small pieces, dried for three days at 80–90°, powdered and the dry material (812 g.) was extracted continuously in a Soxhlet extractor with 4 l. of ethanol for seven days until the extract was colorless. The dark brown solution was evaporated to dryness under reduced pressure and the residue (125 g.) was extracted continuously with ether until no more color was removed (5 hours). The ether extract did not contain alkaloids (Mayer reagent) and gave only traces of oily material when processed in the usual manner for triterpenes. The dark brown, semi-crystalline, ether-insoluble glycosidic fraction (103 g.) was refluxed for three hours with 1.5 l. of methanol and 300 cc. of concd. hydrochloric acid. During the hydrolysis a large amount of solid separated which after cooling and dilution with water was extracted with ether, washed with 10% potassium hydroxide solution, water and dried. Evaporation gave 11.4 g. of neutral material which was chromatographed on 200 g. of deactivated alumina.[20] Elution with benzene–ether (9:1) gave 2.7 g. of colorless crystalline material which crystallized from acetone as needles, m.p. 235–237°, $[\alpha]^{25}\mathrm{D}$ +80°, $\lambda_{\max}^{\mathrm{CHCl_3}}$ 2.78 μ; no selective ultraviolet absorption above 215 mμ. The melting point was not depressed on admixture with **erythrodiol**, m.p. 235–237°, $[\alpha]^{25}\mathrm{D}$ +76°, prepared as described below, and the infrared absorption spectra of the two specimens were identical.

Anal. Calcd. for $C_{30}H_{50}O_2$: C, 81.39; H, 11.38. Found: C, 81.25; H, 11.20.

Erythrodiol diacetate was obtained in nearly quantitative yield (acetic anhydride–pyridine, room temperature, 20 hours) as needles after crystallization from methanol, m.p. 183–185°, $[\alpha]^{25}\mathrm{D}$ +58°, $\lambda_{\max}^{\mathrm{CHCl_3}}$ 5.81 and 8.00 μ. Identity with the sample of erythrodiol diacetate described below was established by infrared and mixture melting point comparison.

Anal. Calcd. for $C_{34}H_{54}O_4$: C, 77.52; H, 10.33. Found: C, 77.77; H, 10.26.

Isolation of Longispinogenin.—Further elution of the previously described chromatogram column with benzene–ether (1:1) gave 3.3 g. of colorless crystalline material, m.p. 240–242°, which after several crystallizations from acetone separated as needles with m.p. 247–249°, $[\alpha]^{25}\mathrm{D}$ +53°, $\lambda_{\max}^{\mathrm{CHCl_3}}$ 2.75 and 2.86 μ, no selective ultraviolet absorption above 215 mμ, yellow color with tetranitromethane.

Anal. Calcd. for $C_{30}H_{50}O_3$: C, 78.55; H, 10.99. Found: C, 78.71; H, 10.95.

Longispinogenin triacetate, prepared by the acetic anhydride–pyridine method (room temperature), crystallized from methanol as needles with m.p. 219–221°, $[\alpha]^{25}\mathrm{D}$ +73°, $\lambda_{\max}^{\mathrm{CHCl_3}}$ 5.80 and 8.00 μ. Repeated acetylation using more vigorous methods (acetic anhydride–perchloric acid and acetic anhydride–pyridine under reflux for 14 hours) gave the same triacetate.

Anal. Calcd. for $C_{36}H_{56}O_6$: C, 73.93; H, 9.65; acetyl, 22.01. Found: C, 73.95; H, 9.59; acetyl, 22.17.

Isolation of Oleanolic Acid.—The alkaline solution from the previously described hydrolysis deposited a semi-crystalline potassium salt which was filtered, dissolved in ethanol and acidified with dilute hydrochloric acid. The precipitated acid was filtered, washed with water and dried to give 22.4 g. of crude oleanolic acid (m.p. 288–292°) which after two crystallizations from ethanol had m.p. 306–308°, $\lambda_{\max}^{\mathrm{Nujol}}$ 2.88 and 5.88 μ. The infrared absorption spectrum was identical with that of oleanolic acid and no depression in m.p. was observed on admixture with an authentic specimen. The acetate had m.p. 263–265° undepressed on admixture with an authentic specimen of oleanolic acid acetate; $\lambda_{\max}^{\mathrm{CHCl_3}}$ 5.80, 5.90 and 7.98 μ; the infrared spectrum was identical with that of oleanolic acid acetate. The methyl ester, prepared by diazomethane treatment in ether–methanol solution, crystallized from methanol–chloroform, m.p. 197–199°, undepressed on admixture with methyl oleanolate.

