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The Structure of Longifolene. The Longifolic Acids[1]

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The longifolic acids are shown to be $C_{15}H_{24}O_2$ and not $C_{14}H_{22}O_2$ monobasic acids as previously reported by other workers. This result together with other data proves the unsaturation in longifolene to be of a methylenecyclopentano form and not of a vinyl type. The acid isomerization of longifolene to β-longifolene is also described.

The simultaneous appearance of three communications relating to the structure of longifolene[2-4] prompts us to place on record work which we have completed and presented recently in verbal form.[1] While one portion of our work is coincidental with that reported by Naffa and Ourisson[3] both in design and result, another is not only novel but is also of considerable significance in the reactions of longifolene.

It has been reported by Simonsen[5] that oxidation of the tricyclic sesquiterpene, longifolene, $C_{15}H_{24}$, in acetic acid with chromium trioxide and in sulfuric–acetic acid with potassium dichromate leads in the first case to longifolic acid and in the second to isolongifolic acid. These acids were considered to be isomeric and of the formula $C_{14}H_{22}O_2$ on the basis of neutralization equivalent determinations, analysis of the silver salt of longifolic acid, combustion analyses and the isomerization of longifolic acid to isolongifolic acid in mineral acid. In addition to the acids a yellow α-diketone, $C_{15}H_{22}O_2$, was isolated from the neutral fractions of both oxidations. Later, Bradfield, Francis and Simonsen[6] obtained formaldehyde and a third acid, α-longifolic acid, also considered to be of the C_{14} variety, from the ozonization of longifolene. The isolation of these three acids was used as proof of a vinyl formulation of the monounsaturation in longifolene.

The uncertain relationships between these acids and the apparently anomalous formation of the C_{15}-diketone, longifdione, led us to repeat these oxidations. The three acids and the diketone were obtained identical in m.p. to those previously described. Lithium aluminum hydride reduction of methyl isolongifolate or of isolongifolic acid yielded as sole product, isolongifolol, m.p. 112°, $[\alpha]_D$ $-46.9°$. Oxidation of isolongifolol with dichromate in sulfuric–acetic acid regenerated isolongifolic acid. However, similar reduction of longifolic acid gave isolongifolol in predominant yield and a second alcohol, longifolol, m.p. 78.5–80.5°, $[\alpha]_D$ $+23.5°$. Furthermore, reduction of α-longifolic acid also led to isolongifolol and a series of impure alcohol fractions rich in isolongifolol. It is apparent, therefore, that longifolic and α-longifolic acids are not homogeneous acids but are mixtures predominating in isolongifolic acid. From the treatment of isolongifolol with phosphorus pentachloride in ether at room temperature an olefin was isolated which proved to be *longifolene* on the basis of optical rotation and infrared spectrum. Clearly, isolongifolic acid cannot be a C_{14}-acid. Similar treatment of the longifolol obtained above gave a hydrocarbon mixture which appeared to contain longifolene. These results suggest that longifolic and α-longifolic acids are at least in part epimeric mixtures. Neutralization equivalent determinations of all three acids in our hands gave correct values for $C_{15}H_{24}O_2$ monobasic acids. This conclusion has been reached also by Naffa and Ourisson.[8]

Examination of the neutral fractions from the ozonization and acidic oxidations of longifolene revealed the presence of large quantities of a monoketone whose infrared spectrum characterized it as a 5-membered ring ketone (5.73 μ). This ketone is undoubtedly the same as the C_{14}-ketone isolated by Naffa and Ourisson from the same sources. After cleavage of this ketone with peracid, an uncharacterized crystalline hydroxy acid was obtained *via* a 6-membered lactone (5.76 μ). All these data, together with the infrared absorption bands of longifolene at 3.25, 6.01 and 11.46 μ, prove that the double bond in longifolene is methylenic and exocyclic to a 5-membered ring. The C_{15}-acids must arise, therefore, by terminal oxidation in the same way as the camphenilanic acids are formed from camphene.

Longifolene is isomerized slowly in sulfuric–acetic acid at 80° over a period of 14 days. The course of the isomerization is followed easily by the change in rotation from $+33°$ to a value of $-16°$ and by the gradual and complete disappearance of the infrared absorption bands due to methylenic unsaturation. The olefin, β-longifolene, which is recovered, arises from the migration of the exocyclic double bond with rearrangement, since its infrared spectrum indicates completely different olefinic unsaturation (12.26 μ, possibly $R_1CH{=}CR_2R_3$).

Dehydration of isolongifolol or longifolol with potassium bisulfate at 220° produces hydrocarbons whose infrared spectra are similar to one another in that they have absorption bands at 6.10 and 11.28 μ as compared to 6.01 and 11.46 μ in the spectrum of longifolene itself. This shift of absorption indicates new unsaturation of the $R_1R_2C{=}CH_2$ type.

