The Relationship between Longifolic and Isolongifolic Acids

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(Received March 4, 1955)

Naffa and Ourisson[1] and later Zeiss and Arakawa[2] observed that the longifolic acids are monobasic with formula $C_{15}H_{24}O_2$ and not $C_{14}H_{22}O_2$. The present author obtained the same results, and furthermore confirmed the fact that the logifolic and isolongifolic acids are isomers in endo- and exo-forms.

Simonsen[3] and others[4] reported that the oxidation of longifolene with chromic acid in acetic acid or with potassium dichromate in sulfuric-acetic acid furnishes isolongifolic and α-longifolic acids besides longifolic acid, that longifolic and isolongifolic acids are isomers having formula $C_{14}H_{22}O_2$, that longifolic acid isomerizes to isolongifolic acid on treatment with mineral acid, and that longifolic acid is considered to be one of the C_{14}-acid varieties.

Zeiss and Arakawa obtained these acids by the oxidation of longifolene with potassium dichromate and reduced them as well as their esters with lithium-aluminum hydride. Namely, when isolongifolic acid and methyl isolongifolate were reduced with the reagent, they were converted into isolongifolol ($C_{15}H_{26}O$), m. p. 112°C. Longifolic acid was converted mainly into isolongifolol and partly into longifolol, m. p. 78.5–80.5°C. α-Longifolic acid gave isolongifolol and impure alcohols rich in isolongifolol. From these results it is obvious that longifolic and α-longifolic acids are mixtures consisting chiefly of isolongifolic acid.

Further, oxidation of isolongifolol with potassium dichromate in sulfuric-acetic acid regenerated isolongifolic acid. On treatment with phosphorus pentachloride in ether at room temperature, it gave an olefin which proved to be longifolene on the basis of optical rotation and infrared spectrum. From these results Zeiss and Arakawa presumed that longifolic and α-longifolic acids are probably epimeric mixtures, and determined that they are monobasic acids of formula $C_{15}H_{24}O_2$.

Longifolene used in the present experiments was regenerated from longifolene hydrochloride (m. p. 59–60°C). The former was oxidized with chromic acid in acetic acid under the same conditions as used by Simonsen[5] and others. Longifolic acid obtained by this treatment was esterified with dimethyl sulfate in the usual manner, and the ester was separated by distillation to give methyl longifolate and methyl isolongifolate, m. p. 54–55°C, which on saponification with alcoholic potash gave longifolic acid, m. p. 152–153°C, and isolongifolic acid, m. p. 136–137°C, respectively. These melting points agreed with other workers' results. Analyses and experiments described below gave values for C_{15}-acid. When dihydrolongifolene, obtained by the catalytic hydrogenation of longifolene, was oxidized similarly, isolongifolic acid was produced. When methyl longifolate and methyl isolongifolate were treated with phenyl magnesium bromide, a crystalline carbinol,

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[1] P. Naffa and G. Ourisson, *Chem. and Ind.*, **1953**, 917.

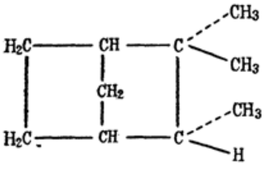
[2] H.H. Zeiss and M. Arakawa, *J. Am. Chem. Soc.*, **76**, 1653 (1954).

[3] J. L. Simonsen, *J. Chem. Soc.*, **1920**, 117, 578; ibid., **1923**, 125, 2624.

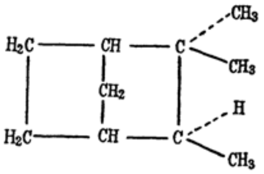
[4] A.E. Bradfield, E.M. Francis and J.L. Simonsen, *J. Chem. Soc.*, **1934**, 118.

[5] J.L. Simonsen, loc. cit.

m. p. 120.5–121.5°C, was obtained from the former, and another carbinol, m. p. 117–118°C, from the latter. On trating it with formic acid, or with potassium bisulfate, or on distilling under diminished pressure, the two carbinols gave the same dehydration product, m. p. 109–110°C, the carbinol of m. p. 117–118°C being dehydrated more easily. These results assumptively show that the two carbinols differ in the steric arrangments of the diphenyl carbinol group and the hydrogen atom ttached to the ring carbon atom which originally possessed the carboxyl group in the longifolic acids. Thus, longifolic and isolongifolic acids are stereo-isomers as regards the carboxyl group and the hydrogen atom. This relationship is imaginable from the results of Zeiss and Arakawa. Just as the endo form (I) and the theoretically possible exo form (II) in dihydrocamphene[6], longifolic and isolongifolic acids may be considered to be in a similar relation.

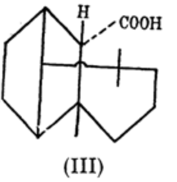


(I)

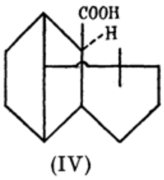


(II)

According to the structural formula presented by Naffa and Ourisson, the relationship is represented as forms (III) and (IV).