Erythrodiol (II) from **Oleanolic Acid** (I).—Oleanolic acid (1.15 g.) was dissolved in tetrahydrofuran (30 cc.) and added dropwise to a stirred suspension of lithium aluminum hydride (4.5 g.) in 300 cc. of ether. After continuous stirring for 25 hours the excess of reagent was decomposed by addition of water and the inorganic material taken into solution by addition of 300 cc. of 10% sulfuric acid. The organic layer was separated and washed with potassium hydroxide solution and water until neutral, dried and evaporated, yielding 0.935 g. of white crystalline material. Filtration through alumina in chloroform solution and crystallization from methanol gave **erythrodiol** (II), m.p. 235–237°, $[\alpha]^{25}\mathrm{D}$ +76°.[21] A sample was sublimed in high vacuum for analysis.

Anal. Calcd. for $C_{30}H_{50}O_2$: C, 81.39; H, 11.38. Found: C, 81.42; H, 11.49.

Erythrodiol diacetate prepared by the usual method had m.p. 184–185°, $[\alpha]^{25}\mathrm{D}$ +59°.[22] This diacetate as well as the free diol were identical with the corresponding derivatives described above which had been isolated from the cactus.

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[20] A suspension of 200 g. of activated alumina (Alcoa, grade F-20) in benzene was shaken with 6 cc. of 10% aq. acetic acid for 2 hours and then used directly.

[21] J. Zimmermann (ref. 10 and *Helv. Chim. Acta*, **19**, 247 (1936)) reported m.p. 232°, $[\alpha]\mathrm{D}$ +75.4°.

[22] Reported[21] m.p. 186°, $[\alpha]\mathrm{D}$ +59°.

DETROIT, MICHIGAN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF DELAWARE]

The Configuration of Some Dichlorocamphanes

BY HAROLD KWART

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The dipole moments of the compounds known as bornyl dichloride and β-chlorocamphane have been measured. The configurational relationships of the two chlorine atoms in these compounds is deducible from the data. The steric course of the reactions by which these substances are formed is clearly understandable in terms of existing theory.

The structure of the principal dichlorination product of α-pinene (I) described by Aschan and others[1] has been identified as 2,6-dichlorocamphane on the basis of tricyclene formation when this product is treated with zinc or sodium. Although referred to by Simonsen and others[2] as bornyl dichloride, the previously reported evidence has not permitted a configurational assignment of the chlorine atoms; *i.e.*, whether *exo* or *endo*.

In general, the determination of configuration by methods involving reaction must depend on an intimate knowledge of the steric requirement for the reaction and other features of the reaction mechanism in entirely analogous systems. Conversion to tricyclene (V), therefore, affords no basis for configurational assignment, since these factors concerned with the process of formation are not sufficiently well understood. Furthermore, such

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[1] O. Aschan, *Ber.*, **61**, 38 (1928); O. Brus, *Compt. rend.*, **180**, 1507 (1925).

[2] J. L. Simonsen, "The Terpenes," Vol. II, Oxford University Press, 1949, p. 167, and elsewhere in the text. See also reference 7.

well understood reactions of acyclic and aliphatic systems as addition, displacement and elimination are frequently attended by deep seated rearrangements[3] when they occur in bicyclic systems, presenting thereby a further complication to the use of reaction derivatives for structural determination.

A unique feature of camphane structures, however, is their relative rigidity as compared with the parent cyclohexane and, as is the case with such structures, good agreement may be expected between calculated and observed dipole moments of their polyhalogen derivatives. Reference to Table I indicates that the three alternative configurations of a sterically pure 2,6-dichlorocamphane may be distinguished by measurement of the product dipole moment.