Inasmuch as Naffa and Ourisson are continuing their study of longifolene and its derivatives, we propose to limit our work to the investigation of β-longifolene and the dehydration products obtained in this Laboratory.

Experimental[7]

Longifolene.—The longifolene used in the following experiments was isolated from the oleoresin of the Japanese

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(1) Presented at Chicago, Ill., September 10, 1953, Abst. 124th Meeting, Amer. Chem. Soc., p. 89–O.

(2) R. H. Moffett and D. Roger, *Chem. and Ind.*, 916 (1953).

(3) P. Naffa and G. Ourisson, *ibid.*, 917 (1953).

(4) G. Ourisson, *ibid.*, 918 (1953).

(5) J. L. Simonsen, *J. Chem. Soc.*, **123**, 2642 (1923). See also J. L. Simonsen and D. H. R. Barton, "The Terpenes," Vol. III, Cambridge Univ. Press, 1952.

(6) A. E. Bradfield, E. M. Francis and J. L. Simonsen, *J. Chem. Soc.*, 188 (1934).

(7) All melting points are corrected. Rotations were measured in 95% ethanol unless otherwise specified. Microanalysis were performed by the Schwarzkopf Microanalytical Laboratories and neutralization equivalents by Mr. M. Tsutsui.

pine, *Pinus densiflora*, Sieb. and Zucc., and supplied to us by the Arakawa Forest Products Company of Osaka, Japan. The sesquiterpene was distilled from sodium before use and had the following constants: b.p. 144–146° (30 mm.), n^{25}D 1.5000, α^{25}D +38.14°; **hydrochloride**, m.p. 58.5–59.5°, $[\alpha]^{25}$D +9.8° (in $CHCl_3$); hydrobromide, m.p 69°. Simonsen[8] reports these constants for longifolene obtained from Indian terpentine oil: b.p. 150–151° (36 mm.), n^{30}D 1.495, αD +42.73°; hydrochloride, m.p. 59–60°, $[\alpha]$D +7.1° (in $CHCl_3$); hydrobromide, m.p. 69–70°.

Longifolene hydrobromide was dehydrobrominated in 10% alcoholic potassium hydroxide at reflux for 11 hr. to longifolene. The hydrochloride was considerably more resistant to this treatment.

Anal. Calcd. for $C_{15}H_{24}$: C, 88.16; H, 11.84. Found: C, 88.12; H, 11.51.

The Longifolic Acids.—Longifolene was oxidized and ozonized according to the procedures of Simonsen.[5,6] Discrepant values are given: longifolic acid, $[\alpha]$D +5.6° (opt. inact.[9]); neut. equiv., 233, 234 ($C_{15}H_{24}O_2$ requires 236); isolongifolic acid, neut. equiv., 236, 236; α-longifolic acid, neut. equiv., 239, 239.5.

The Longifolols.—Methyl isolongifolate (3.2 g.), m.p. 54–55° (54–55°),[9] was reduced in ether with excess lithium aluminum hydride. After working up in the usual manner, the crude alcohol was crystallized from petroleum ether, yielding 2.8 g. of pure isolongifolol, m.p. 111–112°, $[\alpha]^{25}$D −46.9°. Similar reduction of isolongifolic acid gave the same product.

Anal. Calcd. for $C_{15}H_{26}O$: C, 81.02; H, 11.79. Found: C, 80.98; H, 11.38.

Reduction of longifolic acid (3.0 g.) yielded 1.6 g. of crude alcohol, m.p. 50–90°. Crystallization of this material from petroleum ether gave as fraction 1, isolongifolol (0.46 g.), m.p. 111–112°, $[\alpha]$D −46.4°; as fraction 2, crude longifolol, m.p. 75–80°, whose m.p. became constant at 78.5–80.5° after two recrystallizations from the same solvent: 0.21 g., $[\alpha]$D +23.5°.

Anal. Calcd. for $C_{15}H_{26}O$: C, 81.02; H, 11.79. Found: C, 81.03; H, 11.52.

The reduction of α-longifolic acid (1.4 g.) gave 1.1 g. of crude alcohol, m.p. 57–90°. Fraction 1 from petroleum ether proved to be slightly impure isolongifolol (0.3 g.) which further crystallization failed to improve: m.p. 107–109°, $[\alpha]$D −45.0°. fraction 2 (0.2 g.), m.p. 63–66°, $[\alpha]$D −23.5°, and fraction 3 (0.3 g.), m.p. 63–70°, $[\alpha]$D −29.2°, also were not improved by recrystallization. The infrared spectra of the three first fraction isolongifolols were identical, and those of fractions 2 and 3 from the reduction of α-longifolic acid were very similar to that spectrum of isolongifolol.

