded an oil (0·70 g), whose IR spectrum was identical with that of XXIII(R = H). This crude product was treated with Jones' reagent to give a crystalline acidic fraction (0·35 g, 43% overall) which after successive recrystallizations from aqueous MeOH and light petroleum had m.p. 100–102°, $[\alpha]_D^{16}$ +95 (*c* 1·16, $CHCl_3$). The IR spectrum of this acid was identical with that of XV synthesized from (±)-camphenilone.

Tricycloekasantalic acid (VI)

A commercial mixture of α- and β-santalol (Fluka) was oxidized with $KMnO_4$.[22] The acid crystallized as colourless plates, m.p. 76–77° (lit.[22] m.p. 76–77°), $[\alpha]_D^{18}$ +21·2 (*c* 5·88, $CHCl_3$) (lit.[15] $[\alpha]_D$ +19·4). The methyl ester, prepared by treating the acid with ethereal diazomethane, was homogeneous as judged by VPC (150′ Apiezon capillary column, 150°).

Lactone mixture from tricycloekasantalic acid (VI)

(a) Tricycloekasantalic acid (1·10 g) was heated under reflux with 25% H_2SO_4aq (100 ml) for 15 min. The cooled solution was poured into water, and after ether extraction yielded an acidic

[21] G. Büchi, W. D. MacLeod and J. Padilla O, *J. Amer. Chem. Soc.* **86**, 4438 (1964).
[22] A. C. Chapman, *J. Chem. Soc.* **79**, 134 (1901).
[23] A. E. Bradfield, A. R. Penfold and J. L. Simonsen, *J. Chem. Soc.* 309 (1935).

fraction consisting of starting material (0·5 g), and a neutral fraction (0·52 g), m.p. 85–95°, whose IR spectrum was virtually identical with that of the lactone mixture from camphene, and had a composition as shown in Table 1. After 3 recrystallizations from light petroleum, the product, m.p. 101–103°, was a mixture (69:31) of IV and V resp.

(b) The acid (0·21 g) was heated under reflux with formic acid (98%; 20 ml) for 30 min. The cooled solution was diluted with water, and ether extraction gave the lactone mixture (62:38) of IV and V resp. as plates (0·19 g), m.p. 94–97°. After 4 recrystallizations from light petroleum, the product, m.p. 101–103° was a mixture (73:27) of IV and V resp.

(c) The acid (0·20 g) was added to 98% H_2SO_4 (10 ml) which had been cooled to −10°—the mixture became homogeneous after being shaken for 2–3 min. After being kept at −10° for 25 min, the solution was poured onto crushed ice. Ether extraction yielded a crystalline neutral product (0·18 g), which after recrystallization from hexane gave colourless plates (0·10 g); ν_{max} 1780 (γ-lactone) and 1745 cm^{-1} (δ-lactone) (both of equal intensity); NMR τ 9·02 (singlet, tertiary CH_3), 8·76 (singlet, CH_3—C—O—CO— of δ-lactone) and 8·70–7·64 (complex, —CH_2— and —CH—). From the Me signal areas, the product was a mixture (ca. 1:1) of γ- and δ-lactones resp. For VPC analysis see Table 1.

In another experiment, tricycloekasantalic acid was shaken with 98% H_2SO_4 at −10° for 5 min. The product was again a mixture (ca. 1:1) of γ- and δ-lactones as judged by its IR spectrum. In an attempt to separate the lactones, the mixture (0·10 g) was heated under reflux with 0·6N NaOH (4 ml) for 3–4 min. The clear solution was cooled to 0°, acidified with dil H_2SO_4aq and immediately extracted with ether. The ether extract was washed with dil NaOHaq, but acidification and ether extraction of the alkaline layer did not yield any material. Concentration of the ether layer gave back the original mixture (0·090 g).

(d) Tricycloekasantalic acid (2·35 g) was heated under reflux with 15% H_2SO_4aq (350 ml) for 45 min. Ether extraction gave a neutral product (2·1 g), m.p. 72–100°. The IR spectrum indicated the presence of some X (shoulder at 1750 cm^{-1}) while VPC analysis showed it to be a mixture of IV (47%), V (39%) and X (14%). Two recrystallizations from hexane yielded colourless plates (1·4 g), m.p. 100–104°, $[\alpha]_D$ +15 (*c* 4·32, $CHCl_3$), shown to be a mixture (73:27) of IV and V resp.

LAH *reduction of the lactone from tricycloekasantalic acid*

The lactone, $[\alpha]_D$ +15, used was that prepared as described in (d) above. A solution of the lactone (1·60 g) in ether (50 ml) was added to a suspension of LAH (1·0 g) in ether (50 ml), and the mixture was stirred at room temp for 2 hr, and was then heated under reflux for 1 hr. The cooled mixture was carefully treated with water, yielding a colourless waxy product (1·5 g) which showed strong hydroxyl but lacked carbonyl absorption in its IR spectrum. The product was crystallized from ether (50 ml) to give XIV (R = R′ = H) as long colourless needles (0·60 g, 38%), m.p. 132–133°, $[\alpha]_D^{19}$ +22·7 (*c* 1·50, EtOH) (lit.[16] m.p. 112°, $[\alpha]_D^{28}$ +1.94). Recrystallization from benzene raised the m.p. to 133–134°, $[\alpha]_D^{20}$ +25·0 (*c* 2·00, EtOH). A sample in admixture with the (±)-*endo*-diol (IX, R = R′ = H) melted at 65–115°. (Found: C, 73·0; H, 11·1. $C_{12}H_{22}O_2$ requires: C, 72·7; H, 11·2%.)