TABLE I

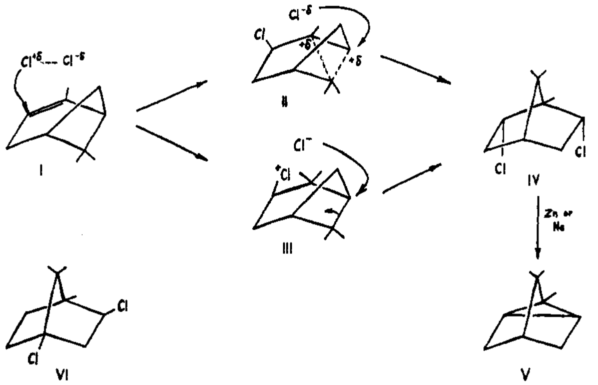
Possible configuration	μ,[a] D Calcd.	Obsd.
2,6-DICHLOROCAMPHANE		
exo–exo	2.3	
exo–endo	2.5	
endo–endo	4.2	4.0
2,4-DICHLOROCAMPHANE (VI)		
2-*exo*	2.5	2.5
2-*endo*	2.5	

[a] The dipole moments of bornyl and isobornyl chlorides were determined (see Experimental section) and found to be identical. This value of the C–Cl bond moment (2.1 D) was used in calculating the moments of all possible configurations.

The result of such measurements appears to confirm the *endo–endo* relationship of the two halogen atoms in bornyl dichloride. Furthermore, this result is most fortunate in that it is the only unequivocal configurational assignment possible among the several alternatives and confirms, at once, the steric purity of the product and the stereospecificity of the reaction leading to borny dichloride.

To verify the validity of this result and as an estimate of the sensitivity of our method we made a similar measurement of the dipole moment of β-chlorocamphane (VI). This substance is an isomer of bornyl dichloride with a 1,3-relationship of chlorine atoms on a camphane skeleton. The configuration of the bridgehead chlorine atom is fixed by the geometry of the camphane skeleton and the isobornyl configuration of the 2-chlorine atom has been deduced in interesting fashion by Houben and Pfankuch[4] from considerations on the optical activity of the product. For our purposes, however, neither the correctness of their deduction nor the steric purity of the product nor a knowledge of the geometry of an isobornyl configuration need be assumed since both of the possible alternatives possess the same calculated moment. The observed moment is seen from Table I to be identical with the calculated. This result provides considerable confidence in our method of identification of the configuration of bornyl dichloride.

The *endo–endo* configuration chosen as most consistent with the data holds particular interest for several reasons. Considering the method of formation from α-pinene, chlorination has resulted in a rearrangement of the carbon skeleton. The stereochemical specificity of the reaction can be nicely accounted for by the generalized theory of Bartlett[5] in terms of a chloronium ion intermediate II or by the more recent bridged ion III concept elaborated by Neville, De Salas and Wilson, *et al.*,[6] to accommodate many instances of Wagner–Meerwein rearrangement, as illustrated in the accompanying figure. The operation of purely polar factors in these mechanisms has been inferred from the observation of Henderson and Marsh[7] that bornyl dichloride, as would be expected in a polar halogenation, also arises from the chlorination of α-pinene in aqueous solution alongside of pinene glycol and chlorohydrin.



In view of the presently established configuration of bornyl dichloride, the formation of tricyclene appears to have involved a *cis* elimination of the elements of chlorine. The normal steric requirement for halogen elimination in alicyclic systems has been shown[8] to be *trans*. However, similar elimination reactions with zinc in bicyclic systems appear[9] to occur with facility in cases of both *cis*- and *trans*-vicinal halogen substituents.

A further source of interest in the configuration IV of 2,6-dichlorocamphane bears on the long contested question of whether a bornyl structure corresponds to the *exo* or *endo* configuration and *vice versa* for the isobornyl.[10] The work of Asahina and his associates[10] leaves little doubt on this score but it may be pointed out that further support for their conclusions is potentially derivable from reduction of IV to bornyl chloride. The symmetry of the halogen atoms, both in *endo* configurations, presents this clear possibility of establishing unequivocally the *endo* configuration of a bornyl structure. We have not succeeded thus far in our

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(3) O. Aschan, *Ber.*, **40**, 2750 (1907); *Ann.*, **387**, 1 (1912); B. Arbusov, *Ber.*, **68**, 1430 (1935); see also reference X.