Longifolene from Isolongifolol.—Pure isolongifolol (2.0 g.) was dissolved in 50 **ml.** of anhydrous ether and 2.0 g. of phosphorus pentachloride was added. While the mixture stood for 36 hours at room temperature the solid pentachloride lying initially at the bottom of the flask slowly dissolved. The clear solution was poured into water, and the ether layer was removed. This ether layer was washed with water, then with dilute sodium hydroxide solution, again with water and finally dried over sodium sulfate. Evaporative distillation of the residue, remaining after evaporation of ether, at 100° (1 mm.) gave 0.2 g. of longifolene, $[\alpha]$D +36.2°, whose infrared spectrum was superimposable upon that of the sesquiterpene described above. If the ether solution of the reaction product is concentrated, a white crystalline substance is deposited, m.p. 121–123°, as major product, and this material, which gave a positive phosphate test, is believed to be the phosphate ester of isolongifolol.

Isomerization of Longifolene.—Longifolene (10 g.), $[\alpha]$D +33.7°, was added to 20 ml. of sulfuric acid, 50 ml. of acetic acid and 70 ml. of water. This mixture was maintained at *ca.* 80° on the steam-bath for 14 days, during which time aliquots were withdrawn for rotation and infrared measurements. Specific rotation changes were: +33.7° (0 days), +21.1° (1), +10.1° (2), +1.8° (3), −3.9° (4), −7.2° (5), −9.6° (6), −15.4° (8), −15.7° (9), −15.0° (11), −16.5° (14).

The isomerized product, β-longifolene, decolorized permanganate solution and bromine in carbon tetrachloride.

Anal. Calcd. for $C_{15}H_{24}$: C, 88.16; H, 11.84. Found: C, 87.72; H, 11.80.

Dehydration of Isolongifolol.—Isolongifolol (1.3 g.) was heated with 0.9 g. of freshly fused potassium bisulfate between 220–230° for 1.5 hours. The product was extracted with ether, washed and dried. Evaporative distillation at 100° (1 mm.) yielded 0.5 g. of colorless, liquid hydrocarbon, $[\alpha]$D −62.6°.

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(8) J. L. Simonsen, *J. Chem. Soc.*, **117**, 570 (1920).

(9) Value reported by J. L. Simonsen.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TORONTO]

Cyclitols. VI. A New Tetrol and Enediol from Cyclohexadiene-1,4 by the Prevost Reaction[1]

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Cyclohexadiene-1,4 in excess reacts with silver iodine dibenzoate to give *trans*-cyclohexenediol-4,5 dibenzoate, which can be saponified to *trans*-cyclohexenediol-4,5. The diene in deficiency reacts to give cyclohexanetetrol-1,2,4,5 tetrabenzoate (m.p. 181°), which on ammonolysis gives a new cyclohexanetetrol-1,2,4,5 of m.p. 208°. Acetylation of the tetrol gives a tetraacetate of m.p. 148° The benzoylation of cyclohexenediol-3,4 is described. New Prevost reaction products of cyclohexene are reported.

Continuing our investigations on cyclitol chemistry,[1] we wish to report the synthesis of a new cyclohexanetetrol III and a new cyclohexenediol V. The cyclohexanetetrols are of interest because of their close relationship to the naturally occurring betitol,[3] quercitols and inositols. Cyclohexenediol-4,5 and -3,4 were needed for use in a configurational determination which is still in progress.

It previously had been shown that tetrols or enediols can be prepared by the hydroxylation (or acyloxylation) of cyclohexadienes with suitable reagents. Products of *cis* configuration are obtained with potassium permanganate[4] or osmium tetroxide,[5] while the perbenzoic acid method[6] gives *trans* prod-

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(1) For previous (unnumbered) papers in this series, see G. E. McCasland and E. Clyde Horswill, THIS JOURNAL, **75**, 4020 (1953), and references there cited.

(2) Fellow of the National Research Council, 1952–1953.

(3) Betitol, a dextrorotatory cyclohexanetetrol, was isolated in 1901 from beet sugar molasses; see *Ber.*, **34**, 1159 (1901). If it has a 1,2,4,5-structure it could conceivably be an active form of our inactive tetrol now reported.

(4) (a) N. D. Zelinski and A. N. Titowa, *ibid.*, **64**, 1399 (1931); (b) N. D. Zelinski, J. I. Denisenko and M. S. Eventova, *Chem. Zentr.*, **106**, II, 3765 (1935).

(5) T. Posternak, *Helv. Chim. Acta*, **36**, 251 (1953).

(6) (a) P. Bedos and A. Ruyer, *Compt. rend.*, **196**, 625 (1933); (b) **204**, 1350 (1937); (c) **195**, 802 (1932).