

Studies on the Constitution of Shonanic Acid, One of the Two Characteristic Volatile Acids from the Wood of *Libocedrus formosana*, Florin. IV. On Dihydroshonanyl Alcohol and the Optical Activity of Shonanic Acid and its Derivatives.

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In a previous communication,<sup>(1)</sup> the author has reported the presence of a dimethylmethylen group in the molecule of shonanic acid as a result of the investigations on the oxidation products of shonanic acid with permanganate. Next, with a view to examine the oxidation products of dihydroshonanic acid, the author attempted to prepare a sufficient quantity of the acid. But, as has been reported, the preparation of dihydroshonanic acid from shonanic acid by reduction with sodium and ethyl alcohol is always accompanied by the formation of by-products such as tetrahydroshonanic acid or isoshonanic acid, and furthermore, the separation of dihydroshonanic acid from these impurities can hardly be accomplished by the fractional distillation as there is but little difference between their boiling points. Attempt to separate it in the pure state by fractional crystallization of its metallic salts was also unsuccessful.

The author tried, hereupon, to prepare dihydroshonanyl alcohol, the unsaturated primary alcohol corresponding to dihydroshonanic acid, and to oxidise it, as such oxidation should lead to the same conclusion as might be expected from the oxidation of the dihydro-acid.

Thus, dihydroshonanyl alcohol was prepared from ethyl shonanate by reduction with sodium and ethyl alcohol. According to H. Rupe and P. Lauser<sup>(2)</sup> the yield of camphorcarbinol increased with the molecular weight of the ester-forming radicals e.g. 10–15% by ethyl ester, 22% by isobutyl ester, 25% by isoamyl ester, 64% by  $\beta$ -naphthyl ester, and 94–96% by phenol ester. The present author, in order to increase the yield of the desired alcohol, prepared phenyl shonanate and reduced it with sodium and ethyl alcohol, but contrary to the expectation the yield of carbinol-compound did not improved at all.

When oxidised with chromic acid, dihydroshonanyl alcohol gave the corresponding aldehyde ( $C_{10}H_{16}O$ , semicarbazone m.p. 149–150°) and

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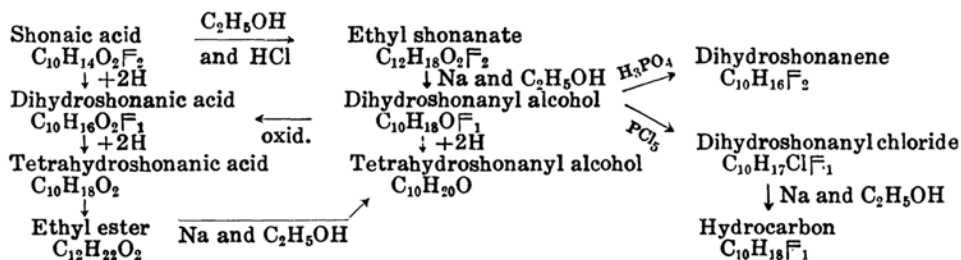
(1) This Bulletin, **12** (1937), 243.

(2) *Helv. Chim. Acta*, **3** (1920), 272.

acid, and when reduced catalytically with palladium and hydrogen it afforded tetrahydroshonanyl alcohol ( $C_{10}H_{20}O$ ), the same as obtained from ethyl tetrahydroshononate by reduction with sodium and ethyl alcohol, which gave tetrahydroshonanic acid on oxidation. On digesting dihydroshonanyl alcohol with phosphorus pentachloride, the corresponding chloride ( $C_{10}H_{17}Cl$ ) was obtained, which could be transformed into a hydrocarbon of the formula  $C_{10}H_{18}F_1$  by reduction with sodium and ethyl alcohol. The dehydration of shonanyl alcohol with phosphoric acid afforded a hydrocarbon  $C_{10}H_{16}F_2$  (dihydroshonanene), but the attempt to obtain its hydrochloride, nitrosochloride and nitrosite in crystalline state was not successful.

These hydrocarbons, judging from their physical properties, viz., boiling points, specific gravities and refractive indices, seem likely to be compounds of six-membered ring type, hence shonanic acid is most likely a cyclohexene derivative.