(4) J. Houben and E. Pfankuch, *Ann.*, **501**, 219 (1933).

(5) P. D. Bartlett, THIS JOURNAL, **59**, 822 (1937).

(6) T. P. Neville, E. De Salas and C. L. Wilson, *J. Chem. Soc.*, 1188 (1939); W. E. Doering, abstracts 113th meeting of the American Chemical Society, Chicago, Ill., April 19–23, 1948, p. 41L; S. Winstein, *et al.*, THIS JOURNAL, **74**, 1130 (1952).

(7) G. G. Henderson and J. E. Marsh, *J. Chem. Soc.*, **119**, 1492 (1921).

(8) D. H. R. Barton and E. Miller, THIS JOURNAL, **72**, 370 (1950).

(9) Unpublished results from these laboratories.

(10) K. Alder and G. Stein, *Ann.*, **514**, 211 (1934); H. Bode, *Ber.*, **70**, 1167 (1937); G. Komppa and G. A. Nyman, *ibid.*, **69**, 334 (1936); W. Hückel, *Die Chemie*, **55**, 227 (1942); Y. Asahina and T. Sano, *Ber.*, **69**, 343 (1936).

attempts to effect this reduction but are continuing our efforts.

Experimental

Isobornyl chloride was prepared according to Meerwein and van Emster.[11] The product thus obtained was recrystallized once from *n*-amyl alcohol (dried over calcium oxide) and twice from nitromethane (Eastman Kodak Co. white label) dried over anhydrous calcium sulfate, m.p. 162° (uncor.). It was dried thoroughly in vacuum before use. The camphene used in this synthesis was provided through the courtesy of the Hercules Powder Company Experiment Station.

Bornyl chloride was prepared by the addition of dry HCl to pinene (Hercules grade distilled over sodium) according to the procedure discussed by Thurber and Thielke.[12] It was recrystallized twice from low boiling 30–60° petroleum ether (distilled from sodium), m.p. 131° (uncor.) and stored in a vacuum desiccator over calcium chloride before use.

TABLE II

DIPOLE MOMENT DATA

Compound	Concn., moles/cc. × 10^4	ϵ	η^2	S_0	μ_D
Isobornyl chloride	6.989	2.6121	2.1363	0.0535	2.1
	3.494	2.4167	2.1298		
	1.747	2.3208	2.1269		
	0.874	2.2725	2.1255		
	0.000	2.2250	2.1240		
Bornyl chloride	10.0469	2.7932	2.1392	.0535	2.1
	5.0235	2.5072	2.1322		
	2.5117	2.3650	2.1281		
	1.2558	2.2963	2.1261		
	0.0000	2.2250	2.1240		
	Mole %				
2,6-Dichlorocamphane	1.51	2.5450	2.1298	.0188	4.0
	2.20	2.6534	2.1336		
	4.11	3.0242	2.1406		
	6.05	3.4015	2.1456		
	0.00	2.2372	2.1243		
	Moles/cc. × 10^3				
2,4-Dichlorocamphane	4.5094	2.565	2.1342	.0720	2.5
	2.2547	2.3919	2.1307		
	1.1274	2.3094	2.1281		
	0.5637	2.2687	2.1266		
	0.000	2.2324	2.1252		

2,6-Dichlorocamphane[13] was prepared according to the method of Aschan.[1] For dipole moment measurements it was recrystallized three times from absolute ethanol and stored in a vacuum desiccator over calcium chloride before use, m.p. 170–171° (uncor.).

2,4-Dichlorocamphane was prepared from synthetic camphor (U.S.P. du Pont) by the procedure suggested by Doering and Schoenewaldt.[14] The product was recrystallized twice from absolute methanol saturated with dry hydrogen chloride and stored in a vacuum desiccator over calcium chloride before use, m.p. 178° dec. (uncor.).