Oxidation of the exo-*diol* (XIV, R = R′ = H). *Preparation of pure* exo-*lactone* (IV)

The diol (0·12 g), m.p. 133–134°, $[\alpha]_D^{20}$ +25, was oxidized with Jones' reagent to yield colourless plates (0·10 g), m.p. 117–119°. Recrystallization from hexane gave pure IV(0·058 g), m.p. 120–121°, $[\alpha]_D^{20}$ +40 (*c* 0·80, $CHCl_3$). The lactone was homogeneous (VPC) and its retention time (peak enhancement) was identical with that of the major component of the lactone mixtures from tricycloekasantalic acid and the lead tetra-acetate reactions.

Lactone from the unsaturated acid (XV)

The (±)-acid (XV; 0·040 g) was heated under reflux with 25% H_2SO_4aq (10 ml) for 10 min, yielding a neutral fraction (0·032 g), m.p. 82–93°, which after recrystallization from light petroleum was a mixture (68:32), m.p. 97–99°, of IV and V, resp.

Acid catalysed equilibrations of the pure lactones IV *and* V

(a) The lactone (0·030–0·050 g) was heated under reflux with the appropriate acid (3–5 ml) for the time indicated in Table 2. The product was isolated by ether extraction, and the composition was determined by VPC analysis (Table 2).

(b) The (+)-*endo*-lactone (V; 0·20 g), m.p. 114–115° was heated under reflux with formic acid (98%, 20 ml) for 90 min. Ether extraction gave a slightly discoloured product (0·20 g) which was a mixture (60:40) of IV and V, resp. After 2 recrystallizations from hexane, the product was a mixture (65:35), m.p. 98–101°, $[\alpha]_D^{20}$ 0 (*c* 1·84, $CHCl_3$), of IV and V, resp.

Degradation of the (+)-exo-*diol* (XIV, R = R′ = H) *to the unsaturated acid* (XV)

The pure XIV(R = R′ = H; 0·44 g), m.p. 133–134°, $[\alpha]_D^{20}$ +25, was converted into XIV(R = H, R′ = $COCH_3$) by treatment with Ac_2O and pyridine at room temp overnight. The crude hydroxyacetate was dissolved in pyridine (50 ml) and $POCl_3$ (5 ml) was added. After being kept at room temp for 1 hr, the mixture was heated at ca. 80° for 1 hr. The cooled mixture was poured into cold water, and after ether extraction gave XXIII(R = $COCH_3$; 0·45 g) contaminated by a small amount of unchanged hydroxyacetate (weak OH absorption in IR spectrum). This product was reduced with an excess of LAH in ether to the liquid XXIII(R = H) which was oxidized with Jones' reagent to give an acidic fraction (0·15 g, 34% overall), m.p. 75–85°. Successive recrystallizations from aqueous MeOH and hexane gave XV as colourless plates, m.p. 95–96°, $[\alpha]_D^{20}$ −118 (*c* 0·574, $CHCl_3$). A mixture of this product and the acid, m.p. 100–102°, $[\alpha]_D^{18}$ +95, melted at 104–105°. The IR spectra of the two samples were identical with that of (±)-XV.

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Note added in proof—As mentioned in the Discussion, the *endo*-lactone (V) in the lactone mixtures formed by the action of acid on tricycloekasantalic acid (VI) must have a negative specific rotation to account for the low rotations of these mixtures. The belief that V is derived from the *exo*-lactone (IV) also requires that the former have a negative specific rotation since its rotation is positive when synthesized from (+)-camphenilone. Since the camphenilone used in the synthesis of V is believed to have been 80% optically pure, optically pure (—)-V should have a specific rotation of −40. On the basis of optical activities, the lactone mixture $[\alpha]_D$ +15 used in the synthesis of (+)-*exo*-lactone (IV) was a mixture (69:31) of IV and V respectively. The agreement with the value (73:27) determined by VPC is thus reasonable.

Since the submission of this manuscript, the following relevant communications have been published.

(a) Bhattacharyya *et al.*[34] have also established that the lactone formed by the action of acid on tricycloekasantalic acid (VI) and bicycloekasantalic acid (XXVII) is a mixture of two components, one of which has physical constants in very good agreement with those of our (+)-*exo*-lactone (IV).

(b) Mechanisms involving exclusive *exo*-methyl group migration have been demonstrated for the π-sulphonation of camphor,[35] and the racemization of camphene.[35] The intervention[36] of some tricyclene, a cyclopropane derivative, in the racemization of camphene shows that the intermediate formation of tricycloekasantalic acid (VI), at least in part, by the action of strong acids on bicycloekasantalic acid (scheme 3) cannot be completely discounted.

(c) Whereas Goering and Schewene[36] used non-classical carbonium ion theory to explain the acid catalysed equilibration of the epimeric 2-norbornyl acetates, Brown[37,38] has suggested a very plausible interpretation involving classical ions.

(d) Brown[37] has also suggested that steric factors, rather than the intermediacy of non-classical ions, are probably responsible for the stereospecifity for *exo*-migration in 3,2-shifts in substituted norbornyl derivatives.

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