The various relations mentioned above are tabulated in the following.



About the oxidation products of dihydroshonanyl alcohol, it will be reported in the next communication.

The values of optical rotatory power exhibited by shonanic acid and its derivatives are as follows, from which it is obvious that the acid is a compound with an asymmetric carbon atom.

Shonanic acid	$[\alpha]_D^{18} = -0.74^\circ$ (in ethyl alcohol)
Shonanic acid dibromide	$[\alpha]_D^{27} = -5.02^\circ$ (in glacial acetic acid)
Ethyl shonate	$\alpha_D^{18} = -4.24^\circ$
Phenyl shonate	$\alpha_D^{28} = -2.40^\circ$
Shonanic amide	$[\alpha]_D^{27} = -9.84^\circ$ (in ethyl alcohol)
Dihydroshonanic acid	$\alpha_D^{30} = -1.36^\circ$
Tetrahydroshonanic acid	$\alpha_D^{26} = -0.84^\circ$
Ethyl tetrahydroshononate	$\alpha_D^{26} = -0.81^\circ$
Dihydroshonanyl alcohol	$\alpha_D^{18} = -2.24^\circ$
Dihydroshonanyl chloride	$\alpha_D^{30} = -2.00^\circ$
Tetrahydroshonanyl alcohol	$\alpha_D^{26} = -1.64^\circ$
Dihydroshonanene	$\alpha_D^{26} = \pm 0^\circ$

### Experimental.

(1) **Preparation of ethyl shonanate.** 10 g. of shonanic acid together with 50 c.c. of ethyl alcohol containing 2.5% of hydrochloric acid was heated on the water-bath for an hour, the product was poured into water, extracted with ether and ethereal solution washed with water and then with dilute sodium bicarbonate solution in order to remove hydrochloric acid and unchanged shonanic acid, dried over anhydrous sodium sulphate and the solvent distilled off. The remainder was then distilled under reduced pressure when a liquid ester with the following properties was obtained. (Yield 9.3 g.) B.p. 106–108°/7 mm., 228–229°/759 mm.;  $d_4^{30}$  0.9568;  $n_D^{30}$  1.4674;  $\alpha_D^{20}$  –4.24°.

(2) **Preparation of dihydroshonanyl alcohol.** 10 g. of ethyl shonanate was dissolved in 200 c.c. of absolute alcohol and 15 g. of metallic sodium was added in small portions. When all the sodium has been taken up the excess of alcohol was distilled away in vacuo and the remainder was poured into 200 c.c. of 10% sodium chloride solution. The oily matter which made appearance was taken up with ether, dried over anhydrous sodium sulphate and then the solvent was distilled off. The product amounted to 3.3 g. corresponding to 41% of the theoretical yield. Several experiments were repeated, in all of which the yield of the alcoholic substance was found to lie between 35–40% of the theoretical. Dihydroshonanyl alcohol showed the following properties: b.p. 104°/7 mm., 228–230°/765 mm.;  $d_4^{30}$  0.9328;  $n_D^{30}$  1.4832;  $\alpha_D^{20}$  –2.24°; M.R. obs. 47.16, calculated for  $C_{10}H_{18}O\bar{F}_1$  47.23. Sample (0.1379 g.) absorbed 0.1476 g. of bromine, while  $C_{10}H_{18}O\bar{F}_1$  requires 0.1433 g. The substance is readily attacked by permanganate solution in cold showing the substance is unsaturated.

(3) **Preparation of dihydroshonanyl alcohol from phenyl shonanate.** Phenyl shonanate was prepared by adding the acid chloride (9.2 g.) dissolved in 100 c.c. of petroleum ether to a solution of 4.7 g. of phenol in 10 c.c. of petroleum ether and heating the mixture on the water-bath until the evolution of hydrochloric acid gas ceased. Ether was then added to the reaction mixture and shaken with 5% sodium hydroxide solution to remove unchanged phenol. The ethereal solution was dried, the solvent distilled off, and then crude phenyl shonanate was distilled under reduced pressure. Yield 11.8 g. (97.5% of the theoretical). B.p. 153–155°/6 mm.;  $d_4^{30}$  1.0415;  $n_D^{30}$  1.5245;  $\alpha_D^{26}$  –2.40°; M.R. obs. 71.16, calculated for  $C_{10}H_{18}O_2\bar{F}_5$  71.36.