Dipole Moment Measurements.—Pure, dry carbon tetrachloride used as the solvent in these experiments was prepared from C.P. Baker grade by the method of Vogel.[15]

The dipole moments were computed from the data shown in Table II, by the method of Guggenheim[16] using the equation

$$\mu_D = 0.0222 \left[\frac{S_0 T}{(\epsilon_0 - 2)(\eta_0^2 - 2)}\right]^{1/2}$$

where

μ_D = the dipole moment in Debyes
S_0 = slope of the plot
T = absolute temp.
ϵ_0 = dielectric of solvent.; ϵ = dielectric of sol.
η_0 = refr. index of solvent; η = refr. index of soln.

Analysis of the error introduced by using this simplified computation according to the suggestion of Palet[17] indicates that an error of no greater than 5% could arise by ignoring consideration of the solution densities in the results reported here. This magnitude of possible error lies beyond the limit which would have significance in our considerations above.

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[11] H. Meerwein and K. van Emster, *Ber.*, **55**, 2526 (1922).

[12] F. H. Thurber and R. C. Thielke, THIS JOURNAL, **53**, 1032 (1931).

[13] This preparation was carried out by Mr. Donald Pascale and Mr. Lloyd Kaplan.

[14] W. von E. Doering and E. F. Schoenewaldt, THIS JOURNAL, **73**, 2333 (1951).

[15] A. I. Vogel, "Textbook of Practical Organic Chemistry," Longmans, Green and Co., New York, N. Y., 1951, p. 174–175.

[16] E. A. Guggenheim, *Trans. Faraday Soc.*, **45**, 714 (1949); J. W. Smith, *ibid.*, **46**, 394 (1950); E. A. Guggenheim, *ibid.*, **47**, 573 (1951).

[17] S. R. Palit, THIS JOURNAL, **74**, 3952 (1952).

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF QUEENSLAND]

Some Properties of Isopropenylic Terpenoids

BY MAURICE D. SUTHERLAND

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Approximate values have been calculated for the refractive indices, densities and boiling points of α-citronellol, α-citronellal and certain other acyclic α-terpenoids which are as yet unknown. For this purpose the hydrocarbons 2,6-dimethyloctene-1 and 2,6-dimethyloctene-2 have been prepared and the density and refractive index of 2-methylhexene-1 has been redetermined. In addition the absence of α-citronellal from the essential oil of *Eucalyptus citriodora* Hook has been demonstrated.

After many years of controversy,[1,2] it is now clear that α-citronellol has not as yet been found in nature, although it may be present in samples of citronellol which have been subjected to acid treatment in the course of isolation[3] or purification.[4] It is also true of the other acyclic oxygenated terpenes of "normal" carbon skeleton that in no case has the α-form or isopropenylic isomer been detected in nature.[4-7] Ocimene also, for many years accepted as isopropenylic, has recently been shown to have an isopropylidenic or β-structure.[8,9]

Thus until recently, the α-terpenoids have been unknown except as inseparable contaminants of the

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[1] L. N. Owen and J. L. Simonsen, *Endeavour*, **8**, 26 (1949).

[2] Y-R. Naves, *Perfumery and Essential Oil Record*, **40**, 41 (1949).

[3] Y-R. Naves, *Bull. soc. chim.*, [5] **18**, 506 (1951).

[4] J. Doeuvre, *ibid.*, [5] **3**, 612 (1936).

[5] Y-R. Naves, G. Brus and J. Allard, *Compt. rend.*, **200**, 1112 (1935).

[6] D. Barnard, L. Bateman, A. J. Harding, H. P. Koch, N. Sheppard and G. B. B. M. Sutherland, *J. Chem. Soc.*, 915 (1950).

[7] M. F. Carroll, R. G. Mason, H. W. Thomspon and R. C. S. Wood, *ibid.*, 3457 (1950).

[8] G. Dupont and V. Desreux, *Bull. soc. chim.*, [5] **5**, 337 (1938).

[9] M. D. Sutherland, THIS JOURNAL, **74**, 2688 (1952).