(III)



(IV)

The infrared spectra of longifolic and isolongifolic acids showed absorptions at 5.93 μ and 5.90 μ respectively in the solid state, and both at 5.87 μ in carbon tetrachloride solution. All these data proved that longifolic and isolongifolic acids are endo and exo isomers, and it was concluded from the infrared spectra that isolongifolic acid is the endo form.

Experimental

1. Longifolene.—Terpentine oil obtained from oleo-resin was distilled under diminished pressure, and the fraction boiling at 149–152°/36 mmHg or 122–125°/10 mmHg was collected. The longifolene fraction was refluxed with metallic sodium for one hour, and then hydrogen chloride was passed for five to eight hours with cooling in ice-water. Longifolene hydrochloride thus obtained in needles melting at 59–60°C was treated with acetic anhydride and sodium acetate under reflux for three hours to give longifolene. 180.5 g. of this longfolene was dried with calcium chloride, and fractionated under a pressure of 10 mmHg as follows:

Fraction	b.p., °C	Yield, g.	d_4^{25}	n_D^{25}
1	–123	0.9	—	—
2	123–124	157.0	0.9300	1.5025
3	124–125	19.3	0.9303	1.5026
4	125–126	2.1	0.9303	1.5028
5	126–	1.2	0.9351	1.5051

Mol. Refract. (Fraction 2); 64.53. Calcd. for $C_{15}H_{24}(F_1)$: 64.40.

Fraction 2 was used in the following experiments.

2. Methylation.—Longifolene was oxidized according to the procedures of Simonsen and others. The acids obtained were dried and esterified with dimethyl sulfate in the usual way. 51.7 g. of the ester were subjected to fractional distillation:

Fraction	b.p. °C (8.5 mmHg)	Yield, g.	d_4^{25}	n_D^{25}
1	139.5–140.5	16	1.0378	1.5012
2	140.5–142	13	1.0278	1.5012
3	142 –143.5	7	1.0382	1.5016
4	143.5–145	2.5	crystals	
5	145 –147	7	〃	
6	147 –150	3	〃	
7	150 –	2	〃	

Recrystallization of the crystalline fractions from alcohol gave a substance melting at 54–55°C, which agreed with methyl isolongifolate obtained by Simonsen and others.

Anal. Found: C, 76.42; H, 10.16. Calcd. for $C_{16}H_{24}O_2$: C, 76.75; H, 10.4%.

Hydrolysis of the crystalline fractions with alcoholic potash gave an acid which melted at 136–137°C which agreed with isolongifolic acid.

Anal. Found: C, 76.16: H, 10.25. Calcd. for $C_{15}H_{24}O_2$: C, 76.22; H, 10.23%.

On the other hand, the acid obtained from fractions 1–3 by similar treatment was identified with longifolic acid, m.p. 152–153°C.

Anal. Found: C, 76.41; H, 9.75. Calcd. for $C_{15}H_{24}O_2$: C, 76.22; H, 10.23%.

Thus, fractions 1–3 were methyl longifolate (yellowish oil) and other fractions were rich in methyl isolongifolate.

3. Grignard Reaction.—Methyl longifolate (30 g.) was treated with a Grignard reagent prepared from brombenzene (47.1 g.) and magnesium (7.2 g.) in ether solution. The ethereal solution was dried, and evaporated left to stand for two or three days, the residue gave the crystalline carbinol melting at 120.5–121.5°C.

Anal. Found: C, 86.29; H, 9.41. Calcd. for $C_{27}H_{34}O_2$:C, 86.58; H, 9.15%. A similar treatment of methyl isolongifolate gave the carbinol melting at 117–118°C, (Found C, 86.49; H, 9.14). The presence of hydroxyl group in these molecules was

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[6] H. Alder and G. Stein, *Ann.*, **525**, 236 (1936).

indicated by the Deniges reagent and by the analysis described above.

4. Dehydration of Carbinols.—The product from methyl longifolate and the Grignard reagent were immediately distilled before the crystals separated out, to give the following results:

Fraction	b.p., °C (10 mmHg)	Yield (g.)	d_4^{25}	n_D^{25}
1	-120	1.5	1.0775	1.5140
2	120–142	2.5	1.0475	1.5240
3	142–146	2.0	1.0413	1.4998
4	146–148	3.0	1.0264	1.5030
5	148–	5.0	crystals	

The residual crystalline substance obtained in the above fractional distillation had a melting point of 109–110°C after recrystallized from alcohol. The presence of a double bond and a phenyl group was inferred from the infrared absorptions at 6.27 μ and 6.70 μ, respectively. Analysis showed it was a hydrocarbon, $C_{27}H_{32}$.

Anal. Found: C, 90.55; H, 9.17. Calcd. for $C_{27}H_{32}$: C, 90.95; H, 9.05%. Another crystalline hydrocarbon, m.p. 67–68°C was obtained from fraction 2. Found: (C, 93.60; H, 6.71). It was not investigated further.

When the carbinols from methyl longifolate and methyl isolongifolate were treated with formic acid or potassium bisulfate under reflux for 1.5 hours, they gave the same hydrocarbon $C_{27}H_{32}$ melting at 109–110°C.

The author is indebted to Prof. T. Kubota, Osaka City University, for his advice and direction, and to Mr. M. Yamaguchi, Osaka City University, for the measurement of the infrared absorption.

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