The phenol ester obtained above (11.8 g.) was dissolved in 120 c.c. of absolute alcohol and was reduced with 9 g. of sodium in the usual manner when 2.2 g. of the corresponding alcohol was obtained, the yield amounting to 29.5% of the theoretical. The yield of the carbinol was 27% and 29% of the theoretical respectively when the reduction was carried out by using smaller (6.5 g.) and larger (11 g.) proportions of metallic sodium. The physical properties of the dihydroshonanyl alcohol are as follows: b.p. 103–103.5°/6 mm.;  $d_4^{30}$  0.9319;  $n_D^{30}$  1.4826;  $\alpha_D^{24}$  –2.09°.

(4) **Hydrogen dihydroshonanyl phthalate.** When heated with equivalent weight of phthalic anhydride in benzene solution dihydroshonanyl alcohol gave its acid phthalic ester. From 1 g. of the sample, 1 g. of phthalic anhydride and 2 c.c. of benzene, the acid phthalic ester was obtained in prismatic needles, which melted at 124° after a recrystallization from ethyl alcohol.

(5) **Oxidation of dihydroshonanyl alcohol with chromic acid.** 10 g. of the alcohol dissolved in 150 c.c. of glacial acetic acid was kept at 10–15° and a solution of chromic acid (10 g.) in a little water and glacial acetic acid (50 c.c.) was added drop by drop with constant stirring. After all the chromic acid solution has been consumed the reaction mixture was warmed on the water-bath at 50–60° for 30 minutes. The reaction mixture was then poured into water and aldehydic and acidic substances were extracted and separated as usual.

(a) *The aldehyde* showed the following properties: b.p. 107–110°/18 mm.;  $d_4^{30}$  0.9630;  $n_D^{30}$  1.4833; M.R. obs. 45.10, calculated for  $C_{10}H_{16}O$  45.78. The substance was a colourless mobile oil with pleasant odour and on testing with Schiff's reagent and Tollens' solution it showed the characteristic reactions of aldehyde.

*Semicarbazone.* A mixture of 1 g. of the sample, 0.8 g. of semicarbazide hydrochloride and 0.6 g. of sodium bicarbonate afforded a semicarbazone as glistening leaflets melting at 149–150° after recrystallizations from ethyl alcohol. (Found: N, 20.88. Calculated for  $C_{11}H_{18}ON_3$ : N, 20.10%.)

(b) *The acidic substance* showed the following properties: b.p. 132°/5 mm.,  $d_4^{30}$  1.022;  $n_D^{30}$  1.4804; M.R. obs. 46.74, calculated for  $C_{10}H_{16}O_2$  47.30. It decolourized permanganate and bromine in cold showing its unsaturated nature. Sample (0.204 g.) absorbed 0.187 g. of bromine, while  $C_{10}H_{16}O_2$  requires 0.194 g.

*Amide.* The amide was prepared by the interaction of the acid chloride and aqueous ammonia. It was glistening scales melting at 130° when recrystallized from 60% ethyl alcohol and was found to be identical by melting in admixture with dihydroshonanamide.

(6) **Preparation of dihydroshonanyl chloride.** When dihydroshonanyl alcohol (3 g. in 10 c.c. of petroleum ether) was treated with phosphorus pentachloride (6.8 g.), the chloride with the following properties was obtained: b.p. 87°/13 mm.;  $d_4^{30}$  0.9984;  $n_D^{30}$  1.4900;  $\alpha_D^{20}$  –2.00°; M.R. obs. 49.95, calculated for  $C_{10}H_{17}Cl$  50.54. At the end of the distillation the hydrocarbon of the following properties came over but its detailed examination was impossible owing to the scarcity of the material. B.p. 172–174°/757 mm.;  $d_4^{30}$  0.8678;  $n_D^{30}$  1.4730. (Found: C, 87.49; H, 12.04. Calculated for  $C_{10}H_{16}$ : C, 88.22; H, 11.78%.)

(7) **Preparation of hydrocarbon  $C_{10}H_{18}$  from dihydroshonanyl chloride.** The chloride (3 g.) mentioned above was dissolved in 50 c.c. of absolute alcohol and 4 g. of metallic sodium was added in small portions. The reaction mixture was then heated on the water-bath and poured into a bulk of water and the hydrocarbon deposited was taken up with ether. The ethereal solution was dried over anhydrous sodium sulphate and the remainder after removal of the solvent was fractionally distilled under the ordinary pressure.

(1) B.p. 163–165° 0.2 c.c.; (2) B.p. 165–166° 1.3 c.c.; (3) B.p. 166–168° 0.3 c.c. The main fraction (2) showed the following properties:  $d_4^{30}$  0.8401;  $n_D^{30}$  1.4658;  $\alpha_D^{26}$  +0.40°; M.R. obs. 45.48, calculated for  $C_{10}H_{18}$  45.60. (Found: C, 87.18; H, 13.14. Calculated for  $C_{10}H_{18}$ : C, 86.96; H, 13.04%.)

(8) **Dehydration of dihydroshonanyl alcohol.** 5 g. of dihydroshonanyl alcohol was heated with 20 g. of phosphoric acid at 200–210° for an hour. The reaction mixture was then poured into water and the oily substance was extracted with ether.

The ethereal solution was next heated with 1 g. of metallic sodium on the water-bath in order to recover the unchanged alcohol and the solvent was distilled off. The extract was then subjected to fractional distillation under the ordinary pressure over metallic sodium. The main fraction showed the following properties: b.p. 168–169°/759 mm.;  $d_4^{30}$  0.8630;  $n_D^{30}$  1.4870;  $\alpha_D$  nil; M.R. obs. 45.32, calculated for  $C_{10}H_{18}F_2$  45.20. (Found: C, 88.28; H, 11.42. Calculated for  $C_{10}H_{18}$ : C, 88.23; H, 11.77%.)

(9) **Preparation of tetrahydroshonanyl alcohol.** Tetrahydroshonanyl alcohol was obtained by catalytic reduction of dihydroshonanyl alcohol on the one hand and by reducing tetrahydroshonamate with sodium and ethyl alcohol on the other.

(a) *Catalytic reduction of dihydroshonanyl alcohol.* 4.438 g. of dihydroshonanyl alcohol, dissolved in 40 c.c. of ethyl alcohol, was catalytically reduced by hydrogen and palladium. Hydrogen absorbed: 644 c.c. (0°, 760 mm.); calculated for  $C_{10}H_{18}OF_1$ : 645 c.c. (0°, 760 mm.). The product showed the following properties: b.p. 100–101°/7 mm.;  $d_4^{30}$  0.9253;  $n_D^{30}$  1.4764;  $\alpha_D^{28}$  –1.64°; M.R. obs. 47.57, calculated for  $C_{10}H_{20}O$  47.52.

(b) *The reduction of ethyl tetrahydroshonamate with sodium and ethyl alcohol.* 5 g. of ethyl tetrahydroshonamate was dissolved in 150 c.c. of absolute alcohol and was reduced by 8 g. of sodium. The alcoholic substance produced showed the following properties, in good accord with those of the product of (a). B.p. 102°/8 mm.;  $d_4^{30}$  0.9250;  $n_D^{30}$  1.4761;  $\alpha_D^{24}$  –1.68°; M.R. obs. 47.57, calculated for  $C_{10}H_{20}O$  47.52.

(10) **Oxidation of tetrahydroshonanyl alcohol with chromic acid.** To a solution of 3 g. of tetrahydroshonanyl alcohol in 70 c.c. of glacial acetic acid, 3 g. of chromic acid was added in small portions with vigorous stirring. The acid produced had the following properties (Yield 1.2 g.): b.p. 120°/2 mm.;  $d_4^{30}$  0.9876;  $n_D^{30}$  1.4650;  $\alpha_D^{26}$  –0.84°; M.R. obs. 47.60, calculated for  $C_{10}H_{18}O_2$  47.70.

*Amide.* The amide prepared from 1 g. of the acid chloride and aqueous ammonia melted at 144° after recrystallization from 60% ethyl alcohol, which showed no depression of the melting point when mixed with an authentic specimen of tetrahydroshonanic amide.

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